Anonyme. The Journal of physical chemistry. Published at Cornell university [3puis3 Published under the auspices of the American chemical society, the Chemical society and the Faraday society]. 1896 [I]-. 1932 . Apr.-june.

1/ Les contenus accessibles sur le site Gallica sont pour la plupart des reproductions numériques d'oeuvres tombées dans le domaine public provenant des collections de la BnF.Leur réutilisation s'inscrit dans le cadre de la loi n°78-753 du 17 juillet 1978 :
*La réutilisation non commerciale de ces contenus est libre et gratuite dans le respect de la législation en vigueur et notamment du maintien de la mention de source.
*La réutilisation commerciale de ces contenus est payante et fait l'objet d'une licence. Est entendue par réutilisation commerciale la revente de contenus sous forme de produits élaborés ou de fourniture de service.

Cliquer ici pour accéder aux tarifs et à la licence

2/ Les contenus de Gallica sont la propriété de la BnF au sens de l'article L.2112-1 du code général de la propriété des personnes publiques.

3/ Quelques contenus sont soumis à un régime de réutilisation particulier. Il s'agit :

*des reproductions de documents protégés par un droit d'auteur appartenant à un tiers. Ces documents ne peuvent être réutilisés sauf dans le cadre de la copie privée sans l'autorisation préalable du titulaire des droits.
*des reproductions de documents conservés dans les bibliothèques ou autres institutions partenaires. Ceux-ci sont signalés par la mention Source Gallica.BnF.fr / Bibliothèque municipale de ... (ou autre partenaire). L'utilisateur est invité à s'informer auprès de ces bibliothèques de leurs conditions de réutilisation.

4/ Gallica constitue une base de données, dont la BnF est producteur, protégée au sens des articles L341-1 et suivants du code la propriété intellectuelle.

5/ Les présentes conditions d'utilisation des contenus de Gallica sont régies par la loi française. En cas de réutilisation prévue par un autre pays, il appartient à chaque utilisateur de vérifier la conformité de son projet avec le droit de ce pays.

6/ L'utilisateur s'engage à respecter les présentes conditions d'utilisation ainsi que la législation en vigueur, notamment en matière de propriété intellectuelle. En cas de non respect de ces dispositions, il est notamment passible d'une amende prévue par la loi du 17 juillet 1978.

7/ Pour obtenir un document de Gallica en haute définition, contacter reutilisation@bnf.fr.

Journal of physical chemistry

Tome 36

Volume 42

Washington 1932

RELATIONS BETWEEN FUNDAMENTAL PHYSICAL CONSTANTS

BY J. E. MILLS

While engaged in an investigation of attractive forces the author calculated some functions involving basic physical constants which would not be calculated from the point of view usually adopted. It was found that certain similar numbers resulted in the most unexpected manner. For example:—

$$\frac{\pi\sqrt{1846.8G}}{\epsilon} = 18861; \quad \frac{c^2}{v^2} = 18850; \quad 3\pi Gc = 18829; \quad \frac{\epsilon^2}{1846.8h} = 18818$$

$$1/2\pi c = 0.53088 \times 10^{-11}; \quad \epsilon/m_o = 0.53035 \times 10^{18}; \quad a = 0.53084 \times 10^{-8};$$

$$4\pi\ 1846.8^2 = 42.859 \times 10^{6}; \quad h^2 = 42.863 \times 10^{-54}; \quad \mu v^2 = 42.861 \times 10^{-12};$$

$$\epsilon = 4.770 \times 10^{-10}; \quad v^2 = 4.7681 \times 10^{16}; \quad \frac{h^2}{(2\pi\epsilon)^2} = 4.7719 \times 10^{-36}$$

For the constants and symbols used see Table I.

TABLE I

Symbols and Constants

π =	Geometrical constant	3.14159
c =	Velocity of light	2.99796×10^{10} cm sec^{-1}
h =	Planck's constant	6.547×10^{-27} erg sec
m_o =	Mass electron	8.994×10^{-28} grams
m_p =	Mass proton	1.6610×10^{-24} grams
ϵ =	Electronic charge	4.770×10^{-10} absolute es units
G =	Gravitation constant	6.664×10^{-8} $\text{cm}^3\ \text{gr}^{-1}\ \text{sec}^{-2}$
τ =	G. N. Lewis temperature unit = $1/k$	7.289×10^{15}
N =	Avogadro's number	6.064×10^{23} mole^{-1}
N m_o =	Atomic weight of electron	5.454×10^{-4}
N m_p =	" " " proton	1.0072346
H =	" " " hydrogen	1.00778
He =	" " " helium	4.00216
O =	" " " oxygen	16.000
μ =	Reduced mass = $\frac{m_p m_o}{m_p+m_o}$	8.9891×10^{-28} grams
mp/m_o =	Ratio mass proton to mass electron	1846.8
M_{He} =	Loss of mass in formation of helium	4.776×10^{-26} grams.
T_o =	Ice point, absolute	273.18°C
A_n =	Normal atmosphere	1.013250×10^{6} dynes cm^{-2}
V_n =	Gram molecular volume	22.4141×10^{3} $\text{cm}^3\ \text{mole}^{-1}$

TABLE I (Continued)

R = Gas constant $= \frac{A_n V_n}{T_o}$ 8.3136×10^{7} erg deg^{-1} mole^{-1}

k = Boltzmann constant $= R/N = 1/\tau$ 1.3710×10^{-16} erg deg^{-1}

α = Fine structure constant $= \frac{2\pi\epsilon^2}{hc}$ 0.7284×10^{-2}

β = Specific heat constant $= h/k$ 4.7753×10^{-11} sec deg

F = Faraday $= N\epsilon$ 2.89253×10^{14} es

v = Velocity of reduced mass in first Bohr orbit $= \frac{2\pi\epsilon^2}{h}$ cms/sec

a = Radius of first Bohr orbit $= \frac{h^2}{4\pi^2\epsilon^2\,\mu}$ cms

ω = Period of reduced mass, first Bohr orbit $= \frac{\mu}{h}\left(\frac{2\pi\epsilon^2}{h}\right)^2$ sec

E_k = Kinetic energy of reduced mass, first Bohr orbit $= \frac{\mu}{2}\left(\frac{2\pi\epsilon^2}{h}\right)^2$ ergs

R_H = Rydberg constant for hydrogen (Spectroscopic value of constants should be used) $= \frac{\mu}{2hc}\left(\frac{2\pi\epsilon^2}{h}\right)^2$

ν = Wave frequency

λ = Wave length of light in cms per sec.

$\bar{\nu}$ = Wave number $= \nu/c$

Atomic weights are from Aston. The values of the other constants are taken mainly from Birge: Phys. Rev. Sup. 1, 1 (1929).

As more and more functions were calculated it became evident that, ignoring the decimal point, nearly all of the functions calculated fell into a comparatively few series of figures. These series of functions and their reciprocals are given in Tables II-XIV.

TABLE II

		Functions related to c	Reciprocals
1	c	2.99796×10^{10}	$.33356 \times 10^{-10}$
2	3	3.0000	$.33333$
5	$\left(\frac{\epsilon}{m_o}\right)^{1/12}$	2.9995×10	$.33339 \times 10^{-1}$
5	$\frac{m_o}{2\pi\epsilon}$	3.0009×10^{9}	$.33323 \times 10^{-9}$
6	$\frac{1}{2\pi a}$	2.9981×10^{7}	$.33354 \times 10^{-7}$
7	$\frac{c^2}{2\pi v^2}$	3.0000×10^{3}	$.33333 \times 10^{-3}$
8	$\frac{h^2}{2\pi\epsilon^2}$	2.9982×10^{-35}	$.33353 \times 10^{35}$

TABLE II (Continued)

		Functions related to c	Reciprocals
9	$\frac{c^2}{2\pi\epsilon}$	2.9989×10^{29}	$.33346 \times 10^{-29}$
10	$\frac{c^4}{2\pi h^2}$	2.9995×10^{94}	$.33339 \times 10^{-94}$
11*	$\frac{\sqrt{1846.8G}}{2\epsilon}$	3.0019×10^{3}	$.33312 \times 10^{-3}$
12	$\sqrt{m_o}$	2.9990×10^{-14}	$.33344 \times 10^{14}$
13	$2\pi\epsilon$	2.9971×10^{-9}	$.33366 \times 10^{9}$
14	$\frac{3Gc}{2}$	2.9967×10^{3}	$.33370 \times 10^{-3}$
24*	$\frac{\epsilon^3}{1846.8\ hc}$	2.9942×10^{-16}	$.33398 \times 10^{16}$
25	$\sqrt{\pi\sqrt{1846.8G}}$	2.9995×10^{-3}	$.33339 \times 10^{3}$
37*	$\frac{1}{2 \times 1846.8\ m_o}$	3.0102×10^{23}	$.33220 \times 10^{-23}$

TABLE III

		Functions related to c^2	Reciprocals
1	c^2	8.9878×10^{20}	$.11126 \times 10^{-20}$
2	3^2	9.0000	$.11111$
5*	$\left(\frac{m_o}{2\pi\epsilon}\right)^2$	9.0054×10^{18}	$.11104 \times 10^{-18}$
6	$\left(\frac{1}{2\pi a}\right)^2$	8.9886×10^{16}	$.11125 \times 10^{-16}$
7	$\left(\frac{c^2}{2\pi V^2}\right)^2$	9.0000×10^{6}	$.11111 \times 10^{-6}$
8	$\left(\frac{h^2}{2\pi\epsilon^2}\right)^2$	8.9892×10^{-70}	$.11124 \times 10^{70}$
9	$\left(\frac{c^2}{2\pi\epsilon}\right)^2$	8.9934×10^{58}	$.11119 \times 10^{-58}$
11*	$\frac{1846.8G^2}{4\epsilon^2}$	9.0114×10^{6}	$.11097 \times 10^{-6}$
12	m_o	8.9940×10^{-28}	$.11119 \times 10^{28}$
13*	$(2\pi\epsilon)^2$	8.9825×10^{-18}	$.11133 \times 10^{18}$
15*	$\frac{\sqrt{1846.8}}{\epsilon}$	9.0093×10^{10}	$.11100 \times 10^{-10}$
16*	$\frac{1}{\sqrt{1846.8G}}$	9.0139×10	$.11094 \times 10^{-1}$
24*	$\frac{\epsilon^3}{1846.8h}$	8.9762×10^{-6}	$.11140 \times 10^{6}$
25	$\pi\sqrt{1846.8G}$	8.9969×10^{-6}	$.11115 \times 10^{6}$

TABLE IV

		Functions related to c^4	Reciprocals
1*	c^4	80.780×10^{40}	$.12379 \times 10^{-41}$
2*	3^4	81.000	$.12345 \times 10^{-1}$
8	$\frac{\epsilon}{hc^2}$	81.064×10^{-6}	$.12336 \times 10^{5}$
12*	m_oc^2	80.836×10^{-8}	$.12371 \times 10^{7}$
15*	$\frac{1846.8}{\epsilon^2}$	81.168×10^{20}	$.12320 \times 10^{-21}$
16*	$\frac{1}{1846.8G}$	81.255×10^{2}	$.12307 \times 10^{-3}$
21	$\frac{h}{m_oc^2}$	80.991×10^{-22}	$.12347 \times 10^{21}$
46	$\frac{\sqrt{1846.8}\, m_o}{\epsilon}$	81.024×10^{-18}	$.12342 \times 10^{17}$

TABLE V

		Functions related to c^6	Reciprocals
1*	c^6	$.7260 \times 10^{63}$	1.3773×10^{-63}
2	3^6	$.7290 \times 10^{3}$	1.3717×10^{-3}
3	$\frac{1}{\sqrt{6\pi}}$	$.7284 \times 10^{-1/2}$	$1.3729 \times 10^{1/2}$
4	$\frac{1}{\sqrt{2\pi c}}$	$.7286 \times 10^{-11/2}$	$1.3725 \times 10^{11/2}$
5	$\sqrt{\frac{\epsilon}{m_o}}$	$.7283 \times 10^{9}$	1.3731×10^{-9}
6	$\sqrt{a}$	$.7286 \times 10^{-4}$	1.3725×10^{4}
7	$\frac{v}{c} = \alpha$	$.7284 \times 10^{-2}$	1.3729×10^{2}
8	$\frac{\epsilon}{h}$	$.7286 \times 10^{17}$	1.3725×10^{-17}
9	$\frac{\sqrt{\epsilon}}{c}$	$.7285 \times 10^{-15}$	1.3727×10^{15}
10	$\frac{h}{c^2}$	$.7284 \times 10^{-47}$	1.3728×10^{47}
11	$\sqrt{\frac{\epsilon}{\pi\sqrt{1846.8\, G}}}$	$.7281 \times 10^{-2}$	1.3733×10^{2}
12	$\frac{1}{\sqrt{2\pi\sqrt{m_o}}}$	$.7285 \times 10^{13/2}$	$1.3727 \times 10^{-13/2}$
13	$\frac{1}{2\pi\sqrt{\epsilon}}$	$.7287 \times 10^{-4}$	1.3723×10^{4}
14	$\frac{1}{\sqrt{3\pi Gc}}$	$.7288 \times 10^{-2}$	1.3721×10^{2}
17	$\sqrt{3\pi}$	$.7280 \times 10^{5/8}$	$1.3736 \times 10^{-5/8}$

TABLE V (Continued)

		Functions related to c^6	Reciprocals
18	$\frac{3}{2\pi h}$	$.7293 \times 10^{26}$	1.3712×10^{-26}
19*	$\tau = 1/k$	$.7294 \times 10^{16}$	1.3710×10^{-16}
20*	$\frac{m_{He}}{h}$	$.7294 \times 10$	1.3709×10^{-1}
21	h/m_o	$.7279 \times 10$	1.3737×10^{-1}
22	$\frac{(2\pi\epsilon^2)^2}{h^3}$	$.7283 \times 10^{43}$	1.3731×10^{-43}
23	$\frac{1}{2\pi 1846.8}\sqrt{\frac{\epsilon}{G}}$	$.7291 \times 10^{-9/2}$	$1.3715 \times 10^{9/2}$
35	$\frac{\epsilon^{1/2}}{m_o^{1/4}\, c^{1/2}}$	$.7284 \times 10^{-3}$	1.3729×10^{3}

TABLE VI

		Functions related to c^8	Reciprocals
1*	c^8	6.5254×10^{83}	$.15324 \times 10^{-83}$
2*	3^8	6.5610×10^{3}	$.15242 \times 10^{-3}$
7	vc	6.5463×10^{18}	$.15276 \times 10^{-18}$
8	$\frac{\epsilon c^2}{h}$	6.5480×10^{37}	$.15272 \times 10^{-37}$
9	$\sqrt{\epsilon c}$	6.5476×10^{5}	$.15273 \times 10^{-5}$
10	h	6.547×10^{-27}	$.15274 \times 10^{27}$
29	$\omega = 2R_Hc$	6.5467×10^{15}	$.15275 \times 10^{-15}$
30	$\frac{(4\pi\epsilon)^2}{c}\sqrt[4]{\frac{8\pi^5}{15}}$	6.5497×10^{-27}	$.15268 \times 10^{27}$
40*	$\sqrt[4]{1846.8}$	6.5557	$.15254$

TABLE VII

		Functions related to c^{10}	Reciprocals
1	c^{10}	5.8649×10^{104}	$.17050 \times 10^{-104}$
2	3^{10}	5.9049×10^{4}	$.16935 \times 10^{-4}$
10	hc^2	5.8843×10^{-6}	$.16994 \times 10^{6}$

This series could be expanded, but the functions do not seem to be of importance.

TABLE VIII

		Functions related to c^{12}	Reciprocals
1*	c^{12}	$.52712 \times 10^{126}$	1.8971×10^{-126}
2*	3^{12}	$.53144 \times 10^{6}$	1.8817×10^{-6}
3	$1/6\pi$	$.53052 \times 10^{-1}$	1.8850×10
4	$\frac{1}{2\pi c}$	$.53088 \times 10^{-11}$	1.8837×10^{11}
5	ϵ/m_o	$.53035 \times 10^{18}$	1.8855×10^{-18}
6	a	$.53084 \times 10^{-8}$	1.8838×10^{8}
7	$\frac{v^2}{c^2}$	$.53051 \times 10^{-4}$	1.8850×10^{4}
8	$\frac{\epsilon^2}{h^2}$	$.53086 \times 10^{34}$	1.8837×10^{-34}
9	ϵ/c^2	$.53072 \times 10^{-30}$	1.8842×10^{30}
10	h^2/c^4	$.53061 \times 10^{-94}$	1.8846×10^{94}
11*	$\frac{\epsilon}{\pi\sqrt{1846.8G}}$	$.53019 \times 10^{-4}$	1.8861×10^{4}
12	$\frac{1}{2\pi\sqrt{m_o}}$	$.53070 \times 10^{13}$	1.8843×10^{-13}
13	$\frac{1}{4\pi^2\epsilon}$	$.53103 \times 10^{8}$	1.8831×10^{-8}
14	$\frac{1}{3\pi Gc}$	$.53110 \times 10^{-4}$	1.8829×10^{4}
17*	$(3\pi)^4$	$.53000^4 \times 10^{5}$	$1.8868 \times 10^{-5}\ {}^{4}$
23*	$\frac{\epsilon}{(2\pi\ 1846.8)^2G}$	$.53161 \times 10^{-9}$	1.8811×10^{9}
35	$\frac{\epsilon}{\sqrt{m_o c}}$	$.53054 \times 10^{-6}$	1.8849×10^{6}
36*	$\frac{8\pi\ 1846.8^3}{3}$	$.52768 \times 10^{11}$	1.8951×10^{-11}

TABLE IX

		Functions related to c^{14}	Reciprocals
1*	c^{14}	4.7377×10^{146}	$.21107 \times 10^{-146}$
2*	3^{14}	4.7830×10^{6}	$.20975 \times 10^{-6}$
4	$\frac{c}{2\pi}$	4.7714×10^{9}	$.20958 \times 10^{-9}$
5	$\frac{\epsilon c^2}{m_o}$	4.7667×10^{38}	$.20979 \times 10^{-38}$
7	v^2	4.7681×10^{16}	$.20973 \times 10^{-16}$
8	$\frac{\epsilon^2 c^2}{h^2}$	4.7706×10^{54}	$.20962 \times 10^{-54}$

TABLE IX (Continued)

		Functions related to c^{14}	Reciprocals
9	ϵ	4.770×10^{-10}	$.20964 \times 10^{10}$
10	$\frac{h^2}{c^2}$	4.7690×10^{-74}	$.20969 \times 10^{74}$
11*	$\frac{\epsilon c^2}{\pi\sqrt{1846.8G}}$	4.7651×10^{16}	$.20986 \times 10^{-16}$
12	$\frac{c^2}{2\pi\sqrt{m_o}}$	4.7698×10^{33}	$.20965 \times 10^{-33}$
13	$\frac{c^2}{4\pi^2\epsilon}$	4.7728×10^{12}	$.20952 \times 10^{-12}$
14	$\frac{c}{3\pi G}$	4.7734×10^{16}	$.20950 \times 10^{-16}$
23*	$\left(\frac{c}{2\pi 1846.8}\right)^2\frac{\epsilon}{G}$	4.7780×10^{11}	$.20929 \times 10^{-11}$
26*	$\frac{1}{\pi G}$	4.7765×10^{6}	$.20936 \times 10^{-6}$
27	$\frac{4\pi\ (1846.8)^2}{c^2}$	4.7685×10^{-14}	$.20971 \times 10^{14}$
28	$\mu\ a$	4.7718×10^{-36}	$.20956 \times 10^{36}$
33*	m_{He}	4.7757×10^{-26}	$.20939 \times 10^{26}$
35	$\frac{\epsilon c}{\sqrt{m_o}}$	4.7684×10^{14}	$.20971 \times 10^{-14}$
38	$\frac{4\pi(1846.8)^2}{m_o}$	4.7653×10^{34}	$.20985 \times 10^{-34}$
47*	$\beta = h/k$	4.7753×10^{-11}	$.20941 \times 10^{11}$

TABLE X

		Functions related to c^{16}	Reciprocals
1*	c^{16}	42.581×10^{166}	$.023483 \times 10^{-166}$
2*	3^{16}	43.047×10^{6}	$.023231 \times 10^{-6}$
4	$c^3/2\pi$	42.884×10^{29}	$.023319 \times 10^{-29}$
9	ϵc^2	42.872×10^{10}	$.023325 \times 10^{-10}$
10	h^2	42.863×10^{-54}	$.023330 \times 10^{54}$
26*	$\frac{c^2}{\pi G}$	42.931×10^{26}	$.023293 \times 10^{-26}$
27	$4\pi 1846.8^2$	42.859×10^{6}	$.023332 \times 10^{-6}$
31*	$\sqrt{1846.8}$	42.974	$.023270$
32	μv^2	42.861×10^{-12}	$.023331 \times 10^{12}$
33*	$m_{He}\ c^2$	42.923×10^{-6}	$.023300 \times 10^{6}$

TABLE XI

		Functions related to c^{18}	Reciprocals
1*	c^{18}	3.8271×10^{183}	$.26127 \times 10^{-183}$
2*	3^{18}	3.8742×10^{8}	$.25812 \times 10^{-8}$
31*	$\sqrt{1846.8}\, c^2$	3.8624×10^{22}	$.25890 \times 10^{-22}$
34*	$\frac{1}{\sqrt{G}}$	3.8737×10^{3}	$.25815 \times 10^{-3}$
39	$\pi\, 1846.8\, G$	3.8664×10^{-4}	$.26864 \times 10^{4}$

TABLE XII

		Functions related to c^{32}	Reciprocals
1*	c^{32}	1813.1×10^{332}	$.55150 \times 10^{-335}$
2*	3^{32}	1853.0×10^{12}	$.53966 \times 10^{-15}$
10*	h^4	1837.25×10^{-108}	$.54429 \times 10^{105}$
32*	$(\mu v^2)^2$	1837.1×10^{-64}	$.54434 \times 10^{61}$
40	m_p/m_o	1846.8	$.54148 \times 10^{-3}$
41	$\frac{\epsilon}{\sqrt{G}}$	1847.8×10^{-9}	$.54118 \times 10^{6}$

TABLE XIII

		Functions related to c^{34}	Reciprocals
1*	c^{34}	1.6296×10^{356}	$.61360 \times 10^{-356}$
2*	3^{34}	1.6677×10^{16}	$.59962 \times 10^{-16}$
42*	m_p	1.6610×10^{-24}	$.60205 \times 10^{24}$
43	$\frac{\epsilon}{\sqrt{1846.8}\, G}$	1.6656×10^{-4}	$.60038 \times 10^{4}$
44	$\sqrt{\frac{1846.8}{G}}$	1.6647×10^{5}	$.60072 \times 10^{-5}$

TABLE XIV

		Functions related to c^{36}	Reciprocals
1*	c^{36}	$.14646 \times 10^{378}$	6.8278×10^{-378}
2	3^{36}	$.15009 \times 10^{18}$	6.6625×10^{-18}
34	$\frac{1}{G}$	$.15006 \times 10^{8}$	6.664×10^{-8}
42*	$m_p\, c^2$	$.14929 \times 10^{-2}$	6.6985×10^{2}
45	$3/2$	.15000	6.6667

TABLE XV

Relations of Physical Constants to Velocity of Light

1	2	3	4	5	6	7	8
3	3	c	2.99796×10^{10}	$2\pi\epsilon$	2.997×10^{-9}	c	2.998×10^{10}
3^2	9	m_o	8.994×10^{-28}	$\pi\sqrt{1846.8G}$	8.997×10^{-6}	c^2	8.988×10^{20}
3^4	81	m_oc^2	80.84×10^{-8}	Series not important		c^4	80.78×10^{40}
3^6	$.729 \times 10^3$	$1/k$	$.7294 \times 10^{16}$	ϵ/h	$.7286 \times 10^{17}$	c^6	$.7260 \times 10^{63}$
3^8	6.561×10^3	h	6.547×10^{-27}	ω	6.547×10^{15}	c^8	6.525×10^{83}
3^{10}	5.905×10^4	hc^2	5.884×10^{-6}	Series not important		c^{10}	5.865×10^{104}
3^{12}	$.5314 \times 10^6$	ϵ/m_o	$.5303 \times 10^{18}$	v^2/c^2	$.5305 \times 10^{-4}$	c^{12}	$.5271 \times 10^{136}$
3^{14}	4.783×10^6	ϵ	4.770×10^{-10}	m_{He}	4.776×10^{-26}	c^{14}	4.738×10^{146}
3^{16}	43.05×10^6	$m_{He}c^2$	42.92×10^6	μv^2	42.86×10^{-12}	c^{16}	42.58×10^{166}
3^{18}	3.874×10^8	$1/\sqrt{G}$	3.874×10^3	$\pi 1846.8G$	3.866×10^{-4}	c^{18}	3.827×10^{188}
3^{22}	3.138×10^{10}	π	3.1416			c^{22}	3.092×10^{230}
3^{32}	1853.0×10^{12}	m_p/m_o	1846.8	$\epsilon/\sqrt{G}$	1847.8×10^{-9}	c^{32}	1813.1×10^{332}
3^{34}	1.668×10^{16}	m_p	1.661×10^{-24}			c^{34}	1.630×10^{356}
3^{36}	1.501×10^{18}	$1/G$	1.501×10^8			c^{36}	$.1465 \times 10^{378}$

In these tables closely related functions are given the same number. In each table one of these numbers is italicized and all functions different numerically from the value of this italicized function by more than one part in a thousand are marked with an asterisk above the number.

Again ignoring the decimal point (see section 6) it will be at once evident that the agreement shown between the figures given in each table could only occasionally be accidental. It was finally found that all of the different series of figures are related one to another and that apparently all were related to the velocity of light. This relationship is brought out clearly in Table XV. In columns 1 and 2 are shown even powers of 3 to 3^{36}. Similarly in columns 7 and 8 are shown even powers of the velocity of light to c^{36}. Ignoring the decimal point the velocity of light differs from 3 by about one part in fifteen hundred. Nevertheless when both have been raised to the thirty-sixth power the divergence is increased to more than two per cent. The basic constants and a few derived constants are shown in columns 3, 4, 5, and 6. All of these constants (except π) and all of the derived functions shown, and nearly all in the extensive series of functions of which they serve only as examples, lie in value between the respective powers of 3 and c.

This result is amazing.

It follows at once that all other similar functions involving these basic constants will similarly be related numerically through the velocity of light.

One may ask "How can light cause the mass of the electron, the electronic charge, Planck's constant and other constants to have their present values?" A little reflection will show that one has an equal right to turn this question backwards and ask "How is it that the mass of the electron, the electronic charge, Planck's constant and other constants, cause light to have its present velocity?" Still further reflection will show that *Table XV really indicates simply a numerical relationship between these basic constants and light and that a similar table could be constructed using any one of the constants as a basis.* From this standpoint there is nothing necessarily unique about the velocity of light. The importance of Table XV as it stands lies in the fact that it reveals a hitherto unknown numerical relationship between the fundamental constants shown.

It becomes important therefore to study this numerical relationship in detail.

1. Could the Relationship shown be Accidental?

When the first few numerical agreements between the gravitational constant and other constants were noted when dealing with functions, which were not known to be related and which differed in their assigned dimensions, the author was skeptical as to the valuable character of such agreement. As the number of similar functions increased, common sense and experience with calculations were sufficient to enable one to conclude with certainty that the relations were not merely accidental coincidences. Now it is quite possible to state the relations in such form that anyone who desires can apply the laws of probability.

Ten numerical functions are involved as follows:

$2, 3, \pi, c, m_0$ or μ, k, h, ϵ, m_p, G.

The mass loss in the formation of helium is omitted from the list as no one is certain of the derivation of the cosmic rays. It may be granted, for the present, that the similarity between 3 and 2.99796 is accidental. Moreover G. N. Lewis has shown that *h* can be calculated from function 30 of Table VI. This reduces the supposedly unconnected numerical constants to eight.

Moreover G. N. Lewis has recognized the fact that ordinary equations connecting some of the remaining constants can be used to derive what he calls ultimate rational units, and has stated that properly defined units will produce always simple numbers. He has made further use of this fact to calculate h, the constant of Stefan's law and a constant in the equation for the entropy of monatomic[1] gases. His reasoning has been rather vigorously disputed.[2] Bridgman states that Planck was the first to suggest a system of ultimate rational units.

These articles do show that extensive numerical simplification would result from changing our system of units. But the articles do not prove the complete numerical simplicity that exists in our present system (see Table XVII) nor show the connection between this simplicity and the velocity of light. Nor do they prove numerically simple relations between the masses of the proton and electron and gravitation. Moreover the views, as advanced, have not been sufficiently proved to lead to a general recognition of their validity.

Now one might assume roughly that each constant is measured to an accuracy of one part in one thousand. In calculating any given function from a combination of these constants, if there is no actual relation between the constants, a new numerical series should be introduced not only with each combination of constants but with every variation in the power of any constant.

An inspection of the functions calculated will show that the constants are used in some of the various functions to the variation in the powers shown below:

Functions	2	π	c	m_0 or μ	k	h	ϵ	m_p	G
Variation in power used	4	5	4	4	1	3	5	5	3

Both the laws of probability and the theories of numbers will show that combinations of unrelated constants as made could produce agreeing numerals only rarely. (Functions that contain 3 as a factor may be based on wholly accidental agreement). Any explanation of the numerical agreement shown as being a mere series of coincidences is utterly impossible. Still more impos-

---

[1] G. N. Lewis and E. Q. Adams: Phys. Rev., (2) 3, 92 (1914); G. N. Lewis: Phil. Mag. 45, 266 (1923); 49, 739 (1925); G. N. Lewis, G. E. Gibson and W. M. Latimer: J. Am. Chem. Soc., 44, 1008 (1922).

[2] Norman Campbell: Phil. Mag., 47, 159 (1924); O. J. Lodge: 45, 276 (1923); 49, 751 (1925).

sible would it be for the various series of numbers showing such agreement to be accidentally related to each other and to the velocity of light in the manner shown.

The numerical agreements shown must be recognized as a basic fact connecting physical constants.

Yet two more facts must be recognized as having a direct bearing upon any possible accidental numerical agreement among the various functions.

a) Strange as it may seem from the character of the functions calculated, very few of these functions were originally calculated for the purpose of showing numerical agreement. Almost all of the forty-seven functions, shown in Table XVIII, to which the others can be immediately reduced, were either previously recognized as being of "natural" significance, or were calculated by the author in the progress of certain theoretical investigations.

b) As shown under Section 5, headed "Can Exact Numerical Agreement be obtained?" only slight changes are necessary in the values of the constants at present adopted to make nearly all of the functions shown in any given series give numbers agreeing to one part in five thousand. With very many functions there would be perfect agreement.

2. The Exactness of the Agreement

Of all of the results shown in Tables II-XIV only the following differ from the underscored function number in each table by more than one part in five hundred (ignoring the decimal point).

Powers of c and 3. c and 3 differ as to the numerals involved by only about one part in 1500. Nevertheless when the numbers are raised to high powers, a serious multiplication of this difference is of course evident.

Functions 37 Table II, 15 Table IV, 16 Tables III and IV, 36 Table VIII, and 31 Table X, all contain 1846.8 as a factor. As is well known, calculations based on spectroscopic evidence lead to the value of this ratio as about 1838. Calculations based on deflection measurements lead to the value 1846.8. Apparently some such divergence is at the bottom of the disagreement shown by these functions. The recent discovery of an isotope of hydrogen must also be considered.

Functions 10 and 32 of Table XII give 1837.25 and 1837.1 as numerals, confirming evidence based on spectroscopic determinations. Function 42 of Table XIV is the only function included in the tables differing from the expected numeral by more than one part in 500 for whose divergence we can at present find no reason.

A few other additional functions as shown by an asterisk differ from the underscored function by as much as one part in a thousand. These differences usually do not probably arise entirely from the uncertainty of the basic constants used. They arise from the fact that 3, m_o, and μ are probably not always correctly used and from the further fact that certain existing disturbances (as for instance a disturbance caused by the physical dimensions of the particle) should be allowed for and were not. It seemed best to the author not to attempt to apply minor corrections to any function, since such an attempt might lead to the feeling that the agreements had been obtained by unjustifiable modifications.

3. The Dimensions of the Functions compared

The author has already been accused even before the publication of this paper of paying no heed to the dimensions of the functions compared. This may indeed be a grievous error. But if it is, the author is not to blame. The mistake was made by nature. All the author has done is to show that a numerical relation actually exists between quantities of different dimensions. Nature, not the author, must be called on to explain why.

The author indeed has no intention of engaging in the oft repeated discussion of dimensions. It is commonly granted that magnetic permeability and the dielectric constant are mutually related to the velocity of light. That discovery marked a big step forward and leaves us with only three dimensions concerning which to worry—mass, length, and time, since temperature is known to be related to kinetic energy. The relativity theory has insisted upon a connection between length and time and the velocity of light is concerned also with that relation. The implied connection found by the author is of a very different character, but again concerns the velocity of light and at any rate the imagination is not further strained. This leaves only mass to worry about. No one knows what causes mass, but it is a step forward to find that mass also is connected with light and time, and again through the velocity of light. Others have advanced ideas concerning the possible electromagnetic nature of mass. Such theories presuppose the possibility of omitting mass as an ultimate dimension.

The idea of dimensions can be made to serve a very useful purpose, but there is often times confusion in their use. One is quite accustomed to the idea that mv represents the momentum of a moving particle and $1/2\ mv^2$ its kinetic energy. But the fact that we have chosen to square the velocity of the particle, and give the name energy to the function thus obtained, has not changed the actual velocity of the particle one iota. The particle still has the same velocity and the dimensions attributable to the particle are still ml/t. We have merely chosen to take two other dimensions l/t, which really belonged to the space traversed by the particle, and have attributed these dimensions also to the particle. This is mathematically very convenient, but it should not be allowed to obscure the fact that energy is in reality a function of the space traversed as well as of the particle, and is dependent on both.

So mass should be regarded as a dimension of a particle only until we realize the true nature of the ultimate property which is its cause. Personally the author believes ultimately that mass will be found to be a property of the physical dimensions of the particle concerned and of the energy of the surrounding space. In other words, it is a property concerned with the distribution of energy in space.

4. The Relationship between 2, 3, π, and c

At first one of the most baffling phases of the numerical relations found to exist was the fact that ignoring the decimal point the following relations were very approximately true:—

TABLE XVI

Relations between 2, 3, π and c

	Corresponding Value of c		Corresponding Value of c
$2 = 1/c^{35}$	3.00005	$3\pi = c^{23}$	3.00015
$3 = c$	3.00000	$4\pi = 1/c^{48}$	2.99985
$3/2 = c^{36}$	2.99995	$6\pi = 1/c^{12}$	2.999565
$\pi = c^{22}$	3.00019	$3/2\pi = c^{14}$	2.99963
$2\pi = 1/c^{13}$	2.999601		

All of the functions can be derived from those for 2π, 4π and 6π, or from any three of the functions that contain the factors 2, 3 and π. The equations do not necessarily exist simultaneously in nature with regard to the same functions and the author thought that a careful determination of the corresponding value of c might lead to the rejection of some one of the relations. But the greatest divergence of any of the values of c from the mean value is as shown in Table XVI, only one part in 10,000. Another surprising result of this check is that all values of c are considerably above the actual observed value. For a discussion of this point see under Section 5.

Actually in nature the relationship probably arises from such equations as

$$1/2\pi c = \text{a function which reduces numerically to } c^{12}, \text{ or}$$

$$4\pi\,(1846.8)^2 = \text{a function which reduces numerically to } c^{16}$$

and from the possible accidental relation numerically of 3 to 2.99796. If the natural relations concerned could be determined all of the others could be discarded as of no consequence in spite of their very close similarity numerically to other naturally arising functions. Curiously enough the first Bohr orbit of the electron and proton is almost exactly $1000/c$ and the orbit which would correspond with a loss of energy equivalent to Millikan's longest cosmic ray is $1/1000c$. The corresponding radii of the orbits are $1000/2\pi c$ and $1/2000\pi c$. Other unique points in nature give rise to similar simple relations and serve to make clear that such relations concerning π as those shown above will exist. Why the orbits are at the points stated is a much more baffling problem.

No reason is known why $8\sqrt[3]{\pi^6/15}$ should be related to c^7,* nor why 3π should be related to $c^{12} \times 10^{-5/4}$.

5. Can Exact Numerical Agreement be obtained?

The best way to answer this question is to choose a single function and calculate all values and constants from this function. For this purpose, we

---

* See G. N. Lewis and E. Q. Adams: Phys. Rev. (2) **3**, p. 92 (1914).

choose the function $2\pi c = 1/c^{12}$. The choice of the function may be regarded for the present as somewhat arbitrary although it was selected because the radius of the first Bohr orbit as stated above is $1000/2\pi c$. The results of the calculation are given in Table XVII.

TABLE XVII

Calculation of Physical Constants from the Equation $1/2\pi c = c^{12}$

		Observed	Calculated
c	c	$(2.99796 \pm 0.00004) \times 10^{10}$	2.99960
c^2	m_o	$(8.994 \pm 0.014) \times 10^{-28}$	8.99761
c^6	$1/k$	$(7.294 \pm 0.0074) \times 10^{15}$	7.28415
c^8	h	$(6.547 \pm 0.008) \times 10^{-27}$	6.55402
c^{14}	ϵ	$(4.770 \pm 0.005) \times 10^{-10}$	4.77401
c^{31}	m_p	$(1.6610 \pm 0.0017) \times 10^{-24}$	1.66014
c^{36}	$1/G$	$(1.5006 \pm 0.0005) \times 10^{7}$	1.49373

The decimal points have again been ignored in making this calculation (See Section 6).

The divergence of $1/k$ is probably due to the size of the molecules of the gas. This point will be considered in a later paper.

As regards the velocity of light it should be borne in mind that if an ether does exist made up of discrete particles, and if a mechanical explanation of the universe is possible, then the velocity of light will differ from the velocity of the particles that cause the wave.

Table XVII at the present time should be taken only as an indication of the possible aid that may be obtained from the relations shown in determining more accurately the value of physical constants. The author regards the constants as calculated at the present time as possible "ideal" constants that would be produced if the ether particles were reduced to points which retained their present properties.

Use can be made of the facts brought out by the table to bring into prominence certain simple relations which should aid in arriving at the underlying cause of the relations shown. Thus it is useful to recognize that using the calculated constants $Gm_om_p = 10^{-58}$ exactly, and that numerous similar exact relations will hold.

The facts given may furnish a clue to the cause of the present discrepancy between certain spectroscopic and deflection measurements.

There are numerous other possibilities suggested. The author was led by a simple speculation in connection with the facts to the discovery that the mass loss causing Millikan's longest cosmic rays is numerically 7.294 times Planck's constant and Planck's constant is of course numerically 7.279 times the mass of the electron. One may indeed be allowed to guess that perhaps the mass loss represented by these rays is more accurately 7.284 times Planck's constant, and that the mass loss represented by the shortest cosmic rays is 7.284 times the mass loss represented by the longest rays.

The first Bohr orbit of the electron and proton is 1000/c in length and the orbit under the same law required for Millikan's longest cosmic rays is 1/1000c. Is it possible that these cosmic rays have their origin in the formation of the proton itself? Is it possible that the proton is produced by two electrons moving in an orbit with semi major axis 1.526×10^{-16} centimeters? Is it possible for an electron to move in an orbit which would normally give to the electron a velocity above the velocity of light? Does the motion of an electron in such an orbit give rise to a positive charge and a large increase in mass? Is the electron an ether particle which has "lost" some of its velocity? At the present time these are mere speculations caused by an attempt to follow back ideas suggested by the relations shown. They are cited here only to show that the facts followed back suggest possibilities from which perhaps the false may be sifted.

6. The Decimal Point

In calling attention to the numerical relationships the decimal point has been ignored. In considering the entire function the decimal point cannot be ignored. As explained, Table XV is artificial in that it appears to make all of the constants depend numerically on the velocity of light. What the table really indicates is a numerical relation among the various constants shown and any constant shown could be made the basis for the table. The correct ultimate table would probably (from the author's point of view) be based in part on more fundamental constants. Between certain constants reciprocal relations exist and one or more physical entities which partly give rise to a property are eliminated. Thus time does not appear directly in Table XV nor does the volume of the masses.

The constants really concerned in the relations appear to be 2, 3, π and c. Using some of these numbers above it is quite possible to write such functions as $h = \frac{3^{11}}{c^3}$, $m_p = \frac{3^{38}}{c^4}$, $\frac{1}{G} = \frac{3^{37}}{c}$, where the 3 is more exactly 2.9996. Numerous similar relations could be written all of no value unless the true relations existing in nature were found. Introducing some theoretical considerations the author suspects strongly that 2, 3, π, and c will all be concerned in the equations which really represent nature. Thus G appears numerically to be related to c^{36}. In reality the relations $G = 2000/c$ and $1/\pi G = 4.7765 \times 10^6$ are probably a somewhat nearer approach to nature, nor is the possible introduction of a logarithmic relation absurd, either theoretically or numerically.

It should be realized that the ratio of the functions in any one of the Tables II-XIV will give a power of 10 very nearly, and that if the calculated constants shown in Table XVII are used then the ratio will often be an exact power of 10. When this fact is considered and it is further realized that we must go one step back of our present physical constants in representing nature in the simplest manner then the fact that we have ignored the decimal point in deriving the relations existing with our present units should not cause any feeling of skepticism. There is nothing mystical concerning the relations.

7. Summary of Functions calculated

A summary of the more important functions calculated are shown in Table XVIII. It appears somewhat strange that the natural functions seldom lead to simple numerical relations involving odd powers of c, though of course a few such functions have assumed some importance.

TABLE XVIII

Summary of Functions

1	c	2.99796	$\times 10^{10}$
2	3	3.00000	
13	$2\pi\epsilon$	2.9971	$\times 10^{-9}$
14	$\frac{3Gc}{2}$	2.9967	$\times 10^{3}$
37	$\frac{1}{2 \times 1846.8m_o}$	3.0102	$\times 10^{23}$
12	m_o	8.994	$\times 10^{-28}$
25	$\pi\sqrt{1846.8G}$	8.9969	$\times 10^{-6}$
24	$\frac{\epsilon^3}{1846.8h}$	8.9762	$\times 10^{-6}$
15	$\frac{\sqrt{1846.8}}{\epsilon}$	9.0093	$\times 10^{10}$
16	$\frac{1}{1846.8G}$	8.1255	$\times 10^{3}$
46	$\frac{\sqrt{1846.8m_o}}{\epsilon}$	8.1024	$\times 10^{17}$
21	h/m_o	7.279	
20	m_{H_o}/h	7.294	
8	ϵ/h	7.2860	$\times 10^{16}$
19	$\tau = 1/k$	7.2886	$\times 10^{15}$
18	$3/2\pi h$	7.293	$\times 10^{25}$
22	$\frac{(2\pi\epsilon^2)^2}{h^3}\frac{v^2}{h}$	7.283	$\times 10^{42}$
10	h	6.547	$\times 10^{-27}$
29	$\omega = 2R_Hc$	6.5467	$\times 10^{15}$
30	$\frac{(4\pi\epsilon)^2}{c}\sqrt[3]{\frac{8\pi^5}{15}}$	6.5497	$\times 10^{-27}$
3	$1/6\pi$	53.052	$\times 10^{-3}$
5	ϵ/m_o	53.035	$\times 10^{16}$
6	a	53.084	$\times 10^{-10}$
4	$1/2\pi c$	53.088	$\times 10^{-13}$
14	$1/3\pi Gc$	53.110	$\times 10^{-6}$
11	$\frac{\epsilon}{\pi\sqrt{1846.8G}}$	53.019	$\times 10^{-6}$
23	$\frac{\epsilon}{(2\pi\ 1846.8)^2G}$	53.161	$\times 10^{-11}$
36	$\frac{8\pi 1846.8^3}{3}$	52.768	$\times 10^{9}$
35	$\frac{\epsilon}{\sqrt{m_oc}}$	53.054	$\times 10^{-8}$
17	3π	53.000	$\times 10^{5}/4$
9	ϵ	4.770	$\times 10^{-10}$
33	m_{H_o}	4.7757	$\times 10^{-26}$
26	$1/\pi G$	4.7765	$\times 10^{6}$
7	v^2	4.7681	$\times 10^{16}$
4	$c/2\pi$	4.7714	$\times 10^{9}$
1	$3/2\pi$	4.7746	$\times 10^{-1}$
47	$\beta = h/k$	4.7753	$\times 10^{-11}$
28	$\mu a = m_oa_o = m_pa_p$	4.7718	$\times 10^{-36}$
38	$\frac{4\pi(1846.8)^2}{m_o}$	4.7653	$\times 10^{31}$
27	$4\pi 1846.8^2$	42.859	$\times 10^{6}$
32	μv^2	42.861	$\times 10^{-12}$
31	$\sqrt{1846.8}$	42.9744	
39	$\pi 1846.8G$	3.8664	$\times 10^{-4}$
40	$\frac{m_p}{m_o}$	1846.8	
41	$\epsilon/\sqrt{G}$	1847.8	$\times 10^{-9}$
42	m_p	1.6610	$\times 10^{-24}$
43	$\frac{\epsilon}{\sqrt{1846.8G}}$	1.6656	$\times 10^{-4}$
44	$\sqrt{\frac{1846.8}{G}}$	1.6647	$\times 10^{5}$
34	$1/G$	.15006	$\times 10^{8}$
45	$3/2$	.15000	

The functions shown in Table XVIII are all dependent upon the relations already discussed between the more fundamental constants 2, 3, π, c, m_o, k, h, ϵ, m_p, and G. The derived functions give however sometimes an unexpected hint as to the nature of the relations between the fundamental constants. Actually a study of the derived functions led to the finding of the numerical relationship between the fundamental constants. Their further study may suggest the complete relationship.

8. Some Suggestions as to the Ultimate Meaning of the Facts

The author does not believe that there is anything in the facts brought out which justifies representing mass or time as a length, or which requires very radical readjustment of primary ideas. A simple numerical relation has been found to exist between fundamental physical constants and these simple relations would be extended by new definitions of atomic weights and certain other constants. But the physical realities existing remain as before.

On the other hand the simple numerical relations proved to exist indicate actual relations between the physical entities concerned of a nature not yet fully realized. For example no simple numerical relation will exist between the mass of an atom of tin or lead and the velocity of light. If therefore a simple relation is found between the mass of the proton and the mass of the electron and the velocity of light a fact has been discovered which requires some sort of an explanation. For there is no *a priori* reason why the complexity of the proton and electron might not prohibit any simple numerical relation between them and between other physical constants.

The author believes that the facts shown are of such a nature as to point rather strongly to the idea that a mechanical explanation of the universe is possible. Certain particles (masses) existed in the universe. A certain amount of motion (energy) was available, and finally distributed itself among the existing particles. As a result we finally have "created" the masses of proton and electron, electronic charge, Planck's constant, the velocity of light, gravitation, and the various attractive forces and results dependent upon them. Protons and electrons apparently exist in equal numbers and the suspicion that both are "created" from some possible simpler particle, such as an ether particle, is increased by the numerical relationships discovered.

Following out the ideas above in a little more detail it seems to the author probable that an ultimate unit of time is desirable and probably would be best defined as the time required for an ether particle to traverse the space which it occupies due to its motion. This is in order to prevent undue multiplication of the space occupied by the particle in relations concerning its motion. Then if it be assumed that this fundamental space traversed in a unit of time bears a simple relation to the orbit which defines the proton and that the diameters of the particles themselves are not greater than 1/12 of the diameter of this orbit, the simple numerical relations shown might possibly follow.

Summary

1. Simple numerical relations have been shown to exist between the constants π, m_o, $1/k$, h, ϵ, m_p, and $1/G$, and the velocity of light, and therefore such relations exist between all functions calculated from them.

2. The fact that such a relation exists proves a connection between the constants not as yet understood.

3. The above constants can be calculated from the equation $1/2\pi c = c^{12}$ and their relation to certain powers of the velocity of light, if the decimal point is ignored. This indicates that the relation which exists is of a very simple nature.

University of South Carolina,
Columbia, S. C.
January 21, 1932.

THE INFLUENCE OF ELECTROLYTES ON THE SPECIFIC HEAT OF WATER[*]

BY FRANK URBAN

The Hofmeister series or lyotropic series[1,2,3,4] was discovered by Hofmeister. It deals with the effects of neutral salts on the protein colloids. The anion series is F^-, ClO_3^-, CO_3^{--}, SO_4^{--}, tartrate, citrate, acetate, Cl^-, Br^-, NO_3^-, I^-, CNS^-; the cation series Ba^{++}, Sr^{++}, Ca^{++}, Mg^{++}, Li^+, Na^+, K^+, $(NH_4)^+$, Rb^+, Cs^+. It is in this order that these ions influence the swelling, osmotic pressure and viscosity of protein colloids. These ions act in an analogous manner on the temperature of gel formation of a gelatine solution, and on the time of gelation. The ions first in the series have the greatest effect. The temperatures at which swelling of starch occurs, also follows the Hofmeister series. It should be noted that the cation series is less definite and less well established than the anion series.

The series is encountered also outside of the field of protein solutions. Thus, it has been shown that the solubility of difficultly soluble substances, especially of gases, is influenced by the addition of neutral salts, in the order of the Hofmeister series. The series is also encountered in the order of the change of the viscosity of water by salts. The saponification of esters, the surface tension of water, and the electrolytic solution pressure are all influenced by neutral salts in the order of the Hofmeister series. The anomalies in the lowering of the freezing point shown by concentrated solutions differ for different salts; the anions may be arranged to form a Hofmeister series.

Bancroft[5] offered good arguments to prove that these phenomena associated with the Hofmeister series may be due to a change in the solvent (water). He showed that they can not be explained on the basis of specific colloidal effects.

That a shift in the equilibrium between different molecular species can bring about decided changes in the property of a solvent has been demonstrated in the case of alcohol. Bancroft[5] mentions the work of Byron and of Lunge who showed that ether plays no direct part in the peptization of pyroxylin by an alcohol-ether mixture. Ether displaces the equilibrium in the direction of the polymer. The latter is the true peptizing agent. If this is so, then it should be possible to peptize pyroxylin at low temperatures by alcohol alone. Kugelmass, McBain, and Byron found that pyroxylin is peptized by alcohol at low temperatures.

---

[*] This communication is based on a thesis submitted for the degree of Doctor of Philosophy at the University of Wisconsin in 1928, under the direction of Professor Farrington Daniels.

[1] Hofmeister: Archiv exp. Pathol., 25, 13 (1888); 28, 210 (1891).

[2] Spiro: Hofmeister's Beitr., 5, 276 (1904).

[3] Odén and Anderson: J. Phys. Chem., 25, 311 (1921).

[4] Hoeber: Physik. Chemie der Zelle, 1, 267 (1922).

[5] Bancroft: J. Phys. Chem., 30, 1194 (1926).

It seemed promising therefore to study the water equilibrium in connection with these questions. A thermodynamic method was chosen for this purpose. We felt that a determination of the specific heats of solutions, containing the anions and cations of the Hofmeister series, from which the partial molal heats of solvent and solute and their temperature coefficients can be calculated would lead to interesting conclusions. It was reasoned that the abnormally high specific heat of water is occasioned by the presence of polymerized molecules which are broken down, as the temperature is raised, into simpler molecules with the absorption of heat. If the presence of ions of the Hofmeister series causes some of these larger molecules to depolymerize then there should be fewer of the large molecules available for absorbing heat and the heat capacity of water in the solution should be less than the heat capacity of pure water.

The object of this particular investigation was not to obtain the greatest possible precision in the measurement of aqueous solutions of electrolytes but rather to cover a considerable range of temperature and concentration with salts which are significant in the Hofmeister series. Dilute solutions, which are particularly significant for theories of ionization, were not investigated but emphasis was placed on concentrated solutions because in them the change in the solvent is most pronounced. The solvent rather than the solute was the center of interest.

Apparatus

For the investigation, an adiabatic calorimeter was used. It is obvious that the heat leakage can be reduced almost to zero, if the system can be made perfectly adiabatic. This result can be achieved by electrolytic heating[6] of the outer bath and by our automatic adiabatic control.

The apparatus used in the determinations of specific heats is shown diagrammatically in Fig. 1. It was a modified form of the apparatus of Williams and Daniels,[7] in which temperatures are measured with a platinum resistance thermometer set in the *outer* bath so as to eliminate thermal leakage along the thermometer to the calorimeter. The readings are taken only when the calorimeter and the outer bath have identically the same temperature as indicated by a zero reading on a thermocouple. The solution was contained in a cylindrical solid silver cup 1, having a capacity of about 0.6 liter supported in an enclosing vessel with an air gap O of 9 mm. between the two. It rested on three Bakelite points. The enclosing vessel 2 was of copper, fitted with a threaded cover of bronze. The cover was provided with an upright tube for the stirrer N, and conical stuffing boxes for the admission of the heater H, and thermocouple C. The heater leads ran through the bath for about 20 cm. to prevent thermal leakage to the air of the laboratory. The cover, with all of the parts supported by it, was screwed into a ring brazed to the copper cylinder. A mixture of oil and graphite in the threads kept the joints tight and acted as a lubricant.

---

[6] Daniels: J. Am. Chem. Soc., 38, 1473 (1916).

[7] Williams and Daniels: J. Am. Chem. Soc., 46, 903 (1924).

The inner stirrer shaft N was made of Bakelite and carried two silver propellers. The Bakelite shaft was screwed to a brass shaft. This upper shaft rotated on two ball bearings. A cap Q attached to it, rotated in the liquid of the outer bath, thus forming a seal and preventing the movement of air, and reducing losses by evaporation to a minimum.

The stirring was found to be most satisfactory at about 130 R.P.M. At this speed, the stirring of the solution was quite efficient and the heat of stirring was of the order of 0.001°C per minute. The exact value was obtained for each determination.

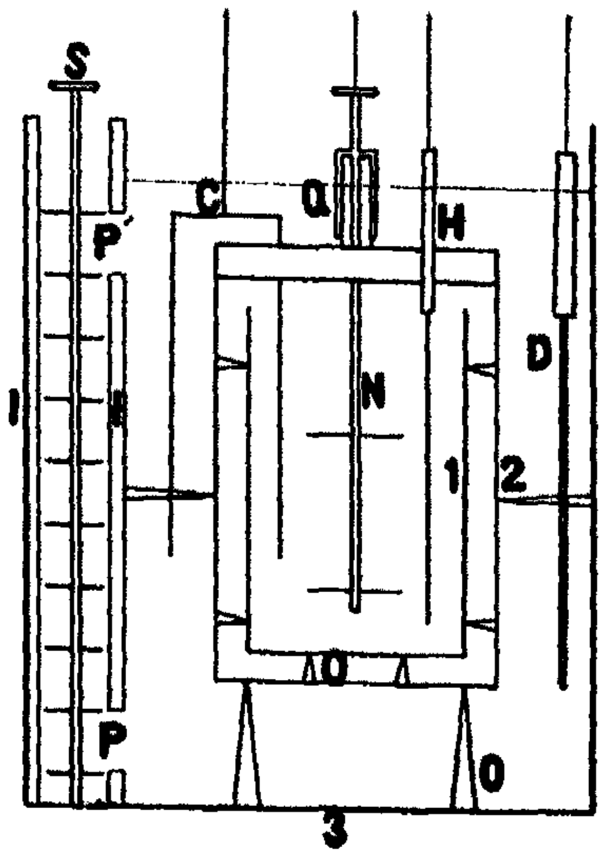


Fig. 1
Calorimeter

A thermel, C, of 16 copper-constantan thermocouples was enclosed in a thin glass tube, and connected to a Leeds and Northrup H. S. galvanometer having a sensitivity of 10 mm. per microvolt at 1 m. The scale was placed at a distance of 4.5 meters from the galvanometer and each cm. of the scale corresponded to a temperature difference of 0.0006°. The resistance of the thermel was 40 ohms. The enclosing tube was filled with a light mineral oil to reduce the thermal lag. At lower temperatures ice water was circulated through a cooling jacket I in the outer bath. Thorough stirring of the outer bath was obtained by means of a stirrer, rotating at about 1800 R.P.M. in the cylindrical compartment S, which sucked the water in at P and emitted it at P′. At temperatures above room temperature, when the outer bath had a tendency to cool off, an adjustable reactance in series with an electric heating coil kept the outer bath nearly up to the temperature of the experiment. This reactance could be set to deliver energy just sufficient to compensate for heat losses by evaporation and cooling.

A Leeds and Northrup calorimetric, platinum-resistance thermometer D, in the outer bath, indicated the temperature of the outside bath. The temperature in the calorimeter was exactly equal to that indicated by the resistance thermometer in the outer bath when the thermel-galvanometer registered zero. If it did not register exactly zero a small correction, amounting to 0.002° or less was applied. Usually, no correction was necessary.

The platinum thermometer was read on a Leeds and Northrup high precision bridge, in connection with a high-sensitivity galvanometer. It was calibrated at the ice point, the boiling point of water and the transition temperature of sodium sulphate. The sensitivity was such that changes of 0.0005° C could readily be detected.

The Automatic Adiabatic Control

The adiabatic control was made automatic with the help of a selenium cell. Light from a 60-watt automobile head light was projected on the mirror of the galvanometer, connected with the thermel. This light was cooled by a stream of water. The galvanometer mirror reflected this light on a selenium cell which was located at a distance of about 4.6 meters from the galvanometer. The cell had a resistance of about 120,000 ohms, when illuminated; in the dark, its resistance increased to about 200,000 ohms. The cell was in series with a grid leak of 250,000 ohms and three dry cells. The terminals of the grid leak were connected to the grid and filament of a radio tube (Cunningham, Type EX-112), respectively. Any change in the resistance of the selenium cell caused a fluctuation in the space current of the radio tube. The space current was about 2 milli-amp. when the selenium cell was in the dark; and 1 milli-amp. when it was illuminated. The space current flowed through a micro-relay. A counter E.M.F., supplied by a storage battery, was put across the micro-relay. It yielded exactly one milliampere and thus the net effect was a current of one milliampere when the cell was dark, but no current passed when the cell was illuminated. If small fluctuations occurred in the space current, the counter E.M.F. was immediately adjusted by varying the resistance in a 10,000 ohm resistance box, in series with the storage battery. The micro-relay in turn actuated larger relays, which controlled the heating of the outer-bath. When the outer bath was colder than the calorimeter the beam of light was thrown to the left of the selenium cell, the micro-relay was closed and the outer bath was heated by the passage of the current through the water. The outer bath then heated up faster than the calorimeter and threw the beam of light of the thermal galvanometer on the selenium cell. The micro-relay was then released, the heating of the outer bath ceased and the beam swung back to the left, whereupon the operation was repeated. A series of small mirrors arranged as a parabola was placed at the right of the selenium cell to reflect the beam back onto the cell in case it swung past, on account of the time-lag of the selenium cell.

The adiabatic control fluctuated between ± 0.0015° and ± 0.004° under average conditions. In order to obtain best results, the conductance of the outer bath had to be properly adjusted, as too high a conductance produced too much heat and caused the beam of light to travel entirely across and beyond the parabolic mirror. In actual operation, the conductance could be satisfactorily maintained by adding distilled water to the outer bath from day to day, as needed, to replace evaporation losses.

Procedure

Before starting a determination, ice water was pumped through the calorimeter jacket I (Fig. 1) and the temperature of the outer bath lowered as much as possible (usually to about 6° or 7°C). In the meantime, the solutions were prepared, by weighing a certain amount of salt and conductance water into a Pyrex flask. This solution was then cooled and poured into the silver can, The can, together with the surrounding copper vessel and brass lid had been previously weighed. The brass lid was screwed on again at once, to avoid condensation of moisture of the air on the cold silver cup. The cap attached to the upper shaft was closed, temporarily, by two halves of a rubber stopper.

The solution was placed in the outer bath of the calorimeter immediately after weighing. Measured amounts of electrical energy were then passed through the heater H, (Fig. 1) for definite time intervals. The time was measured with a calibrated stop watch which read to 0.1 second. While the input of energy into the inner solution continued, the outer bath automatically maintained itself at the same temperature as the solution. After a definite interval, the input of electrical energy into the inner solution was discontinued and its temperature determined, as outlined above. The reading was not taken immediately, but after a period of from 5 to 10 minutes, so as to insure that the solution had come to complete thermal equilibrium. The length of this period was determined and a corresponding correction, for the heat produced by the stirrer, was applied.

Three different heaters were used in the investigation, having resistances of approximately 31, 34 and 40 ohms. They were all made of Constantan wire No. 32, wound in a bifilar manner on a mica strip. The constantan wire was silver-soldered to copper leads. The primary sheath of all three heaters consisted of thin (0.05 mm) copper foil, which was soldered over the heating element. Thin mica sheets served as insulation. Two of the heaters were heavily silver-plated, the plating being more than 0.12 mm. thick. The third heater was not silver-plated, but coated with Bakelite varnish and baked. In no case were we able to detect contamination of our solutions by copper. The fact that the different heaters showed no difference in the specific heat measurements lent confidence to the results.

The electrical system was similar to that described by Williams and Daniels.[8] Ten storage cells supplied the energy which passed through the heater and a standard resistance. In parallel with the heater, there was a volt-box, having a ratio of 20.078:1. The volt-box and standard resistance and standard cell were calibrated by the Wisconsin Electrical Standards Laboratory. The heater, the multiplier, and the standard resistance were all connected to a sensitive potentiometer. The scale was placed at a distance of six meters from the galvanometer.

Determination of Specific Heats

The procedure and calculations are illustrated in Table I with the details of a single experiment.

In this particular experiment the calorimeter contained 584.86 grams (corrected to vacuum) of a 0.500 molal solution of potassium chloride (0.5 mole KCl per 1000 g. of water). In the first column are given the time intervals in seconds during which the electrical heater was turned on. In the second column are given the time intervals which elapsed between turning off the

---

[8] Williams and Daniels: J. Am. Chem. Soc., 46, 908 (1924).

TABLE I

Details of a Calorimetric Measurement

1 Time Heating Seconds	2 Time After Heating	3 Temperature C.	4 Temperature Increase	5 Resist. Heater Ohms	6 Energy Input Joules	7 Input per deg. Joules
0	—	8.6766	—	—	—	—
1830.5	425	12.3220	3.6024	31.872	8652.1	2401.8
1830.1	744	15.9603	3.5949	31.878	8650.7	2406.4
1830.3	724	19.5926	3.3934	31.887	8654.3	2408.4
1830.0	516	23.2210	3.5959	31.889	8652.5	2406.2
1830.1	440	26.8513	3.6015	31.893	8564.3	2403.0
1829.9	611	30.4776	3.5997	31.897	8653.9	2404.1
1830.1	648	34.1009	3.6019	31.901	8656.5	2403.3
1830.1	820	37.7302	3.6082	31.905	8657.6	2399.4

heating current and the measuring of the temperature. The data of the second column are used only in calculating the stirring correction. The temperatures are given in column 3. One of these includes a correction of 0.0015° and another a correction of 0.0022° because the differential thermel was not exactly at zero when the resistance thermometer was read. The others involved no correction. Column 4 gives the actual temperature increase produced by the electrical heating—i.e. the intervals between the figures of column 4 from which has been subtracted the temperature rise due to stirring. This correction due to the heat of stirring was determined over a considerable period of time at the end of each experiment (40°C). Experiments showed that the change in the heat of stirring with the temperature was small enough to neglect.

The current through the system was 0.51066 ampere as measured with the potentiometer across a standard 1 ohm resistance. It was kept constant at all times by raising or lowering a resistance wire in a tube of mercury, placed in series with the heater. The voltage used for measuring the potential drop across the heater drew a small amount of current, 0.01527 ampere, which was subtracted from the total current giving a current of 0.49539 ampere through the heating coil.

The resistances of the heating unit, given in column 5, were obtained by dividing the potential drop across the heater by the current flowing through the heater. The total input of electrical energy in the heater was calculated by multiplying the square of the current through the heater by the resistance and by the time. These values expressed in joules are given in column 6. Division of these values by the temperature interval gives the average number of joules required to raise the calorimeter and the solution through 1°C.

The water equivalent of the calorimeter was determined by similar measurements using pure water, and a curve giving the water equivalent at each temperature was prepared. For the first interval (8.6 to 12.2) it had a value of 78.1 joules per degree. Since 2401.8 joules of heat was required to raise the calorimeter and its contents through 1° in this temperature range, 2323.7

joules was required to raise the contents (584.86 grams of 0.500 molal potassium chloride) through 1°. The heat required to raise one gram of the solution through 1° in this interval is then 3.973 joules or 0.9494 $cal_{15°}$[9].

It is evident that the specific heats calculated in this way are average specific heats covering the temperature interval for which they were determined. This interval varied between 3.5° and 4.5° in the different determinations.

Summary of Results

The average specific heats ($calories_{15°}$ per degree per gram of solution), calculated in the manner just described, were plotted against temperature on a large scale and the interpolated values are summarized in Table II.

TABLE II

Salt	m*	10°	15°	20°	25°	30°	35°	40°
KCl	2.000	.8423	.8431	.8439	.8448	.8457	.8466	.8474
KCl	1.000	.9144	.9123	.9131	.9140	.9148	.9157	(.9166)
KCl	0.500	.9512	.9519	.9526	.9532	.9539	.9547	.9555
KCl	0.100	.9868	.9865	.9862	.9859	.9856	.9853	.9850
$BaCl_2$	1.384	.7332	.7366	.7378	.7389	.7430	.7470	.7482
$BaCl_2$	1.000	.7784	.7875	.7892	.7900	.7906	.7914	.7922
$BaCl_2$	0.500	.8758	.8782	.8798	.8814	.8832	.8848	.8856
$BaCl_2$	0.100	.9615	.9623	.9623	.9620	.9614	.9610	.9606
KCNS	2.625	.8078	.8120	.8146	.8160	.8162	.8156	.8142
KCNS	1.257	.8908^a	.8935	.8950	.8958	.8963	.8963	.8963
KCNS	0.500	.9501	.9517	.9524	.9530	.9534	.9537	.9537
K tartrate	2.000	.7568^b	.7611	.7630	.7639	.7648	.7658	.7667
K tartrate	1.000	.8388^a	.8462	.8473	.8484	.8496	.8507	.8518
K tartrate	0.500	.9104^d	.9116	.9139	.9147	.9155	.9164	.9172
K tartrate	0.100	.9553	.9587	.9597	.9607	.9617	.9627	—
$KC_2H_3O_2$	2.360	.8440^a	.8479	.8515	.8530	.8530	.8526	.8520
$KC_2H_3O_2$	0.974	.9202	.9240	.9266	.9271	.9270	.9266	.9259
$KC_2H_3O_2$	0.479	.9528	.9553	.9561	.9560	.9555	.9548	.9542
$KC_2H_3O_2$	0.249	.9816	.9843	.9849	.9845	.9835	.9824	.9813
KBr	2.000	.7787^c	.7795	.7856	.7853	.7855	.7880	.7888
NH_4Cl	2.000	—	—	.8904	.8915	.8925	.8936	.8946

^{a} = 11°; ^{b} = 12°; ^{c} = 13°; ^{d} = 14° instead of 10°.

* Mols per 1000 grams of water.

---

[9] The conversion factor 4.185 given by Int. Crit. Tables is used in this research.

It is probable that the uncertainty in the data presented in this investigation was usually within 1 or 2 parts per thousand. The errors in the standard resistance, standard cell, volt-box calibration and measurement of time were probably less than 0.02 per cent in each case. The adiabatic control was so perfect that the thermal leakage may be considered entirely negligible. The error due to evaporation of the water, which saturates the air gap in the calorimeter as the temperature is raised, was also negligible. Assuming complete saturation a calculation showed that the evaporation amounted to 0.008 cal. per degree at 7° and 0.04 cal. per degree at 40°. The greatest source of error was involved in the correction for the heat of stirring. Assuming an error of 10 per cent in this quantity the uncertainty in the final result would be 0.1 per cent since the heat of stirring was about 1 per cent of the total heating effect. This error could be reduced with better design and with greater constancy in the rate of stirring.

Partial Molal Heat Capacities

The partial molal heat capacities of potassium chloride $\bar{C}_{p_2}$, were calculated by plotting the apparent molal heat capacity, Φ, against the logarithm of the molality,[10] dividing the slope of the tangent by 2.303 and adding the ordinate. $\bar{C}_{p_2}$ having been found, we obtain $\bar{C}_{p_1}$ (the partial molal heat capacity of the water) by substituting in the equation

$$C_p = n_1 \bar{C}_{p_1} + n_2 \bar{C}_{p_2}.$$

The partial specific heats of the solvent in 0.1 m, 0.5 m, 1.0 m and 2.0 m KCl solutions are shown in Table III.

TABLE III

Partial Specific Heats of Water in Solutions of Potassium Chloride

$\bar{C}_{p_1}$	10°C	15°	20°	25°	30°	35°	40°
0.1 m KCl	.9970	.9965	.9965				
0.5 m KCl	.9948	.9948	.9954	.9952	.9955	.9960	.9971
1.0 m KCl	.9928	.9934	.9940	.9950	.9952	.9961	.9973
2.0 m KCl	.9863	.9899	.9916	.9920	.9929	.9948	.9968

These values have been plotted in Fig. 2. The 25°C value of 0.1 m KCl (Curve 1) is the value of Randall and Rossini.[14] Curves 2, 3, and 4 represent the partial specific heats of water in 0.5 m, 1.0 m and 2.0 m KCl. Rossini's 25°C values, which are believed to be accurate to 0.01%, were used as reference points, i.e., a parallel displacement of our curves was made so that they now run through Rossini's values. The curve AB is the specific heat of pure water, the line CB the ideal specific heat of water which does not contain Type Ice I molecules, according to Tammann.[11]

---

[10] Lewis and Randall: "Thermodynamics and the Free Energy of Chemical Substances," 37 (1923).

[11] Tammann: Z. anorg. Chem., 158, 1 (1926).

It will be easier to understand the significance of these curves, if we know how the partial specific volumes in 0.1 m, 0.5 m, 1.0 m and 2.0 m KCl change with the temperature. For this reason, we have calculated the partial molal volumes of potassium chloride of Baxter and Wallace,[12] by plotting the volume of the solution against the molality and determining the slope of the tangents.[13] The partial specific volumes of water in these solutions, calculated from these values, are shown in Table IV.

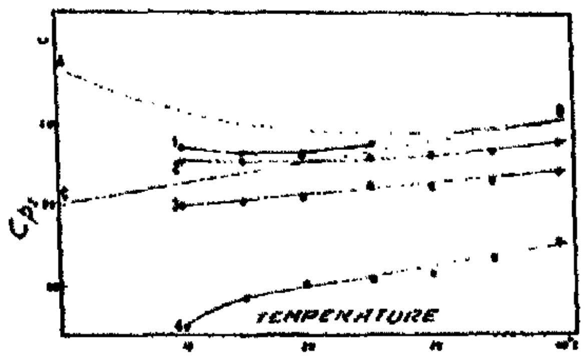


Fig. 2
Partial specific heat capacity of water in solutions of potassium chloride

TABLE IV

Partial Specific Volumes of Water in Solutions of Potassium Chloride

$\overline{V}_{p_1}$	0°C.	25°C.	50°C.	70°C.	100°C.
0.1 m KCl	.9997	1.0019	1.0121	1.0218	1.0430
0.5 m KCl	.99945	1.0022	1.0125	1.0223	1.0429
1.0 m KCl	.9987	1.0043	1.0133	1.0239	1.0414
2.0 m KCl	.9977	1.0085	1.0166	1.0273	1.0321

We have plotted these values of $\overline{V}p_1$ against temperature in Fig. 3. AB is the specific volume curve of pure water. CB is the specific volume curve of water which is free from Type Ice I, according to Tammann's theory.[11] Curves 2, 3 and 4 are the partial specific volume curves for water in 0.5 m, 1.0 m, and 2.0 m KCl solutions. The dotted line represents 0.1 m KCl.

The specific heat data for potassium chloride could be checked directly with Rossini's work at 25° and accordingly they have been treated in detail. The rest of the electrolytes have been studied in a different manner. The partial specific heat of solvent water in molal solutions has been calculated in a simple manner by a recent method.[14,15] This method is particularly suitable when the number of concentrations for which data are available is rather limited. In this method the apparent molal heat capacity, Φ,[16] is plotted against the square root of the molality, $\sqrt{m}$. A smooth line results which is

---

[12] Baxter and Wallace: J. Am. Chem. Soc., 39, 70 (1916).

[13] Reference 10, p. 36.

[14] Randall and Rossini: J. Am. Chem. Soc., 51, 324 (1929).

[15] Rossini: Bur. Standards J. Research, 4, 316 (1930).

[16] Φ = (heat capacity of solution containing 1000 grams of water—heat capacity of 1000 grams of water) ÷ molality.

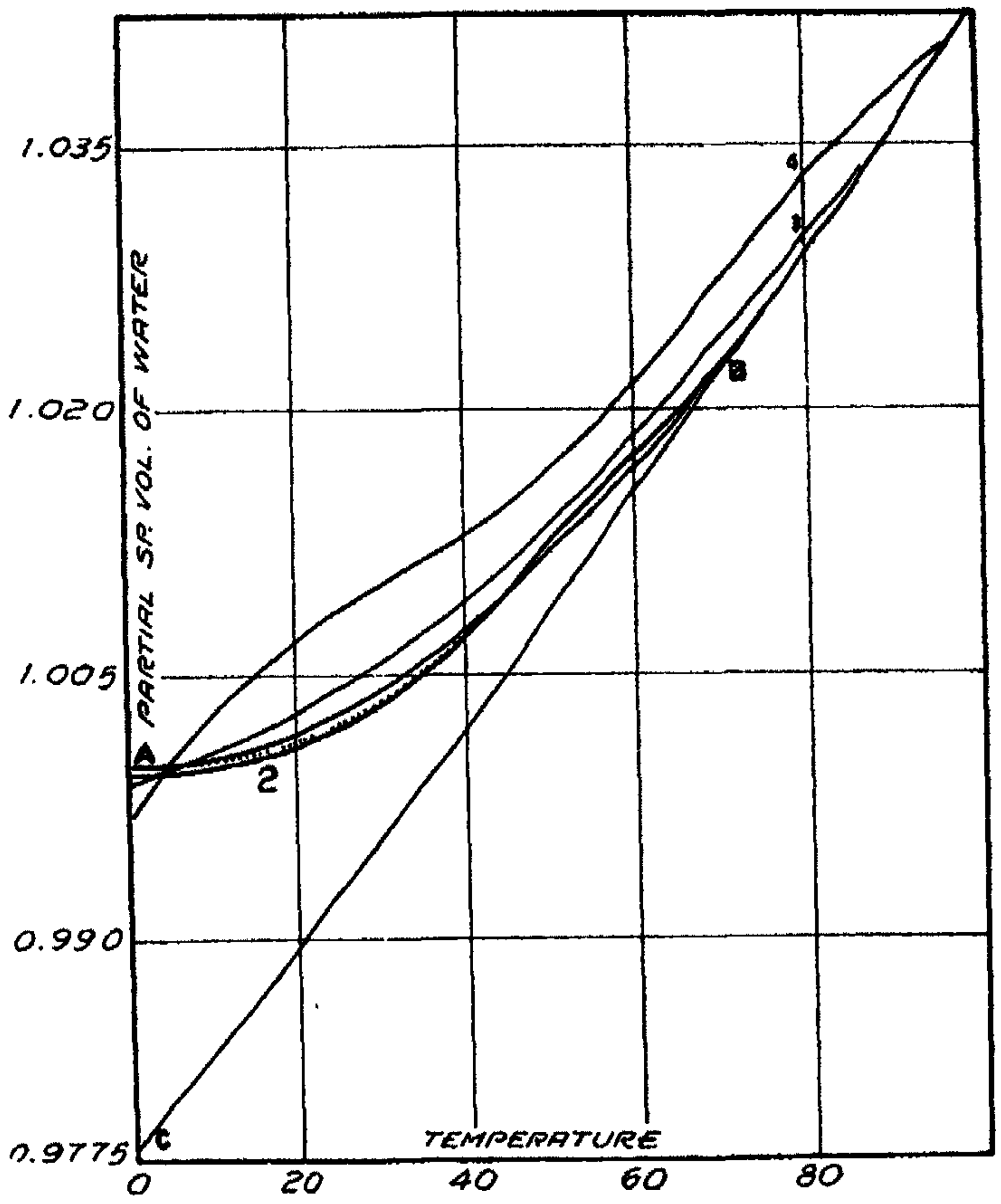


FIG. 3
Partial specific volumes of water in solutions of potassium chloride

often nearly straight over a wide range of concentration. The slope of this line $d\Phi/d\sqrt{m}$ at any concentration is an important quantity. It can be shown by simply differentiating Φ with respect to $\sqrt{m}$ and using the definitions of apparent molal heat capacity and partial molal heat capacity $\overline{C}_p$, that the difference between the partial heat capacity of a mol of solvent water in a large amount of solution, $\overline{C}_{p_1}$, and the heat capacity of a mol of pure water $\overline{C}^\circ_{p_1}$ (i.e. at infinite dilution) is given by the equation

$$\overline{C}_{p_1} - \overline{C}^\circ_{p_1} = -\frac{m}{1000/18}\,1/2\,\sqrt{m}\,\frac{d\Phi}{d\sqrt{m}}$$

For 1 molal solutions $\overline{C}_{p_1} - \overline{C}^\circ_{p_1}$ is simply $-0.0090\ d\Phi/d\sqrt{m}$. Dividing by 18.0 in order to change to the gram basis, the difference between the partial heat capacity of 1 gram of solvent water in solution and the heat capacity of 1 gram of pure water may be indicated as follows,

$$\text{Specific heat}_{\text{Solvent water (1m.)}} - \text{Specific heat}_{\text{Pure water}} = .00050\ d\Phi/dv\sqrt{m}.$$

In Fig. 4, are shown graphs of Φ plotted against $\sqrt{m}$, calculated from the data of Table II. The smoothness (and approximate straightness) of such a line gives an exacting test of the consistency and reliability of the specific heat measurements. The errors are particularly magnified in dilute solutions and in these graphs it has been necessary to exclude the measurements of the 0.1 m solutions. The 35° curve for potassium acetate is not considered in the graph because it would fall below the 25° curve, and such a phenomenon seems unlikely.

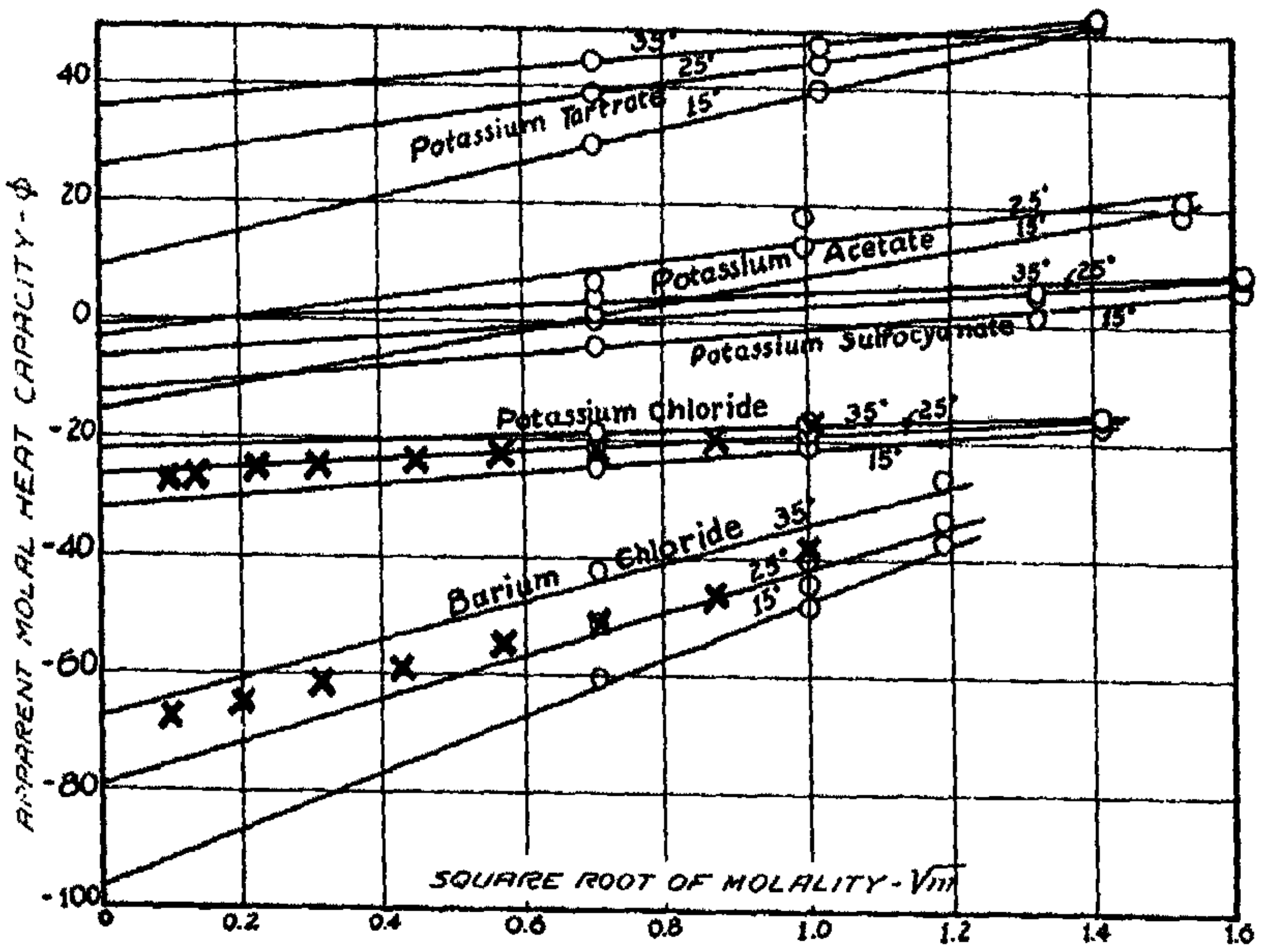


Fig. 4

Apparent molal heat capacity of water in solutions of electrolytes

It is gratifying that where the results can be compared with other accurate work the agreement is excellent. The crosses in Fig. 4 for potassium chloride solutions at 25° are calculated from the determinations of Randall and Rossini;[17] the crosses for barium chloride at 25° are calculated from the determinations of Richards and Dole.[18] The slope of the curves drawn through these points at a concentration of 1 molal is practically identical with ours. The results of these other investigators show that, particularly in the case of barium chloride, the slope changes in the dilute solutions but in considering the shift of the water equilibrium we are concerned, primarily, with the more concentrated solutions.

Fortunately the scope of the present investigation can be extended with valuable data from the experimental data of Randall and Rossini[17] and with

---

[17] Randall and Rossini: J. Am. Chem. Soc., 51, 323 (1929).

[18] Richards and Dole: J. Am. Chem. Soc., 51, 724 (1929).

the data of Richards and his co-workers as recalculated by Rossini.[19] In Table VI all of this material is grouped together. From the values of $\frac{(\bar{C}_{p_1}-\bar{C}^\circ_{p_1})}{18}$ given in the third column and the known specific heat capacity of pure water one can easily calculate the heat capacity of one gram of solvent water in a large quantity of solution as shown in the last column. In the next to the last column, the ions are arranged in the order of the lyotropic or Hofmeister series as determined from the salting out of inert gases and of proteins, and from various colloid phenomena.

TABLE V

Heat Capacity in Calories per Gram of Solvent Water in 1.0 Molal Solutions of Electrolytes at 25°

Electrolyte	$\frac{d\Phi}{d\sqrt{m}}$	$\left(\frac{\bar{C}_{p_1}-\bar{C}^\circ_{p_1}}{18}\right)$	Lyotropic series	"Specific heat" of solvent water in 1 molal solution
Water	—	0	—	0.9985
$BaCl_2$	38	0.0189	Ba^{++}	0.9796
$CaCl_2$	24	0.0122	Ca^{++}	0.9863
$K_2C_4H_4O_6$	20	0.0100	SO_4^{--}	0.9885
K_2SO_4	11	0.0055	$C_4H_4O_6$	0.9930
$KC_2H_3O_2$	10	0.0050	$C_2H_3O_2^-$	0.9935
KCl	8.0	0.0040	Cl^-	0.9945
KNO_3	5.3	0.0025	NO_3^-	0.9960
KCNS	4.0	0.0020	I^-	0.9965
KI	3.3	0.0017	CNS^-	0.9968
NaCl	18	0.0089	Na^+	0.9896
KCl	8	0.0040	K^+	0.9945
Na_2SO_4	14	0.0072	Na^+	0.9913
K_2SO_4	11	0.0055	K^+	0.9930
$NaNO_3$	6.2	0.0031	Na^+	0.9954
KNO_3	5.3	0.0026	K^+	0.9959
NaI	3.8	0.0019	Na^+	0.9966
KI	3.3	0.0017	K^+	0.9968

The influence of temperature on the specific heat capacity of solvent water is shown in Table VI. It is not possible to find recent data for checking this temperature effect.

---

[19] Rossini: Bur. Standards J. Research, 4, 316 (1930).

TABLE VI

Influence of Temperature on the Specific Heat Capacity of Solvent Water in 1 Molal Solutions of Electrolytes

Electrolyte	15°	25°	35°
Water	1.000	0.9985	0.9980
$BaCl_2$	0.9740	0.9796	0.9820
$K_2C_4H_4O_6$	0.9845	0.9885	0.9890
$K_2C_2H_3O_2$	0.9925	0.9935	—
KCl	0.9930	0.9945	0.9960
KCNS	0.9935	0.9965	—

Conclusions

Table VI shows that the idea back of the present investigation was justified and that there is remarkable correlation between the order in which the ions affect the heat capacity of water and the order in which they affect colloid properties—i.e. the Hofmeister or lyotropic series. Those salts which come at the head of the list decrease the heat capacity most and have the greatest ability to salt out dissolved gases or proteins. As a direct result of this property they lead to the highest temperature of gelation of certain colloids. A comparison of the effects of barium and calcium chloride shows that in 1 molal concentration the barium ion is more effective than calcium ion, since the chloride ions are the same in both.

The next seven salts all contain potassium ions and the differences in behavior are due to the anions. Tartrate and sulfate which have the greatest effect are divalent. All the others are univalent. The last group of eight salts in Table V show conclusively that the effect of the sodium ion is always greater than that of the potassium ion for any given anion.

These relationships are not evident when one examines only the heat capacity per gram of solution. They are obscured by the changing of the molecular weights and by other factors and are brought out only by the mathematical relations which involve the way in which the specific heat of the solution changes with the molality. The mathematical formula can be reduced to such a simple form, however, that the order of the effect of electrolytes on the heat capacity of water can be determined by a glance at the slopes of the lines, $d\Phi/d\sqrt{m}$, in Fig. 4.

Thus barium chloride has the steepest slope and potassium sulphocyanate the least. The former has the greatest effect on the heat capacity of water and the latter the least and the other salts line up in their proper order.

The cause of the decrease in heat capacity of water by the presence of ions is complicated. The intrinsic heat capacities of the ions themselves become unimportant in the present method of calculating the partial molal heat capacities of the solvent water. The charge of the ions serves to hold the water molecules in a more rigid manner, restricting free movement of the units and thus decreasing the degrees of freedom and diminishing the heat capacity of the solvent water. The divalent ions are, of course, more effective in this restriction than are the univalent ions. The theoretical treatment of this effect of charge in very dilute solutions has been studied by other investigators. Hydration of the ions is a second effect which may be identical, in part at least, with the restriction of free motion due to the charge, already discussed. If the hydration becomes less as the temperature is raised there must be a tendency to increase the heat capacity on account of the absorption of heat in the process of breaking up hydrates. This increase may more than offset the decrease in heat capacity caused by the decrease in the total number of separate units.

A third effect which may be called the depolymerization of water, we believe to be the most important factor in arranging the ions of a given charge in the order of the lyotropic or Hofmeister series. It is generally believed that the abnormally high specific heat of water, the existence of a minimum heat capacity at 35° and a maximum density at 4° are due to the existence of polymers of water which break down with the absorption of heat as the temperature is raised. It is immaterial for the present discussion whether these polymers are $(H_2O)_3$ or $(H_2O)_n$ or whether they are in the form of clusters of many molecules. It seems likely that these polymers may be broken down also by the presence of electrolytes, and that part of the loss in heat capacity of water produced by the presence of the ions may be attributed to the loss of these heat-absorbing polymers.

Tammann[11] has sought to develop a quantitative theory for the behavior of water based on the depolymerization of polymers, (Type Ice I molecules). In Fig. 3 it will be noted that the specific volume curve of 0.1 m KCl lies slightly below the AB line but that it merges with this line at 40°. According to Tammann's theory Type Ice I molecules have disappeared at 40° in pure water. Therefore, at 40° and above, the partial specific volume curve of the solvent, and the specific volume curve of pure water coincide. Curve 2 (0.5 M KCl) shows exactly the same effect. Since curves 3 and 4 lie considerably above AB, it follows that the above explanation can be only partly true. Certainly the orientation of water molecules by the charged ions must be an important factor also.

The change in the condition of the solvent water by the addition of solutes is supported also by optical measurements. Schade and Lohfert[20] observed a decrease in the intensity of the ultraviolet Tyndall cone of pure water upon the addition of electrolytes in 0.1 N concentration. They held that this decrease was caused by the depolymerization of Type Ice I. Gerlach[21] arrived at similar conclusions based on observations of the Raman bands of water. The change in the Raman spectrum with temperature was similar to the change brought about by the additions of lithium chloride.

The influence of temperature on the partial specific heat capacity of solvent water is interesting. The slopes, $d\Phi/d\sqrt{m}$, as shown in Fig. 4 become less as the temperature is raised from 15° to 35°. Thus, the difference between the

---

[20] Schade and Lohfert: Kolloid-Z., 51, 65 (1930).

[21] Gerlach: Naturwissenschaften, 18, 68 (1930).

heat capacity of the solvent water and pure water becomes less, i.e. the solvent water becomes more like pure water as the temperature is increased up to 35°. This fact is in accord with the suggestion that the electrolytes lead to the depolymerization of water, for if the temperature has already broken down some of these polymers there will be less opportunity for the electrolytes to do so. The temperature of minimum specific heat of water happens to fall at 35° and it would be interesting to have these measurements extended to a higher temperature range.

It is evident that the order of the slopes $d\Phi/d\sqrt{m}$ may not be the same at all temperatures and that the order of the ions may not be exactly the same as that shown in Table V for 25°. Furthermore, the lines in which Φ is plotted against $\sqrt{m}$ are often approximately straight but they are not necessarily so. Particularly in the very dilute solutions the slopes may change to such an extent as to alter $\overline{C}_p$ and change the order in which the ions affect the heat capacity of solvent water. It is predicted, then, that the lyotropic series or Hofmeister series can be influenced by temperature and concentration. Perhaps minor variations in the work of different investigators on the lyotropic series may be attributed to differences in concentration and temperature.

Summary

1. Specific heats have been obtained for solutions of barium chloride and of the potassium salts of hydrochloric, tartaric, acetic and sulfocyanic acids from 0.1 molal to 2 molal at temperatures from 10° to 40°C. Data have been obtained for 2 molal solutions of ammonium chloride and potassium bromide.

2. An adiabatic calorimeter was used with automatic control.

3. The partial specific heat capacities of the solvent water have been calculated for 1 molal solutions of several electrolytes.

4. The partial specific heats with potassium chloride have been calculated at several concentrations and compared with the partial specific volumes at different temperatures.

5. The order in which the ions decrease the heat capacity of the solvent water is practically the same as the order in which the ions appear in the lyotropic or Hofmeister series.

6. The presence of the electrically charged ions restricts the free motion of the water molecules and reduces the heat capacity. The depolymerization of water is suggested as a second factor in reducing the heat capacity, and arranging the ions of a given charge in the order of the lyotropic or Hofmeister series.

The author desires to express his appreciation to Professor Farrington Daniels for his guidance throughout this investigation.

Laboratory of Physical Chemistry,
University of Wisconsin.

THE SYSTEM METHYL ALCOHOL-N-HEXANE AT 45 DEGREES[*]

BY JOHN BRIGHT FERGUSON

The system methyl alcohol-n-hexane was investigated at 45 deg. since Rothmund[1] had found the critical solution temperature to be 42.6 deg. Schukarew[2] determined the total pressures at 43.8 deg. and these and the solubilities are the only measurements which have been reported.

The differences which we encountered were those always associated with the use of anhydrous reagents. Rothmund stressed the importance of dry materials and our experiences amply confirmed his opinion.

Our apparatus was essentially that of Ferguson and Funnell[3] but to it was added a second sample tube container in parallel with the first. This enabled us to introduce the pure liquids into the apparatus. Had we prepared the two-component samples outside the apparatus, more hexane would have been required, contamination by water would have been greater and evaporation losses might have caused appreciable errors in the sample composition owing to the high vapour pressures of the solutions.

Our raw materials were Kahlbaum's best grade methyl alcohol and Eastman Kodak synthetic normal hexane. The alcohol was dried over freshly ignited lime for three weeks at room temperature, decanted off and distilled. In some cases, the alcohol was distilled over sodium in addition and in all cases care was taken to prevent contamination by water. The hexane was washed with 95 percent sulphuric acid until the acid layer remained colourless, with distilled water, with dilute alkaline permanganate solution and with distilled water in the order given. The hexane layer was separated and to it was added metallic sodium. It was left for two days but frequently shaken and then carefully distilled.

The temperature of the water bath was read on a Beckmann thermometer which had been compared with a standard. The vapour pressure of water at 45 deg. was found to be 71.9 mm; the value given in I.C.T. is 71.88 mm.[4] The vapour pressure of hexane was 333.0 mm which agrees with the value of 332.7 mm obtained from I.C.T.[5] and with the value 334.6 mm interpolated from the results of Thomas and Young.[6] For methyl alcohol we obtained a value of 327.9 as compared with 328 mm given by Ramsay and Young[7]

---

[*] An account of the results obtained by Messrs. Beare and McVicar and by Messrs. French and Wright.

[1] Rothmund: Z. physik. Chem., **26**, 433 (1898).

[2] Schukarew: Z. physik. Chem., **71**, 101 (1910).

[3] Ferguson and Funnell: J. Phys. Chem., **33**, 1 (1929); Beare, McVicar and Ferguson: **35**, 1068 (1931).

[4] Inter. Crit. Tables, **3**, 212 (1928).

[5] Inter. Crit. Tables, **3**, 222 (1928).

[6] Thomas and Young: Trans. Chem. Soc., **67**, 1071 (1895).

[7] Ramsay and Young: Phil. Trans., **178**, 313 (1887).

and for our stock hexane 325 mm. Schukarew's value of 309.5 mm for 43.8 deg. agrees with this last value and it would appear that either his hexane was impure or his temperature in error.

The critical solution temperature was determined by the sealed tube method. Our result was 42.4 deg.; Rothmund gives 42.6 deg.

The compositions of the co-existent vapour and liquid phases in the binary system were calculated from the determined vapour densities, the weights of the vapours and the weights of liquids introduced. The details may be found in earlier papers. However, there is one point which must be discussed here. N-hexane vapour is not a perfect gas and the two-component vapours are not perfect gaseous solutions. As a first approximation, it seemed probable that a knowledge of the behaviour of pure hexane vapour might suffice for the calculations. The useful method of treatment recently employed by Cope, Lewis and Weber[8] to correlate the densities of the vapours of the higher hydrocarbons did not yield results of sufficient accuracy nor did a consideration of the experimental results of Thomas and Young, of Ramsay and Steel[9] and of Hicks-Bruun.[10]

The results of Thomas and Young were extrapolated by plotting the observed volume of one gram divided by the corresponding volume calculated from the simple gas laws against the pressure. Hicks-Bruun states that the equation of Berthelot for limiting density is valid for unsaturated hexane vapour and the plot should yield a linear relation within narrow limits. The data, available, indicated that the observed volumes might deviate several percent from the calculated volumes and direct measurements seemed advisable. Our determinations are given in Table I.

TABLE I

Apparent formula weight of n-hexane

Temperature	Pressure	F.Wt.	Observer
48.6	334.1	88.34	Beare and McVicar
48.0	333.3	88.74	" "
49.7	331.0	88.47	French and Wright
		av. 88.5	

Subsequent experiments on the two-component system indicated that our determined vapour compositions would not differ greatly from each other and that the partial pressures would approach the vapour pressures of the pure liquids. When calculations were made using the formula weight for alcohol and the apparent formula weight for hexane just given, the partial pressures of hexane were found to exceed the vapour pressure of pure hexane in a number of cases. These improbable results forced us to calibrate our apparatus with known amounts of the pure vapours.¶ For convenience, we calculated the apparent formula weight of hexane which we

---

[8] Cope, Lewis and Weber: Ind. Eng. Chem., 23, 887 (1931).

[9] Ramsay and Steele: Z. physik. Chem., 44, 348 (1903).

[10] Hicks-Bruun: Bur. Standards J. Research, 5, 575 (1930).

must use to get the right result when the normal formula weight of alcohol was assumed. Our best experiment gave these results: 49.4 deg., 548.5 mm, 75.21 wt. percent hexane; from initial weights—91.09, from weight condensate—91.35. Weight sample taken—5.9411, weight found—5.946, diff-0.0049. Two other experiments were not so satisfactory. One, 49.6 deg., 589.2 mm, 74.92 wt. percent hexane and the other, 49.7 deg., 587.6 mm, 74.37 wt. percent hexane gave respectively the values 90.95 and 90.38 from the weights of the condensates. From these, we concluded that a value, 91.1, would be probable one for this, our analytical constant. It was possible to use but one constant since the vapour compositions did not vary much from those used to determine this.

Our results are given in Table II. The mol. percentages are based upon 32.03 for methyl alcohol and 91.1 for n-hexane and the same units were used for the calculation of the partial pressures.

TABLE II

Liquid Composition		Vapour Composition			Partial Pressure		
Wt. % Hexane	Mol. % Hexane	Wt. % Hexane	Mol. % Hexane	Total Pressure	Hexane	M. Alcohol	Observer
18.06	7.18	72.51	48.1	611.0	293.9	317.1	F. & W.
19.27	7.74	71.96	47.45	601.7	285.6	316.1	" "
20.15	8.15	71.90	47.39	606.9	287.6	319.3	" "
22.0	9.02	73.89	49.86	617.2	307.7	311.5	B. & McV
24.88	10.43	73.47	49.30	618.1	304.7	313.6	F. & W.
28.92	12.51	73.48	49.30	624.1	307.7	316.4	B. & McV.
45.07	22.40	74.04	50.07	628.3	314.7	313.6	F. & W.
46.12	23.13	74.61	50.81	630.3	320.2	310.1	B. & McV.
72.95	48.67	74.06	50.12	630.2	315.8	314.4	" "
89.86	75.82	74.49	50.67	626.4	317.5	308.9	" "
95.72	88.63	75.16	51.56	619.3	319.3	300.0	F. & W.
98.35*	95.5*	79.87	58.28	549.8	320.4	229.4	B. & McV.
100	100	100	100	333.0	Average of detn. of F. & W. and B. & McV.		
0	0	0	0	327.9			F. & W.

Temperature 45.00 ± 0.02°C.

*(Interp.)

The following results are shown graphically in Fig. 1: the total and partial pressures at 45 deg., the total pressures obtained by Schukarew at 43.8 deg. and the solubility curve of Rothmund.

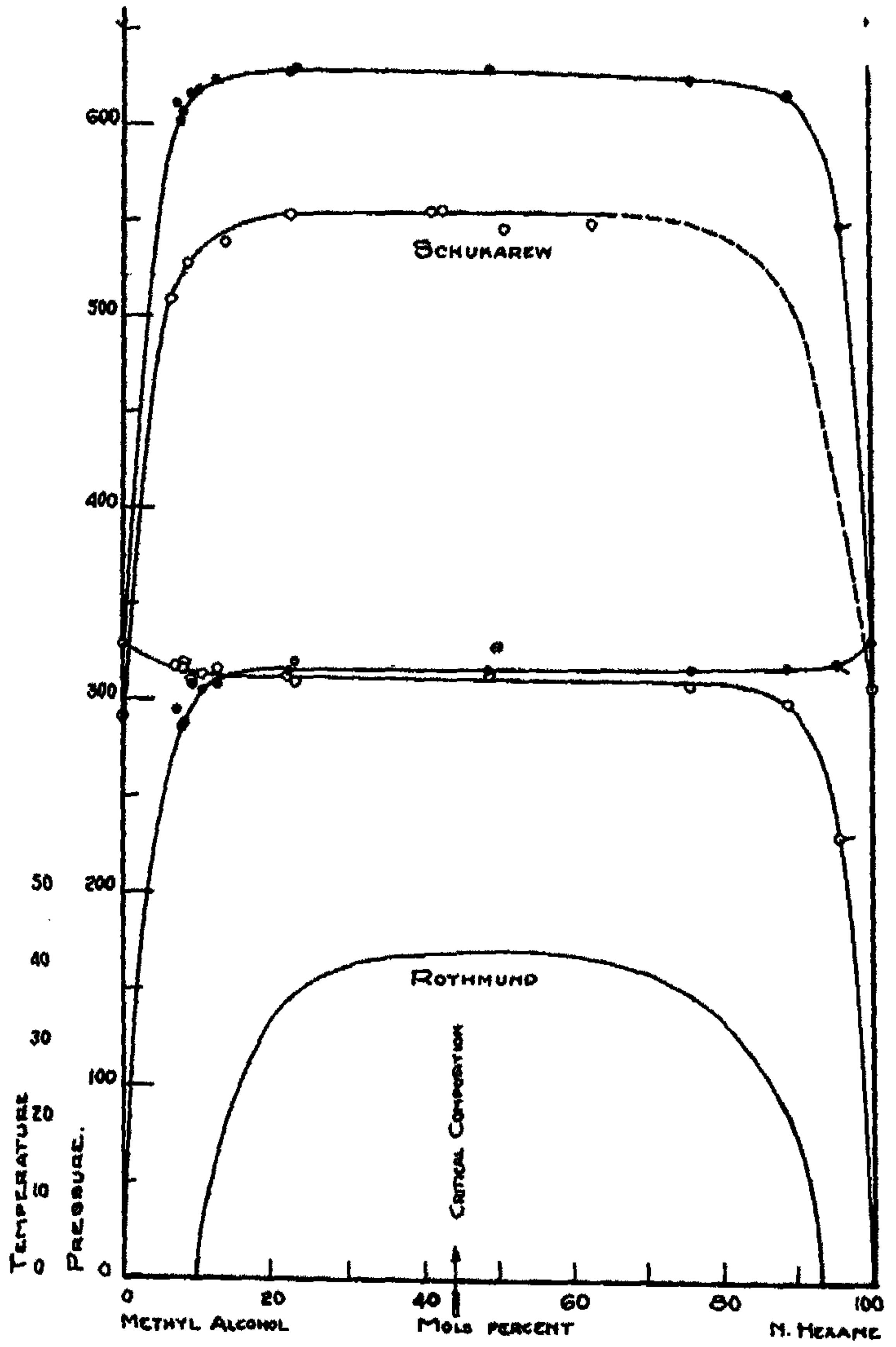


Fig. 1

Discussion

We have called 91.1 an analytical constant although later we have assumed it to be the formula weight of hexane in the vapour phases because we wished to stress the point that our results in weight percentages are independent of any theoretical significance which might be attached to this constant. The apparent formula weight of hexane probably varies from 86.11 for the dilute vapours, to 91.1 for the more concentrated vapours, finally reaching a value of 88.5 for the pure hexane, under our experimental conditions.

Obviously, only one value can be used for the presentation of these results in the customary manner and we have chosen 91.1. We have assumed that the methyl alcohol vapour was normal at all times although it is likely that this assumption is not strictly true. The high value chosen for hexane presents a problem. It seems unlikely that our value for pure hexane is too low since the sources of error other than contamination by water, would lead to higher results and if we ascribe it to the presence of water, we must conclude that it was easier to keep both alcohol and hexane dry than it was to keep hexane, itself. Our results indicate an appreciable volume change on mixing these vapours. It is an interesting fact that the apparent formula weight of hexane obtained from the two-component system is approximately equal to the value obtained by linear extrapolation from zero pressure through the vapour pressure of pure hexane to the vapour pressure of the solutions. This suggests that a study of such phenomena might shed some light on liquid phases in which the factors involved are more difficult to differentiate. One wonders whether such an effect occurs only in those systems, in which liquid immiscibility is found or may be easily produced.

The partial pressure curves are similar and do not indicate compound formation. They are not at variance with the Duhem-Margules equation although the comparison is, of necessity, crude and for theoretical reasons cannot be exact. The nearly horizontal portions of the curves extend over a wide range of liquid compositions which agrees with the results of others on similar systems and is also in accord with theory. The latter will be apparent from an inspection of the following equation given by Lash Miller:[11]

$$\mu_{xy} = \frac{\theta}{\mathrm{T}}\mu'_{xy} - \frac{(\theta-\mathrm{T})}{\mathrm{T}}\chi'_{xy} + \left\{(\theta-\mathrm{T}) - \theta\log_e\frac{\theta}{\mathrm{T}}\right\}\mathrm{C}_{xy}$$

Since the change from an homogeneous to an heterogeneous system occurs over a small temperature range for an extended range of composition, it follows that μ'_{xy} must have a small value in order that the χ_{xy} and C_{xy} terms may be sufficient to give the value of μ_{xy} for the unstable homogeneous phase an opposite sign. If μ'_{xy} is very small, the corresponding partial pressures curves would be nearly horizontal, provided, as seems reasonable, that the deviations from perfect gaseous solutions are insufficient to affect this conclusion.[12]

On the other hand both χ_{xy} and C_{xy} cannot approach zero if μ_{xy} is to change sign on changing the temperature. Thus, the curves of χ and C cannot both be horizontal or linear over the range of compositions for which the partial pressure curves are nearly horizontal.

Such partial pressure curves cannot be explained by the judicious manipulation of the units used to express the liquid composition—a fact which is now generally admitted. One should not segregate such cases and assume that the factors, here important, are negligible in all other types of systems

---

[11] Lash Miller: Chem. Rev., 1, 327 (1925), Equation 9 but with terms rearranged.

[12] In a previous paper (Ferguson: J. Phys. Chem., 31, 762 (1927)), we presented similar deductions but used a slightly different equation.

nor accept, as proved, a degree of association the assumption of which enables one to correlate the experimental results by means of an equation. Siang Chieh Lee[13] has recently emphasized the importance of the "tendency to separate." We, also, believe that the theory of solutions will remain incomplete until a method has been found for the evaluation of the factor, mainly responsible for the nearly horizontal partial pressure curves in these extreme cases and probably important in many other cases as well.

Summary

1. The compositions of the co-existent liquid and vapour phases in the system methyl alcohol-n-hexane have been determined at 45 deg.

2. A study has been made of the densities of hexane vapour and of the two component vapour.

3. The total pressures and the calculated partial pressures have been given and the latter discussed.

Chemical Laboratory,
University of Toronto,
Toronto, Canada,
January 5th, 1932.

---

[13] Siang Chieh Lee: J. Phys. Chem., 35, 3558 (1931).

THE LIESEGANG PHENOMENON APPLIED TO THE LAKE SUPERIOR IRON FORMATIONS*

BY ROBERT J. HARTMAN AND ROBERT McCULLOUGH DICKEY

Introduction

From an economic standpoint, the rock strata known as the Lake Superior iron formations are perhaps the most important natural deposits on the North American continent. To the geologist they afford innumerable and fascinating problems of structure and stratigraphy, of secondary ore concentration, and ultimately of origin. It is with the origin of this formation that this paper proposes to deal, but it will concern itself primarily with a single phase of a hypothetical process of origin, one which has either been completely overlooked heretofore, or which has been passed over with scant notice. The study lies within the legitimate province of the chemist, but his experimental work must be constantly limited by the geologic conditions either known definitely or strongly believed to have existed at the time of formation of these remarkable deposits. If it is possible for the structure and composition of the rocks comprising the iron formations to be synthetically reproduced in the laboratory, within the limitations imposed by the necessity of using only those elements in the reactions which could easily have existed in nature according to the most widely accepted geologic theories of origin, then a considerable advance will have been made. It is not proposed to enter into an involved discussion of the merits of the various hypotheses advanced by geologists to account for the deposition and occurrence of these rocks, except insofar as the results of the work described tend to support or disprove one or the other.

What are generally referred to as the iron formations are not in themselves iron ores. The iron formations proper were probably originally cherty iron carbonate and greenalite ($FeMgSiO_3.nH_2O$) which have undergone varying amounts of oxidation, leaching by circulating meteoric and magmatic waters, and metamorphism, leading to the production of minerals characteristic of these processes during the millions of years which have elapsed since their deposition. They vary from a few feet to one thousand feet in thickness, and contain roughly about 25% iron. The iron ores of the region have developed under favorable geologic conditions through the leaching out of the amorphous or finely crystalline silica of the iron formations and oxidation of the ferrous salts to hematite, limonite, and other of the varied forms of the higher oxides of iron. In short, the development of iron ore in these instances is the result of secondary concentration, through various agencies, of the iron in the primary iron formations.

---

*Contribution from the Laboratory of Colloid Chemistry of Indiana University.

A peculiar and generally well-marked characteristic of these iron formations is their definite banding, which is particularly apparent in the rocks of some localities. Even a cursory examination suggests to the chemist the possibility of reactions in a silica gel having been of some importance in the formative processes. The iron carbonate, oxidized to different degrees, occurs in the iron formations in bands of varying thicknesses separated by other bands of chert, or silica. These bands exhibit no uniformity in thickness. Many attempts to explain this banding have been made, but all fall somewhat short of satisfying the conditions. It is true that no one explanation will suffice for the whole of the iron formations, since they were laid down over an area thousands of square miles in extent and were doubtless subject to the greatest differences in conditions. Nevertheless, it is entirely possible that one type of process may have been dominant, and the attempt to discover this certain type of process has occupied many geologists for a number of years.

Van Hise and Leith[1] assert that most of the iron salts and silica were contributed directly to marine waters by submarine basic lavas, that is, by direct contact of heated igneous material possessing a high ferromagnesian content, with the sea water. They show by a series of laboratory experiments that such a process is adequate to provide all the elements present in the iron formations, and their contention is supported by the close association in the Lake Superior region of vast amounts of weathered basic igneous rocks, greenstones and basalts, with the iron formations. Subordinate to this, they believe, was the weathering of the igneous rocks when cooled, leading to transportation to settling basins by meteoric waters of iron in the form of the ferrous salts of silicic, carbonic, sulphuric, hydrochloric, and other acids. They mention the fact that when iron silicates make contact with calcium carbonate, ferrous carbonate is precipitated, tending to agglomerate into bands separated by free silica.

Gruner,[2] on the other hand, contends that weathering of large land areas covered with greenstones and basalts was the predominant process. He postulates a humid climate, tropical or subtropical in nature, and abundant land vegetation of a low form affording rapid decay and solution of iron and silica as being of fundamental importance. According to his theory, most of the iron was carried to depositional basins as organic colloids or adsorbed by organic colloids, and was precipitated primarily through the influence of living algae and bacteria. Thus he subordinates inorganic reactions to organic.

An elaboration of the Gruner theory is offered by Maynard and Moore,[3] wherein they enter more thoroughly into the colloidal aspects. They contend that the banding is due to differential rates of precipitation of iron and silica, combined with seasonal changes causing varying quantities of these substances to be brought into the basins of deposition at different times of the

---

[1] C. R. Van Hise and C. K. Leith: U. S. Geol. Sur., Mon. 52.

[2] Gruner: Econ. Geol., **17**, 407 (1922); **18**, 612 (1923).

[3] E. S. Moore and J. E. Maynard: Econ. Geol., **24**, 272, 365, 506 (1929).

year. The emphasis of the banding, according to their idea, is due to metamorphic processes, although the distinctness of the banding for the most part may be regarded as primary. They have produced banding of a rough order by differential settling in sea water of well-agitated ferric hydroxide and silica. Mention is made of the possibility of Liesegang's rings having been of some importance. They prepared a gel of equal volumes of 1.16 density sodium silicate and 3 N sulphuric acid which was made 0.1 N with respect to ferric chloride. The gel formed in a day or two, and was covered with ammonium hydroxide. In a month, ferric hydroxide bands developed. However, the authors claim that this process is inadequate to account for great thicknesses of the iron formation.

Experimental

The experimental work detailed in this paper tends to support the theories of Van Hise and Leith. It demonstrates conclusively that reactions in a silica gel will produce, under proper conditions, well-defined bands of ferrous carbonate, separated by silica bands. The banding peculiar to the iron formations is faithfully reproduced by this method. Briefly, the geologic considerations entailed are the presence of ferrous iron, non-oxidizing conditions in the gel tending to keep the iron in its ferrous form, sodium silicate, carbon dioxide (hence some form of life), and relatively quiescent conditions. All these can be reconciled with the direct submarine magma contribution theory. The sodium silicate and iron could readily have been supplied from the magma itself. Van Hise and Leith[1] found that when fresh basalt is heated to 1200° Centigrade, so that the surface is fused, and the mass is plunged into salt water, sodium silicate is produced, together with small amounts of iron salts.

Nitrogenous material and carbon dioxide may have been furnished by organisms; however, some of the carbon dioxide may have been supplied through action of the magma itself. Chamberlin and Salisbury[2] assert that carbon dioxide increases greatly in relative abundance with expiration of volcanic activity. If such is the case, most of this substance could have been supplied at a time when the period of violent igneous activity had passed and quiescent conditions had set in.

When the Simplon tunnel was dug through the Alps, the workmen cut through a vein of silicic acid soft enough to dig out with the hand.[3] It is the contention of the authors that this iron formation was no doubt at one time in similar gelatinous form and that while in this state a reaction, analogous to the Liesegang phenomenon, took place, giving rise to the ferrous carbonate bands. Dehydration, pressure, etc., through the ages leaves the iron formation in its solid state with its ferrous iron having been trapped and isolated from air, preventing it from further oxidation.

---

[1] C. R. Van Hise and C. K. Leith: U. S. Geol. Sur., Mon. 52, 516.

[2] Chamberlin and Salisbury: "Text-Book of Geology," 1, 590 (1904).

[3] Holmes: "Laboratory Manual of Colloid Chemistry," p. 136.

Of importance in this connection, it may be observed here that the authors have found that passage of carbon dioxide gas through sodium silicate solution will cause it to form a very firm silicic acid gel in a short time.

From approximately seventy-five different experimental preparations, the fifteen showing the best banding are pictured in Plate I.

The first horizontal row of test tubes (A) in Plate I contains gels prepared by mixing equal volumes of 1.06 density water glass and normal ammonium carbonate solution. The horizontal row, B, consists of gels formed by mixing equal volumes of 1.06 density water glass and 0.8 N ammonium carbonate solution. The test tubes in the third horizontal row, C, contain gels prepared by mixing equal volumes of 1.06 density water glass and 0.5 N ammonium carbonate solution.

The row A gels set in approximately five minutes, the row B gels in ten minutes, and the row C gels in an hour.

In order, from left to right, to the first test tube in each horizontal row was added approximately seven cubic centimeters of 0.1 N ferrous ammonium sulfate solution. To the second test tube in each horizontal row was added the same amount of 0.3 N ferrous ammonium sulfate solution, to the third 0.5 N ferrous ammonium sulfate solution, to the fourth 0.8 N ferrous ammonium sulfate solution and to the fifth normal ferrous ammonium sulfate solution.

The ferrous ammonium sulfate solutions were changed once each day for three days, and then were replaced twice daily for three days. Following this they were permitted to stand untouched for three days, at the end of which time the photographs were made.

Due to the oxidation of the ferrous salt, it was found necessary to use in each instance freshly prepared solutions of ferrous ammonium sulfate of identical concentrations.

Test tubes containing the same respective concentrations of ammonium carbonate in the gels and of ferrous ammonium sulfate in the solutions above the gels (as in Plate I) were prepared, and allowed to stand without replacing the ferrous ammonium sulfate solutions. It was found that ferrous carbonate bands formed. However, those bands formed when the ferrous ammonium sulfate solutions were changed at regular intervals were more numerous and more distinct.

Since the photographs were taken (three weeks), the gels below the bands have in most instances become grayish-white in color almost to the bottoms of the test tubes, without, however, formation of any bands other than those pictured. This is probably due to the diffusion of ferrous carbonate throughout the gel.

Concentrations of ferrous ammonium sulfate lower than 0.1 N failed to produce bands. Equal volumes of 1.06 density water glass and 0.3 N ammonium carbonate solution were mixed and a gel set in approximately one hundred hours. This gel was unsatisfactory for use, as shrinkage due probably to evaporation over a long standing period gave rise to cracks at the surface

PLATE I

PLATE II

of the gel. Concentrations of ammonium carbonate solution less than 0.3 N did not produce gelation upon mixing with an equal volume of 1.06 density water glass.

From a comparison of the tubes in Plate I, it may be said that no general relationship between the concentration of ammonium carbonate in the gel and distinctness and number of bands formed may be deduced. With increasing concentration of ferrous ammonium sulfate in the solution placed above the gel, it can be stated that the bands become wider, and less sharply defined. This may be observed in each horizontal row of tubes, where the concentration of the soluble iron salt increases from left to right.

It is interesting to note that some very white bands of ferrous carbonate occur in the gels. The unusual lightness of these bands is probably due to the fact that they are formed in the absence of air.

Plate II shows four separate specimens of the iron formation from the Crystal Falls district of Michigan, whose faces have been polished so as to better reveal the structure. For purposes of comparison, two test tubes illustrating banding of the type produced in the laboratory have been included. As may readily be seen, the similarity between the synthetic and the natural products is very marked. The banding in the tube on the left was formed in a gel composed of equal volumes of 0.5 N ammonium carbonate solution and 1.06 density water glass, and placing over this a solution of ferrous ammonium sulfate to which was added approximately 0.5 grams of ferrous ammonium sulfate crystals daily for five days. The bands in the tube on the right were formed in the same manner, with the difference that the gel was prepared of equal volumes of normal ammonium carbonate and 1.06 density water glass.

Conclusion

In short, then, the authors contend that the peculiar banding of the iron formations, *in some localities*, has been brought about by slow diffusion of soluble ferrous salts through a gel formed by the interaction of basic nitrogenous substances, carbon dioxide, or carbonates with sodium silicate, giving rise to irregularly spaced bands of varying thicknesses of insoluble ferrous carbonate separated by silica. It is the opinion of the authors that in many cases this is the most logical explanation of the formation of the rock structure in question. Further work concerning the application of the Liesegang phenomenon to the geology of this iron formation is being carried out by the latter author while the former is making further study of the formation of ferrous carbonate bands in gels.

A COMPARISON OF COLORIMETRIC AND ELECTROMETRIC METHODS IN THE DETERMINATION OF pH VALUES OF VARIOUS GELATIN SOLUTIONS*

BY R. J. HARTMAN AND I. F. FLEISCHER

Introduction

The colorimetric methods have been resorted to almost entirely by investigators and by manufacturers in determining the pH value of various gelatin solutions. Walter S. Hughes,[1] however, measures the potential of a 1% gelatin solution by means of a glass electrode and a hydrogen electrode. The potential of this solution is changed by the addition of sodium hydroxide and hydrochloric acid solutions. A curve is then obtained by plotting the potential measured by the hydrogen electrode against that of the glass electrode. A similar curve is constructed from measurements of a solution where no gelatin is present. The former curve assumes the general shape of the latter but the potential measured by the glass electrode gives values lower than in the case where gelatin was not present. This phenomenon is explained by stating that the presence of gelatin produces substances other than hydrogen-ions which affect the glass surface potential. It is further asserted that before any acid or alkali was added to the gelatin solution the glass surface potential was 0.531 and the hydrogen potential 0.560. This difference is accounted for by saying that the presence of electrolytes has some influence on the adsorption of gelatin on the glass surface. It was further found that the potential measured by the glass surface electrode depends upon both the nature of the solution and the time of contact.

Allen E. Stearn[2] has studied the nature of isoelectric gelatin in solution. It was found that when a solution of a certain pH value was mixed with a basic dye of the same pH value, there was a very significant decrease in pH. The opposite was noted with acid dyes. In explanation two apparent mechanisms are presented.

$$\mathrm{DCl + HGe = DGe + HCl}$$

or better

$$\mathrm{D^+ + HGe = DGE + H^+}$$

where D^+ is the dye cation and Ge the gelatin radical. An adsorption mechanism depending on the equilibrium is the other explanation offered.

$$\mathrm{DCl + HOH = DOH + HCl}$$

It is definitely shown by Stearn that, when an acid dye reacts with a gelatin solution, the hydrogen-ions from the protein molecule are used up or, in the

---

* From the Laboratory of Colloid Chemistry, Indiana University.

[1] Hughes: J. Am. Chem. Soc., 44, 2860 (1922).

[2] Stearn: J. Phys. Chem., 34, 973 (1930).

case of a basic dye, hydroxyl-ions are used up. The disappearance of ions from a gelatin solution upon the addition of crystal violet (basic dye) is shown by a decrease in the conductivity of such solution.[3] It would have been indeed interesting had the two investigators above mentioned compared the pH values they obtained by potentiometric methods with values obtained from colorimetric indicators.

Stearn has conclusively shown that a gelatin molecule in solution combines chemically with either an acid or basic dye. From this it is reasonable to assume that in the colorimetric determination of the pH value of a gelatin solution the indicator chemically unites with the gelatin molecule arresting any free acid or basic ions due to the hydrolysis of a gelatin in solution. The work of Stearn indicates the existence of an ampholyte ion in gelatin solutions. This ion would, accordingly, prevent equilibrium in potentiometric determinations since it would not be combined chemically and would be free to react with other ions in solution.

This investigation was undertaken to compare the pH values obtained from two colorimetric methods with those obtained from three potentiometric methods and to study the variation of values yielded from the potentiometric methods with time, or, the time necessary for equilibrium.

Experimental

Material used. The hide glue used in this investigation was furnished through the courtesy of Conrad-Kammerer Glue Company, New Albany, Indiana, the bone glue through the courtesy of Armour Glue Company, Chicago, Illinois. The casein glue was prepared in this laboratory by the grain-curd process. The vegetable glue was prepared in this laboratory by digesting on a boiling water bath 50 grams of tapioca flour with 150 cubic centimeters of water containing 5.6 grams of caustic soda and then adding 5-100 cc. portions of water. This material was dried in an oven between 40-50° C. over night. The dry product was granulated for use.

The solutions to be tested were prepared in the following manner:

Two grams of the gelatin was allowed to soak in water over night and then heated to 62°C. at which temperature the solution became homogeneous after a 15 minute period. The solution was then permitted to come to room temperature. Ten cubic centimeter portions were used in all colorimetric determinations while fifty cubic centimeter portions were used in all potentiometric determinations with readings at definite time intervals. Redistilled water was used throughout the entire investigation.

Equipment. The pH of each gelatin solution was first determined using Clark and Lubs standard colorimetric indicators. The indicators were obtained from Coleman and Bell Company, Norwood, Ohio. The Hellige Colorimetric Comparator was also used in determining the pH value. This comparator and the standard indicator solutions were obtained from the Hellige

---

[3] Reference 2, p. 981.

Klett Company, Inc., New York, New York. In each instance the two colorimetric methods gave the same pH value.

The three electrodes used in the potentiometric methods were the hydrogen, quinhydrone and glass, each in combination with a saturated calomel-half cell. With the hydrogen and glass electrodes Leeds and Northrup hydrogen-ion potentiometer (no. 7665) was used. Leeds and Northrup quinhydrone pH indicator (no. 7654) was used in making determinations with the quinhydrone electrode. The quinhydrone and hydrogen electrodes were obtained from the same company.

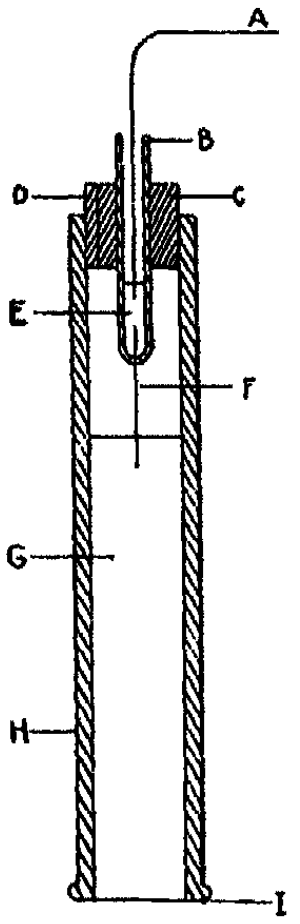


Fig. 1

A	Copper wire.
B	Glass tube.
C	Cork.
D	Groove in cork C to prevent pressure inside electrode.
E	Mercury.
F	Platinum wire.
G	Saturated KCl solution.
H	Glass tube 10 cm. long and about 1.5 cm. in diameter.
I	Thin sheet of glass.

The glass electrode was prepared by welding a very thin sheet of glass to a piece of glass tubing about 10 centimeters long and 1.5 centimeters in diameter as shown in Fig. 1. The thin sheet of glass was prepared by blowing a large thin-walled bulb from a piece of soda glass tubing.

The lower end of the glass was heated to dull red heat when it was pressed against the thin sheet of glass, which was placed on a piece of clean asbestos slate. Tests were made for leakage by filling the tube with saturated potassium chloride solution.

The hydrogen used with the hydrogen electrode was electrolytic hydrogen purified by passing through a train consisting of hot copper, concentrated sulphuric acid, glass wool and caustic soda sticks.

A convenient and inexpensive saturated calomel-half cell was devised by using a small clean wide mouth bottle arranged as shown in Fig. 2.

Data. Table I shows the values of E.M.F. and pH obtained by the various methods with the different gelatins. In carrying out the potentiometric determinations, readings were taken at various time intervals in an attempt to determine the length of time for equilibrium to take place in the solution. Horizontally is listed the various gelatins studied while vertically the E.M.F. and pH values are given with the time of reading. All of the readings were taken over a temperature range of 24 to 30°C. Correction for same was made in the calculation of each pH value.

From the following table it is noted that the two colorimetric methods, Clark and Lubs, and Hellige, gave identical pH values. The results obtained from the hydrogen electrode of each gelatin can in no way be compared with the value obtained from the colorimetric methods. At the expiration of 60 minutes in the potentiometric determination of the hide gelatin, a value

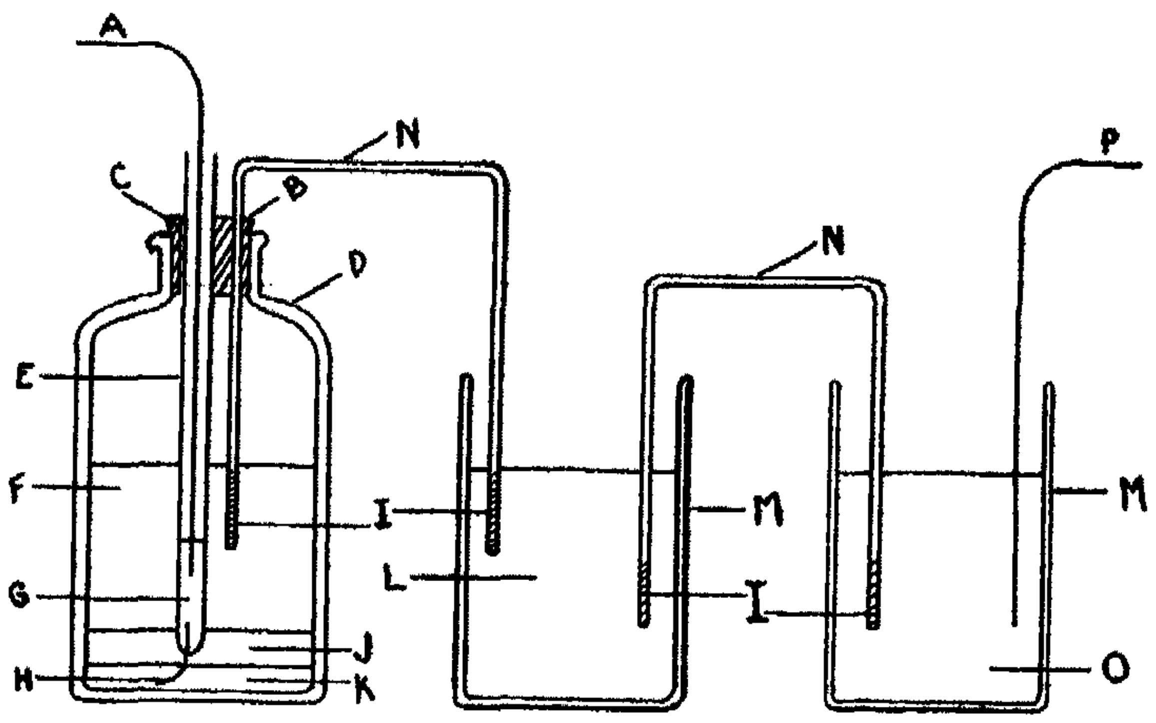


FIG. 2

A	Copper wire.
B	Cork.
C	Groove in cork B to prevent pressure inside cell.
D	100 cc. wide mouth bottle.
E	Glass tube.
F	Solution saturated with respect to KCl and calomel.
G	Mercury.
H	Platinum wire.
I	Agar gel or crushed filter paper.
J	Calomel paste.
K	Mercury.
L	Saturated KCl solution.
M	100 cc. beaker.
N	Saturated KCl bridge.
O	Solution to be tested.
P	Opposite electrode.

similar to that received with the colorimetric indicators is obtained. Since, however, the values received prior to the expiration of 60 minutes were much less than 6.6, and, since those values received after expiration of 60 minutes were greater than 6.6, this fact is coincidental.

In general, the pH values obtained with the quinhydrone electrode did not vary with time to the same extent as the values obtained from the hydrogen electrode.

Apparent equilibrium was reached in the quinhydrone determinations of the hide and casein gelatins after about 25 minutes. The values obtained at this point, however, are quite different from those obtained by the colorimetric indicators. The pH value obtained from the quinhydrone electrode with bone gelatin at the expiration of 40 minutes compared with that obtained with the two colorimetric methods. Since, however, the pH values continued to vary before and after the expiration of 40 minutes, this again may be considered coincidental.

The pH values obtained from the glass electrode did not vary with time to the same extent as the values obtained from the hydrogen electrode and in each case the pH values obtained from this method were very much lower than those obtained by the colorimetric methods.

TABLE I

Comparison of EMF and pH Values of Different Gelatin Solutions as measured by Various Methods

Gelatin	Bone			Hide		
Colorimetric pH values by Clark and Lubs, and Hellige Comparator	5.6			6.6		
	Time in Minutes	EMF Volts	pH Calculated	Time in Minutes	EMF Volts	pH Calculated
Hydrogen Electrode	15	.0707	—	5	.2513	0.143
	19	.0224	—	10	.5427	5.007
	28	.2360	—	15	.5980	5.930
	37	.4477	3.55	30	.6120	6.160
	53	.5356	4.89	45	.6180	6.260
	65	.5410	4.98	60	.6220	6.580
	83	.5476	5.28	130	.6418	6.920
	103	.5439	5.01	235	.6473	7.020
	123	.5449	5.04			
	280	.4144	2.86			
Quinhydrone Electrode	5	−.126	5.35	5	−.1210	5.60
	20	−.123	5.45	12	−.1235	5.65
	40	−.118	5.60	23	−.1235	5.65
	60	−.120	5.50	44	−.1220	5.60
	215	−.122	5.55	85	−.1210	5.60
				120	−.1210	5.60
Glass Electrode	5	.3299	(2)	5	.1150	(2)
	14	.3141		20	.1263	
	26	.3268		40	.1336	
				55	.1350	
		Electrode		75	.1336	
		Fractured		100	.1324	
				115	.1297	
				120	.1289	

TABLE I (Continued)

Comparison of EMF and pH Values of Different Gelatin Solutions as measured by Various Methods

Gelatin	Casein			Vegetable		
Colorimetric pH values by Clark and Lubs, and Hellige Comparator		4.0		9.0 (Phenol phthalein) (Hellige comparator not used)		
	Time in Minutes	pH EMF Volts	Calculated	Time in Minutes	EMF Volts	pH Calculated
Hydrogen Electrode	10	.4101	2.78	1.5	.1000	—
	20	.4173	2.91	5.0	.4243	3.19
	25	.4201	2.95	10.0	.6843	7.38
	35	.4242	3.01	15.0	.8087	9.46
	50	.4244	3.02	30.0	.8185	9.62
	60	.4250	3.03	48.0	.8187	9.63
	75	.4253	3.04	80.0	.8170	9.60
	90	.4256	3.05	100.0	.8167	9.58
	105	.4258	3.05	120.0	.8162	9.57
	120	.4270	3.07			
	180	.4274	3.19			
Quinhydrone Electrode	5	−.3240	2.15	28	.2540	(1)
	10	−.3290	2.07	75	.2558	
	25	−.3320	2.05	95	.2589	
	46	−.3330	2.02	120	.2408	
	62	−.3330	2.02			
	108	−.3335	2.02			
	128	−.3335	2.02			
Glass Electrode	7	.3214	(2)	5	.0867	(2)
	10	.3302		10	.1320	
	17	.3290		15	.1419	
				30	.1221	
		Electrode Fractured		45	.1301	
				60	.1391	
				80	.1574	
				105	.1382	
				120	.1426	

(1) It is known that the quinhydrone electrode will not give correct values for pH when the alkalinity is pH = 9 or greater.

(2) The pH values were not calculated in this case due to the fact that sufficient information is not available.

The accuracy of the pH determinations does not seem to vary with gelatins made from different materials.

In view of the fact that the readings obtained potentiometrically in no case reached a constant value, it is apparent that equilibrium in solution is not obtained. This quite likely could be due to the existence of an ampholyte ion in solution. This ampholyte ion may form inner salts or react with other ions which are no doubt in solution as impurities. In the colorimetric determination this ampholytic ion is probably united chemically with the organic indicator, thus yielding pH values more correct and constant.

If the variations of the pH values with time is due to an ampholytic ion, which is probably the case, equilibrium would not be expected in unbuffered solutions such as those tested. Values of pH constant with time also agreeing with the colorimetric values could be probably obtained if the solutions could be buffered. Further work along this line conducted by the authors will appear in a later issue of this journal.

Conclusion

1. The pH values obtained from the glass, quinhydrone and hydrogen electrodes in the potentiometric determination of the various gelatin solutions do not agree with the pH values obtained colorimetrically.

2. Of the methods employed in this investigation, only the colorimetric methods can be relied upon.

3. There was no equilibrium reached in the potentiometric determination of the gelatin solution over the period of time studied.

4. The data indicates the existence of ampholyte ions in each of the gelatin solutions studied as first pointed out by Stearn.

5. Of the three electrodes studied, the pH values obtained with the quinhydrone electrode seemed to give readings most constant with time, but these values did not agree with the colorimetric determinations.

THE ENTROPY OF STEAM, AND THE WATER-GAS REACTION

BY A. R. GORDON AND COLIN BARNES

The Entropy of Steam and the Water-Gas Equilibrium

A knowledge of entropies provides the most direct method of obtaining free energies of reaction, equilibrium constants, etc. from purely thermal data. The entropies of many diatomic gases at moderate temperatures have now been calculated from the formulae of quantum mechanics and the data of spectroscopy, and a few polyatomic molecules have been treated as symmetrical rotators, a structure of limited applicability.

The entropy of steam is of fundamental importance in many thermodynamic problems, but so far the calculation has not been made for such an asymmetrical top. In this paper we shall compute the entropy, and check the result against the experimental values of the free energy and heat of formation of water. A second check on our value can be obtained from the water-gas reaction whose equilibrium constant is now accurately known. Values of the entropy obtained by using an "effective" moment of inertia[1] have been previously employed to determine the "integration constant" for this reaction, but a more exacting test is to calculate the equilibrium constant itself, which, after all, is the quantity given directly by experiment. This latter calculation requires also the entropies and heat capacities of hydrogen, carbon monoxide and carbon dioxide for temperatures from 600°K. to 1200°K. These three gases are treated by a uniform method applicable to diatomic (and pseudo-diatomic) gases, and since the process[2] is now a familiar one, only a very brief description of the essential points in the calculation is given. The heat capacities are computed and tabulated with the accuracy necessary for the calculation of the water-gas equilibrium; the so-called experimental values[3] are of no use; they still need a critical revision and a sharp distinction between laboratory values and numbers derived by extrapolation.

As is usual, we get the contributions to the entropy of steam from the translational, vibrational and rotational parts of the energy. We believe that for this molecule the process gives reasonably good results up to 1200°K., though of course the interactions must eventually be taken into account. If the energy state ϵ_n occurs with the weight p_n we define the "state-sum" Σ_1 and the "energy-sum" Σ_2 by

$$\Sigma_1 = \sum_n p_n \cdot e^{-\epsilon_n/kT} \qquad (1)$$

---

[1] See for example Eucken: Physik. Z., 30, 818 (1929).

[2] See for example Rodebush: Chem. Rev., 9, 319 (1931).

[3] Inter. Crit. Tables, 5, 79. This point has already been noted by Bryant: Ind. Eng. Chem., 23, 1019 (1931).

$$\Sigma_2 = \sum_n p_n \cdot (\epsilon_n/kT) \cdot e^{-\epsilon_n/kT} \qquad (2)$$

The entropy is then

$$S = R(\Sigma_2/\Sigma_1) + R \ln \Sigma_1 \qquad (3)$$

Here ϵ_n is the energy of a vibrational or rotational state. The translational entropy is given by the usual Sackur-Tetrode expression corrected where necessary for the deviation of the gas from ideality.

We have used the following values of the constants:[1] $R = 1.9858$ cals./deg.; $k = 1.372 \times 10^{-16}$ ergs/deg.; $h = 6.55 \times 10^{-27}$ ergs/sec.; $N = 6.06 \times 10^{23}$; 1 atmosphere $= 1.0133 \times 10^6$ dynes/cm.[2] All temperatures are in degrees Kelvin, pressures in atmospheres, and entropies and heat capacities in cals./deg.

§ 1: THE TRANSLATIONAL AND VIBRATIONAL ENTROPY OF STEAM.

The translational entropy is given by the familiar expression

$$S_T = R \ln[(2\pi/h^2N)^{3/2}.k^{5/2}.e^{5/2}] + 5R/2 \ln T - R \ln P + 3R/2 \ln M + s \qquad (4)$$

where M is the molecular weight in grams, s is the correcting term for deviation from ideality, and the other symbols have their usual significance. To compute s, we used the equation of state for water vapour given by Steinwehr;[2] the magnitude of s is obvious from a comparison of the entries in the second and third columns of Table II; at 300° for saturated steam it amounts to −0.003 in the entropy, while for 400° and 1 atmosphere it is about ten times as great.

There must be three fundamental frequencies in the vibration spectrum of the H_2O molecule; two of them are reasonably certain, the third is doubtful. Fortunately, the smallest frequency, which is by far the most important, is fairly accurately known. We adopted the values of Mecke[3]

$$\omega_1 = 3930 - 95_{n_1} \quad \omega_2 = 3950 - 100_{n_2} \quad \omega_3 = 1600 \text{ cm}^{-1}.$$

The corresponding energy levels are

$$hc(n_1\omega_1 + n_2\omega_2 + n_3\omega_3)$$

There are no weight factors when the summations involved run over all possible zero and integral values of n_1, n_2 and n_3. The contributions at the various temperatures are listed in the column headed S_V in Table II. At 1200° the vibrational entropy amounts to 1.215 with perhaps an error from the uncertainty in the frequencies of five per cent, while at 300° the vibrational entropy is only 0.008.

§ 2: THE ROTATIONAL ENTROPY OF STEAM.

The H_2O molecule, so far as rotational states are concerned, is an asymmetrical top; its three principal moments of inertia are not known very accurately, and we selected the values 0.98×10^{-40}, 1.80×10^{-40} and 2.80×10^{-40}, given by Mecke.[4] Fortunately, a moderate change in the moments of inertia

---

[1] Standard table (1926) Handbuch der Physik.

[2] Steinwehr: Z. Physik, 3, 466 (1920).

[3] Mecke: Physik. Z., 30, 907 (1929).

[4] Mecke: Trans. Faraday. Soc., 26, 214 (1930).

causes only a relatively slight change in the entropy; for example, the use of Bailey's values[1] (0.97×10^{-40}, 1.91×10^{-40}, 2.91×10^{-40}) would lead to a rotational entropy only 0.09 higher than that entered in Table I.

The energy levels of an asymmetrical rotator are now well known; the equations for the first nine sets $J = 0$ to $J = 8$ have been conveniently summarized by Dennison,[2] and need not be given here. The energy depends not only on J but also on a subsidiary number τ which takes the $2J+1$ values $-J, -J+1, -J+2, \ldots J-1, J$. As regards the symmetry of the rotational states, we have (for even values of J) symmetrical levels $\tau = -J, -J+2, \ldots$ and antisymmetrical levels $\tau = -J+1, -J+3, \ldots$ while for odd values of J, the levels $\tau = -J, -J+2, \ldots$ are antisymmetrical and the levels $\tau = -J+1, -J+3, \ldots$ are symmetrical.[3] Moreover each level has the usual weight $2J+1$. In addition, the symmetrical and antisymmetrical rotational states must be weighted differently on account of the two hydrogen atoms, each with nuclear spin, in the molecule; the relative weights here are 3 and 1. It makes no practical difference (less than 0.001 in the entropy) whether the symmetrical or antisymmetrical states are given the weight 3, a circumstance which justifies the separate treatment of the vibrational contributions, for the symmetry of the vibrational part of the wave function changes for every change by unity in the quantum number n_3. In our calculation, we gave the complete weights $3(2J+1)$ to the symmetrical rotational levels and $2J+1$ to the antisymmetrical.

The rotational energy levels $\epsilon_{J\tau}$ for $J = 0$ to $J = 8$ were found by solving the exact equations;[4] for higher J values asymptotic formulae were used.[5] It may be of interest for subsequent calculations to sketch briefly the use of these formulae. From the levels $J = 8$, the quantity

$$\lambda_0 = 8\pi^2.\epsilon_{J\tau}/h^2J(J+1) \tag{5}$$

is plotted against $(J + \tau + 2\beta)/(J + 1/2)$ where $\beta = 0$ for $\tau = J, J-2, \ldots$ and is equal to $1/2$ for $\tau = J-1, J-3, \ldots$ From this graph we can

---

[1] Bailey: Trans. Faraday. Soc., 26, 203 (1930).

[2] Dennison: "Reviews of Modern Physics," 3, 280 (1931).

[3] This assignment of symmetry and antisymmetry to the rotational part of the wave function corresponds to Dennison's case *b* (loc. cit. p. 332) and assumes that the intermediate moment of inertia lies along the axis of symmetry of the molecule (cf. Mecke: Trans. Faraday Soc. 26, 214). If the smallest moment of inertia were assumed to lie along the axis of symmetry, as in Eucken's early model for the water molecule, Dennison's case *a* would apply, and for either odd or even J, the levels $\tau = -J, -J+3, -J+4, \ldots$ would be symmetrical, and the levels $\tau = -J+1, -J+2, -J+5, -J+6, \ldots$ would be antisymmetrical. As far as the calculation of the entropy is concerned, either *a* or *b* leads to the same numerical value for 300° within 0.002.

[4] The actual levels in wave numbers are given below; they may be of interest as showing the general distribution of the levels for such an asymmetrical top.
$J = 0$: 0. $J = 1$: 25.2, 38.1, 43.6. $J = 2$: 74.3, 83.1, 99.5, 138.1, 139.5. $J = 3$: 144.9, 149.8, 182.5, 213.8, 220.4, 292.6, 292.8. $J = 4$; 235.0, 237.5, 290.8, 315.3, 330.8, 395.8, 397.4, 501.4, 503.3. $J = 5$: 344.7, 345.7, 422.1, 436.7, 470.3, 524.9, 530.8, 632.4, 632.7, 769.9, 769.9. $J = 6$: 473.6, 474.0, 574.0, 582.1, 637.3, 679.4, 694.5, 788.3, 789.7, 925.0, 1093.1, 1093.1. $J = 7$: 622, 625, 731, 745, 823, 858, 889, 980, 1001, 1106, 1107, 1272, 1273, 1473, 1473. $J = 8$: 790, 790, 934, 937, 1042, 1061, 1113, 1179, 1194, 1316, 1317, 1478, 1482, 1679, 1679, 1909, 1910.

[5] Kramers and Ittmann: Z. Physik, 58, 217 (1929).

read off values of λ_0, and hence of $\epsilon_{J\tau}$, for higher values of J and for positive values of τ not too near zero. Another graph of the same two quantities but with $\beta = 1/2$ for $\tau = -J, -J+2, \ldots$ and $\beta = 0$ for $\tau = -J+1, -J+3, \ldots$ gives the value of λ_0 for negative values of τ not too near zero. Finally, the values of λ_0 for τ equal to or near zero are found directly from Eq. 47 of Kramers and Ittmann.[1] The graphical method gives the mean positions of the pairs into which the rotational states fall for high J's, and for the present purpose it is unnecessary to compute the separations. Checks on the accuracy of the process were obtained by getting the sums for J = 8 from the levels J = 7; the exact method for J = 8 gives

2.688 (sym) 0.805 (anti) 12.169 (sym) 3.506 (anti)

as the contributions to the state and energy sums respectively (see Table I), while the approximation gives the corresponding values

2.667 (sym) 0.828 (anti); 12.083 (sym) 3.684 (anti).

Since the contribution to the energy sum from states with J > 8 is only about 5% of the whole sum, and the contribution to the state sum from the same levels is less than 2%, we see that the error introduced into the entropy by the approximation cannot exceed 0.005.

TABLE I

Rotational Entropy of Steam at 300°K

	State Sum		Energy Sum	
J	Sym. Terms	Antisym. Terms	Sym. Terms	Antisym. Terms.
0	3.000	0.000	0.000	0.000
1	7.502	5.095	1.365	0.828
2	27.555	5.947	13.295	3.040
3	23.016	10.602	22.322	9.966
4	27.591	7.072	41.568	10.840
5	15.555	6.431	33.665	13.906
6	11.417	3.190	32.971	9.133
7	5.094	1.982	18.495	7.247
8	2.688	0.805	12.169	3.586
9	1.025	0.355	5.514	1.933
10	0.396	0.129	2.550	0.826
11	0.134	0.045	0.997	0.338
12	0.042	0.014	0.360	0.120
13	0.012	0.004	0.117	0.039
14	0.003	0.001	0.033	0.011
15	0.001	0.000	0.006	0.002
	125.03	41.67	185.43	61.82

$\Sigma_1 = 166.70$ $\Sigma_2 = 247.25$

$$
\begin{aligned}
S_R &= R(\Sigma_2/\Sigma_1) + R \ln \Sigma_1 \\
&= 1.9858 \times 247.25/166.70 + 4.5725 \times 2.2219 \\
&= 13.104 \text{ cals./deg.}
\end{aligned}
$$

---

[1] Kramers and Ittmann: *loc. cit.*

The calculation of the rotational entropy was carried out for 300° and 400°; the former calculation is summarized in Table I. The rotational entropy for 400° exceeds that for 300° by $(3R/2)$.ln $4/3$ so that we are justified in using the complete "classical" excitation of the rotational energy to get the rotational entropies at higher temperatures from our values at 300°; the numbers so obtained are entered in the column headed S_R in Table II.

Classical methods,[1] using an "effective" moment of inertia, the Ehrenfest "symmetry number" and an added constant $2R \ln 2$ (which allows for spin), lead to a rotational entropy at 300° only 0.007 greater than the value in Table I; if this agreement is not fortuitous, it suggests that for thermodynamic calculations the older formula should be quite satisfactory for asymmetrical rotators, and that the very laborious calculations sketched above could be avoided.

§3: THE ENTROPY OF SATURATED STEAM AT 300°.

Since the vapour pressure of water at 300° is 26.739/760 atm., the translational entropy of saturated steam at this temperature, including the correction from the equation of state, is 41.278. From Table I, $S_R = 13.104$ and $S_V = 0.008$; hence the entropy of saturated steam at 300° is 54.39.

The heat of formation per mole of liquid water at 298.1° and 1 atm. is 68270 cals.[2] and the free energy of formation, under the same conditions, is 56560 cals. Hence

$$S_{H_2O\,(l)} - S_{H_2} - 1/2\, S_{O_2} = -11710/298.1 = -39.29$$

Since S_{H_2} is here[3] 33.98 and S_{O_2} is[4] 49.03, this gives for 298.1° $S_{H_2O\,(l)} = 19.21$ and for 300°, $S_{H_2O\,(l)} = 19.33$. The latent heat of vaporization[5] at 300° is 2432 joules/gram = 10470 cals./mole; hence the molar entropy of saturated steam at 300° is $19.33 + 10470/300 = 54.23$, in satisfactory agreement with our calculated value 54.39.

Had we worked from our spectroscopic entropy value for steam at 300°, using the heat of formation, the latent heat of vaporization, and the spectroscopic entropies of hydrogen and oxygen, we should have arrived at a value for the free energy of formation of liquid water at 298.1° only 50 calories higher than the accepted 56560; this difference is well within the limits of possible error.

For higher temperatures and for 1 atmosphere pressure, the entropy of steam is entered in Table II for reference.

---

[1] See, for example, Eucken: Physik. Z., 30, 818 (1929).

[2] Inter. Crit. Tables, 7, 258.

[3] Giauque: J. Am. Chem. Soc., 52, 4816 (1930).

[4] Giauque and Johnston: J. Am. Chem. Soc., 51, 2300 (1929).

[5] Inter. Crit. Tables, 5, 138.

TABLE II

Molar Entropy of Steam at 1 Atmosphere

T°K.	S_T (ideal)	S_T (actual)	S_R	S_V	S
400	36.062	36.025	13.959	0.043	50.03
500	37.170	37.152	14.626	0.115	51.89
600	38.075	38.066	15.167	0.222	53.46
700	38.840	38.835	15.626	0.346	54.81
800	39.503	39.501	16.024	0.494	56.02
900	40.088	40.088	16.375	0.657	57.12
1000	40.611	40.611	16.688	0.831	58.13
1100	41.084	41.084	16.972	1.020	59.08
1200	41.516	41.516	17.231	1.215	59.96

§4: THE WATER-GAS EQUILIBRIUM.

In Tables III, IV and V, are tabulated the entropies of hydrogen, carbon monoxide and carbon dioxide for temperatures ranging from 300° to 1200° and for 1 atmosphere pressure. In the case of hydrogen, the rotational-vibrational entropy was calculated by the method of Giauque[1], though a direct calculation in the standard way using a moment of inertia 0.48×10^{-40} and a fundamental frequency $\omega_0 = 4262 - 113.5n$ gives entropy values differing from those obtained by his method by 0.04 at most. For carbon monoxide,[2] the moment of inertia used is 14.9×10^{-40} and $\omega_0 = 2155 - 12.7n$, while for carbon dioxide, the moment of inertia[3] is 70.2×10^{-40} and $\omega_1 = 2295$, $\omega_2 = 672.5$ and $\omega_3 = 1223.5$ cm^{-1} (Eucken's frequencies).[4] In the case of carbon dioxide, alternate rotational levels ($J = 1, 3, \ldots$) are missing, and

TABLE III

Molar Entropy of Hydrogen at 1 Atmosphere

T°K.	S_T	S_{RV}	S
300	28.110	5.894	34.00[5]
400	29.538	6.461	36.00
500	30.646	6.910	37.56
600	31.551	7.279	38.83
700	32.316	7.594	39.91
800	32.979	7.872	40.85
900	33.564	8.123	41.69
1000	34.087	8.354	42.44
1100	34.560	8.572	43.13
1200	34.992	8.778	43.77

---

[1] See Giauque: J. Am. Chem. Soc., 52, 4817 (1930), Table I.

[2] Mulliken: Phys. Rev., (2) 32, 206 (1928).

[3] Houston and Lewis: Proc. Nat. Acad. Sci., 17, 231 (1931).

[4] Eucken: Z. Physik, 37, 714 (1926).

[5] Giauque's value viz. 33.98 for 298.1° would correspond to 34.02 for 300°; the slight discrepancy arises from our use of R = 1.9858 while he used R = 1.9869.

TABLE IV

Molar Entropy of Carbon Monoxide at 1 Atmosphere

T°K.	S_T	S_R	S_V	S
300	35.948	11.369	0.000	47.32
400	37.376	11.940	0.008	49.32
500	38.484	12.383	0.031	50.90
600	39.389	12.745	0.075	52.21
700	40.154	13.051	0.137	53.34
800	40.817	13.316	0.215	54.35
900	41.402	13.550	0.303	55.26
1000	41.925	13.759	0.397	56.08
1100	42.398	13.948	0.495	56.84
1200	42.830	14.121	0.591	57.54

TABLE V

Molar Entropy of Carbon Dioxide at 1 Atmosphere

T°K.	S_T (ideal gas)	S_T (actual gas)	S_R	S_V	S
300	37.294	37.282	13.072	0.838	51.19
400	38.722	38.715	13.643	1.458	53.82
500	39.830	39.825	14.086	2.224	56.14
600	40.735	40.732	14.448	2.981	58.16
700	41.500	41.498	14.754	3.716	59.97
800	42.163	42.163	15.020	4.414	61.60
900	42.748	42.748	15.253	5.076	63.08
1000	43.271	43.271	15.463	5.702	64.44
1100	43.744	43.744	15.652	6.295	65.69
1200	44.176	44.176	15.825	6.860	66.86

TABLE VI

Molar Heat Capacities in Cals. Deg.$^{-1}$
at Constant Pressure (1 atm.)

T°K.	Steam	Hydrogen	Carbon Monoxide	Carbon Dioxide
300	—	6.91[1]	6.96	8.99
400	8.26	6.96	7.00	9.98
500	8.45	6.97	7.11	10.79
600	8.68	6.99	7.27	11.44
700	8.93	7.03	7.44	11.96
800	9.19	7.08	7.61	12.39
900	9.46	7.13	7.77	12.74
1000	9.74	7.20	7.91	13.04
1100	10.02	7.28	8.03	13.28
1200	10.29	7.38	8.13	13.49

[1] Extrapolated from Giauque: J. Am. Chem. Soc., 52, 4821 (1930).

the frequency ω_2 has the weight $n_2 + 1$; the correction for deviation from ideality was obtained by using a van der Waals equation of state, and amounts to 0.012 at most (see Table V).

The heat capacities of these three gases and of steam were computed by means of the relation $C_P = T(\partial S/\partial T)_P$, and are entered in Table VI.

If Q is the heat of reaction at T° for $CO + H_2O \rightarrow H_2 + CO_2$ and if S_X is the entropy of a constituent X at a partial pressure P_X, then at equilibrium

$$Q = T(S_{CO} + S_{H_2O} - S_{H_2} - S_{CO_2}) \qquad (6)$$

Hence, if K stand for $P_{CO}.P_{H_2O}/P_{H_2}.P_{CO_2}$,

$$R \ln K = -Q/T + \Sigma S' \qquad (7)$$

where $\Sigma S'$ stands for a quantity identical in all respects with that enclosed in the brackets in Eq. 6 except that all the entropies are now for T° and 1 atmosphere.

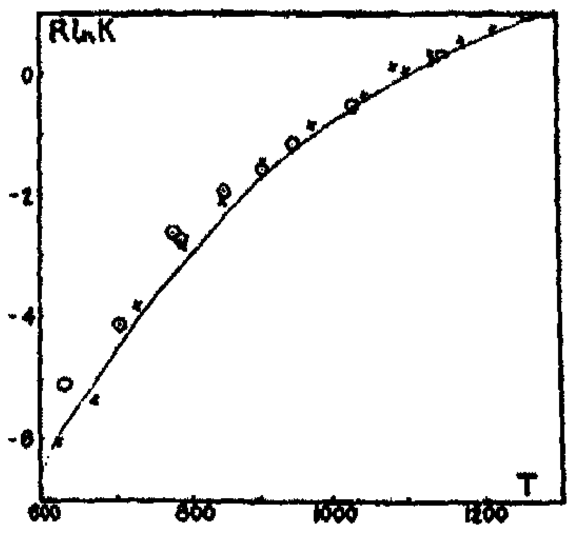


Fig. 1

In the second line of Table VII values of Q/T are entered for a range of T from 600° to 1200°; they were obtained from Bryant's value[1] of Q for 298°, viz. 9751 cals., by graphical integration of the specific heat curves. The mean heat capacity of steam between 298° and 373° was taken to be 7.81, which is consistent with the latent heats of vaporization[2] at these two temperatures and with the mean heat capacity of water (18.02) over the same range. Between 373° and 400° the heat capacity of steam was taken to be 8.23, a value obtained in the same way as the numbers entered in Table VI; the other heat capacities needed for the calculation were taken from that table. The values of $\Sigma S'$ were obtained from Tables II, III, IV and V, and R ln K (see Table VII) was found by difference; the numbers so found were used to construct the curve in the figure. The experimental values of Neumann and Köhler[3] are shown for purposes of comparison; their values when approaching equilibrium from the CO, H_2O side are indicated by small circles, and those when approaching equilibrium from the CO_2, H_2 side, are indicated by small crosses.

---

[1] Bryant: Ind. Eng. Chem., 23, 1019 (1931).

[2] Inter. Crit. Tables, 5, 138.

[3] Neumann and Köhler: Z. Elektrochemie, 34, 218 (1928), Tables 12 and 13.

TABLE VII

The Equilibrium Constant for the Water-Gas Reaction

T°K	600	700	800	900	1000	1100	1200
Q/T	15.30	12.75	10.82	9.33	8.13	7.16	6.36
ΣS′	8.68	8.27	7.92	7.61	7.33	7.10	6.87
R ln K	−6.62	−4.48	−2.90	−1.72	−0.80	−0.06	+0.51

The calculated curve lies in general about 0.2 cals./deg. below the best curve drawn through their points. This difference is within the limit of error of a calculation such as ours, and could be made to disappear by slight adjustments in the moments of inertia; for example, if we had used the conventional 63.5×10^{-40} for carbon dioxide instead of the more recent 70.2×10^{-40}, our calculated curve would have been 0.2 higher throughout.

Our entropy values for 300° (together with Bryant's value for the heat of reaction) lead to a free energy change at 298.1° for the water gas reaction ($-\Delta F^{\circ}_{298.1}$ in Lewis and Randall's notation) of 6810 calories as compared with Bryant's 6750-6830 calories.

Summary

The entropy of saturated steam for 300° and of superheated steam at 1 atmosphere from 400° to 1200° is calculated, using the rotational levels for an asymmetrical rotator and the spectral constants of Mecke. In conjunction with the calculated entropies of hydrogen, carbon monoxide and carbon dioxide, the equilibrium constant of the water-gas reaction for the range 600°-1200° is then calculated. The divergence of the calculated results from these of experiment is no greater than would be expected to arise from the uncertainties in the data used for the calculation.

The University of Toronto,
Toronto, Canada.
January, 1932.

REMARKS CONCERNING THE CLAUSIUS-MOSSOTTI LAW*

BY PIERRE VAN RYSSELBERGHE

It is well known that the dielectric constant of a dielectric which is *perfect*, *homogeneous* and *isotropic* obeys the Clausius-Mossotti law[1,2,3]:

$$\frac{\epsilon-1}{\epsilon+2}\cdot\frac{M}{d} = \text{Constant} = P \tag{1}$$

in which ϵ is the dielectric constant,
M the molecular weight,
d the density.

The constant has the dimensions of a volume and is called the molecular polarization. It is defined by the relation

$$P = \frac{4\pi}{3} N\alpha \tag{2}$$

in which N is Avogadro's number and α is the molecular polarizability.

The Clausius-Mossotti law can also be written as follows:

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} n\alpha \tag{3}$$

in which n is the number of molecules per unit volume.

When the Clausius-Mossotti law is written as above, the use of the Gauss C. G. S. system of units (dielectric constant and magnetic permeability of vacuum both equal to unity), or of the electrostatic C. G. S. system of units (dielectric constant of vacuum and velocity of light both equal to unity) is required. The law cannot be used as such in the electromagnetic system of units (magnetic permeability of vacuum and velocity of light both equal to unity) or the practical system of units (unit of length = 10^9 cm., unit of mass = 10^{-11} gm., unit of time = 1 second, magnetic permeability of vacuum and velocity of light both equal to unity). In these two systems of units the numerical value of the dielectric constant of vacuum is 1/900.

The purpose of this note is to give the Clausius-Mossotti law a form independent of the system of units and to derive it in a general way applicable to all dielectrics which are *perfect*, *homogeneous* and *isotropic*, including those which are permanently polarized. The derivations of the Clausius-Mossotti law usually given in text-books implicitly suppose that the Gauss C. G. S. or the electrostatic C. G. S. system of units are used and fortuitously give the correct result for permanently polarized dielectrics.

---

* Contribution from the Chemical Laboratory of Stanford University.

[1] O. F. Mossotti: Mem. di mathem. e fisica in Modena, 24 II, 49 (1850).

[2] R. Clausius: "Die mechanische Wärmetheorie," 2, 62 (1879).

[3] P. Debye: "Polare Molekeln," 7 (1929).

A *perfect, homogeneous* and *isotropic* dielectric is a dielectric for which the polarization vector $\bar{I}$ is given by

$$\bar{I} = \bar{I}_0 + k\bar{H} \tag{4}$$

$\bar{I}_0$ being the polarization corresponding to a total electrostatic field zero,
$\bar{H}$ being the total electrostatic field,
k being the electric susceptibility
and for which k is independent of $\bar{H}$ and of the coordinates.[4] The electrostatic induction $\bar{B}$ is given by:

$$\bar{B} = \epsilon_0\bar{H} + 4\pi\bar{I} \tag{5}$$

in which ϵ_0 is the dielectric constant of vacuum.
The vector

$$\bar{R} = \bar{H} + \frac{4\pi}{3\epsilon_0}\bar{I} \tag{6}$$

is the total force acting on a punctual charge of unity when the volume of a spherical alveolus dug around the charge tends towards zero. It is called the "electric resultant."[5]
Debye's "inner field" $\bar{F}$[6] is related to R by:

$$\bar{F} = \epsilon_0\bar{R} \tag{7}$$

We see that $\bar{R}$ has the dimensions of an electrostatic field ($\epsilon_0^{-1/2}L^{-1/2}M^{1/2}T^{-1}$) while $\bar{F}$ has the dimensions of an electrostatic induction ($\epsilon_0^{+1/2}L^{-1/2}M^{1/2}T^{-1}$). Applying equation (4) we deduce from (5) and (6):

$$\bar{B} = \epsilon\bar{H} + 4\pi\bar{I}_0 \tag{8}$$

$$\bar{R} = \frac{\epsilon + 2\epsilon_0}{3\epsilon_0}\bar{H} + \frac{4\pi}{3\epsilon_0}\bar{I}_0 \tag{9}$$

with

$$\epsilon = \epsilon_0 + 4\pi k \tag{10}$$

ϵ is the dielectric constant of the dielectric. We see that

$$\frac{B}{H} = \epsilon + 4\pi\frac{I_0}{H} \tag{11}$$

when $\bar{I}_0$ and $\bar{H}$ are parallel.
Let us write:

$$\bar{I} = n\alpha\epsilon_0\left(\bar{H} + \frac{4\pi}{3\epsilon_0}\bar{I}\right) + \left(1 - \frac{4\pi n\alpha}{3}\right)\bar{I}_0 \tag{12}$$

which is equivalent to:

$$\bar{I} = n\alpha\bar{F} + \left(1 - \frac{4\pi n\alpha}{3}\right)\bar{I}_0 \tag{13}$$

in which n is the number of molecules per unit volume and α the molecular polarizability.

---

[4] Th. De Donder: "Théorie mathématique de l'électricité," 90 (1925).
[5] Th. De Donder: loc. cit., p. 79.
[6] P. Debye: loc. cit., p. 6.

From (12) we deduce:

$$\bar{I} = \frac{n\alpha\epsilon_0}{1 - \frac{4\pi n\alpha}{3}} \bar{H} + \bar{I}_0 \qquad (14)$$

Comparing this relation with (4) we see that:

$$k = \frac{n\alpha\epsilon_0}{1 - \frac{4\pi n\alpha}{3}} \qquad (15)$$

Introducing the value of I as given by (14) into (5) we find:

$$\bar{B} = \epsilon_0\bar{H} + \frac{4\pi n\alpha\epsilon_0}{1 - \frac{4\pi n\alpha}{3}} \bar{H} + 4\pi\bar{I}_0 \qquad (16)$$

while equation (8) gives

$$\bar{B} = \epsilon\bar{H} + 4\pi\bar{I}_0 \qquad (17)$$

From (16) and (17) we deduce:

$$\frac{\epsilon - \epsilon_0}{\epsilon + 2\epsilon_0} = \frac{4\pi n\alpha}{3} \qquad (18)$$

and

$$\frac{\epsilon - \epsilon_0}{\epsilon + 2\epsilon_0} \cdot \frac{M}{d} = \frac{4\pi N\alpha}{3} \qquad (19)$$

which is the general form of the Clausius-Mossotti law. If instead of (12) we write:

$$\bar{I} = n\alpha\epsilon_0 \left(\bar{H} + \frac{4\pi}{3\epsilon_0}\bar{I}\right) \qquad (20)$$

(16) becomes:

$$\bar{B} = \epsilon_0\bar{H} + \frac{4\pi n\alpha\epsilon_0}{1 - \frac{4\pi n\alpha}{3}} = (\epsilon_0 + 4\pi k)\bar{H} = \epsilon\bar{H} \qquad (21)$$

and the correct Clausius-Mossotti formula could be deduced from this equation. (20) and (21) are however both wrong because $\bar{B}$ is not equal to $\epsilon\bar{H}$ when $\bar{I}_0$ is different from zero. A correct reasoning would be to start by differentiating (5), (8) and (12). One has then:

$$d\bar{B} = \epsilon_0 d\bar{H} + 4\pi d\bar{I} \qquad (22)$$

$$d\bar{B} = \epsilon d\bar{H} \qquad (23)$$

$$d\bar{I} = n\alpha\epsilon_0 \left(d\bar{H} + \frac{4\pi}{3\epsilon_0} d\bar{I}\right) \qquad (24)$$

Replacing $d\bar{I}$ in (22) by its value deduced from (24) and equating the two expressions of $d\bar{B}$ one obtains again the Clausius-Mossotti formula. The dielectric constant is defined by equation (23), the constant of integration being $4\pi\bar{I}_0$, as shown by (17).

If $\bar{I}_0 = 0$ the dielectric is said to be *soft*. We have in this case:

$$\epsilon = \frac{dB}{dH} = \frac{B}{H} \tag{25}$$

Summary

A general expression of the Clausius-Mossotti law, independent of the system of units and valid for all dielectrics which are perfect, homogeneous and isotropic has been established.

Stanford University,
California.

AN IMPROVED COMMUTATOR AND SOME SOURCES OF ERROR IN THE COMMUTATOR METHOD FOR THE MEASUREMENT OF OVERVOLTAGE*

BY A. L. FERGUSON AND G. M. CHEN[1]

Two methods have been extensively used for the measurement of overvoltage commonly known as the direct and commutator methods. Investigators have found that invariably the direct method gives values higher than the commutator method. For more than forty years an explanation has been sought for these observations; and during this time hundreds of researches have been carried out. The explanation offered may be classified into two groups. According to one the discrepancy is due to the existence of a resistance that is different from the ordinary electrolytic resistance between the electrode and the adjacent electrolyte. This resistance has been given various names such as surface resistance, contact resistance, film resistance, transfer resistance, etc. According to the other group the interrupter, which is a necessary part of the equipment for the commutator method, does not permit the measurement of the total discharge potential because of the rapid drop in potential during the interval between the interruption of the current and the measurement of the potential. The question is one of great importance because the values obtained by the two methods in many instances have been found to differ by a large amount and no complete theory of overvoltage, passivity or valve action can be formulated as long as this situation exists.

Several years ago a thorough investigation of this subject was started in this laboratory and has been in progress intermittently since that time. In the first article[2] it was shown beyond any doubt that practically all data obtained with a commutator by previous investigators were open to serious criticism. It was proven that the commutator gives values that are averages over the whole charge or discharge interval. This means that such commutators could never give, directly, values as high as those obtained by the direct method, and offered a possible explanation for the discrepancies between the two methods.

In the second paper[3] an attempt was made to show that the value at the beginning of the discharge interval is the same as at the end of the charge interval; in which case there would be no reason to postulate the existence of transfer resistance. The data all pointed strongly in that direction but the design of the commutator was such that values could not be obtained within 4° of the end of the charge interval, and about 4° of the beginning of

---

*Contribution from the Chemical Laboratory of the University of Michigan.

[1] Rewritten from a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Michigan.

[2] Trans. Am. Electrochem. Soc., 45, 311 (1924).

[3] Trans. Am. Electrochem. Soc., 47, 227 (1925).

the discharge interval. The potential was changing so rapidly, particularly on discharge, that it was not safe to extrapolate through these ranges. There were grounds to suspect, also, that the brushes introduced some uncertainties, particularly when the commutator was used at more than one speed.

Before the present work was started the commutator was completely rebuilt with different design to eliminate the difficulties that had been discovered. A new system for the manipulation of the brushes also was employed, which made it possible to explore the region much nearer the end of charge and beginning of discharge than could be done with the old interrupter. In the previous work it was necessary to change the speed of the commutator, which was shown to be a serious disadvantage. By the new arrangement it was not necessary to stop the commutator or change its speed during a complete series of measurements.

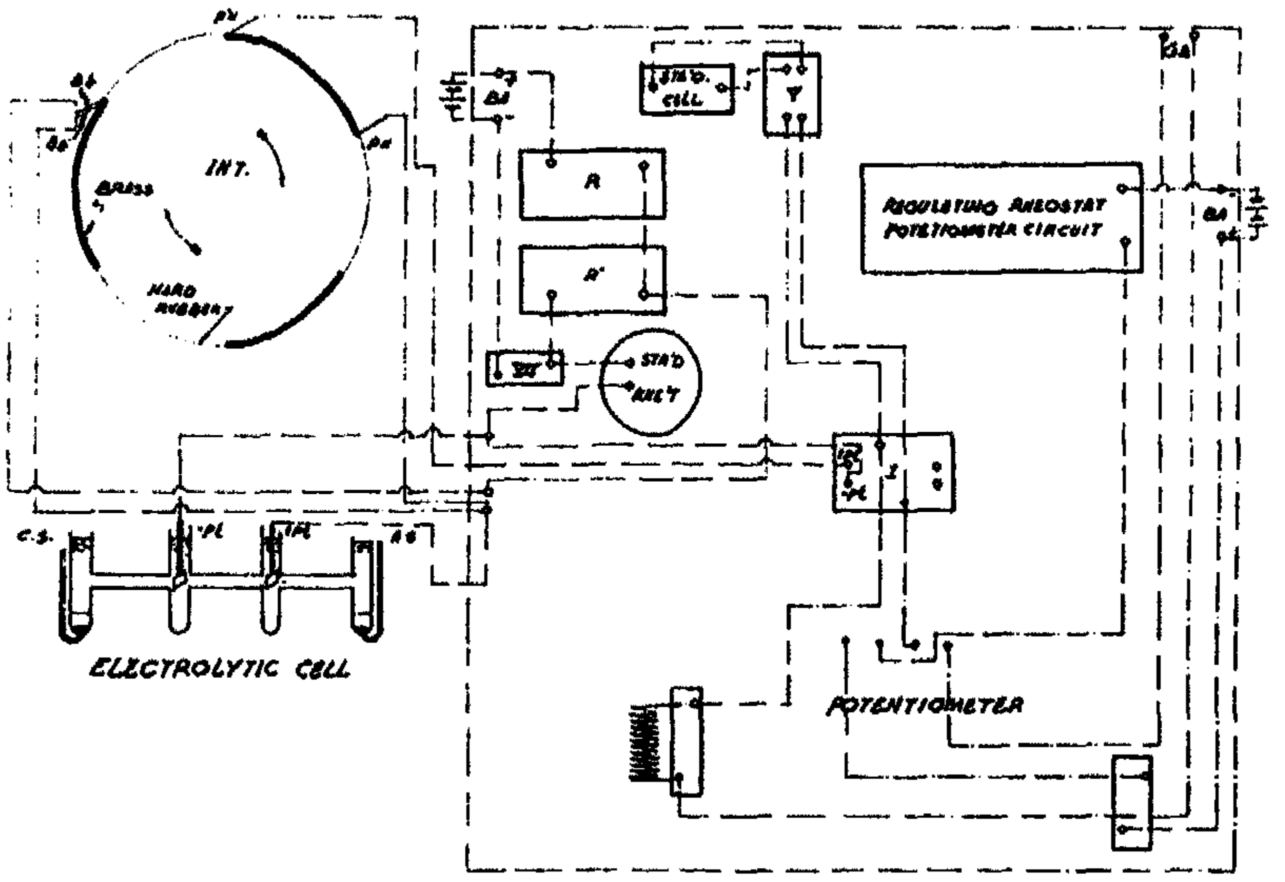


Fig. 1
The essential parts of a potentiometer-commutator assembly for the measurement of decomposition potentials.

Apparatus

The most essential parts of the set-up are shown in Fig. 1. The desired potential, which is obtained as an I.R. drop over resistance R′, may be applied to the cell through the charging brushes (Bb and Bb′), represented in contact with a brass section of the interrupter (Int). The potentiometer is connected to the anode and cathode of the cell through the brushes P_n and P_n' represented in contact with another brass segment near the ends.

The commutator consists of two interrupters directly connected to a ½ horse power motor (see Fig. 2). Each interrupter is made of a disk of hard rubber 2.8 cm. wide and 20 cm. in diameter. The edge is divided into 360°

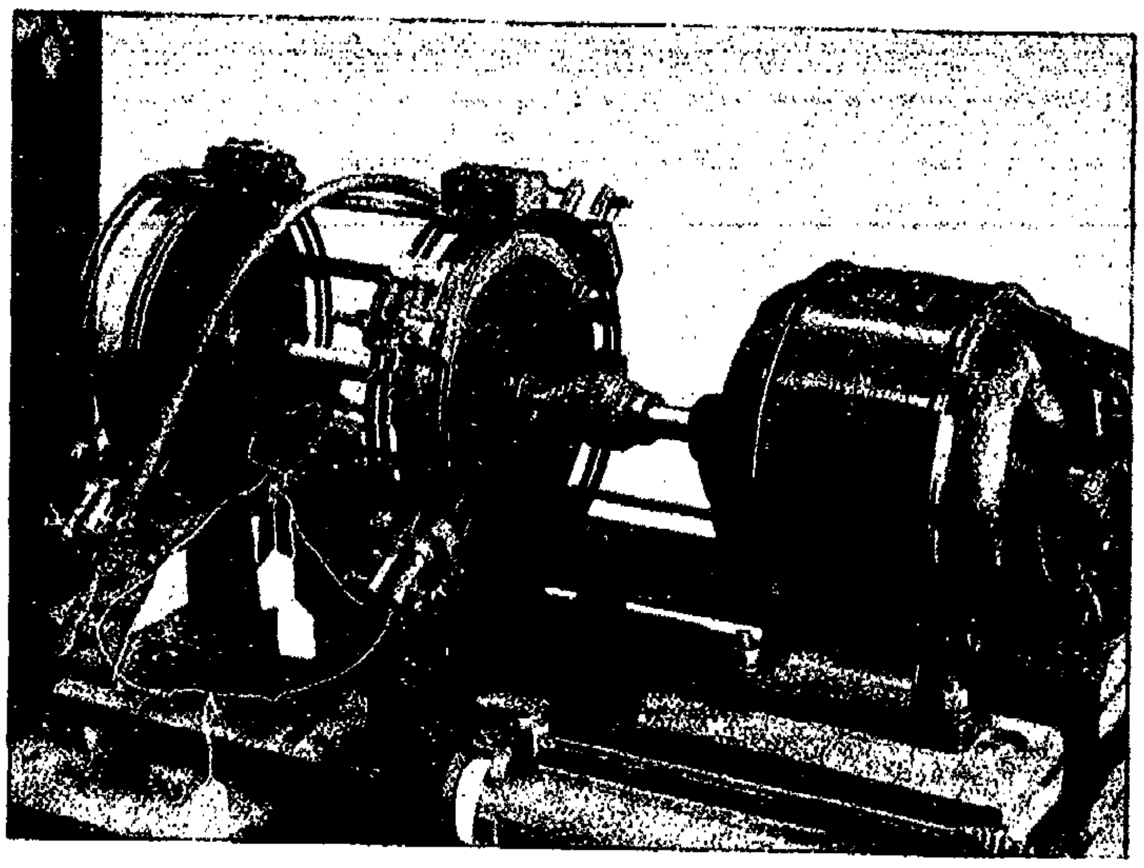


FIG. 2
A direct driven two-disk commutator.

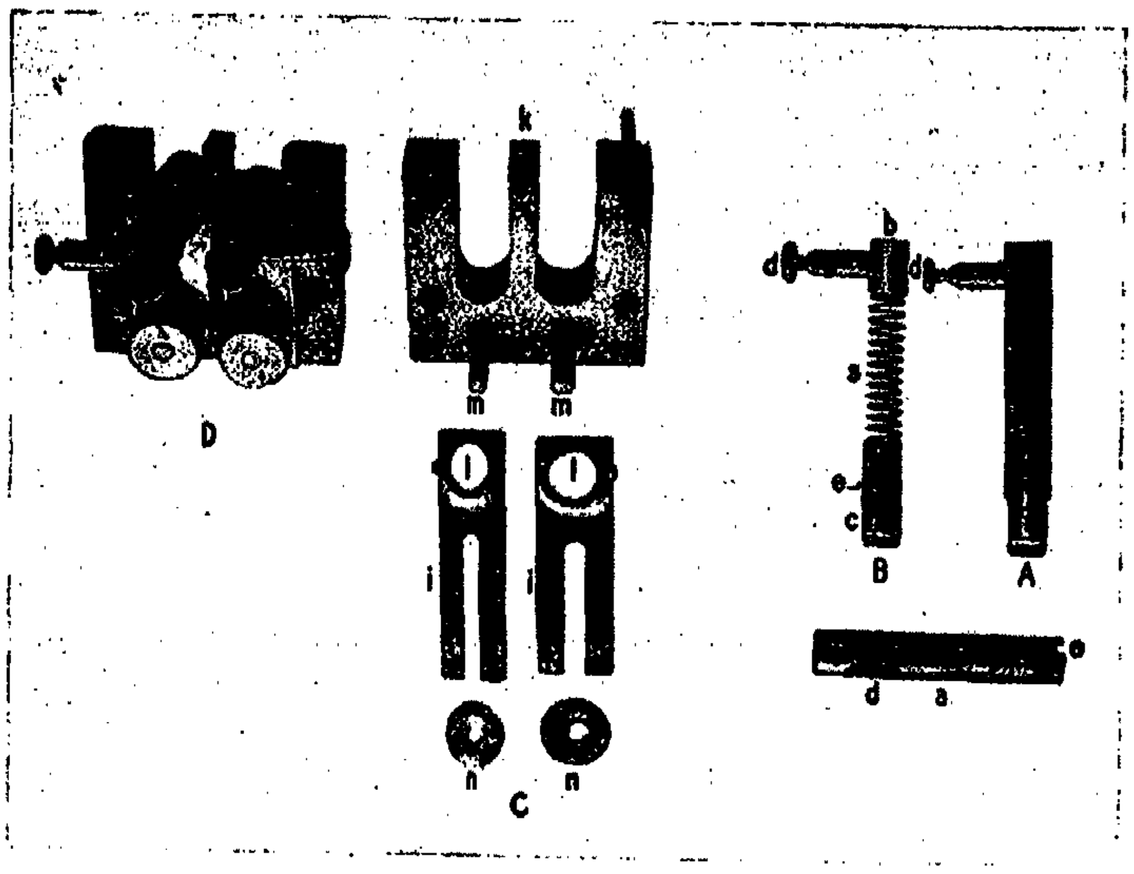


FIG. 3
Brush and brush holder assemblies.

by a scale. In the surface three brass sections each 60° long are set 60° apart, and separated by three hard rubber sections of equal length. The surfaces of the disks are wide enough so that two brushes may be mounted in parallel and thus make contact with the brass segments at the same time. The disks may be shifted to any position on the shaft.

The various parts and the construction of the brushes and brush holders are represented in Fig. 3. The complete brush and holder assembly is shown in (A), and the various parts in (B). The brush proper is made of solid copper of a shape indicated by (c). This is soldered to a spring (S) the other end of which is soldered to a piece of brass (b). The holder (a) is a piece of brass tubing with two narrow openings (d) and (e). The assembly consisting of brush (c), spring (S) and brass piece (b) all slipped inside the holder (a) and held in place by the binding post (d) which passes through opening (d) on the holder. There is a small projection (e) on the brush that fits into the opening (e) and keeps the brush in the proper position. By means of the spring, and the binding post operating in slot (d) the tension of the brush on the interrupter can be changed.

Surrounding each disk of the commutator is an arrangement for supporting the brushes in position (see Fig. 2). Some of the details of a brush support are shown in (C) and (D) of Fig. 3; the various parts are shown in (C) and the assembly in (D). It consists of two parts, the brass strip (i) and the hard rubber support (k). The brass strip has a neck (l) at one end through which the brush assembly (A) may pass; at the other end is a deep slot which enables the brush to be adjusted to any position in the slot of the hard rubber support (k) and held in place by the bolt (m) and nut (n) as illustrated in (D). This whole assembly may be mounted in any position on the frame surrounding the disks as shown in Fig. 2.

The electrolytic cell system is represented diagrammatically in Fig. 1. Two-normal sulfuric acid was used throughout. The reference electrodes were mercurous sulfate and the electrodes in the decomposition cell were platinized platinum.

Experimental

Many experiments were carried out to study such conditions as current density, speed of interrupter, kind of brushes, tension of brushes, length of time commutator was operated, presence of dissolved gases, position of tip of reference electrode, etc. Only a few typical sets of data are recorded, however, in this report.

Table I shows the influence of current density. The time in column (1) is given in seconds from the beginning of the charge or discharge interval. The potentials of the anode against the anode standard are given in column (2); cathode against cathode standard in column (3); the total applied potential minus the I.R. drop through the solution, or, in other words, the sum of (2) and (3) in column (4), the total discharge potential in column (5); and the difference between the total charge potential at the end of charge and the beginning of discharge in column (6). In all experiments conditions were the same except current density and this was made greater in each succeeding experiment.

TABLE I

Comparison of Charge and Discharge Potentials at Different Current Densities

Platinized platinum electrodes. Time is given in sec. after beginning of charge or discharge. The applied potential is greater for each succeeding experiment.

(1) Time $\times 10^{-1}$	(2) Pt.$^+$−A.S. (charge)	(3) Pt.$^-$−C.S. (charge)	(4) Pt.$^+$+Pt.$^-$ (3) + (2)	(5) Pt.$^+$−Pt.$^-$ (discharge)	(6) End of charge minus beginning of discharge
Experiment (1) Average C.D. = .0006 amp./cm^2					
24	1.126	0.716	1.842	1.855	0.000
end	1.138	0.717	1.855	1.841	
Experiment (2) Average C.D. = .0016 amp./cm^2					
17	1.210	0.726	1.936	1.954	0.000
end	1.228	0.726	1.954	1.936	
Experiment (3) Average C.D. = .0021 amp./cm^2					
11	1.222	0.732	1.954	1.979	0.001
end	1.248	0.732	1.980	1.954	
Experiment (4) Average C.D. = .028 amp./cm^2					
14	1.312	0.758	2.070	2.059	0.069
end	1.369	0.759	2.128	1.984	

The data in column (6) show that at high current densities there is still an appreciable difference between the values for the end of charge and the beginning of discharge. The fact that the agreement is good at low but not at high current densities supports the idea that there is a contact resistance at the interface between electrodes and solution as many investigators have contended. Such a resistance would use up some of the measured charge potential before it reached the electrode. More information on this point is furnished by the data in Table II.

If the differences observed in Table I are due to surface resistances these should be appreciably different at the two electrodes. To test this point the charge and discharge potentials were measured separately for each electrode at a series of current densities. The data are recorded in Table II. Column (2) gives the anode charge potential at the end of charge; column (3), at the beginning of discharge; and column (4) the difference between (3) and (2). Columns (6), (7) and (8) give similar data for the cathode. It should be observed that the differences increase with current density as in Table I. If the differences are due to I.R. drops then the resistances may be obtained by dividing the values in columns (4) and (8) by the corresponding currents. The values thus obtained are recorded in columns (5) and (9).

TABLE II

Anode and Cathode Potentials on Charge and Discharge

(1) Time $\times 10^{-4}$	(2) Pt.$^+$–A.S. (End of charge)	(3) Pt.$^+$–A.S. (Discharge)	(4) Pot. diff.	(5) Resistance	(6) Pt.$^-$–C.S. (End of charge)	(7) Pt.$^-$–C.S. (Discharge)	(8) Pot. diff.	(9) Resistance
Experiment (1) current 0.0024								
0		1.106	0			0.698	0	
9		1.105				0.698		
578		1.098				0.698		
609	1.106				0.698			
Experiment (2) current 0.0086								
0		1.190	0.004	.5		0.732	0.004	.5
8		1.187				0.731		
578		1.157				0.724		
609	1.194				0.736			
Experiment (3) current 0.0143								
0		1.234	0.016	1.1		0.734	0.011	.8
9		1.230				0.733		
660		1.178				0.731		
708	1.250				0.745			
Experiment (4) current 0.0265								
0		1.270	0.027	1.0		0.743	0.019	.8
7		1.265				0.741		
506		1.198				0.736		
543	1.297				0.762			
Experiment (5) current 0.0365								
0		1.283	0.043	1.2		0.745	0.031	.9
8		1.279				0.743		
565		1.193				0.737		
649	1.326				0.776			
Experiment (6) current 0.046								
0		1.295	0.054	1.2		0.744	0.042	.9
9		1.289				0.742		
660		1.196				0.734		
708	1.349				0.786			
Experiment (7) current 0.054								
0		1.316	0.061	1.1		0.747	0.052	.9
8		1.305				0.745		
565		1.203				0.736		
649	1.377				0.799			

The surprising fact is the resistances are practically the same for each electrode and do not change with current density and are, therefore, not due to transfer resistances. In fact it was shown later that the resistances were due to the combined resistances of the electrodes and lead wires of the charging circuit between the electrodes and the points where the potentiometer circuit made contact. In all later work the leads were reduced in length as much as possible and when necessary corrections were made.

To study the nature of the resistance of the commutator brushes an arrangement represented in Fig. 4 was used. The two sets of brushes a and a′ and b and b′ were set 60° apart and in parallel position on the interrupter. The brushes a and b, also, a′ and b′ were connected through the switch I. The potential divider R′ was used as the source of current which passed through the ammeter and either the set of brushes b and b′ or a and a′ depending upon which was in contact with a brass segment. The voltmeter measured the fall of potential over whichever pair of brushes was carrying the current. The voltmeter reading divided by the ammeter reading gave the resistance in the brush contacts.

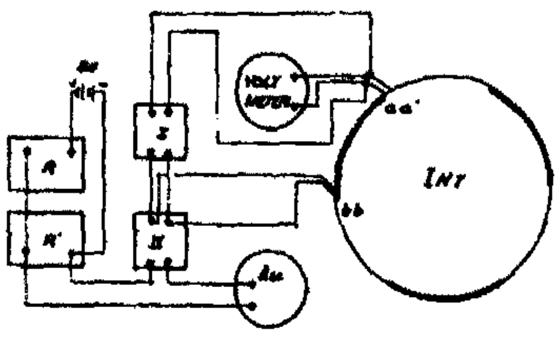


Fig. 4
Diagram of the arrangement for producing a continuous direct current through the brushes of a rotating commutator.

Measurements were taken with three different current densities and various r.p.m.s. and are represented in Fig. 5. The curve shows that the resistance of the commutator brushes increases with increase of r.p.m. but is independent of current density. The results are surprisingly reproducible as shown by the agreement of the three sets of data.

Since, in the commutator method, the current passes through the brushes on the interrupter, an I.R. drop at the contact is inevitable. This drop is very small at low, but is considerable at high current densities, particularly at high commutator speeds. As a result, the applied potential that actually reaches the electrodes from a common source varies with these factors. In other words, the potential from a common source that actually reaches the electrodes is different in the commutator method and the direct method. This subject was studied more fully with an arrangement similar to Fig 4, which permitted the applied potential to be measured in three ways.

The data are recorded in Table III. The first column indicates the method used. In the *direct method* (a) a direct continuous potential was applied to the cell without passing through the interrupter; in the *commutated direct method* (b) a direct continuous potential was applied through the interrupter by two sets of brushes arranged as indicated in Fig. 4; in the *commutator method* (c) a direct intermittent potential was applied through the interrupter which is the regular commutator arrangement; and in the "*direct method*" (d) the system was the same as (a) except a resistance equal to the

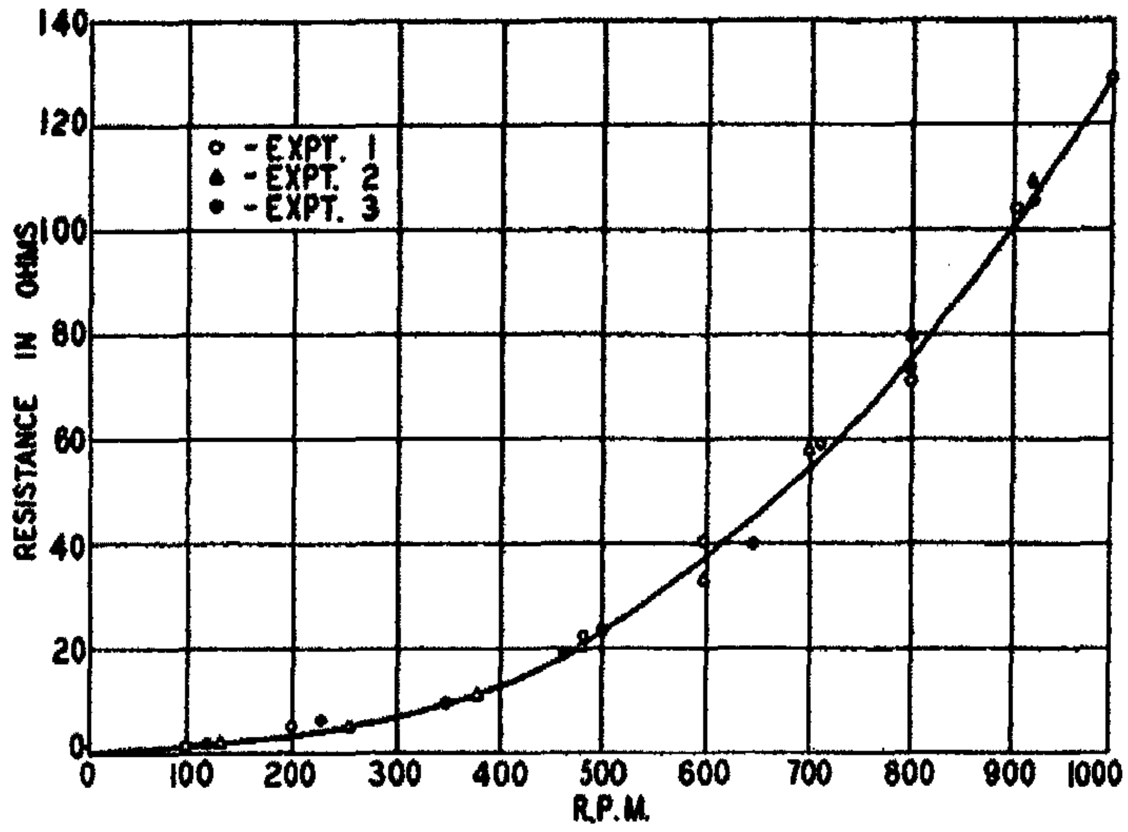


FIG. 5
Curve showing change of brush contact resistance with speed of rotation of commutator.

TABLE III
Comparison of Four Methods for measuring Polarisation

(1) Method	(2) R−R′	(3) Pt.⁺−Pt.⁻ (Charge)	(4) Pt.⁺−A.S. (Charge)	(5) Pt.⁻−C.S. (Charge)	(6) (4) + (5) Pt.⁺−Pt.⁻	(7) Pt.⁺−Pt.⁻	(8) I (Amp.)
Experiment (1)							
(a)	2.037	2.000	1.145	0.734	1.879		0.00338
(b)	2.043	1.995	1.145	0.734	1.879		0.00320
(c)	2.018	1.937	1.121	0.729	1.850	1.850	0.00350
(d)	2.042	1.995	1.145	0.734	0.879		0.00320
Experiment (2)							
(a)	2.322	2.229	1.232	0.750	1.982		0.00844
(b)	2.345	2.200	1.229	0.748	1.977		0.00740
(c)	2.233	2.011	1.210	0.738	1.948	1.943	0.00804
(d)	2.347	2.205	1.230	0.748	1.978		0.00740
Experiment (3)							
(a)	2.498	2.345	1.265	0.757	2.022		0.0136
(b)	2.518	2.298	1.228	0.757	1.985		0.0126
(c)	2.520	2.283	1.219	0.750	1.969	1.946	0.0131
(d)	2.517	2.298	1.226	0.756	1.982		0.0126
Experiment (4)							
(a)	3.084	2.770	1.312	0.768	2.080		0.0273
(b)	3.177	2.789	1.312	0.765	2.077		0.0240
(c)	3.120	2.665	1.289	0.749	2.038	2.015	0.0249
(d)	3.161	2.789	1.312	0.764	2.076		0.0240

brush resistance determined in (b) was inserted in series with the electrolytic cell. The measurements were taken by all four methods at the same time with the same ratio of resistances R'/R of the potential divider used as the source potential. The magnitude of the source potential is given in column (2). In the various experiments all conditions were held constant except the ratio of resistances in the potential divider, and this was changed so as to give a higher source potential for each succeeding experiment.

A comparison of the results in rows (b) and (d) for the various experiments shows that for all measurements made by the commutated direct method (b) and "direct method" (d) the data obtained are practically the same. This indicates that passing the charging current through the resistance of the commutator brushes is equivalent to passing it through a constant carbon resistance. A comparison of the data in rows (a) and (b) shows that in all cases the current (column 8) and also the polarisation (columns 3, 4, 5 and 6) are greater in the direct method (a) than in the commutated direct method (b). This is due to the fact that in the latter the brush resistance is included in the circuit and prevents the total source potential from reaching the electrodes. It may be observed, further, from the data in rows (a), (c) and (b) (column 2) that the source potentials in the former two are less than in the latter though the ratio of resistances on the potential divider is the same. The variation of this common source potential is undoubtedly caused by the change of the apparent resistance of the potential divider as the result of the addition, in the parallel circuit, of the resistance of the commutator brushes in the commutated direct method and by the change of e.m.f. of the cell in these two methods. The resistance of the commutator brushes is of course equal to zero in the direct method.

An inspection of the data in rows (c) (column 8) shows that the current is higher than in (b) and (d) but lower than in (a). It is lower than in (a) because of the added resistance of the brushes and it is higher than in (b) and (d) because it is an intermittent current while in (b) and (d) the current is continuous. An intermittent current of the same value as a continuous one produces less average polarisation. This conclusion is borne out by the observed data recorded in columns 6, 7, and 8 as pointed out above.

These data show that any resistance which develops at the brushes will cause an increase in source potential at the potential divider but will at the same time diminish the charging current; which means that, in a comparison of the direct and commutator methods for measuring overvoltage, the experimenter may apply a certain potential to the cell by the direct method and obtain a certain polarisation potential, then he may apply supposedly this same potential through a commutator and expect that he should get the same polarisation, and in case he does not, he may conclude that the two methods do not give the same value. The data in Table III show that he is not justified in this assumption but rather should expect a lower polarisation, as he actually finds, in the latter case because of the lower current which the data show is always obtained. It is advisable, therefore, in a comparison of the two methods to use a low speed of rotation of the commutator in order to minimize the resistance of the commutator brushes. It should be pointed out, also, that commutator data obtained at definite intervals of charge or discharge, to be used for extrapolation purposes, must be obtained at the same r.p.m., a point that has not been given sufficient consideration in the past.

Some investigators have contended that in a comparison of the two methods the current densities employed in the two methods should be the same. The data in *Table III*, columns 6 and 8, show that this conclusion is not true. The current by the commutator method is in all cases slightly higher than by the methods (b) and (d), yet the polarisation is in all cases less. If the current were made equal in the two cases then the difference in polarisation would be even greater, which means that it is not to be expected that the polarisation should be the same by the two methods at the same current density. The reason for this is evident; in the commutator method the current flows intermittently and thus produces less polarisation, or to put it differently, during the time the intermittent current is not flowing the polarisation decreases a little.

Summary

1. A commutator is described which makes it possible to measure charge or discharge potentials within 0.0003 sec. from the beginning or end of the charge and discharge intervals for the electrodes either combined or separately.

2. Several sources of error that may enter into the measurements of polarisation potentials by the commutator method have been pointed out.

THE MEASUREMENT OF POLARISATION BY THE DIRECT AND COMMUTATOR METHODS*

BY A. L. FERGUSON AND G. M. CHEN[1]

In the previous article the authors have described a new commutator which possesses several desirable features and eliminates some of the undesirable features found in other commutators. Some important sources of error, also, were pointed out.

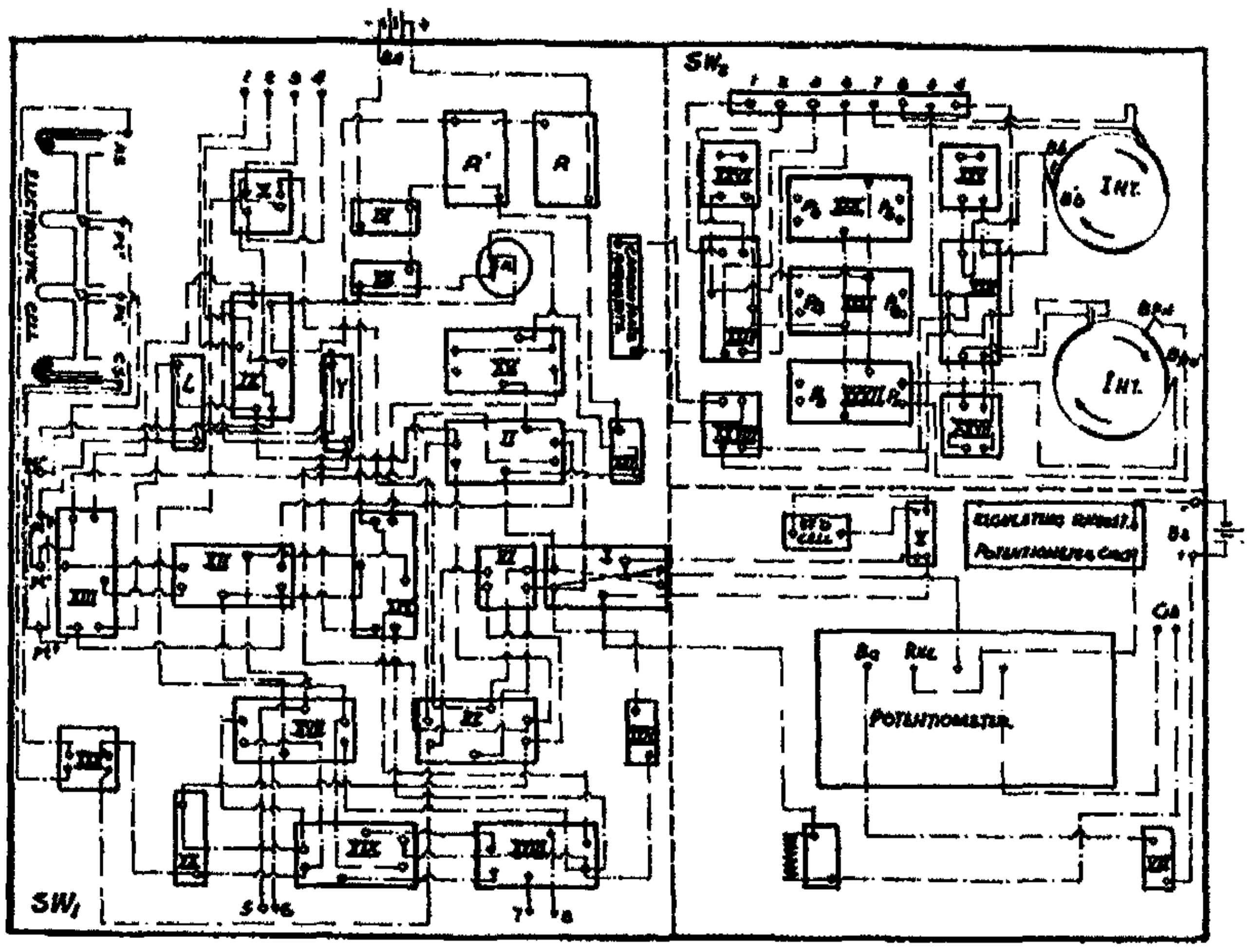


FIG. 1
Complete wiring diagram of switch-board used in polarisation measurements.

In the present work it was found advisable to introduce several additions to the set-up in order to measure the potential over every part of the circuit, even including the lead wires; the object being to make certain that all potentials were correctly measured and that there was no potential or I.R. drop in any part of the circuit unaccounted for. By this arrangement the sum of all the separate potentials in the whole circuit could be checked with the source potentials.

The final system is represented in Fig. 1. A summary of the manipulation of the switches necessary for the more important measurements is given in Table I. To make a measurement, the switches listed following that measurement should be closed and all others opened.

---

* Contribution from the Chemical Laboratory of the University of Michigan.

[1] Rewritten from a thesis presented in partial fulfillment of the requirement for the degree of Doctor of Philosophy at the University of Michigan.

TABLE I

A. Charge potential with the interrupter rotating.

Switches XXIII and XXIV closed down and P_n closed
(P_n indicates the P_1, P_2, P_3, etc. required)

Potential to be measured	Switches to be closed
Charge	I, II (right), XII (right).
Pt.$^{+}$ – A.S.	I, III (left), XII (left), XIII (down), XXII.
Pt.$^{-}$ – C.S.	I, III (right), XII (left), XIII (up), XXII, XX.
A.S. – C.S.	I, VI, XXII, XVII (left).
Brushes	I, X (right), XIV (up).
S.R.	I, XV (right), XIV (up).
Box Pot.	I, XVI, XIV (down), XXIX.

B. Discharge potentials with interrupter rotating.

Switches XXIII and XXIV closed up and P_n closed

Potential to be measured	Switches to be closed
Discharge	I, II (left), II (down), r.
Pt.$^{+}$ – A.S.	I, III (left), IX (down), XXII.
Pt.$^{-}$ – C.S.	I, III (right), II (up), XX, XXII.

C. Direct method.

Switches XXIII closed up, XXV and XXVI closed

Potential to be measured	Switches to be closed
Charge	I, II (right), XII (right).
Pt.$^{+}$ – A.S.	I, III (left), XII (left), XIII (down).
Pt.$^{-}$ – C.S.	I, III (right), XII (left), XIII (up).
A.S. – C.S.	I, VI, XXII, XVII (left).
Brushes	I, X (right), XVII (right), XXIX.
S.R.	I, XIV (up), XV (right).
Box Pot.	I, XIV (down), XVI, XXIX.

Symbols used for various potentials:

Pt.$^{+}$ – A.S. = anode potential vs anode standard.
Pt.$^{-}$ – C.S. = cathode potential vs cathode standard.
Pt.$^{+}$ – C.S. = anode potential vs cathode standard.
Pt.$^{-}$ – A.S. = cathode potential vs anode standard.
Pt.$^{+}$ + Pt.$^{-}$ = sum of the single electrode potential of anode and that of cathode.
Pt.$^{+}$ – Pt.$^{-}$ (charge) = potential, anode vs cathode, including the I.R. drop through the solution.
Pt.$^{+}$ – Pt.$^{-}$ (discharge) = potential, anode vs cathode, equal to the sum of electrode potentials on discharge.
C.D. = current density.
Box Pot. = common source of potential taken from the potential divider.
Hg.$^{+}$ – Hg.$^{-}$ or I.R. = I.R. drops through the solution, or potential between two reference electrodes.
Br. = potential across the brushes.
S.R. = potential across the standard resistance.

The electrolytic cell system was changed somewhat from that used before. The new arrangement is shown in Fig. 2. This more complex system was designed to prevent the diffusion of mercurous ions into the decomposition cell from the reference electrodes, and to eliminate any I.R. drop between the electrode of the decomposition cell and the reference electrode. Two normal sulfuric acid was used in all experiments. In some experiments the electrodes were platinized and in others bright.

The heart of the whole equipment is, of course, the commutator. For a description see the previous paper. An end view of one of the interrupters giving considerable detail is shown in Fig. 3.

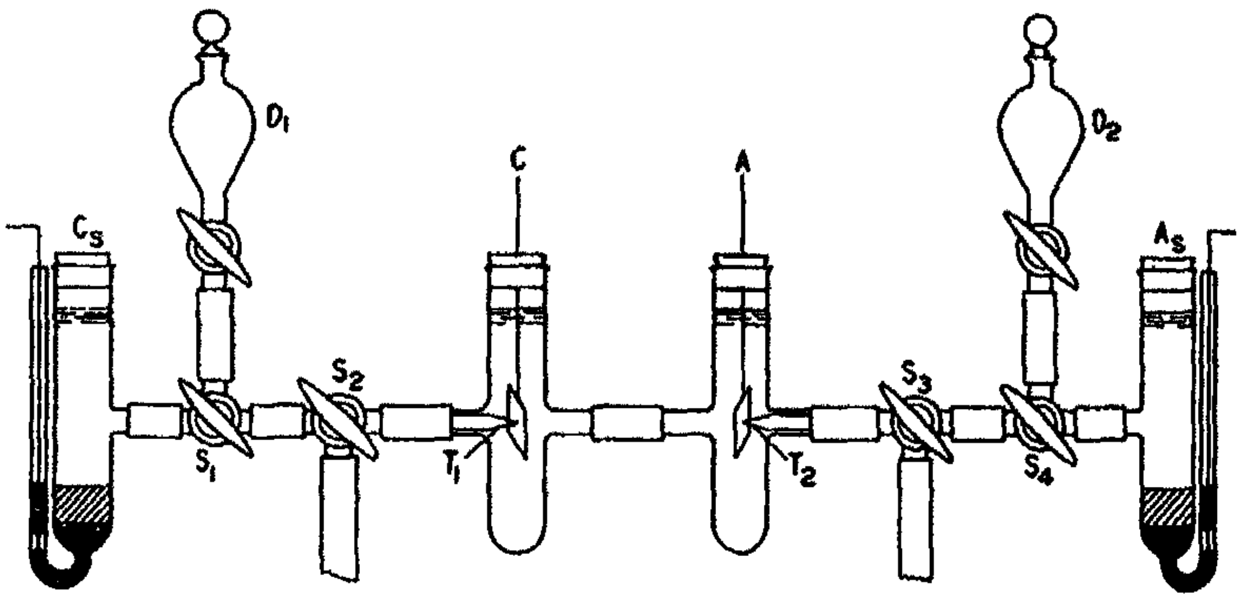


FIG. 2
Cell system for polarisation measurements.

The charging brushes B_b are set in parallel so that both make contact at the same instant. The potentiometer brushes B_{p1} and $B_{p1'}$ are set 59° apart which means they close the potentiometer circuit during only one degree once every 1/3 of a revolution. The potential measured is, then, the average during a time interval equal to lx(1/360) × (60/r.p.m.) sec. If the interrupter rotates clockwise and has come to the position shown in Fig. 3, the charging brushes have made contact on a brass plate for one degree and during this same time the potentiometer brushes B_{p1} and $B_{p1'}$ have made connection to the potentiometer through switch P_1 in S_{w2} of Fig. 1. The potential measured is the average value of the potentials during only this one first degree of charge, since, after the interrupter has turned more than one degree the connection to the potentiometer is broken at B_{p1}. After 7 degrees, connection is made again for a period of one degree by brushes B_{p2} and $B_{p2'}$. In a similar manner other pairs of brushes are used to measure either charge or discharge or both after any desired known intervals of time at constant r.p.m. and practically simultaneously.

If the potentiometer contact be made for one degree and the potentiometer brushes commence to make connection after the charging brushes have been in contact with the brass section of the interrupter for "d" degrees, then the time interval after charge starts corresponding to the potential measured is $d - \frac{1}{2}$ degrees or in seconds is given by the expression

$$(d - \tfrac{1}{2})\ (1/350 \times 60/\text{r.p.m.})$$

One might think, at first, that with the apparatus here described it should be possible to reduce the discharge time interval to any desired value by increasing the speed of the interrupter. From the formula it is evident the time interval may be changed by decreasing or increasing the R.P.M. Several factors enter in, however, which place a limit upon the time-interval and still obtain reliable data. In the first place, as will be shown later, sufficient time must be allowed for the charge to reach a maximum during each charge interval. In the second place, the discharge potential at the instant the current is interrupted cannot be measured because the charging brushes

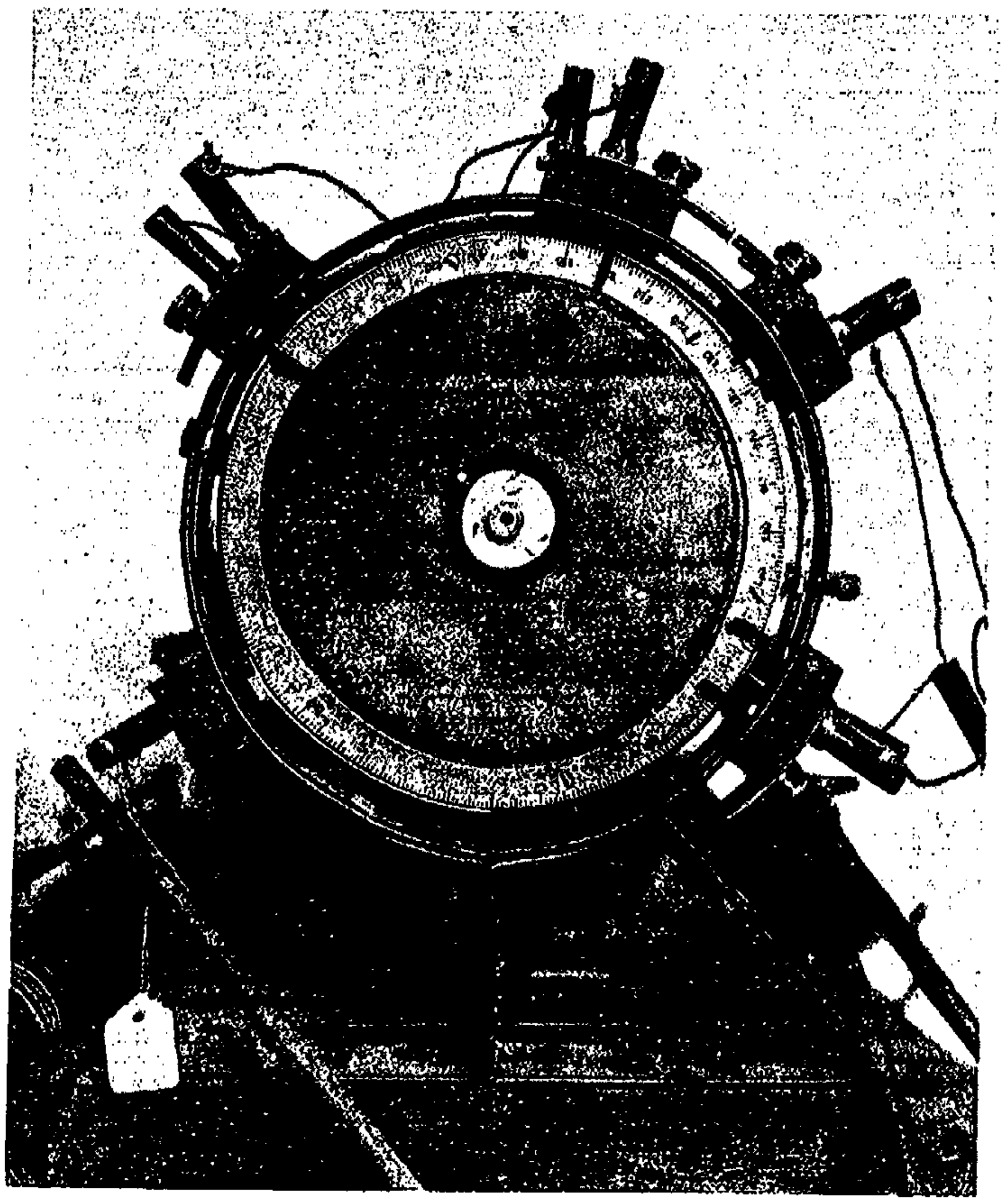


Fig. 3
End view of one disk of commutator.

must have completely left the brass section of the interrupter before the potentiometer contact is made. This interval amounts to about 0.0001 second at 400 R.P.M. for the brushes used; and they are as thin (1 mm.) as other conditions will permit. In the third place, in order that the potentials shall be measured accurately to one millivolt the potentiometer circuit must be closed at least 0.0005 second. If, now, the electrode potential at the beginning of discharge is determined as soon as the apparatus will permit after the interruption of the current at the R.P.M. 400 and at a time interval just necessary for the potentiometer contact, the time during which the average potential is obtained is .0006 second. By assuming the average potential to be the actual potential at a time equal to half of the total interval, the shortest possible discharge interval at which potential can be measured is 0.0003 seconds after discharge has begun. These limitations are imposed by the very nature of equipment required in the commutator potentiometer method.

Among the advantages of the equipment used in this work not possessed by those previously used may be listed the following: (1) measurements may be made by both the direct and commutator methods at the same time; (2) both charging and discharging potentials may be measured at different and known intervals of charge and discharge without stopping the interrupter; (3) potentials can be determined as near the end of charge and beginning of discharge as the physical limitations inherent in the potentiometer commutator method will permit; (4) Anode, cathode and total potentials can be measured practically at the same time; (5) The I.R. drop between the electrodes may be measured directly; (6) Every individual potential throughout the charging circuit may be measured and their sum compared with the total potential delivered to the system; (7) Only one speed of the interrupter is required for a complete set of measurements.

Experimental

Hundreds of measurements were made with this outfit which were highly reproducible and satisfactory; but only a few typical sets are included in this report.

It was stated that the charge potential requires some time to reach a maximum value and that in a comparison of the direct and commutator methods care must be taken to see that sufficient time is allowed for the maximum to be reached. This is clearly evident from the curves of Fig. 4, where charge and discharge potentials are plotted against time from the beginning of the charge interval. Curves (a) and (a′) are the charge and discharge curves for a current density of 9 m.a., and (b) and (b′) for 90 m.a. For each set of curves the current density was held constant, also, the speed of rotation of the interrupter. Each point was determined by a separate set of brushes. Readings were taken in rapid succession and then repeated as a check. It was found advisable in all cases to pass a continuous direct current through the cell for at least half an hour before starting the interrupter. Measurements were not taken until the intermittent current had been flowing about five minutes. These curves make clearly evident the following points. (1) It is possible, by means of the interrupter used, to obtain definite values for any part of either the charge or discharge interval and thus to plot a complete cycle. (2) The rate of charge and discharge at the various portions of the charge and discharge intervals depends upon the current density and is much greater at the start the higher the current density. (3) The time required to reach maximum charge is greater the lower the current density. (4) The only way to be certain the charge potential has reached its maximum value is to determine the charge curve.

The curves in Fig. 5 show the relation between current and cell potential as both change with time. The current increases much more rapidly than the potential and reaches a maximum after which it shows a slight but characteristic decrease as the potential increases.

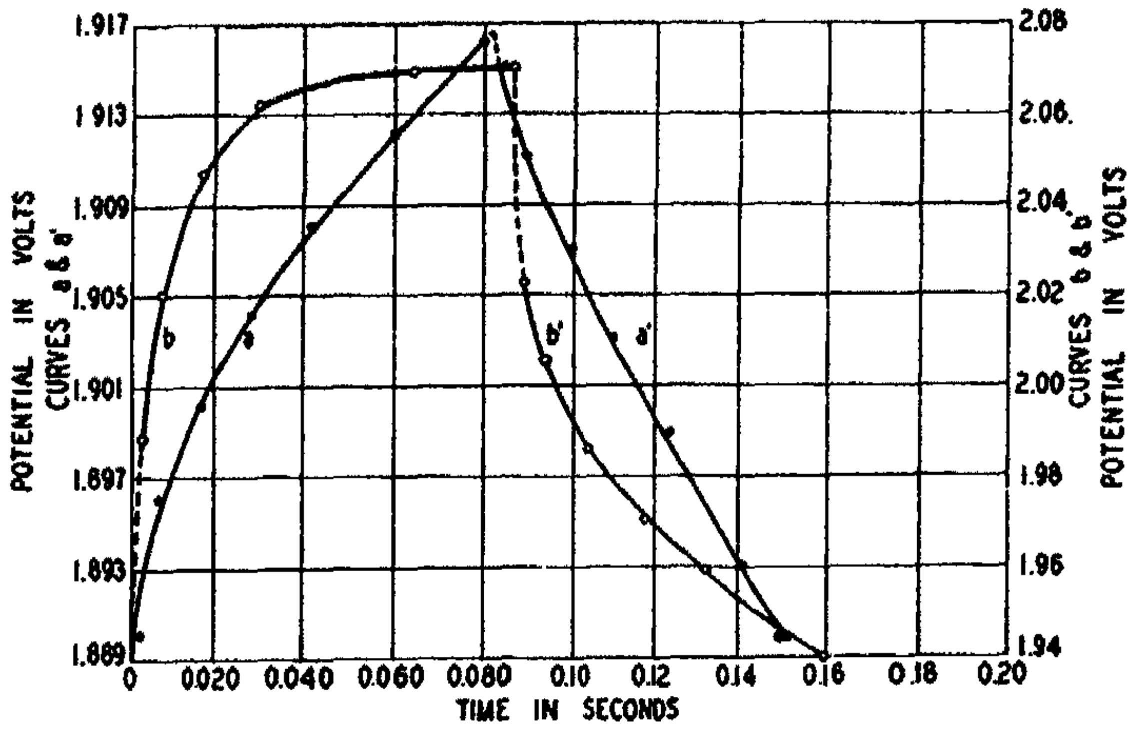


Fig. 4
Charge and discharge curves by commutator potentiometer method.

Attention was concentrated especially upon the portions of the curves at the end of charge and beginning of discharge as these are the parts which are of greatest interest and the portion which the redesigned commutator made it possible to study. The work reported earlier indicated that if measurements could be made close enough to the end of charge and the beginning of discharge the values would be found equal and thus proof furnished that there is no such thing as transfer or any other kind of surface resistance.

A typical set of data is given in Table II. The time in seconds recorded in column (1) corresponds to the interval after discharge has begun. Only one value for charge is recorded and that is for the time corresponding to 59° and is considered that at the end of charge since the charge had reached a maximum.

The average current density was determined by measuring the I.R. drop over a standard resistance during the total charge interval. Columns (3) and (7) contain the single electrode potentials at the end of charge minus the I.R.

drop through the connecting wires. The resistance of the electrode and connecting wire to the point where the potential was determined was in these experiments 0.24 ohms. The electrode potential values in columns (4) and (8), at zero time of discharge were obtained by extrapolation from the discharging curves. In each of the eight experiments, conditions were maintained constant except the current density which was made higher in each succeeding experiment. As the current density increases from 3.8 m.a. to 149 m.a. the polarisation of the cathode increases only 24 m.v. but the anode increases 282 m.v. The cathode drops two or three millivolts during the first few thousandths of a second then remains constant during the remainder of the discharge interval. The anode potential drops much more rapidly and continues to drop throughout the whole discharge interval. The anode potentials for some of the experiments are represented as curves in Fig. 6. The ends of the charge curves are represented as horizontal dotted lines since the potential had reached a constant maximum value. It should be noticed that the first point on the discharge curves was taken about 0.0008 sec. after the beginning of the discharge interval and the greatest extrapolation was only 9 m.v. The differences in potentials between the end of charge and zero time of discharge are given in columns (5) and (9). They amount to about 2 m.v. which is practically within the limits of experimental or extrapolation errors. This is the first time that anything like so close agreement has been found for such high current densities.

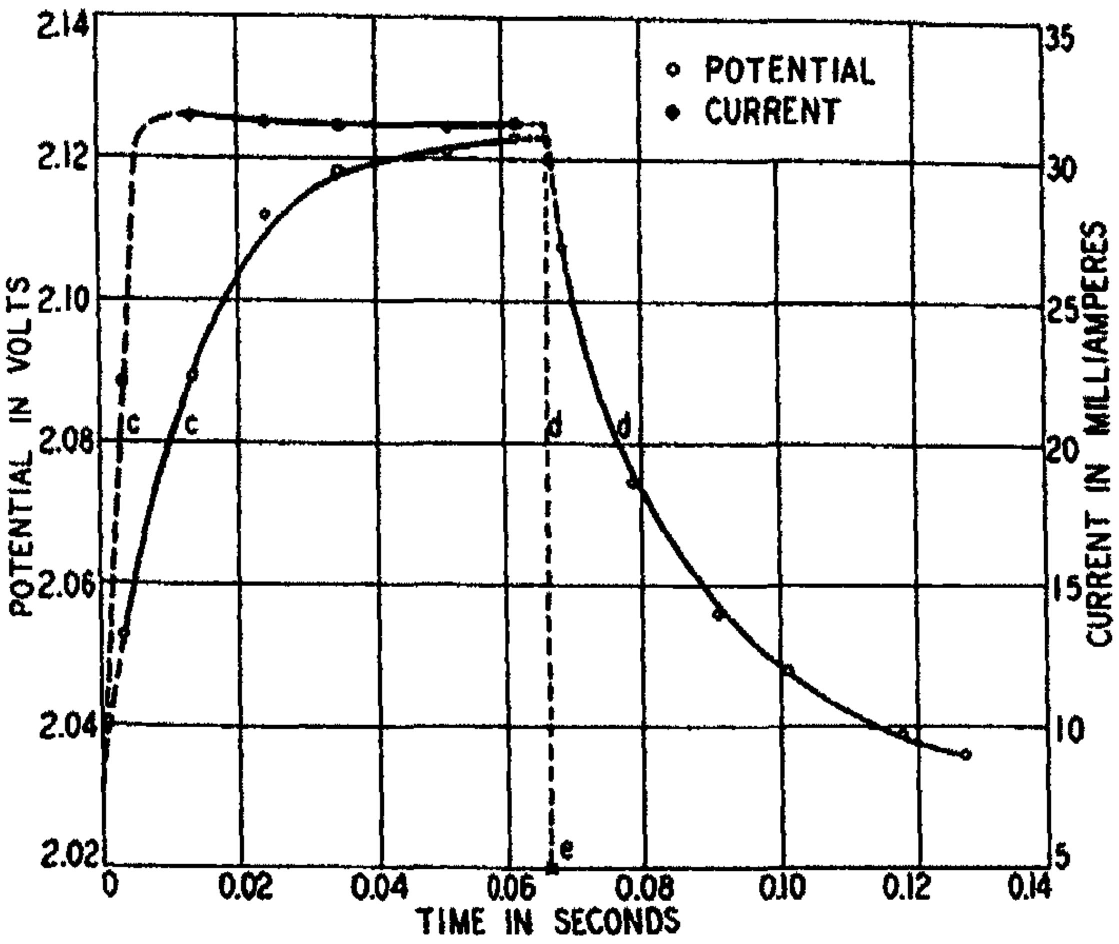


Fig. 5

Current and potential charge and discharge curves.

TABLE II

Relation between single electrode potentials on charge and on discharge at various current densities. Platinized electrodes. Time is in Sec. × 10^4.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
	$Pt.^+$−A.S.		Pt^+.−A.S.		$Pt.^-$−C.S.		$Pt.^-$−C.S.	
Time × 10^4	End of charge	Pot. corr.	Dis-charge	Pot. diff. m.v.	End of charge	Pot. corr.	Dis-charge	Pot. diff. m.v.
Experiment (1) Average C.D. = 0.0038								
0			1.040	−1			0.707	0
8			1.039				0.706	
40			1.038				0.705	
140			1.036				0.705	
460			1.032				0.705	
550			1.031				0.705	
590	1.039	1.039			0.707	0.707		
Experiment (2) Average C.D. = 0.0178								
0			1.165	0			0.722	−1
8			1.164				0.721	
40			1.162				0.719	
140			1.153				0.719	
460			1.138				0.719	
550			1.131				0.719	
590	1.167	1.165			0.723	0.721		
Experiment (3) Average C.D. = 0.0284								
0			1.210	−1			0.725	−2
8			1.209				0.724	
40			1.204				0.722	
140			1.193				0.722	
460			1.167				0.722	
550			1.161				0.722	
590	1.212	1.209			0.726	0.723		
Experiment (4) Average C.D. = 0.0436								
0			1.254	−1			0.728	−1
8			1.252				0.727	
40			1.246				0.725	
140			1.225				0.725	
460			1.197				0.725	
550			1.193				0.725	
590	1.259	1.253			0.723	0.727		

TABLE II (continued)

(1) Time $\times 10^4$	(2) Pt.$^+$–A.S. End of charge	(3) Pot. corr.	(4) Pt.$^+$–A.S. Dis-charge	(5) Pot. diff. m.v.	(6) Pt.$^-$–C.S. End of charge	(7) Pot. corr.	(8) Pt.$^-$–C.S. Dis-charge	(9) Pot. diff. m.v.
Experiment (5) Average C.D. = 0.0722								
0			1.272	−2			0.729	−1
7			1.268				0.728	
33			1.256				0.726	
129			1.231				0.726	
423			1.200				0.726	
506			1.193				0.726	
543	1.278	1.270			0.736	0.728		
Experiment (6) Average C.D. = 0.0936								
0			1.290	−2			0.729	−2
8			1.286				0.728	
40			1.272				0.726	
140			1.249				0.726	
460			1.210				0.726	
550			1.204				0.726	
590	1.299	1.288			0.738	0.727		
Experiment (7) Average C.D. = 0.1228								
0			1.296	+2			0.730	0
7			1.290				0.729	
32			1.277				0.727	
122			1.250				0.727	
400			1.210				0.727	
479			1.201				0.727	
513	1.313	1.298			0.745	0.730		
Experiment (8) Average C.D. = 0.1490								
0			1.322	+2			0.731	+1
7			1.313				0.730	
33			1.293				0.729	
129			1.264				0.729	
423			1.220				0.729	
506			1.214				0.729	
543	1.342	1.324			0.750	0.732		

These data confirm the prediction made in an earlier paper that the potential at the beginning of charge and the end of discharge would be found equal if reliable measurements could be made. This means that transfer resistance or any other kind of resistance is not present at the surface of electrodes for the system just described.

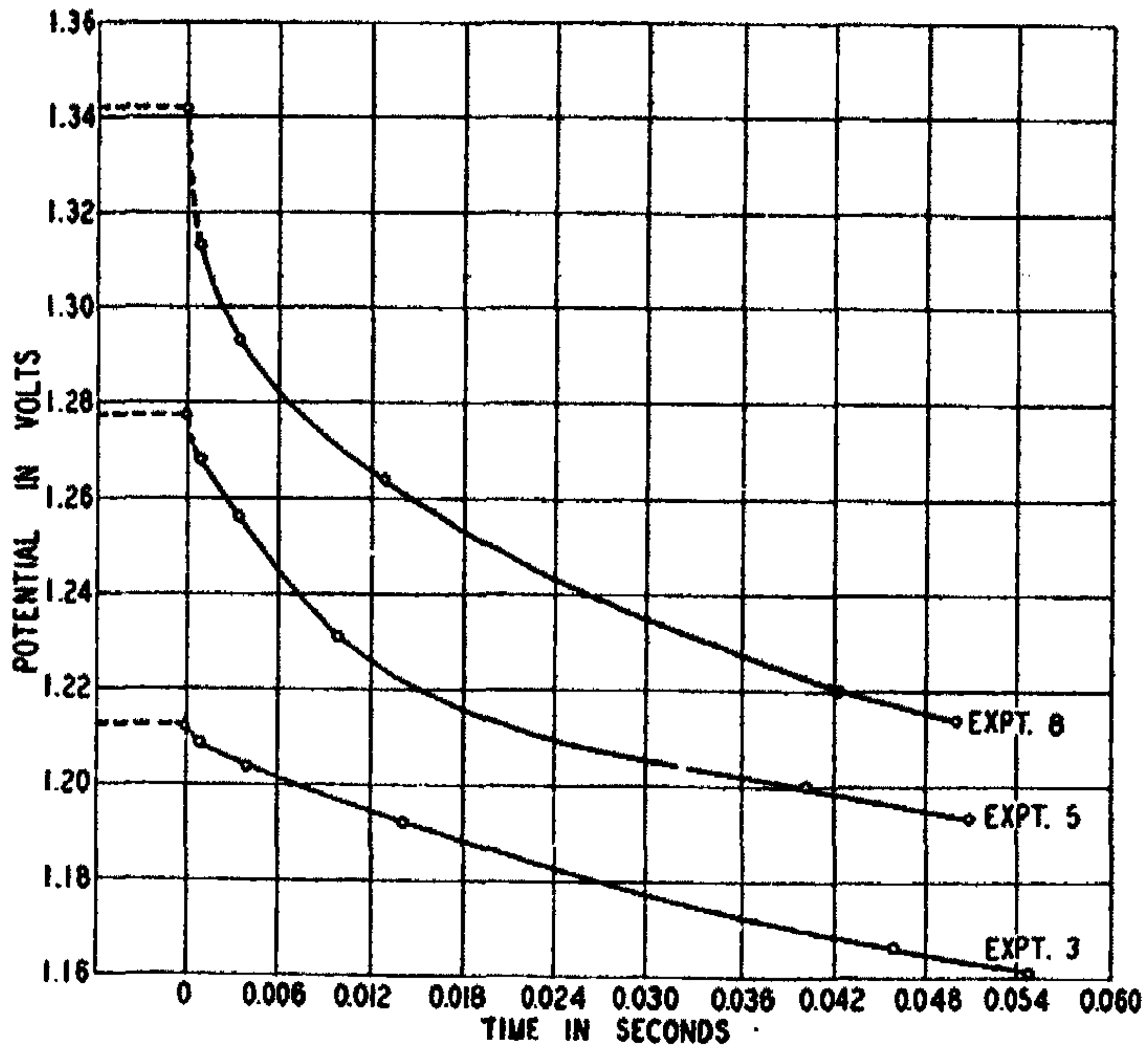


FIG. 6
Anode discharge curves for platinized electrodes.

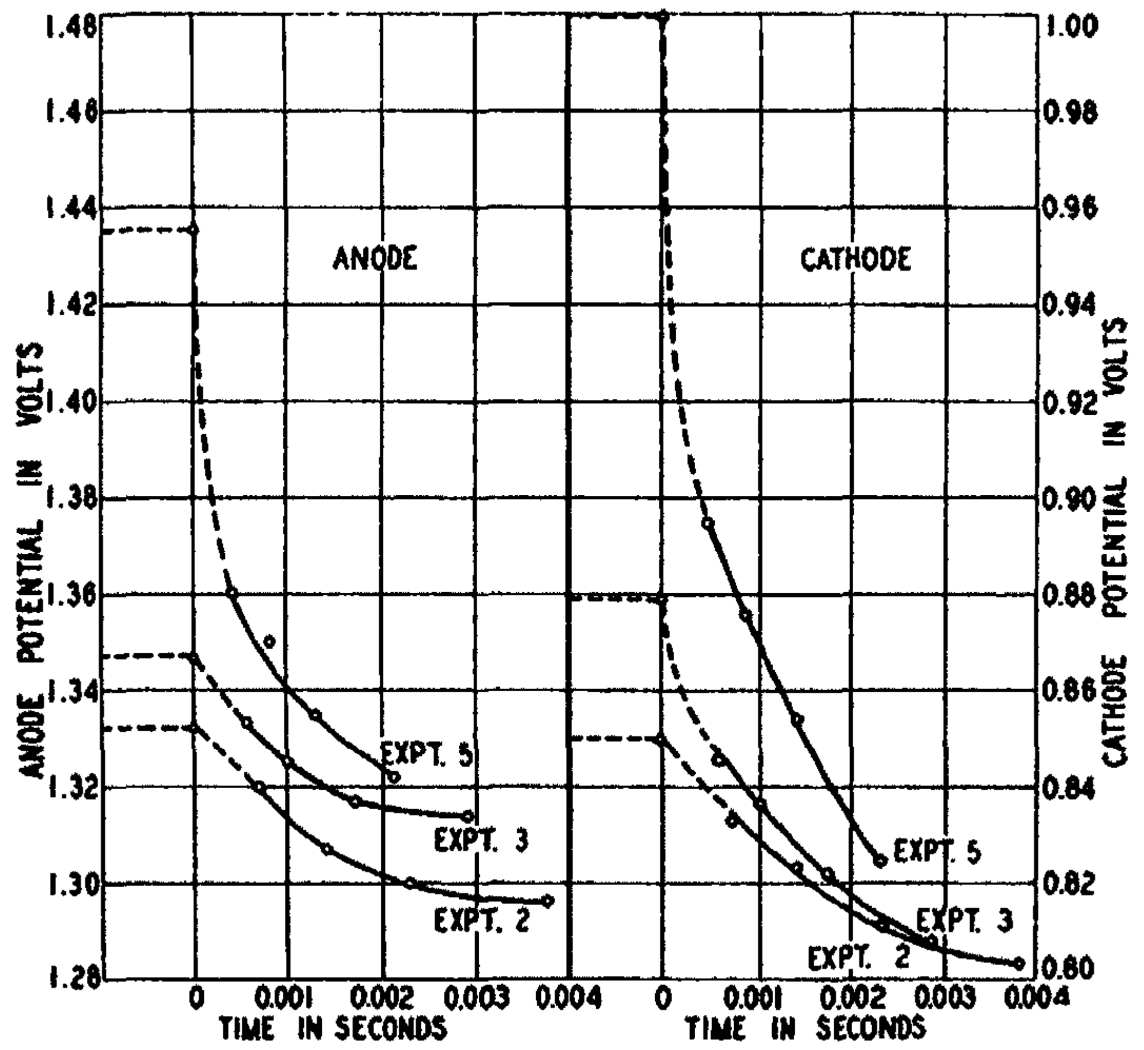


FIG. 7
Anode and cathode discharge curves for bright platinum electrodes.

Table III

Relation between single electrode potentials on charge and on discharge at various current densities. Smooth platinum electrode.

(1) Time $\times 10^{-4}$	(2) Pt.$^+$–A.S. End of charge	(3) Pot. corr.	(4) Pt.$^+$–A.S. Discharge	(5) Pot. diff. m.v.	(6) Pt.$^-$–C.S. End of charge	(7) Pot. corr.	(8) Pt.$^-$–C.S. Discharge	(9) Pot. diff. m.v.
Experiment (1) R.P.M. = 210, Average C.D. = 0.0001								
0			1.183	0			0.689	1
8			1.182				0.688	
15			1.181				0.688	
24			1.181				0.688	
40			1.181				0.687	
470	1.183	1.183			0.690	0.690		
Experiment (2) R.P.M. = 220, Average C.D. = 0.0016								
0			1.333	1			0.850?	0?
7			1.320				0.833	
14			1.307				0.824	
23			1.300				0.811	
38			1.296				0.803	
443	1.332	1.332			0.850	0.850		
Experiment (3) R.P.M. = 290, Average C.D. = 0.0026								
0			1.347?	0?			0.862?	17?
5.7			1.333				0.846	
10			1.325				0.837	
17			1.317				0.822	
29			1.314				0.807	
336	1.347	1.347			0.879	0.879		
Experiment (4) R.P.M. = 400, Average C.D. = 0.0360								
0			1.366?	20?			0.892?	24?
4			1.355				0.855	
8			1.344				0.833	
13			1.335				0.821	
21			1.325				0.811	
248	1.390	1.386			0.920	0.916		
Experiment (5) R.P.M. = 360, Average C.D. = 0.0500								
0			1.380?	49?			0.920?	74?
4.6			1.360				0.895	
8.3			1.350				0.876	
14			1.335				0.854	
23			1.322				0.825	
271	1.435	1.429			1.000	0.994		

Measurements were next carried out with smooth platinum electrodes. The data are recorded in Table III, and some are represented as curves in Fig. 7. A comparison of the data in Table III with those in Table II shows some pronounced differences. This is especially noticeable for the cathodes. While the platinized cathode increased in potential only 24 m.v. for a change in current density from 3.8 m.a. to 149 m.a., the smooth platinum changed about 200 m.v. for a current density change from 0.1 m.a. to only 50 m.a. The smooth platinum anode, on the other hand showed a considerably smaller change with current density than the platinized anode. The rate of decrease in potential on discharge was much greater for both anode and cathode with smooth than with platinized platinum, and here again the rate of decrease was much greater for the cathode than for the anode. At extremely low current densities smooth and platinized electrodes for both electrodes do not show these abnormal effects. It is clearly evident from the curves that, even though the first points on the discharge curves were obtained only about 0.0004 sec. after discharge started the potential had dropped probably 50 to 75 m.v. This is much too great a rate of change for safe extrapolation to zero time. This means that the commutator potentiometer method can not be relied upon to give satisfactory results for smooth platinum electrodes.

Summary

1. A commutator was used which enabled potentials to be measured within 0.0005 sec. from end of charge or beginning of discharge.

2. The system permitted the measurement of every potential drop in the complete circuit, and their sum could be compared with the source potential.

3. Measurements were made for anode, cathode and total potentials at several points on the charge and discharge intervals, practically simultaneously, without stopping the interrupter, so that curves could be plotted for complete cycles.

4. It was proven that for platinized electrodes in two-normal sulfuric acid there is no surface resistance of any kind for current densities between 3.8 and 150 m.a.

5. With smooth platinum electrodes the decrease in discharge potential is so rapid that satisfactory results can not be obtained with the interrupter potentiometer system.

DETERMINATION OF ADHESION TENSION OF LIQUIDS AGAINST SOLIDS. A MICROSCOPIC METHOD FOR THE MEASUREMENT OF INTERFACIAL CONTACT ANGLES[1]

BY F. E. BARTELL[2] AND E. J. MERRILL[3]

The primary purpose of the present investigation was to obtain evidence concerning the validity of certain assumptions made in the development of the method of Bartell and Osterhof[4] for the determination of adhesion tension of solids against liquids. It was desired to obtain an independent check on the contact angle values and the corresponding adhesion tension values as determined by them. In their work contact angles were determined indirectly by a pressure of displacement method; in the work described herein, contact angles were measured directly by a microscopic method.

In this paper only a brief review of the pressure of displacement method can be included. Over a century ago Thomas Young[5] pointed out that a simple relationship existed between the different interfacial tension values of interfaces in contact and the resultant angle of contact formed by their intersection, and proposed that the following relation should hold,

$$S_1 - S_{12} = S_2 \cos \theta_{12} \qquad (1)$$

S_1 = the surface tension of the solid.
S_2 = the surface tension of the organic liquid.
S_{13} = the interfacial tension of water against the solid.
S_{23} = the interfacial tension of water against organic liquid.
A_{12} = the adhesion tension of an organic liquid against a solid.
A_{13} = the adhesion tension of the water against the solid.
θ_{12} = the liquid-air-solid contact angle.
θ_{23} = the interfacial contact angle between liquid-liquid interface and the solid.

---

[1] Presented at the Minneapolis meeting of the American Chemical Society, September, 1929. The material presented in this paper is from a dissertation submitted by Mr. Merrill to the Graduate School of the University of Michigan in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1929.

This paper contains also a relatively small part of the results obtained in an investigation on "The Displacement of Petroleum Oils from Oil-bearing Sands by Means of Selected Aqueous Solutions," listed as Project No. 27 of American Petroleum Institute Research. The microscopic method data here presented tends to confirm the correctness of the displacement pressure method used in much of the oil displacement work. Other papers will follow. Financial assistance in this work has been received from a research fund of the American Petroleum Institute, donated by the Universal Oil Products Company. This fund is being administered by the Institute with cooperation of the Central Petroleum Committee of the National Research Council.

[2] Director, Project 27, American Petroleum Institute Research.

[3] American Petroleum Institute Research Assistant.

[4] Bartell and Osterhof: Ind. Eng. Chem., 19, 1277 (1927).

[5] Phil. Mag., 1805, 165.

Freundlich[1] more recently suggested that the adhesion tension of a liquid against a solid (A_{12}) should be given by the expression,

$$A_{12} = S_1 - S_{12} = S_2 \cos \theta_{12} \qquad (2)$$

If the contact angle formed by a liquid-air-solid system were greater than a zero angle, then with equation (2) the adhesion tension value for the liquid against solid could be determined by measuring the surface tension of the liquid and the angle of contact. In a few instances this procedure is possible, but with nearly all liquids the contact angle is zero and hence the adhesion tension values become indeterminate. To overcome this difficulty, Bartell and Osterhof made use of the following formulation:

$$A_{13} - A_{12} = S_{12} - S_{13} = S_{23} \cos \theta_{23} \qquad (3)$$

With the A_{12} value determined for a single liquid by equation (2), it was possible, by obtaining the interfacial tension of liquid against liquid, S_{23}, and the interfacial contact angle, θ_{23}, to determine the adhesion tension of water, A_{13}, according to equation (3). When once the adhesion tension of water was thus determined, the adhesion tension of other (organic) liquids against the solid could be found by using the same equation and again determining the interfacial tensions and the contact angles of these other water-organic liquid-solid systems.

In order to measure contact angles, Bartell and Osterhof used an apparatus consisting of a cell with an inlet tube at one end and an attached manometer at the other. In one half of the cell was packed water-wet solid while in the other half, the organic liquid-wet solid. When powdered silica was used as the solid material, the water tended to displace the organic liquid from the powder and in so doing set up a pressure which was read with a manometer. Assuming that the pores of the powder served as a multiple capillary system, and assuming that an equilibrium contact angle was formed in each of the pores, they calculated the value of this contact angle by the formulation,

$$\cos \theta_{23} = gPr/2\ S_{23},$$

in which g = gravitational constant.
P = manometer pressure in gms/cm^2.
r = average effective radius of all capillaries.

In accepting measurements of this nature it is evident that three fundamental assumptions were made:

(1) That the fine pore structure of the solid is equivalent to a large cluster of single capillary tubes.

(2) That within each system a state of equilibrium is finally reached which includes in effect an equilibrium contact angle in each pore.

(3) That the formulations of Young and of Freundlich, and likewise their own derivations from these, are sound and hence give valid results.

It is the substantiation of all three of these hypotheses that this paper primarily undertakes.

---

[1] "Colloid and Capillary Chemistry," 157 (1926).

The Photomicrographic Method

Casual microscopic observations of liquid-air-solid menisci and of liquid-liquid-solid interfaces set up in small capillary tubes suggested that true representations of these might be secured by means of a photomicrographic apparatus. Then if it could be shown that such interfaces, when located in small capillaries, are either hemispherical or sectors of spheres, or that the variance therefrom is so small as to lie within the range of other experimental errors, it should be possible to project these photographic images upon the screen under large magnification and to make a fairly accurate measurement of the contact angles. Transparent capillary tubes were made available by using transparent quartz. This material was desirable since much of adhesion tension data obtained in this laboratory had been procured with silica.

Experimental Method and Apparatus

Satisfactory capillary tubes with diameters ranging from 0.2 mm. to 0.6 mm. were drawn from larger sized transparent quartz tubing. Only those were accepted for use which were found to have a uniform cylindrical bore. At first attempts were made to clean the tubes after drawing them. After much experimentation it was found that the washing of the inside walls of the tubes with acids produced undesirable changes on these surfaces and hence the practice thereafter was to use tubes just as taken from the fire in the drawing process. Glass capillaries were prepared for use in the same manner.

The method of studying the curvature and the contact angle was that of obtaining the photomicrograph of the liquid interface or meniscus upon a photographic plate which could be used as a lantern slide. With this negative, projections were then made upon a screen of white paper.

The photomicrographic apparatus consisted of an arc lamp, condensers, filters, heat absorption cell, adjustable light shutter, an immersion cell with constant temperature control for the capillary tubes, a microscope, an attached camera and a projection lantern.

Perhaps the greatest difficulty encountered in the work was that of overcoming the effect due to the different indices of refractions of the various parts of the different systems. This applied to the tube material, the liquid contained within, and the air or second liquid. It will be evident that the simplest system to study would be one composed of a liquid, air and a solid of which the liquid and the solid have the same index of refraction. An example of this kind is that of carbon tetrachloride-air-silica. By using an immersion liquid in the immersion cell which also had the same index of refraction as the silica, there would come through the microscope to the photographic plate a true image of the meniscus and of the contact angle.

To determine whether the curvature of the menisci, in the size of capillaries that were to be used, were actually constant, a number of liquids possessing the same index of refraction as the material of the capillary walls were first studied. Figs. 1-8 inclusive show photographs of the menisci of such liquids. It is apparent that the contact angles formed in the first four cases are greater than zero, and that those in the last four are zero or at least nearly so. Careful measurement showed them to be zero angles. By the aid of the projection lantern and a pair of dividers, a large number of such menisci were studied upon the screen at magnifications of 1000 diameters or greater. In no case could the slightest deviation from a constant curvature be found when the photographs had been accurately made with correct illumination. The need of the latter must be duly recognized. A small air bubble trapped within the liquid of one of the above systems serves as a desirable means of checking this factor. Illumination must be adjusted so as to give the circular outline of the bubble in the center of the tube image.

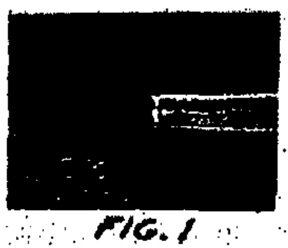


FIG. 1


FIG. 2

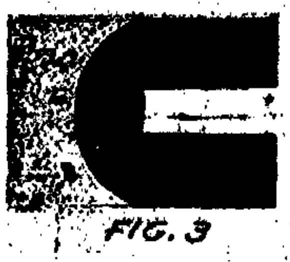


FIG. 3


FIG. 4

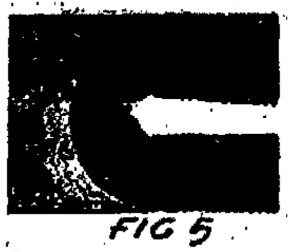


FIG 5

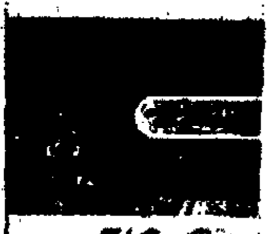


FIG. 6


FIG. 7


FIG. 8

That the curvatures are constant is further substantiated by the fact that when angle values were later calculated upon the basis of this assumption, duplicate values for the same liquid in different tubes could be obtained even though the diameters of the tubes differed by as much as 300 percent. The work of Richards and Carver[1] also tends to check this conclusion.

Accepting the premise that the curvature of such menisci are constant, the method for measuring the value of the contact angle is shown in Fig. 9. ACB represents a cross section of the meniscus of the system, AB is the diameter of the tube and OB the radius of curvature. PQ is drawn tangent to the curve at point B. The angle of contact, θ, will then be equal to the angle θ', and the measurement of the latter will give the value sought. When the contact angle is greater than zero the points A and B are readily located as shown. If the angle is of zero value, the radius of curvature and the radius of the tube will be identical.

Not all liquids have the same index of refraction as that of the material of the capillary wall. With such liquids the meniscus will appear distorted, Fig. 10, and a need of some modification of the previous method might at first thought appear to be demanded. The premise of the constant curvature of the meniscus will, however, still stand, for there is no reason for believing that the refractive index of a liquid will in any way affect the meniscus curvature. Furthermore, it is apparent that the point C on the meniscus, Fig. 11, will appear in its true position regardless of refractive index, since the light from this point will pass directly through the liquid and on through the wall

---

[1] Richards and Carver: J. Am. Chem. Soc., 43, 827 (1921).

of the tube without deflection. Observations will further show that, in spite of the differing indices of refraction of the liquid and the wall of the tube, the true positions of A and B are clearly indicated, due to the difference in light dispersion produced by the liquid and the air at the line of intersection. And so, while the meniscus will appear to be, in such cases as these, either in some position as A'CB' or as A''CB'', the true positions of A, C, and B will still establish the true curvature and thus serve as the basis for measuring the true contact angle. The method is in effect the same as was used in the previous case.

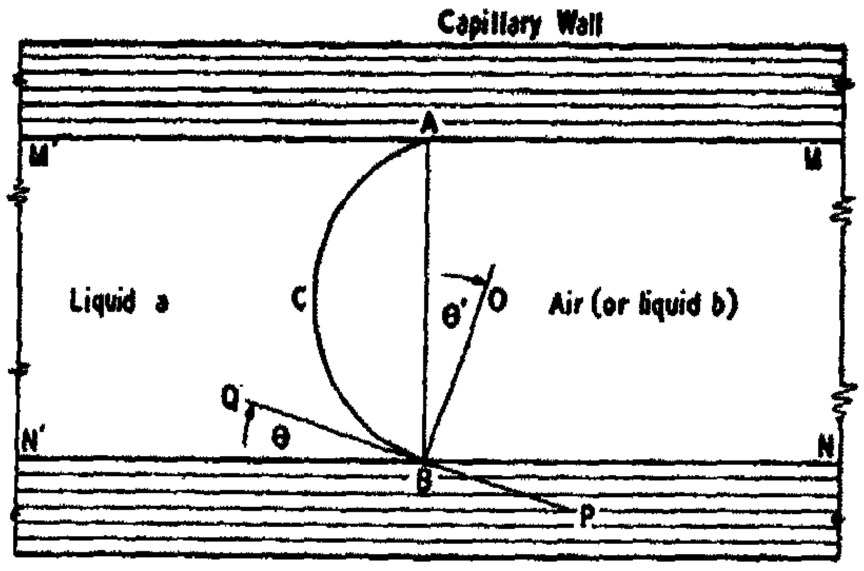


FIG. 9
Contact Angle. Liquid (or liquids) with index of refraction same as that of capillary wall.

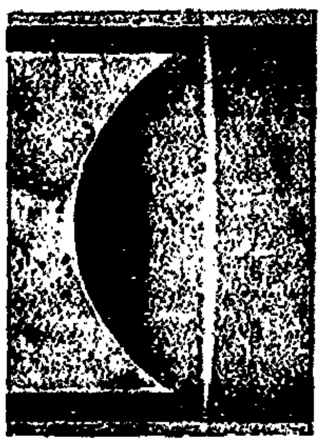


FIG. 10

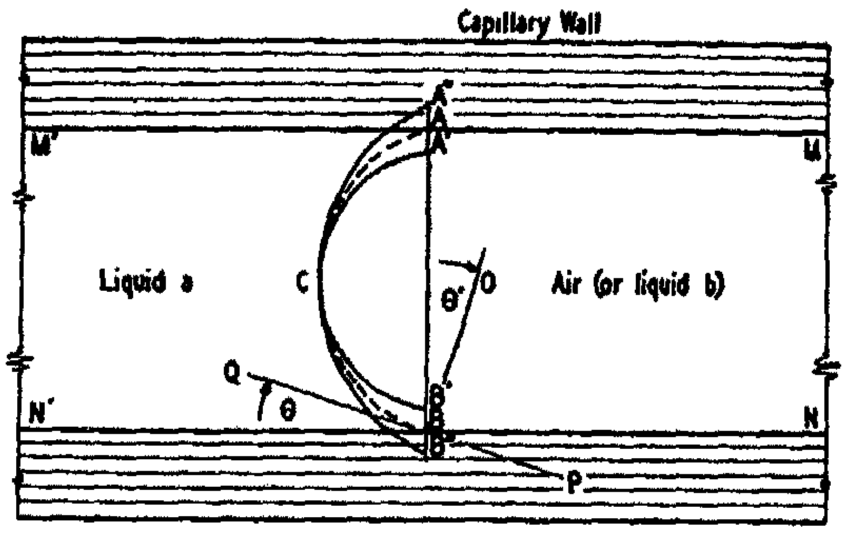


FIG. 11
Contact Angle. Liquid (or liquids) with index of refraction different from that of capillary wall.

Liquid-liquid-solid Systems.—In bringing the surfaces of two liquids together in a capillary tube for the measurement of the interfacial contact angle, a small amount of the organic liquid was first allowed to rise in the end of the tube. Water was then permitted to displace the organic liquid so that the water-organic liquid interface was carried to some convenient position in the capillary. The water end of the tube was then quickly sealed. The capillary was then kept at a constant temperature.

In a manner identical with that used to determine the type of curvature of the meniscus of the liquid-air-solid systems, liquid-liquid-solid interfaces were likewise found to possess constant curvatures. In determining this, pairs of immiscible liquids, each having the same index of refraction as the capillary wall material, were brought together and a study made as before. Figs. 12 and 13 show photomicrographs of two such interfaces. For liquids having different indices of refraction the discussion given above applies. The method used for measuring the interfacial contact angle was identical with that of the liquid-air-solid systems.

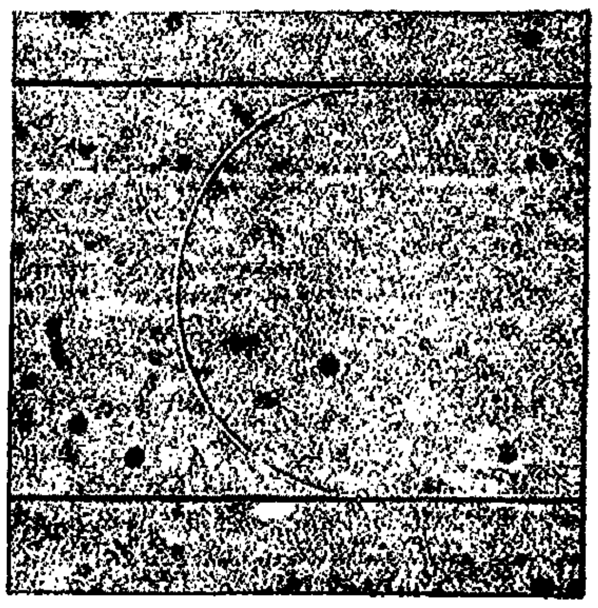


FIG. 12

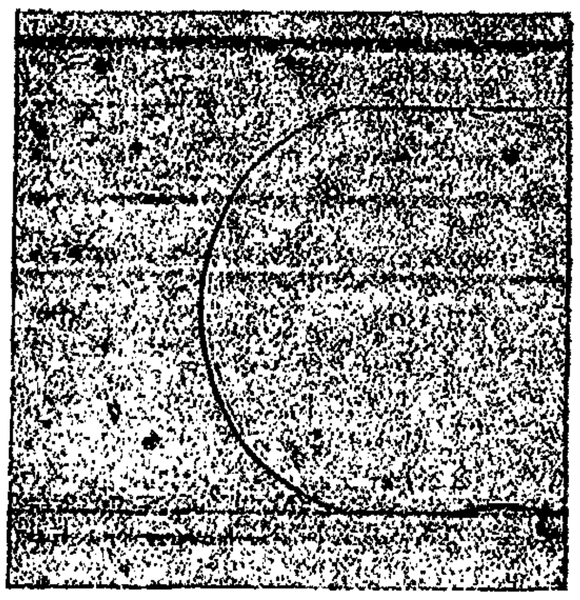


FIG. 13

The values of some liquid-air-solid and of liquid-liquid-solid contact angles as formed in capillaries of silica and of different glasses are given in Tables I and II.

Equilibrium Contact Angles

Much discussion is to be found in the literature relative to the formation of equilibrium contact angles between liquids and solids. Rayleigh[1] appears to have been one of the first to note the presence of the so-called advancing and receding contact angles. His work was confirmed by that of Miss Pockels.[2] Sulman[3] concluded that "when a liquid reaches its final state of equilibrium by spreading over the dry surface of a solid, the contact angle is greater than when the liquid reaches its final state of equilibrium by receding from a previously wetted surface." He calls this the "hysteresis" of the contact angle, suggesting that the difference in the two angles is due to a changing surface tension of the solid once it is wet by the liquid. This view is shared by Bosanquet and Hartley.[4] Adams and Jessup[5] choose to consider this phenomenon as caused by friction of the liquid and the solid. Thus

---

[1] Rayleigh: Phil. Mag., 30, 397 (1890).
[2] Pockels: Physik. Z., 15, 39 (1914).
[3] Sulman: Trans. Inst. Min. Met., (1920).
[4] Bosanquet and Hartley: Phil. Mag., 42, 456 (1921).
[5] Adams and Jessup: J. Chem. Soc., 127, 1863 (1925).

additional energy is expended in order to overcome friction as the liquid moves out over the solid surface. Still others[1] conclude that the energy of adsorption of the liquid by the solid constitutes the determining factor.

TABLE I

Liquid-Air-Solid Contact Angles

Liquid	Silica	Pyrex	Lead Glass	Soda-lime Glass
Acetylene tetrabromide	28° 00′	30° 30′	22° 30′	21° 15′
Alphabromnaphthalene	21° 00′	20° 30′	6° 45′	5° 00′
Methylene iodide	33° 00′	29° 30′	30° 00′	29° 00′
Tribromhydrin	20° 15′	—	15° 30′	17° 00′
Alphachlornaphthalene	15° 00′	—	13° 30′	10° 30′
Iodobenzene	12° 10′	—	12° 15′	0° 15′
Bromoform	24° 30′	—	13° 00′	16°
Turpentine	0°	0°	0°	0°
Acetic acid	0°	0°	0°	0°
Glycerine	0°	0°	0°	0°
Carbon-tetrachloride	0°	0°	0°	0°
Xylene	0°	0°	0°	0°
Olive oil	20° 00′	21° 45′		
Oleic acid	27° 00′	27° 30′		

TABLE II

Liquid-Liquid-Solid Contact Angles
(Water—Organic Liquid-Solid)

Liquid	Silica	Lead glass	Soda-lime Glass
Acetylene tetrabromide	30° 30′	34° 15′	0°
Alphabromnaphthalene	33° 00′	37° 30′	0°
Methylene iodide	33° 30′	—	0°
Tribromhydrin	25° 15′	29° 30′	0°
Alphachlornaphthalene	25° 00′	30° 00′	0°
Iodobenzene	25° 30′	—	0°
Bromoform	24° 30′	22° 15′	0°
Benzene	28° 40′		
Toluene	35° 00′		
Carbon tetrachloride	25° 15′		
Hexane (synthetic)	25° 30′		
Nitrobenzene	42° 30′		
Carbon disulfide	42° 30′		
Amyl alcohol	55° 30′		
Butyl acetate	45° 00′		

---

[1] Ablett: Phil. Mag., 46, 244 (1923); Rideal: "Surface Chemistry" (1926).

A rigorous treatment of the subject of advancing, receding and equilibrium contact angles has been the subject of another investigation in this laboratory and so will not be further touched upon in this paper; suffice it to say that it now appears that where systems are contained in such small-sized capillary tubes as were used in this investigation, the forces of surface and interfacial tension appear to overcome any distorting effects due to gravity and should quickly bring a meniscus or interface to an equilibrium position and thereby establish an equilibrium contact angle. In this work it was not possible to bring two liquid surfaces together in a capillary tube at precisely such points as will later prove to be the true equilibrium contact points. Hence it is to be expected that some time must elapse before equilibrium will occur; usually from 10 to 24 hours is sufficient. Table III includes two series of readings for contact angle values as they were measured over consecutive periods of time in two different water-benzene-silica systems. It will be observed that even though the first readings were greater or were less than those of the values finally obtained, both systems eventually gave angles of the same value. These readings are typical of those for all systems studied. Furthermore, the consistent duplication of contact angle values for the same liquids in different tubes which were set up at different times and therefore under somewhat different conditions, makes but one conclusion possible; namely, that although the angle formed before equilibrium conditions are reached may vary and may be either smaller or larger than the final angle, in due time a definite and constant angle will be formed. This latter angle we designate as the equilibrium contact angle. The evidence appears to be conclusive that with both liquid-air-solid and with liquid-liquid-solid systems in single capillary tubes a definite and reproducible contact angle is formed.

Table III

Advancing and Receding Contact Angles

Time required to reach equilibrium values

System 1. Water-benzene-silica

	Value of angle	
Time of standing	First tube	Second tube
1 hr.	15° 00′	30° 30′
6 hrs.	23° 15′	—
10 "	—	28° 50′
1 day	28° 45′	28° 20′
2 days	28° 00′	—
3 "	28° 30′	28° 40′
4 "	28° 40′	—

Preferential Adsorption

The equilibrium positions taken by the menisci of the liquid-air-solid systems were found to remain always the same no matter how long they were allowed to stand. On the other hand many of the liquid-liquid-solid interfaces after weeks, or perhaps not until after months, of standing were observed to change and finally to form zero contact angles. A close study of these changing systems showed that water droplets were forming between the organic liquid surface and the wall of the capillary. These drops increased both in number and in size as time went on and then eventually all coalesced into one continuous film of water which completely surrounded the organic liquid column. Such a condition is nearly reached in the system as shown in the photograph of Fig. 14. It seems probable that as the two liquids stood in contact with each other they became mutually saturated. Since the silica has a greater attraction for water than for the organic liquid, the water was preferentially adsorbed by the silica, thus displacing the organic liquid. A slight change in temperature may have induced the initial drop formation and thereby caused the appearance of the water phase at the surface. Further adsorption and drop, or film formation, produces a growth of the film until it becomes continuous. When this happens the contact angle must necessarily become zero.


FIG. 14

The above behavior raises the question: have true equilibrium angles really been formed when admittedly the angle may eventually undergo change? Strictly speaking, the angle is not an equilibrium angle, otherwise it would not change. The change is probably due to an alteration in nature of the contiguous phases. The surface of the solid phase becomes altered, it passes from essentially a surface of pure solid to a surface of water, which phase finally covers the solid phase. The preferential adsorption of the water by the capillary wall material is a matter quite secondary to the original condition which gave the apparent equilibrium angle. This latter angle is probably in fact the characteristic angle for the phases in contact at the moment. Although considerable time may be required to obtain this angle, it will remain at a constant value for a comparatively long time. It is believed that this angle can be used to give fairly accurate values for adhesion tension. Further, it should be pointed out that interfacial contact angles measured by the microscopic method have shown good agreement with the interfacial angles obtained by the Bartell-Osterhof displacement pressure method.

Adhesion Tension Values from Contact Angles

It has been previously pointed out that a fundamental value in the determination of the adhesion tension of most organic liquids is the adhesion tension of water itself. To obtain this, it is necessary first to find some liquid or liquids which give a finite contact angle with air and the solid. Table IV gives such liquid-air-solid contact angle values, together with the adhesion tension values for the six liquids used. Table V gives the adhesion tension value of water for silica as determined independently using each of these different liquids. The close agreement of the six values thus found for water is of much significance. Not only does it give a multiple check on the adhesion tension value for water against silica, but it goes far in checking the validity of the method used, together with all formulations which lie back of it. Similar data for these liquids and lead glass are also given in Tables VI and VII. Table VIII shows the contact angle and adhesion tension values for the organic liquids and soda-lime glass. The adhesion tension of water against this glass cannot be determined since all interfacial contact angles involved are of zero value.

TABLE IV

Liquid-Air-Silica Contact Angles, θ_{12}

Adhesion tension values, liquid-silica, A_{12}

Organic Liquid	θ_{12}	S_1*	A_{12}
Acetylene tetrabromide	28° 00′	49.07	43.32
Tribromhydrin	20° 15′	44.76	42.00
α-Br-naphthalene	21° 00′	44.00	41.07
α-Cl-naphthalene	15° 00′	41.20	39.77
Iodobenzene	12° 10′	39.10	38.22
Bromoform	24° 30′	40.93	37.25

TABLE V

Interfacial Contact Angles, θ_{23}

Adhesion tension of water-silica, A_{13}

Organic Liquid	θ_{23}	A_{12}	S_{23}*	A_{13}
Acetylene tetrabromide	30° 30′	43.32	38.32	76.34
Tribromhydrin	25° 15′	42.00	38.00	76.37
α-Br-naphthalene	33° 00′	41.07	41.57	75.93
α-Cl-naphthalene	25° 00′	39.77	40.24	76.24
Iodobenzene	25° 30′	38.22	41.34	75.53
Bromoform	19° 30′	37.25	40.35	75.28

Average value of A_{13} = 75.92

*All surface tension and interfacial tension values found in the data of this paper are those from the "Critical Tables" corrected to 25°C. In some instances temperature coefficient values were not available and values which appeared to represent justifiable approximations were used. Any errors thus introduced are surely not greater than the experimental errors of our method.

TABLE VI

Liquid-Air-Lead Glass Contact Angles, θ_{12}

Adhesion tension values, liquid-lead glass, A_{12}

Organic liquid	θ_{12}	S_1	A_{12}
Methylene iodide	30° 00′	50.16	43.73
Tribromhydrin	15° 30′	44.76	43.13
α-Br-naphthalene	6° 45′	44.00	43.61
α-Cl-naphthalene	13° 30′	41.20	40.05
Iodobenzene	12° 15′	39.10	38.70
Bromoform	13° 00′	40.93	39.86

TABLE VII

Interfacial Contact Angles, θ_{23}
Adhesion tension values of water-lead glass, A_{13}

Organic liquid	θ_{23}	A_{12}	S_{23}	A_{13}
Methylene iodide	Reaction, no results.			
Tribromhydrin	29° 30′	43.87	38.00	76.18
α-Br-naphthalene	37° 30′	44.16	41.57	76.59
α-Cl-naphthalene	30° 00′	40.65	40.24	74.90
Iodobenzene	Reaction, no results.			
Bromoform	22° 15′		40.35	77.30
	Average value of A_{13}, (all independent) =			76.16

TABLE VIII

Liquid-Air-Soda Lime Glass Contact Angles, θ_{12}
Adhesion tension values, liquid-soda lime glass, A_{12}

Organic liquid	θ_{12}	S_2	A_{12}
Acetylene tetrabromide	21° 15′	49.07	45.71
Tribromhydrin	17° 00′	44.76	40.68
α-Br-naphthalene	5° 00′	44.00	44.00
α-Cl-naphthalene	10° 15′	41.20	40.20
Iodobenzene	0°	39.10	> 39.10
Bromoform	16° 30′	40.93	39.24

By making use of the determined adhesion tension of water for silica and for lead glass, the adhesion tension of several other organic liquids for these solids were obtained and are given in Tables IX and X. The data of Table XI compares the values of the adhesion tension of several liquids as determined by this, the microscopic method, with those obtained by the Bartell-Osterhof displacement pressure (fine pore) method. It should be pointed out that the silica used in the latter method was specially treated tripoli or diatomaceous earth instead of transparent quartz. This would surely affect the results to a certain degree for the natures of the two surfaces would not be the same. A comparison should therefore be made on the basis of comparative values. For instance, the adhesion tension of water as determined by the two methods differs by nearly 7 dynes, a corresponding deviation holds also for the other liquid systems. Further evidence that the difference in values may be due to the different natures of the two forms of the silica is found in the work by Bartell and Miller[1]. With the displacement pressure method the adhesion tension of water for fine sand was found by them to be 74.10 dynes, a value even lower than that found by this method for fused quartz. With the above in mind, it is quite apparent that the values for the different liquids agree very well, which fact gives substantial evidence as to the soundness of both methods, their fundamental formulations, and

---

[1] Bartell and Miller: unpublished.

developments, and at the same time indicates that the so-called adhesion tension of a liquid for a solid represents a specific and definite property of that system.

TABLE IX

Interfacial Contact Angles, Liquid-Water-Silica, θ_{23}

Adhesion tensions, organic liquid-silica, A_{12}

Liquid	A_{13}	θ_{23}	S_{23}	A_{12}
Water	75.92			
Amyl alcohol		55° 30′	4.96	73.13
Ethyl carbonate		55° 00′	12.65	68.74
Butyl acetate		45° 00′	13.17	66.60
Nitrobenzene		42° 30′	25.32	57.25
Toulene		35° 00′	35.86	46.54
Benzene		28° 40′	34.76	45.43
Carbon disulfide		42° 30′	48.10	40.46
Carbon tetrachloride		25° 15′	44.50	35.67
Hexane (synthetic)		25° 30′	51.00	29.90

TABLE X

Interfacial Contact Angles, Liquid-Liquid-Lead Glass

Adhesion tension, organic liquid-lead glass, A_{12}

Liquids	A_{13}	θ_{23}	S_{23}	A_{12}
Water	76.16			
Amyl alcohol		0°	4.96	<71.00
Ethyl carbonate		0°	12.67	<63.25
Butyl acetate		0°	13.17	<62.75
Nitrobenzene		27° 30′	25.32	53.50
Toluene		26° 30′	35.86	43.82
Benzene		0°	34.76	<41.66
Carbon disulfide		33° 40′	48.10	44.25
Hexane		36° 30′	51.00	34.92

TABLE XI

Comparison of Adhesion Tension Values; Fine Pore vs. Microscopic Methods

Liquids	A_{12} Fine pores	A_{12} Microscopic
Water	82.82	75.92
Butyl acetate	73.45	66.60
Carbon tetrachloride	40.69	35.67
Toluene	54.70	46.54
Benzene	52.43	45.43
Carbon disulfide	45.94	40.46

Conclusions

It is believed that this investigation has given the following rather conclusive evidences:—

1.—That equilibrium contact angles are formed when solid-liquid-air phases are in contact; likewise definite contact angles are formed between liquid-liquid-solid phases. These angles can be formed within capillary tubes; they are quite independent of the size of the tubes and can be measured fairly accurately.

2.—That the adhesion tension as measured is specific and definite for a given solid-liquid system.

3.—That the formulations used in the determination of adhesion tension were justified.

4.—That the data obtained by the microscopic method show good agreement with the results obtained by the Bartell-Osterhof pressure of displacement method and tends to substantiate the correctness of the assumptions made in connection with their work.

Department of Chemistry,
University of Michigan.

A STUDY OF THE ADSORPTION OF SUGARS AND NITROGENOUS COMPOUNDS[1]

BY VASILY KNIASEFF

The purpose of the present work is to study the phenomena of adsorption of sugars and nitrogenous compounds and to obtain data particularly on the question of specificity of adsorption and the influence of certain factors which appear to be of practical importance.

We may divide our work into two parts. We shall first present material on the adsorption of different sugars on Norit and on fuller's earth. In the second part we shall give our results on the adsorption of nitrogenous compounds by fuller's earth only. In both studies we determined the effects of different factors on the phenomenon of adsorption, limiting our work practically to those factors which influence the liquid phase.

We chose, because of its convenience, to analyze by appropriate method the solutions before and after adsorption. In some cases volumetric and in other cases gravimetric methods were used. For analyzing sugar solutions titration with Fehling's solution according to the method outlined by Leach[2] was used. The solutions of nitrogenous compounds were analyzed by direct weighing or by titration.

Procedures used for determining Adsorption

Charcoal (Norit) and fuller's earth were used as adsorbents. Both adsorbents were used without thorough purification; fuller's earth was washed, however, several times with water, dried at 140° C, and passed through 200-mesh sieve. Therefore the adsorptions were of such kind as are used in commercial practice.

Fifty cc. of .029 molar solutions of sucrose, lactose, maltose, glucose, levulose, and galactose were placed with 1 gram of charcoal in Erlenmeyer flasks and shaken for a period of one-half hour; the same amount of solution was used for shaking with 1 gram of dried fuller's earth for one and one-half hours. Duplicate experiments in each case were run in parallel. The solutions after shaking were rapidly filtered through a Gooch crucible by suction. In order to obtain exact results, the following precautions were taken in filtration of solution: several cubic centimeters were passed through the filter paper and discarded; also the vacuum was kept as low as possible and constant. The filtrate was analyzed by titration against Fehling's solution.[3]

The amount of sugar adsorbed was calculated in the following way. The amount of sugar found by titration in a portion of the filtrate from adsorbent

---

[1] An extract from a thesis presented in partial fulfillment of the requirements for the degree of Master of Science, University of Oregon, December, 1927.

[2] Leach: "Food Analysis."

[3] Leach: "Food Analysis."

treated solution was subtracted from the amount of sugar present in an aliquot portion of original sugar solution. The Fehling's solution was standardized separately for each type of sugar solution. The duplicate titration agreed to within hundredths of cubic centimeter.

In carrying out the experiments on adsorption of nitrogenous compounds by fuller's earth, there were some variations in the procedure and analysis of the filtrate.

In the analysis of caffeine and urea a direct weighing method was used. Ten cubic centimeters of the filtrate were placed in a weighed crucible and evaporated to dryness in a drying oven and reweighed to constant weight. The crucibles were ignited and weighed again in order to determine if any amount of the adsorbent had passed through the filter. The difference between the second and the last weight was taken as the amount of the substance in 10 cc. of the solution. In order to verify the accuracy of the method, 10 cc. of the original standard solution were treated in the same way and very close checks were obtained. In the analysis of piperidine the titration method was used with methyl orange as indicator.

Rate of Adsorption

In making adsorption tests it is important to know the time required for equilibrium to be established between the amount of adsorbed solute on the adsorbent and the amount of solute in solution.

A series of solutions of the same concentration of lactose were shaken for different periods of time with 1 gr. of charcoal and with 1 gr. of fuller's earth. The results of the experiment are exhibited in Tables I and II.

From following tables it is easy to see that the amount of lactose adsorbed by charcoal is almost constant after fifteen minutes of shaking, while the adsorption by fuller's earth is not complete in an hour.

TABLE I

Rate of Adsorption of Lactose by Charcoal[1]

Time of shaking	¼ hour	½ hour	¾ hour	1½ hour
Amount of adsor. sugar in grs.	.0844	.0822	.0844	.0844
Concentration of solution at equilibrium in mmols.	27.5657	27.5710	27.5657	27.5657
Concentration of adsorbent at equilibrium in grs.	1	1	1	1

---

[1] 1 gr. of charcoal was shaken with 50 cc. of .029 mol. solution of lactose at natural pH.

TABLE II

Rate of Adsorption of Sugars by Fuller's Earth[1] (Lactose)

Time of shaking	¼ hour	½ hour	¾ hour	1½ hour
Amount of adsor. sugar in grs.	.0024	.004	.0152	.0167
Concentration of solution at equilibrium in mmols.	27.1933	27.7999	27.7578	27.7537
Concentration of adsorbent at equilibrium in grs.	1	1	1	1

Maltose

Time of shaking	½ hour	1½ hour
Amount of adsorbed sugar in grs.	.0144	.166
Concentration of solution at equilibrium in mmols.	27.7579	27.3389
Concentration of adsorbent at equilibrium in grs.	1	1

Relative Adsorption of Different Sugars by Charcoal and Fuller's Earth

The next step in our study was to determine the relative adsorption of different sugars by the two adsorbents studied. The results of experiments on different sugars are given in Tables III and IV.

TABLE III

Adsorption of Different Sugars by Charcoal[2]

Names of sugars: Mol. weights	Maltose 360.25	Lactose 360.25	Sucrose 342.18	Glucose 198.4	Galactose 180.13	Levulose 180.13
Adsor. from .029 m. sol.						
grs.	.0844	.0825	.0816	.0375	.0375	.0366
mmols.	.2343	.2290	.2388	.1890	.2049	.2036
Concentration of solution at equilibrium in mmols.	28.7657	28.7710	28.7612	28.8110	28.7951	28.7964
Concen. of adsor. at equilibrium in grs.	1	1	1	1	1	1

---

[1] 1 gr. of fuller's earth was shaken with 50 cc. of .029 mol. solution of lactose and maltose at natural pH.

[2] ½ hour of shaking; 1 gr. of charcoal.

Table IV

Adsorption of Different Sugars by Fuller's Earth[1]

Names of sugars: Mol. weights	Maltose 360.25	Lactose 360.25	Sucrose 342.18	Glucose 198.4	Galactose 180.13	Levulose 180.13
Adsor. from .029 M. sol.						
grs.	.01388	.01422	.0144	.01254	.00196	.00182
mmols.	.0385	.0395	.0421	.0632	.0109	.0101
Concentration of solution at equil. in mmols.	28.9615	28.9605	28.9579	28.9368	28.9891	28.9899
Concen. of adsor. in grs.	1	1	1	1	1	1

The results of these experiments show that charcoal adsorbs different sugars about equally but that fuller's earth adsorbs certain sugars much more readily than others.

Effect of pH on the Adsorption of Sugars by Charcoal and Fuller's Earth

A series of equivalent concentration of lactose and glucose solutions but with different adjusted pH values were prepared by the indicator method and a series of tests were made on each solution. Fifty cubic centimeters of the solution of .029 M. concentration were placed with 1 gr. of charcoal or fuller's earth in Erlenmeyer flasks and shaken for one half hour; the filtrates were analyzed as before. The results of these tests are given in Tables V-VIII.

Table V

The Effect of pH of Solution on the Adsorption of Lactose by Charcoal

pH of original solution	6.9	5.4	4.5	4.0
pH of filtrate	8.4	5.6	4.9	5.6
Amount of adsorbed sugar in:				
grs.	.1270	.1382	.1344	.14385
mmols.	.3525	.3836	.3731	.3993
Concentration of solution at equilibrium in mmols.	28.6475	28.6164	28.6269	28.6007
Concentration of adsorbent at equilibrium in gr.	1	1	1	1

The results of the experiments show that the adsorption of lactose by charcoal is not greatly affected by change of pH in the acid range with a tendency toward higher adsorption when the pH is lower.

Different results were obtained with fuller's earth as adsorbent, which can be seen from Table VI.

---

[1] 1½ hours of shaking; 1 gr. of fuller's earth.

TABLE VI

The Effect of pH of Lactose Solution on Adsorption by Fuller's Earth and Change of pH of Solution

pH of original solution	4.1	5.5	7.4
pH of filtrate	5.6	5.6	7.1–7.0
Amount adsorbed in grs.	−.00027	−.00018	+.00237
in mmols.	−.000007	−.0000053	+.0000069

The data show that adsorption decreases with diminishing value of pH of solution; also negative adsorption was observed at pH 4.1 and 5.5.

TABLE VII

Adsorption of Glucose by Fuller's Earth at Different pH of Solution and Change of pH of Original Solution

pH of original solution:	4.0	4.3	5.5	6.4	6.75	7.4	8.4
pH of filtrate:	6.9	6.85	6.9	6.95	6.8	6.95	6.9
Adsorption in mgrs:	4.81	4.65	3.99	3.83	3.65	3.01	2.84
Adsorption in mmols:	.0247	.0234	.0201	.0193	.0184	.0152	.0143
Concentration of solution at equilibrium in mmols.	28.9753	28.9766	28.9799	28.9807	28.9816	28.9848	28.9857
Concentration of adsorbent at equilibrium in grs.	1	1	1	1	1	1	1

It can be seen from this table that a regular increase of adsorption with decrease of pH value of original solution took place, although this change is very negligible, almost zero.

Adsorption of Nitrogenous Compounds

Experiments were next conducted in order to study the adsorption of nitrogenous compounds by fuller's earth. For the present work sufficiently soluble nitrogenous compounds which were readily available were chosen. The largest number of experiments were done with caffeine, which possesses amphoteric properties. ($K_a = >1 \times 10^{-14}$; $K_b = 4 \times 10^{-14}$). As it was observed by Grettie[1] that fuller's earth adsorbs only basic substances, therefore three other nitrogenous compounds which possess different basic properties from caffeine were used for comparative study. These substances were piperidine, which is strongly basic ($K_b = 1.2 \times 10^{-14}$), and urea ($K_b = 1.5 \times 10^{-14}$) which is slightly basic.

We followed almost the same scheme of work as that used in case of adsorption of sugars; the only difference being that we studied the influence of some other factors, which affect adsorption besides those which were mentioned in the case of adsorption of sugars.

Rate of Adsorption

In the study of the rate of adsorption of nitrogenous compounds the same general method was applied as in the case of sugars. Twenty-five cc. of .01 M caffeine solution were shaken with .1 gr. of fuller's earth for different periods of time, the results obtained are given in Table VIII.

TABLE VIII

Rate of Adsorption of Caffeine by Fuller's Earth

Time of shaking in minutes	3	5	10	38
Amount of adsorption in grs.:	.0049	.0053	.0054	.0056
Amount of adsorption in mmols.:	.0232	.0251	.0255	.0260
Concentration of solution at equilibrium in mmols:	9.9768	9.9749	9.9745	9.9740
Concentration of adsorbent at equilibrium in grs.	.1	.1	.1	.1

The experiments demonstrate that the equilibrium is reached after a few minutes of shaking.

The Effect of pH of Solution on Adsorption of Caffeine by Fuller's Earth

A series of 25 c.c. of .01 M concentration of caffeine were shaken for five minutes with .1 gr. of fuller's earth. The results of these experiments are given in the Table IX.

---

[1] J. Am. Chem. Soc., 50, 668 (1928).

TABLE IX

Adsorption of Caffeine at Different pH of Solution

pH of original solution:	4	4.7	5.4	6.4	6.9	7.3	7.9	8.8	9.4
pH of filtrate:	7.9	7.1	7.2	7.4	7.2	7.2	7.2	7.5	9.0
Caffeine adsorbed in mgrs.:	5.43	5.58	5.33	5.48	5.33	5.33	5.33	5.38	4.88
Caffeine adsorbed in mmols.:	.0255	.0263	.0251	.0251	.0251	.0251	.0251	.0253	.0229
Concentration of solution at equilibrium in mmols.:	9.9745	9.9737	9.9749	9.9749	9.9749	9.9749	9.9749	9.9747	9.9771
Concentration of adsorbent at equilibrium in gr.	.1	.1	.1	.1	.1	.1	.1	.1	.1

These results show that practically no change of adsorption of caffeine with change of pH value could be observed.

Influence of Mass of Adsorbent on the pH of Solution

A series of 25 c.c. of .01 M solution of pure caffeine were shaken with the following quantities of fuller's earth: .5 g., .1 g., .05 g., and .01 g.

The results of experiment are given in Table X.

TABLE X

Amount of fuller's earth used in grs.:	.5	.25	.1	.05	.01
Caffeine adsorbed in mgrs.:	19.1	9.45	7.48	3.6	.48
Caffeine adsorbed in mmols.:	.090	.0555	.0352	.0168	.0022
Concentration of solution at equilibrium in mmols.:	9.9100	9.9445	9.9648	9.9832	9.9978
Initial pH of solution:	6.8	6.8	6.8	6.8	6.8
pH of filtrate:	8.4	7.6	7.4	7.0	6.8

This table shows that the change of pH of solution (increase) is proportional to the amount of earth added.

The Effect of the Nature of the Solvent

It was observed that the nature of solvent has a great effect on adsorption of solute. This may be seen clearly if we compare the results reported here on adsorption of nitrogenous compounds in alcohol solution with those obtained by Grettie,[1] who performed experiments on the adsorption of the same compounds only from water solution. In both cases the conditions of experiment were identical, namely 25 c.c. of .01 M solution were shaken for five minutes with .5 gr. of fuller's earth. The results are shown in Table XI.

TABLE XI

The Effect of the Nature of the Solvent on the Adsorption of Caffeine, Piperidine, and Urea

Names of compounds:	Piperidine	Caffeine	Urea
Amount adsorbed from water solution in %:	73.8	92.3	5
Amount adsorbed from water solution in mmols.:	.1840	.0923	.0125
Concentration of solution at equilibrium in mmols.:	9.8160	9.9077	9.9875
Amount adsorbed from alcohol solution in %:	33.6	73.5	.95
Amount adsorbed from alcohol solution in mmols.:	.0347	.0735	.0024
Concentration of solution at equilibrium in mmols.:	9.9653	9.9265	9.9976
Concentration of adsorbent at equilibrium in grs.:	.5	.5	.5

The experimental data shows that the adsorption of nitrogenous compounds is less in alcohol solution than in water solution.

Displacement Type of Adsorption

We thought when caffeine is shaken with fuller's earth the caffeine unites with the earth and calcium is liberated.

In order to test out is our idea true we carried out several experiments on adsorption of caffeine by fuller's earth and analyzed the filtrate for both caffeine and calcium. These experiments were performed with both washed and unwashed fuller's earth with solutions of different concentration and with solutions of different pH values. The results obtained are indicated in Tables XII-XIV.

---

[1] J. Am. Chem. Soc., 50, 668 (1928).

TABLE XII

The Displacement of Calcium by Caffeine from Fuller's Earth

	Washed fuller's earth	Unwashed fuller's earth
Caffeine adsorbed in grs.:	.1188	.1225
Caffeine adsorbed in mmols.:	.56	.58
Calcium found in filtrate in gr.:	.000278	.000991
Calcium found in filtrate in mmols.:	.00695	.0247

The results indicate some displacement of calcium from fuller's earth but the quantity is negligible and not directly proportional to the amount of caffeine adsorbed.

The experiment on displacement was repeated with small variation, namely different concentrations of caffeine solutions were used. The results are given in Table XIII.

TABLE XIII

Displacement of Calcium in Adsorption of Caffeine at Different Concentration of Solution

(1 gr. of fuller's earth used)

Concentration of solution in mols.:	.1	.05	.01
Caffeine adsorbed in grs.:	.0696	.0592	.02008
Caffeine adsorbed in mmols.:	.327	.278	.093
Calcium found in filtrate in mmols.:	0	.0033	.0155

Also experiments on the displacement of calcium by caffeine at the different pH of solution were carried out and the following results were obtained which are given in Table XIV.

TABLE XIV

Displacement of Calcium in Adsorption of Caffeine at the Different pH of Solution[1]

pH of Initial Solution:	4.0	7.1	7.9
Caffeine adsorbed in grs.:	.0727	.094	.096
Caffeine adsorbed in mmols.:	.343	.442	.451
Calcium found in filtrate in mgrs.:	.71	.74	.53
Calcium found in filtrate in mmols.:	.017	.018	.013

The amount of calcium present in the filtrate was irregular and seems to have nothing to do with the pH of solution; the displacement of calcium does not conform to the law of multiple proportion.

Summary

1). In the adsorption of sugars by charcoal (Norit) equilibrium is reached in a few minutes. Adsorption of sugars by fuller's earth does not reach equilibrium in less than an hour.

2). The various sugars tested were adsorbed about equally by charcoal but fuller's earth adsorbed certain sugars much more readily than others.

3). The adsorption of lactose by charcoal is not greatly affected by change of pH in the acid range, but there is a tendency toward higher adsorption when the pH is lower. The adsorption of lactose by fuller's earth decreases with diminishing values of pH. Negative adsorption of this sugar was observed at pH 4.1 and pH 5.5. In case of the adsorption of glucose by fuller's earth a regular but very small increase of adsorption with decrease of the pH value of original solution was noted.

4). In the adsorption of caffeine by fuller's earth the equilibrium is reached in a few minutes of shaking.

5). Adsorption was practically unaffected by pH of original solution, when 25 c.c. of .01 mol. solution of caffeine were shaken with .1 gr. of fuller's earth.

---

[1] 1 gr. fuller's earth shaken with 25 cc. of .05 M. sol. caffeine.

6) There is a shift of pH of original solution of caffeine after shaking with fuller's earth; this shift is also proportional to the amount of fuller's earth used.

7). The adsorption of three typical nitrogenous compounds by fuller's earth is less from alcoholic solution than from water solution.

8). Calcium was found in the filtrate of caffeine solution shaken with fuller's earth; the amount of calcium was practically negligible and not directly proportional to the amount of caffeine adsorbed; the amount of calcium present in the filtrate was irregular at the different pH values of the caffeine solution.

This work was done under the direction of Dr. R. J. Williams, to whom I wish to express my sincere thanks for his able guidance and helpful suggestions.

Department of Chemistry,
University of Oregon,
Eugene, Oregon.

CHEMICAL ACTIVITY AND PARTICLE SIZE

II. The Rate of Solution at Slow Stirring of Anhydrite and Gypsum*

PAUL S. ROLLER**

Natural anhydrite is an unstable phase[1] of calcium sulphate at 20°C. and is about 1½ times as soluble as gypsum,[2] yet its rate of solution is much less than that of the dihydrate.[3,4] It seemed possible that the dissolution of the anhydrite might be activated by a reduction in the particle size, entirely apart from the ordinary effect resulting from an increase in specific surface.

Three reasons appeared to lead to this conclusion, as follows:

1. The Nernst-Brunner[5,6] theory postulates that the rate of solution of a solid in a liquid is governed by the rate of diffusion from a saturated layer adjacent to the surface through an adhering film. By calculation the thickness of this film at ordinary stirring speeds (100 to 500 r.p.m.) is 20 to 50 microns.[6,7] It seemed altogether reasonable to suppose that, other conditions remaining the same, the thickness of this film in contact with particles of the order of 1 to 50 microns in size would be modified from its value at a plane surface. Hence, since the specific rate of solution according to the Nernst theory varies inversely as the film thickness, a specific effect should be observed for such particles beyond the effect due to changes in the surface exposed.

2. Probably the strongest support of the Nernst diffusion theory of heterogeneous reaction has been in the results of Van Name and his coworkers[8] which showed that the relative rate of oxidation of a number of metals in KI_3 solution was independent of the nature of the metal; on the other hand it must be remembered that the same authors[9] have found that the rate of oxidation by ferric sulphate and chromic acid in H_2SO_4 and ferric chloride in HCl solution was in the same order as the e.m.f. series of the metals. This result is contrary to the assumption of the Nernst theory that reaction at the solid-liquid interface is instantaneous.

---

* Published by permission of the Director, U. S. Bureau of Mines.

Presented before the meeting of the American Chemical Society in Buffalo, September, 1931. (Not subject to copyright).

** Associate Chemist, U. S. Bureau of Mines, Nonmetallic Minerals Experiment Station, New Brunswick, N. J.

[1] van't Hoff: Z. physik. Chem., **45**, 257 (1905).

[2] Roller: J. Phys. Chem., **35**, 1133 (1931).

[3] McCaleb: Am. Chem. J., **11**, 31 (1889).

[4] Wildermann: Z. physik. Chem., **66**, 445 (1909).

[5] Nernst: Z. physik. Chem., **47**, 52 (1904).

[6] Brunner: Z. physik. Chem., **47**, 56 (1904).

[7] Wagner: Z. physik. Chem., **71**, 401 (1910).

[8] Van Name and Edgar: Am. J. Sci. (4) **29**, 237 (1910); Van Name and Bosworth: **32**, 207 (1911); Van Name and Hill: **36**, 543 (1913); Van Name: **43**, 449 (1917).

[9] Van Name and Hill: Am. J. Sci. (4), **42**, 301 (1916).

Similarly, the rate of solution of anhydrite in water may be governed not by diffusion but by the rate of reaction at the surface. That this is the situation for the solution of metals in acids is indicated by the fact that the rate of solution is independent of the rate of stirring when the latter is sufficiently high;[10] this has also been observed for benzoic acid in water at a stirring speed above 400 r.p.m.[4] The fundamental importance of the rate of reaction at the surface is also indicated by the fact that different crystal faces of the same substance have different rates of solution,[7,11] although in contrast to the early considerations of Curie and Wulff the saturation solubility for each of these faces is the same or imperceptibly different.[12,18,35]

As regards the interaction at the surface, recent evidence indicates that such interaction between a solid and a fluid takes place not uniformly over the surface of the solid but at "active spots" as first propounded by Taylor.[13] These active spots may correspond to the "crystal defects" observed by Smekal,[14] and also to the edges and corners as observed by Volmer[15] and theoretically considered by Stranski,[16] Kossel,[17] and Brandes.[18] Assuming that the surface activity is nil, then, if the rate of solution were governed solely by reaction at the edges, it should increase with the inverse square of the particle size, and if governed by the corners, with the inverse cube of the particle size.[19] If as seems probable for the solution process, the surface activity plays a part, then, assuming the latter to be constant for different sizes of particles, the rate should increase inversely with a power of the particle size lying between 1 and 3.

3. Since many individual microscopic particles constitute a given weight of solute, the physical interaction of these particles, differing in general with particle size, will have an effect on the rate of solution. In this work the microscopic crystals were in most cases contiguous to one another. Consequently, neighboring particles will affect the availability of the solvent to an individual particle under consideration. The degree of the interference will depend on the particle size (less than a given value) and on conditions of the experiment.

Results of this present work show, as previously found at a stirring speed of 470 r.p.m.,[2] that there is an enhanced or activated rate of solution for both anhydrite and gypsum with decrease in particle size below 50 microns.

---

[10] Centnerszwer and Zablocki: Z. physik. Chem., **122**, 455 (1926); Centnerszwer and Straumanis: **128**, 369 (1927); Centnerszwer: **137**, 352 (1928); **141A**, 297 (1929).

[11] Becke: Tschermak Min. and Pet. Mitt., **11**, 349 (1890); Schenk: Z. Min. **1900**, 313; Rinne: Cent. Min., **1904**, 116; Korbs: Z. Krist., **43**, 434 (1907); Gross: **57**, 145 (1922); Glauner: Z. physik. Chem., **142**, 67 (1929); Tammann and Sartorius: Z. anorg. Chem., **175**, 197 (1929).

[12] Valeton: Ber. math. physik. sächs Ges. Leipsig, **67**, 1915; Physik. Z., **21**, 606 (1920).

[13] Taylor: Proc. Roy. Soc., **108A**, 105 (1925); J. Phys. Chem., **30**, 145 (1926).

[14] Smekal: Physik. Z., **26**, 707 (1925); Z. angew. Chem., **42**, 489 (1929; Z. Elektrochemie, **35**, 567 (1929).

[15] Volmer: Z. physik. Chem., **102**, 270 (1923).

[16] Stranski: Z. physik. Chem., **135**, 259 (1928); **11B**, 342 (1930).

[17] Kossel: Nachr. Ges. Wiss. Göttingen math. physik. Kl., **1927**, 135.

[18] Brandes: Z. physik. Chem., **126**, 198 (1927).

[19] Schwab and Pietsch: Z. Elektrochemie, **35**, 573 (1929).

Briefly, as regards the above theories, it is demonstrated that the Nernst film, if it exists, is considerably smaller than the expected 20 to 50 microns in thickness. In fact, it is less than 0.2 of a micron—i.e., less than one-hundredth of the theoretically accepted value. Evidence is presented from the recent literature which substantiates this conclusion and, still further, indicates that any film at the surface must be indefinitely thin, of the order of a monomolecular adsorption layer. Consequently in heterogeneous reaction the supposition of diffusion through an adhering Nernst film as the fundamental *modus operandi* is untenable, and can not be used to explain the results of this work.

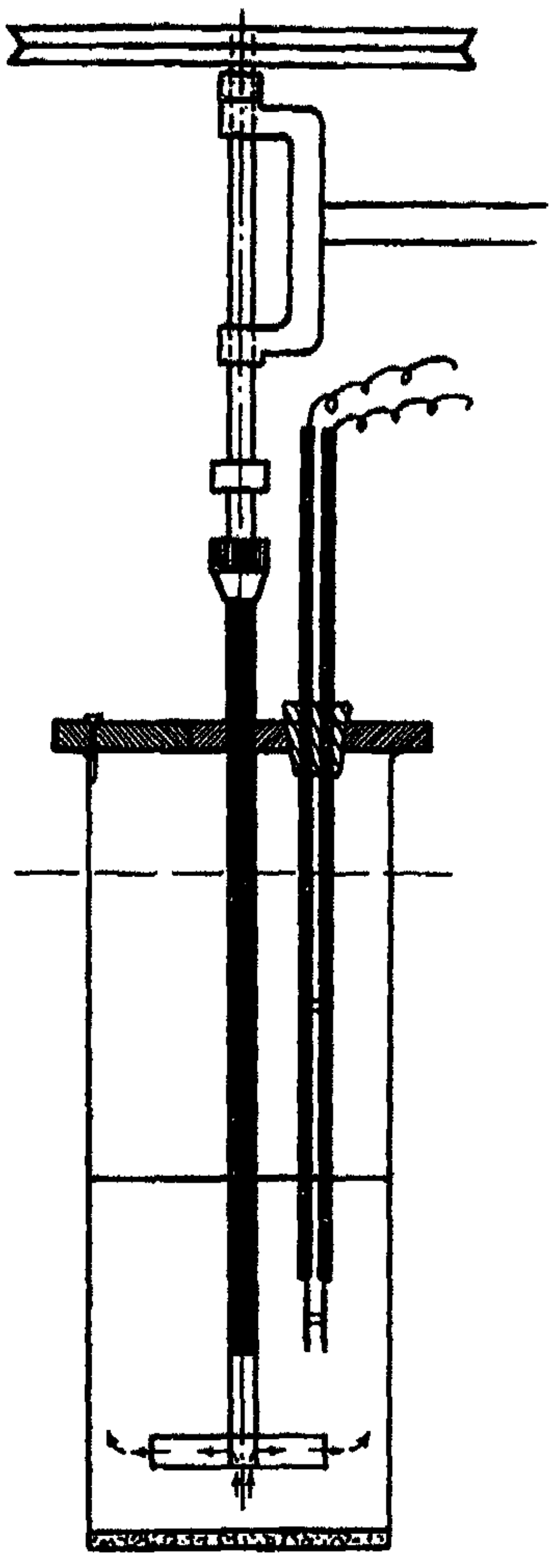


FIG. 1

With the solute added dry to the solvent, the enhanced effects appear to be intimately associated with the structure of the dissolving sediment. When the solute (anhydrite) is initially dispersed in a small amount of water, this situation also obtains for particles between 8 and 50 microns in size. However, for particles below 8 microns, the enhanced rate of solution is apparently due to the effect of edges and corners superimposed upon solution directly from the surface, apparently by way of active centers of the latter.

Apparatus

The apparatus, which is the same as that previously used,[2] is shown in Fig. 1. The slightly tapered cylindrical Kavalier glass beaker was 4.9 cm. in diameter, at the lower end, and 13 cm. deep, the water reaching to a height of 5.5 cm. above the bottom. The stirrer that passed through a split ebonite cover consisted of a 5.5-mm. solid glass rod, to the bottom of which was fused a hollow glass inverted "T," the arms of which were 3 cm. across. With rotation of the stirrer, a circulation of the water was set up in the hollow T as shown by the arrows. The end of the T was in all cases 12 mm. above the bottom of the beaker. The thickness of the dissolving sediment, 0.4 to 1.5 mm., was negligible in comparison to this distance.

The conductivity of the solution was measured by unprotected platinized platinum electrodes that were frequently checked. The electrodes were

15 mm. long by 9 mm. across, the upper edge being 5 mm. below the surface of the water.

In some auxiliary experiments a cylindrical Pyrex beaker 5.3 cm. wide at the bottom and 10 cm. deep was used.

Materials

The distilled water had a conductivity that was checked before each experiment of 2-3 × 10^{-6} r.o.

The anhydrite was the same pure crystalline product as was used before.[2][*] The gypsum was Baker's c.p. grade. Both materials were finely ground and then air-separated to secure the desired particle-size fractions. The gypsum

TABLE I

Microscopic Analysis of Particle Size Fractions of Anhydrite

Fraction							
I	0–1	1–2	2–3	3–4			Microns
	56.2	11.9	12.3	19.6			Weight per cent
	96.2	2.5	0.8	0.5			Number per cent
II	0–1	1–2	2–3	3–4	4–5	5–6	Microns
	24.8	5.0	3.0	38.6	15.9	12.7	Weight per cent
	95.2	2.2	0.4	1.8	0.3	0.1	Number per cent
III	2–3	3–5	5–7	7–9			Microns
	2.6	22.2	24.3	50.9			Weight per cent
	25.2	50.5	13.4	10.9			Number per cent
IV	7–10	10–15	15–20				Microns
	3.4	40.3	56.3				Weight per cent
	16.4	55.2	28.4				Number per cent
V	15–20	20–25	25–30	30–40			Microns
	9.0	28.7	33.0	29.3			Weight per cent
	23.0	26.0	14.5	36.5			Number per cent
VI	26–35	35–55	55–80				Microns
	1.7	40.2	58.1				Weight per cent
	7.3	60.7	32.0				Number per cent
VII	85–100	100–150	150–200	200–250			Microns
	3.5	41.0	40.5	15.0			Weight per cent
	12.7	65.5	17.3	4.5			Number per cent
VIII	125–150	150–200	250–275				Microns
	2.8	53.1	44.1				Weight per cent
	11.4	67.2	21.4				Number per cent

---

[*] *Courtesy of the U. S. Gypsum Co.*

TABLE II

Microscopic Analysis of Particle Size Fractions of Gypsum

Fraction								
	0–1	1–2	2–3	3–4				Microns
I	50.7	28.2	17.0	4.1				Weight per cent
	92.8	6.5	0.7	0.1				Number per cent
II	0–1	1–2	2–3	3–4	4–5	5–7	7–9	Microns
	6.5	4.2	10.1	20.6	29.7	14.3	14.6	Weight per cent
	84.6	6.7	3.8	2.8	1.6	0.3	0.2	Number per cent
III	3–6	6–8	8–10	10–12	12–15			Microns
	3.8	18.1	23.5	27.4	27.2			Weight per cent
	33.4	29.5	19.2	11.5	6.4			Number per cent
IV	5–10	10–13	13–16	16–19	19–22	22–25		Microns
	3.5	8.2	22.3	21.2	22.3	22.5		Weight per cent
	28.4	19.4	25.4	11.9	9.0	5.9		Number per cent
V	12–18	18–24	24–30	30–36	36–42	42–50	50–60	Microns
	2.0	3.3	23.5	34.0	11.0	14.5	11.7	Weight per cent
	18.4	10.2	33.7	26.5	5.1	4.1	2.0	Number per cent
VI	26–35	35–55	55–80					Microns
	2.3	55.4	42.3					Weight per cent
	10.0	71.6	18.4					Number per cent
VII	100–150	150–200	200–250					Microns
	19.6	75.1	5.3					Weight per cent
	33.3	65.0	1.7					Number per cent
VIII	150–250	250–400						Microns
	30.5	69.5						Weight per cent
	50.8	48.2						Number per cent

was separated in an air analyzer;[20] later an enlargement of this apparatus was constructed[21] that permitted the securing of considerable quantities of the fractions in a much shorter time; this apparatus was used for the anhydrite separations. The two coarsest fractions between 150 and 250 microns were obtained by sieving between the 50 and 200 mesh sieve. These fractions in spite of prolonged sieving still retained appreciable quantities of adhering "fines" that showed up in preliminary rate of solution measurements; the sieved fractions were therefore treated in the air analyzer, the fines being thus effectively removed.

---

[20] Roller: U. S. Bureau Mines Tech. Paper, No. 490 (1931).

[21] Roller: Ind. Eng. Chem. Anal. Ed., 3, 212 (1931).

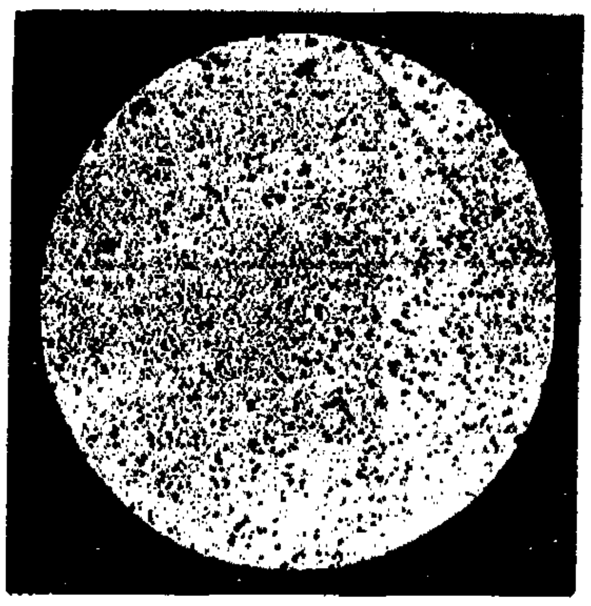


Fig. 2
335 ×

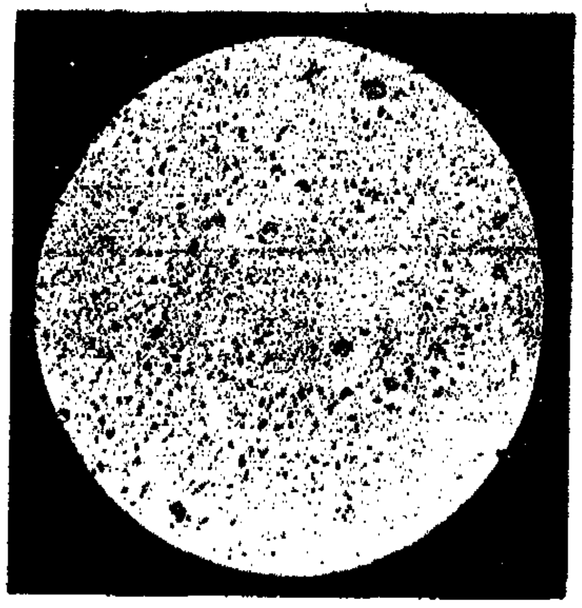


Fig. 3
335 ×

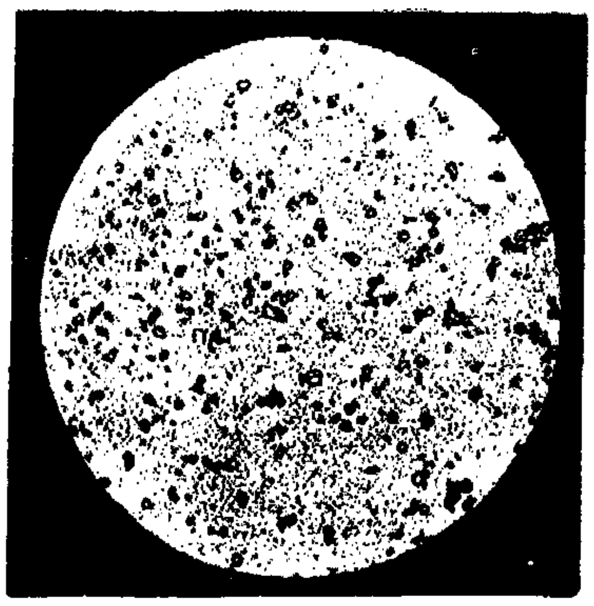


Fig. 4
335 ×

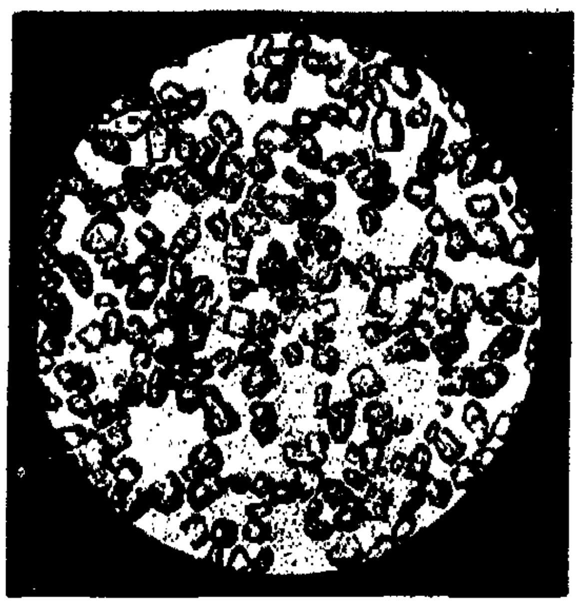


Fig. 5
335 ×

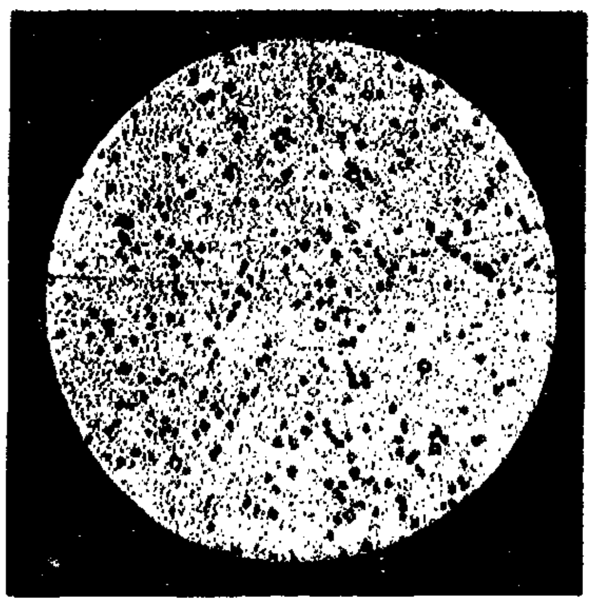


Fig. 6
45 ×

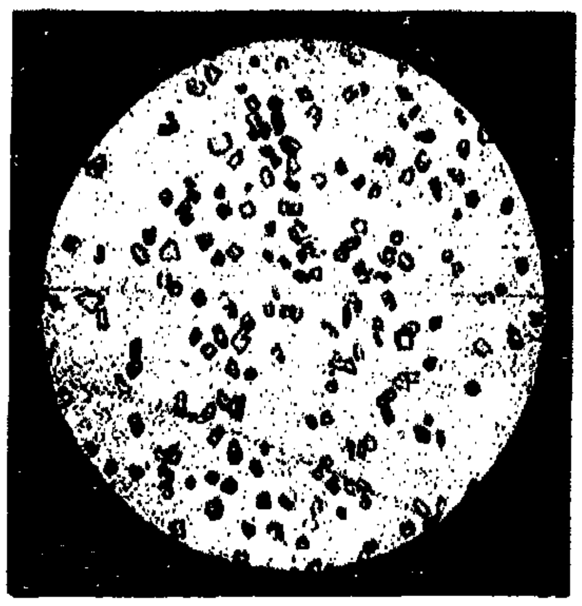


Fig. 7
45 ×

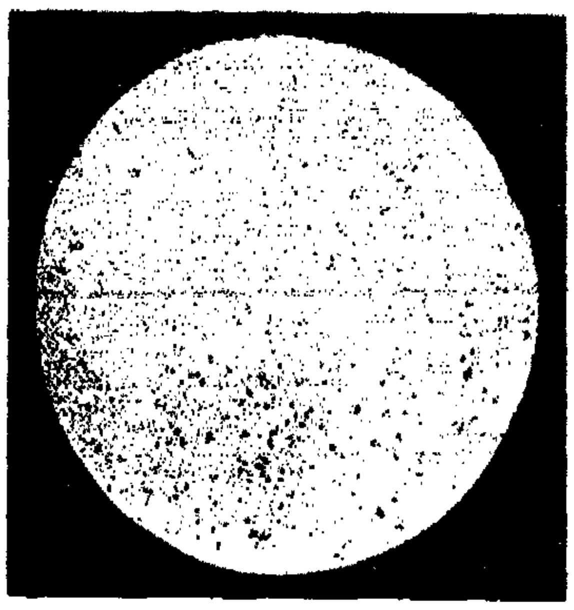


Fig. 8
335 X

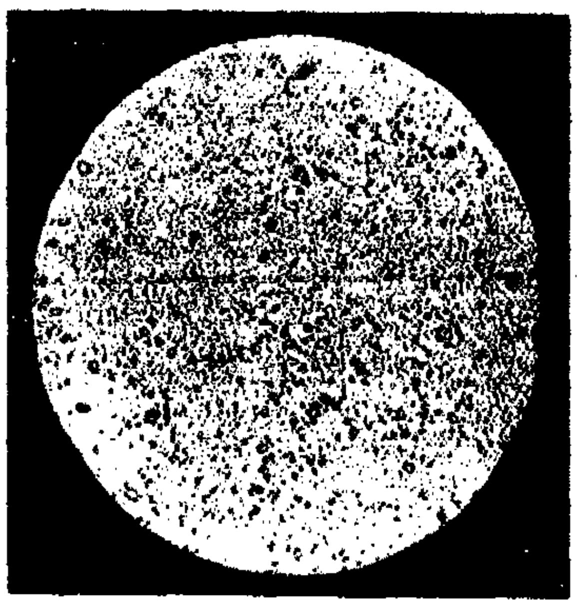


Fig. 9
335 X

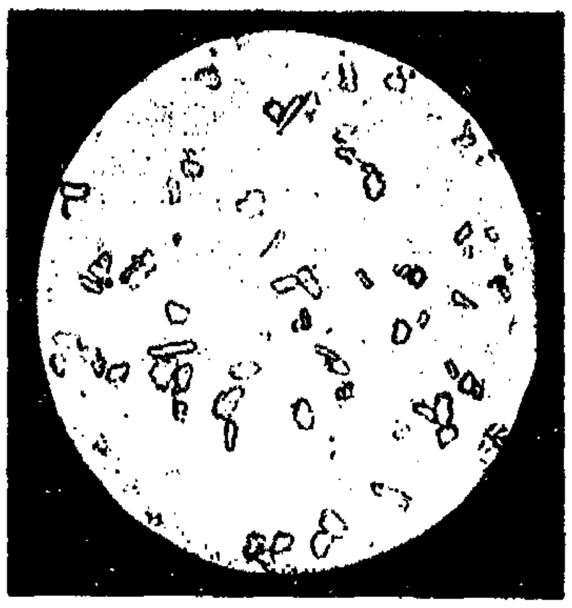


Fig. 10
335 X

Fig. 11
335 X

Fig. 12
70 X

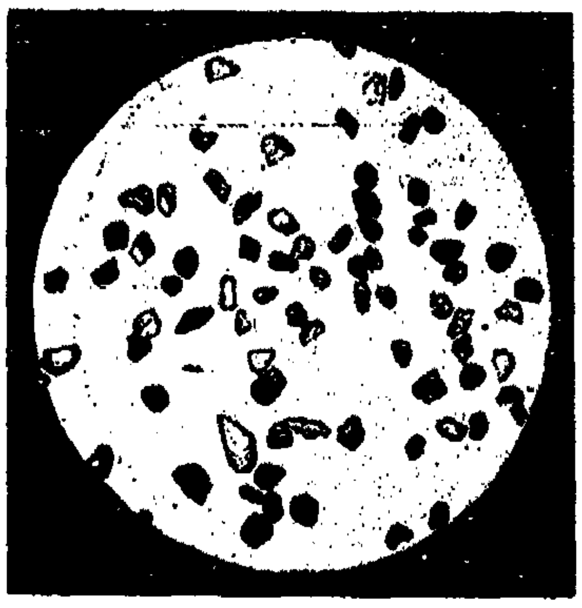


Fig. 13
70 X

To counteract the dehydrating effect of the grinding and air separation, the gypsum fractions previous to microscopic measurement were superficially rehydrated by stirring with water at room temperature for 1 or 2 hours, filtered, washed with 50% alcohol, 95% alcohol, and ether, and dried at 70°C. The fractions then showed a specific conductivity of 1.965×10^{-3} r.o. at 20°C., the value found by Böttger[22] being 1.970×10^{-3} r.o. at 19.94.°

Figs. 2 to 7 are photomicrographs of the air-separated anhydrite fractions I to VI respectively, and Figs. 8 to 13 are of the same gypsum fractions. In Tables I and II are given summarized microscopic counts of the particles contained in the anhydrite and gypsum fractions, respectively. It should be noted that fraction II in each case overlaps fraction I due to "attrition" of the soft powder by the air current at this particle size separation.

The surface mean diameter, d_s, of each of these fractions, as previously,[2] is defined by equation (1) in which d is the arithmetic mean of the length and width of a particle and the summation is taken over all the measured particle sizes.

$$(1) \quad d_s = \Sigma d^3/\Sigma d^2$$

The calculated values of d_s are shown in Table III.

TABLE III

Surface Mean Diameter of Anhydrite and Gypsum Fractions

Fraction	Anhydrite	Gypsum
I	1.10	1.10
II	1.89	3.22
III	5.9	9.8
IV	14.7	17.3
V	26.5	35.3
VI	53.8	53.1
VII	157.	177
VIII	250	286

Method

The procedure in measuring the dissolution was the same as formerly[2] except that 100 c.c. of water instead of 135 c.c. was used and 0.8 gram was taken as a standard weight in place of 0.7 gram. Also, the stirring speed was now 130 r.p.m. instead of 470 r.p.m.

In these experiments the solute was added to the water in two different ways. After the solvent and powder had come to temperature in a water bath maintained at 20.0 ± .03°C. the solute was spread out in the weighing tube and was added to the water during stirring of the latter. In the second method of addition of the solute, the powder was first dispersed, generally with 2 c.c. of water, and the suspension added to the water in the beaker. For all fractions of the powder added dry, settling took place within a period of 5 seconds, the rotating stirrer helping to spread the powder over the bottom of the beaker.

---

[22] Böttger: Z. physik. Chem., 46, 602 (1902).

Conductivity readings were converted into concentrations by means of Hulett's formula as before, but for concentrations below 0.1 gr./100 c.c. the somewhat more accurate data of Kohlrausch and Grüneisen[23] were used. All runs were made at least twice and the results averaged. The error of the average for the powder added dry was ± 4%; with fractions III and IV, between 5 and 15 microns, the results were somewhat erratic, due apparently, at the low rate of stirring, to the powder occasionally falling off in a lump to one side of the beaker or clinging at the surface. The discordantly low values thus obtained were neglected in obtaining the average. This "lumping" tendency of fractions III and IV which seemed to be influenced by the humidity was largely overcome by shaking and spreading the powder out in a large weighing tube and then uniformly adding it to the solution. Due to fluctuations the accuracy for these fractions was ± 8%.

With the powder dispersed in water the results for all the fractions were quite reproducible, the accuracy being ± 1%.

The average error in d_s was ± 8%; for fractions I and II the error was smaller than ± 4%.

Results for Anhydrite and Gypsum added dry

The time-concentration values for anhydrite and gypsum added dry are shown in Tables IV and V and are plotted in Figs. 14 and 15. It is seen that the rate of solution is initially high but falls off rapidly in the first two or

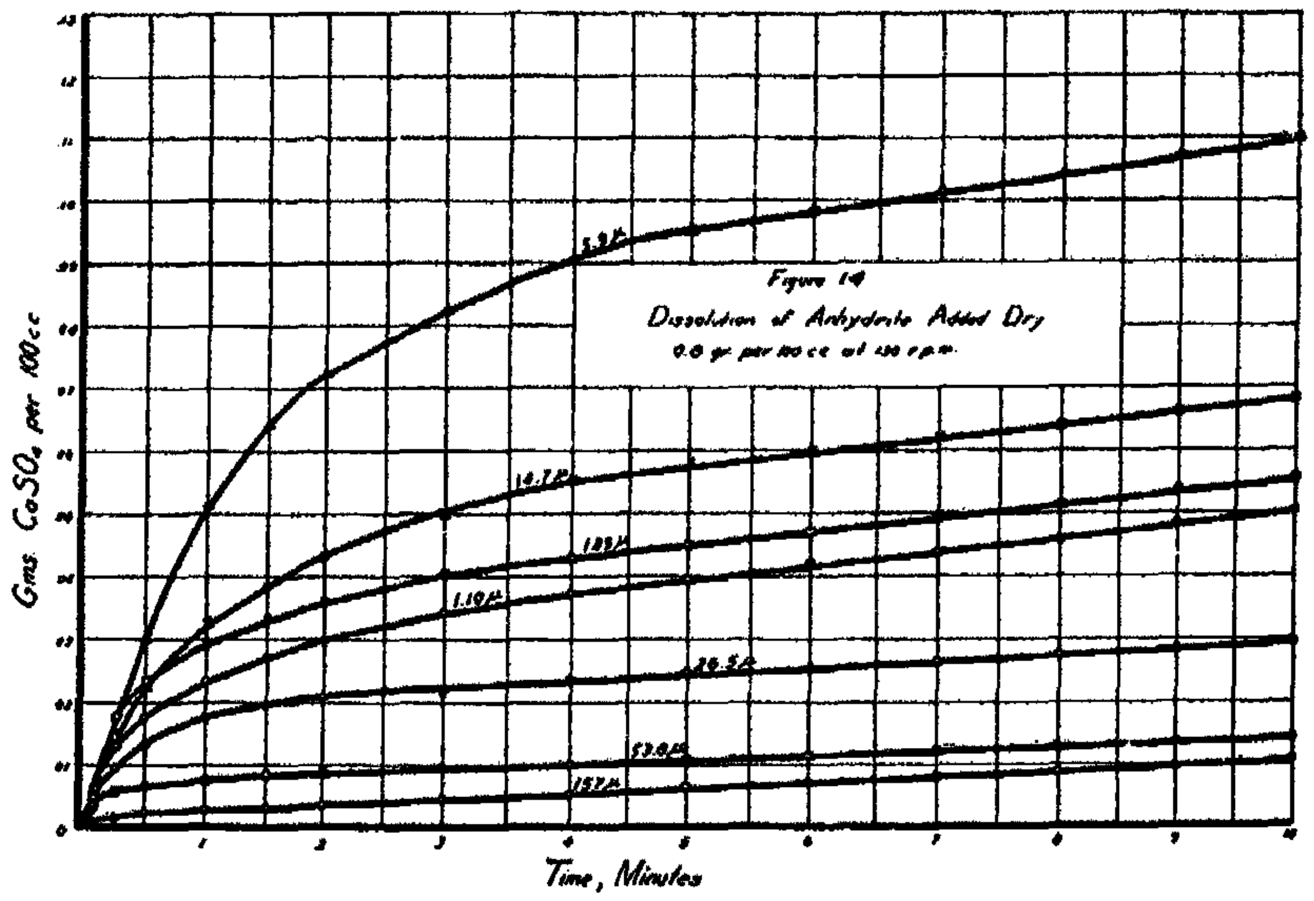
TABLE IV

Dissolution of 0.8 Gram of Anhydrite added dry to 100 c.cm. of Water at a Stirring Speed of 130 r.p.m.

	I	II	III	IV	V	VI	VII	VIII	Fraction
			Surface Mean Diameter						
	1.10	1.89	5.9	14.7	26.5	53.8	157	250	Microns
Min.			Grams $CaSO_4 \times 10^2$/100 c.c.						
0.1	.37	.59	.59	.45	.43	.30	.10	.07	
0.25	1.32	1.75	1.51	1.30	.97	.59	.16	.11	
0.50	1.77	2.33	3.02	2.22	1.38	.65	.21	.16	
1.0	2.33	2.85	5.17	3.28	1.75	.75	.28	.23	
1.5	2.70	3.33	6.42	3.92	1.95	.82	.34	.28	
2.0	2.98	3.60	7.25	4.35	2.08	.88	.39	.33	
3.0	3.42	4.02	8.25	5.03	2.17	.95	.48	.42	
4.0	3.75	4.30	9.06	5.52	2.38	1.01	.56	.51	
5.0	3.98	4.50	9.52	5.80	2.47	1.08	.65	.59	
6.0	4.22	4.70	9.83	6.00	2.58	1.14	.72	.66	
7.0	4.38	4.92	10.16	6.20	2.66	1.20	.81	.75	
8.0	4.60	5.15	10.45	6.42	2.76	1.26	.89	.83	
9.0	4.83	5.38	10.73	6.62	2.84	1.33	.98	.91	
10.0	5.02	5.58	11.08	6.81	2.92	1.40	1.06	.99	

---

[23] Kohlrausch and Grüneisen: Landolt-Börnstein Tab., 2, 1081 (1923).



three minutes; thereafter the rate of increase in concentration is relatively slight and is about the same for the different fractions. During the settling period of less than 5 seconds the amount dissolved of the solute added dry is small; indeed, for the finer fractions I to IV, that is, below about 17 microns, there is an induction period of 4 or 5 seconds in which the amount dissolved is virtually nil.

The unexpected low rate of solution of the fine fractions I and II, i.e. below about 3 microns, should be noted. These fractions dissolve more

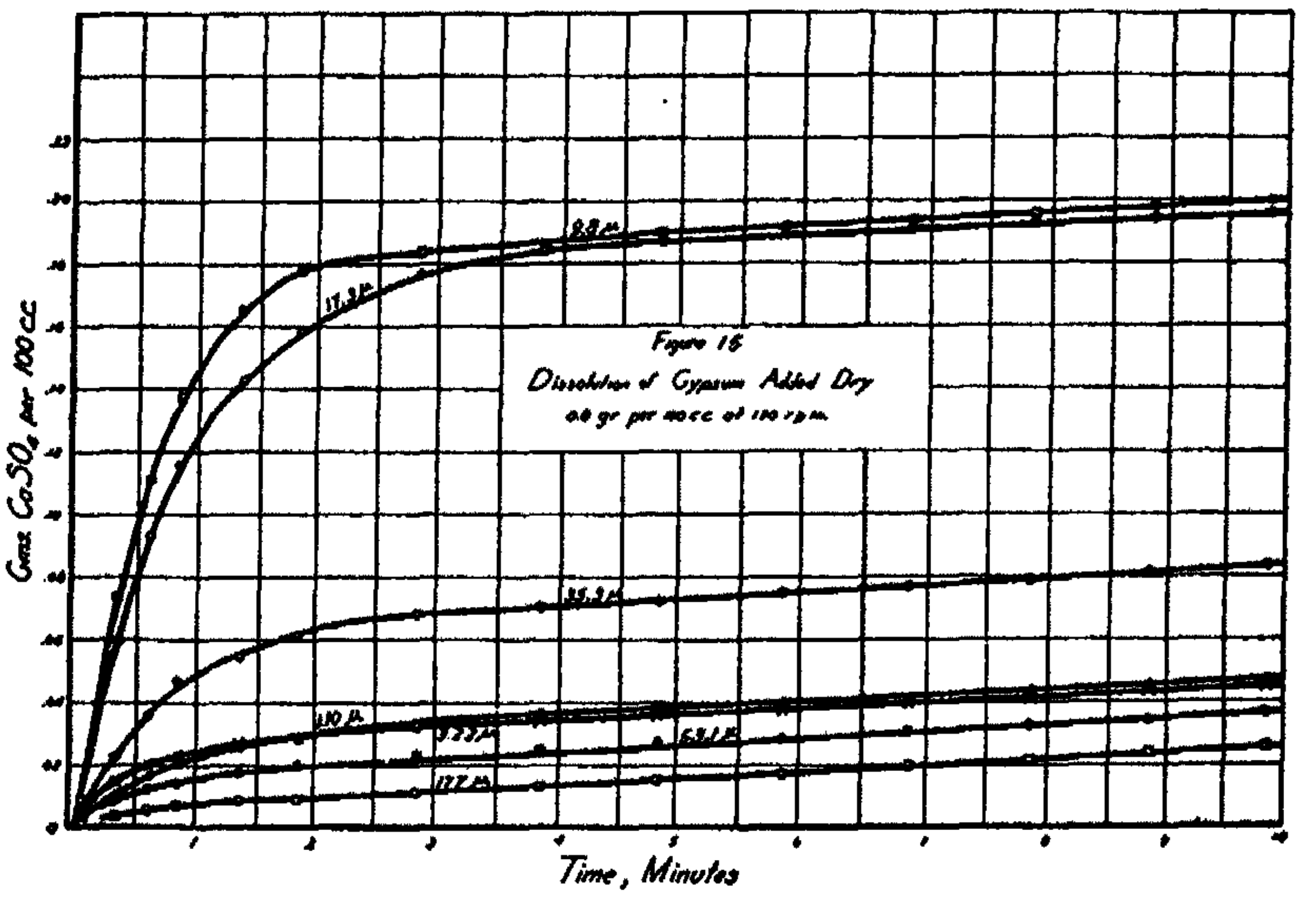


Table V

Dissolution of 0.8 gram of Gypsum added dry to 100 c.cm. of Water at 130 r.p.m.

Time Min.	I	II	III	IV	V	VI	VII	VIII Fraction
Surface Mean Diameter	1.10	3.22	9.8	17.3	35.3	53.1	177	286 Microns
	Grams $CaSO_4 \times 10^2$/100 c.c.							
0.10	0.27	0.37	0.94	0.90	0.45	.41	.21	.09
0.35	1.05	1.51	7.40	6.00	2.29	.91	.35	.20
0.60	1.69	2.02	11.10	9.36	3.57	1.26	.61	.30
0.85	2.08	2.26	13.76	11.64	4.67	1.47	.71	.38
1.35	2.62	2.67	16.50	14.37	5.53	1.81	.85	.53
1.85	2.95	2.91	17.91	15.91	6.20	2.02	.96	.68
2.85	3.35	3.26	18.37	17.72	6.88	2.35	1.16	.95
3.85	3.66	3.51	18.72	18.53	7.06	2.58	1.35	1.19
4.85	3.96	3.74	18.97	18.75	7.26	2.75	1.55	1.41
5.85	4.12	3.96	19.08	18.97	7.50	2.92	1.76	1.66
6.85	4.31	4.17	19.35	19.07	7.73	3.12	1.98	1.90
7.85	4.50	4.38	19.62	19.25	7.94	3.30	2.19	2.20
8.85	4.68	4.58	19.84	19.41	8.08	3.45	2.39	2.48
9.85	4.86	4.79	20.23	19.60	8.38	3.63	2.60	2.75

slowly than the 14.7 micron fraction in the instance of anhydrite and more slowly than the 35.3 micron fraction in the instance of gypsum. The inertness of these fractions at slow stirring is therefore more pronounced for gypsum than for anhydrite. This fact is further evidenced by the closeness of the rate of solution of fractions III and IV of gypsum in contrast to the distinct difference for the similar fractions of anhydrite.

The above results for fractions I and II added dry can be understood if it is considered that solution takes place by penetration of the solvent into the sediment formed by the finely divided crystal grains. Owing to their mutual attraction, the particles constituting the dry fractions below about 3 microns tend to cluster together into ball-like aggregates;[20] on the other hand, this tendency rapidly diminishes with increase in size of particle so that it has largely disappeared in fraction III. As a result of this highly aggregated state of fractions I and II it is difficult for the solvent to penetrate the sediment (which will have formed rapidly by settling due to the same aggregation of the particles and in spite of their individual fineness), so that the rate of solution is extremely small.

Gypsum being softer than anhydrite, it may be expected that the stray fields of force at the surface are greater and consequently also the mutual attraction of the fine particles. This will explain the fact that fractions I and II of the dihydrate added dry to the solvent are relatively more inert than the corresponding fractions of anhydrite. In fact, in contrast to the other fractions, the rate of solution of fractions I and II under the slow stirring conditions is actually greater for anhydrite than for gypsum.

Conversely to the results at 130 r.p.m., the two finest fractions of anhydrite I and II (1.96 and 3.17 microns) added dry at the higher stirring speed of 470 r.p.m., showed a much greater rate of solution[2] than fraction III (7.56 microns). This difference is due to the fact that the penetration by the solvent of the sediment grains is relatively more effective with increase in the speed of stirring for the finer clustered grains than for the coarser. In the same way preliminary experiments showed that the rate of solution of fractions I and II of the gypsum added dry at the higher stirring speed was, in contrast to the result at slow stirring, considerably greater than that of the corresponding fractions of anhydrite. Thus it is seen that increase in the speed of stirring selectively increases the solution rate of the finest particles below about 5 microns when added dry to the solvent to a value approaching normal.

It seemed possible that the observed low rate of solution at slow stirring for fractions I and II of anhydrite and gypsum might be due to a tenaciously adsorbed air film. For example, Ehrenberg and Schultze[24] found that the displacement by water of the air film surrounding a finely divided soil and lampblack was a slow process. To test out this hypothesis the rate of solution of anhydrite fraction II (1.89 μ mean diameter) was measured in a heavy walled Pyrex beaker described above. After three-quarters of a minute, stirring was interrupted and the beaker evacuated at 30 mm. of mercury. Release of small air bubbles took place and terminated in the course of several minutes. Stirring was then continued and conductivity readings taken as before. For comparison the rate of solution was also measured by first dispersing the powder in 2 c.c. of water.

From the results which are shown in Table VI, it is seen that with removal of the air that doubtless adhered to the surface of the powder in the form of minute bubbles, the rate of solution increased, but the effect is quite small compared with that obtained by first dispersing the grains.

TABLE VI

Comparison of Dissolution of 0.8 Gram of Fraction II of Anhydrite (1.89 microns) with and without Evacuation at 30 mm. Hg.

	Grams $CaSO_4 \times 10^2/100$ c.c. after 6 min.
Added dry	4.41
Added dry with evacuation	6.05
Initially dispersed	16.97

In another type of experiment evacuation was carried out in a small thin bulb, the powder wetted in vacuo, and the contents added to the solvent by shattering the bulb. Here again the effect of a possible adhering air film was found to be negligible.

---

[24] Ehrenberg and Schultze: Kolloid-Z., 15, 183 (1914).

It may be noted at this point that just as for the anhydrite, a great increase in the rate of solution of fraction I of gypsum was obtained by first dispersing in 2 c.c. of water. With 0.8 of a gram thus taken for solution saturation was reached in slightly less than 1 minute.

Rate of Solution versus Particle Size for Anhydrite and Gypsum added dry

In determining the relative rate of solution of the different particle sizes, a definite method of comparison must be fixed upon. It was found that the initial rates of the different fractions could not be directly compared, first, because of the very rapid way in which they changed, and second, because of the presence of initial disturbances caused by the varying sedimentation and the presence in some cases of a slight induction period. Comparison of the times required to reach a definite concentration or to span a definite

TABLE VII

Comparison of Concentration Ordinates for Anhydrite added dry at 130 r.p.m.

Fraction	Surface Mean Diameter microns	Grams taken for Solution	Concentration at 6 min. Gr. $CaSO_4 \times 10^2$/100 c.c.
I	1.10	0.8	4.22
		1.6	6.35
II	1.89	0.8	4.68
		1.6	6.75
		2.4	8.62
III	5.9	0.8	9.83
IV	14.7	0.8	6.00
		1.6	7.12
		2.4	8.55
V	26.5	0.8	2.58
		1.6	3.52
		3.2	5.32
VI	53.8	0.8	1.14
		1.6	1.65
		2.4	2.29
VII	157	0.8	.72
		1.6	.90
		2.4	1.08
VIII	250	0.8	0.67
		1.6	0.81

concentration interval was also ruled out because of the existence practically of two stages in the solution process, namely, an initially fast stage covering the first 2 or 3 minutes, and then a uniformly slow stage. It was in most cases impossible to confine the time comparisons for any two fractions to the same stage. Consequently, the method was pursued that was previously employed,[2] of comparing after a given time the concentration ordinates of multiple weights of a given fraction with the concentration of a standard weight of the next adjacent finer fraction. The assumption involved is that for a given fraction the rate of solution as measured by the concentration is proportional to the surface exposed. This appears to be borne out by the fact that for all the fractions, under the *same set of conditions*, equal increments in weight of solute resulted in equal increases in concentration in the range covered.

As larger quantities of the fractions were now available than heretofore, an ascending scale of multiple weights of 0.8, 1.6, 2.4, etc., grams was uniformly employed. A small correction to the surface of the solute for the amount dissolved was made as before.

TABLE VIII

Comparison of Concentration Ordinates for Gypsum added dry at 130 r.p.m.

Fraction	Surface Mean Diameter	Grams taken for Solution	Concentration Gr. $CaSO_4 \times 10^3/100$ c.c. 2.85	6.85 min.
I	1.10	0.8		4.31
II	3.22	0.8	3.22	4.17
		1.2	5.91	7.34
		1.6	7.92	
		2.0	10.60	
III	9.8	0.8	18.37	
IV	17.3	0.8	17.72	19.07
		1.2	19.30	
V	35.3	0.8		7.73
		1.6		12.38
		2.4		16.29
VI	53.1	0.8		3.12
		1.6		4.68
		2.4		6.14
VII	177	0.8		1.98
		1.6		2.41
		2.4		2.89
VIII	286	0.8		1.90
		1.6		2.20

In Tables VII and VIII are given the concentration ordinates at the end of a fixed time of multiple weights of each of the fractions of anhydrite and gypsum, respectively. From these values the relative specific rate of solution of the fractions taken in pairs was calculated, with results as shown in Tables IX and X.

TABLE IX

Relative Rate of Solution of Different Particle Size Fractions of Anhydrite added dry at a Stirring Speed of 130 r.p.m.

Fraction	Surface Mean Diameter	Relative Surface in Pairs	Relative Rate in Pairs	Relative Specific Rate in Pairs	Dissolution Factor
I	1.10	1.72	.82	0.477	.32
II	1.89	3.12	.26	0.083	.68
III	5.9	2.49	4.31	1.73	8.14
IV	14.7	1.80	4.87	2.71	4.70
V	26.5	2.03	3.59	1.77	1.74
VI	53.8	2.93	3.34	1.14	0.98
VII	157	1.59	1.37	.86	0.86
VIII	250	1.00	1.00	1.00	1.00

TABLE X

Relative Rate of Solution of Different Particle Size Fractions of Gypsum added dry at a Stirring Speed of 130 r.p.m.

Fraction	Surface Mean Diameter microns	Relative Surface in Pairs	Relative Rate in Pairs	Relative Specific Rate in Pairs	Dissolution Factor
I	1.10	2.92	1.02	.35	.07
II	3.22	3.04	.20	.067	.20
III	9.8	1.77	1.23	.69	3.00
IV	17.3	2.04	3.77	1.85	4.35
V	35.3	1.50	4.16	2.77	2.35
VI	53.1	3.33	3.53	1.06	0.85
VII	177	1.61	1.29	0.80	0.80
VIII	286	1.00	1.00	1.00	1.00

The dissolution factor shown in column 6 of Tables IX and X is obtained by setting the rate of solution of the coarsest fraction (VIII) equal to unity. It is, therefore, the relative specific rate of solution of each fraction referred to the coarsest as standard.

In Fig. 16, the dissolution factor for anhydrite at 130 r.p.m. is plotted from Table IX in comparison with the values previously obtained at 470 r.p.m.;[2] in Fig. 17 the values of the dissolution factor for gypsum at 130 r.p.m. are plotted from Table X in comparison with those for anhydrite at the same stirring speed.

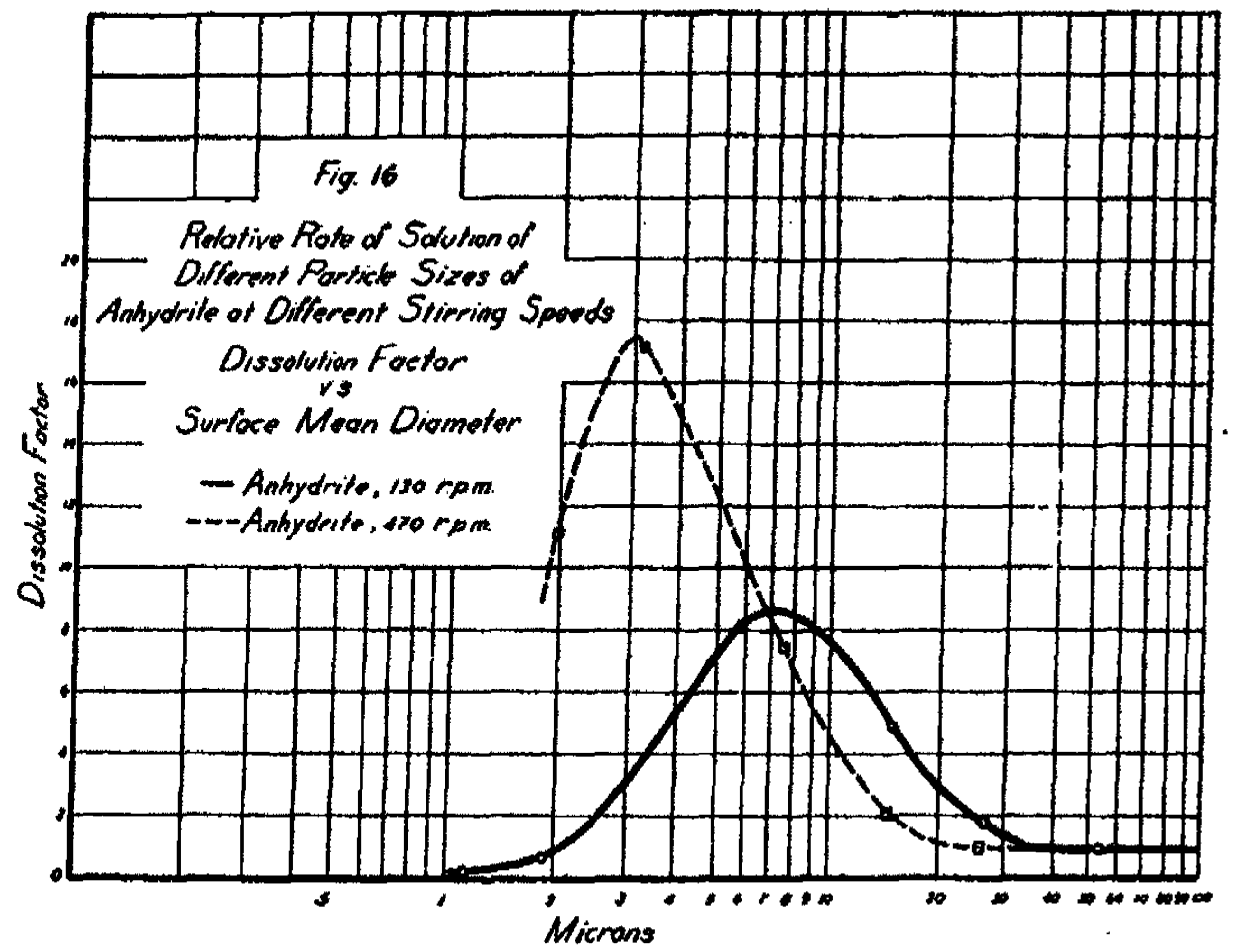


Fig. 16

Relative Rate of Solution of Different Particle Sizes of Anhydrite at Different Stirring Speeds

Dissolution Factor vs Surface Mean Diameter

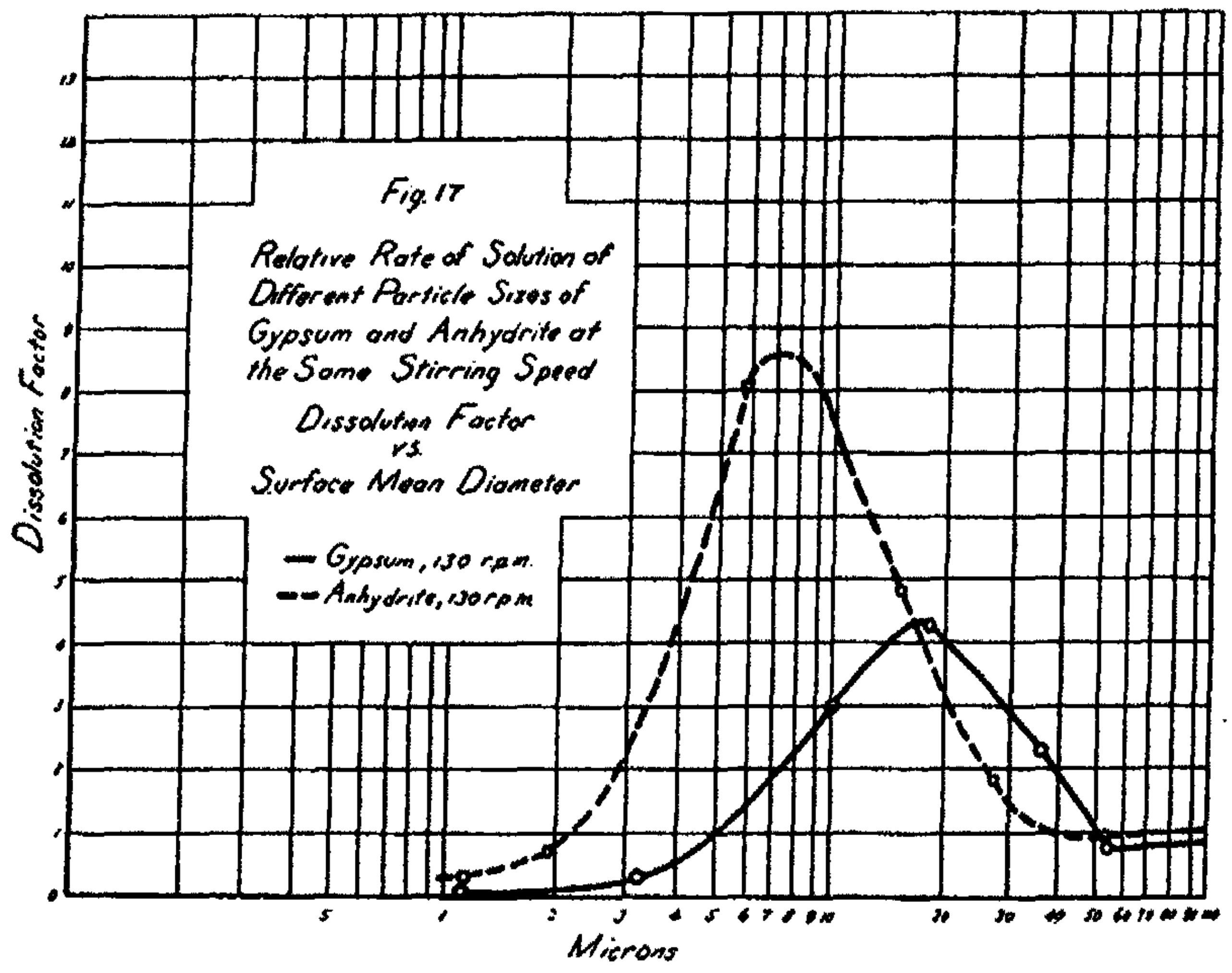


Fig. 17

Relative Rate of Solution of Different Particle Sizes of Gypsum and Anhydrite at the Same Stirring Speed

Dissolution Factor vs. Surface Mean Diameter

Considering from these figures the results for anhydrite and gypsum added dry at the same slow stirring speed of 130 r.p.m., it is seen that below 50 microns the dissolution factor is enhanced above the normal value unity and reaches a maximum. This maximum is for anhydrite 8.6 at a particle size of 7.0 microns. For gypsum the maximum is about half as great, 4.4, and is displaced to a coarser particle size of 16.5 microns. With decrease in particle size below the maximum, the dissolution factor reaches the normal value unity at 2.1 microns for anhydrite and at 5.1 microns for gypsum; thereafter with further decrease in particle size it diminishes to very low values. As already indicated the maximum in the dissolution factor and subsequent decrease are to be ascribed to the effect of mutual attraction and adherence of the grains when simply added dry to the solvent.

At the higher stirring speed, as shown in Fig. 16, the maximum for anhydrite is now 17.6 as against 8.6, and is displaced from 7.0 microns at slow stirring to a particle size of 2.8 microns. This shows the selective increase in the dissolution of the finest grains added dry by increase in stirring speed. For particles greater than 50 microns the specific rate of solution is close to the normal value unity. For fraction VII at about 150 microns the value is nevertheless distinctly less both for anhydrite and gypsum. This corresponds to the relatively high rate of solution of the coarsest fraction VIII with which VII was compared and for which the dissolution factor is unity as standard. Due to the small number of grains involved, the solute of fraction VIII did not completely cover the bottom of the beaker and this probably explains the somewhat high rate observed for this fraction compared to VII.

Rate for Anhydrite dispersed in Water

Since it had been found that initial dispersal of the fine grains of fraction II of anhydrite enormously increased the rate of solution at slow stirring, it was decided to run a series of experiments with the anhydrite powder initially dispersed, similar to that with the powder added dry.

Preliminary trial showed that the use of 3 c.c. of dispersing water gave the same rate of solution as 2 c.c., except for fraction I (1.10 microns). In this instance the amount dissolved after 6 minutes from 0.8 gram was 0.1915 grams $CaSO_4$/100 c.c. with 3 c.c. against 0.1686 grams per 100 c.c. with 2 c.c. Accordingly the larger quantity of dispersing water was used with this fraction and also, for the sake of uniformity, with fraction II (1.89 microns).

Correction of the measured concentrations was made for the amount dissolved in the 2 or 3 c.c. of dispersing water. It was found for all the fractions but VI that the dispersing water was saturated so that the correction was 0.0030 gram per c.c.[2] For 0.8 gram of fraction VI the water was three-fourths saturated. Runs were not made with the coarsest fractions VII and VIII because of the formation of an adherent sludge in the weighing tube.

The time-concentration values are shown in Table XI. Fig. 18 in which these results are plotted shows that the dissolution curves are of the same form as for the anhydrite and gypsum added dry (Figs. 14 and 15). It is seen that the rate of solution of fractions I and II initially dispersed is enormously increased over that of the same solute added dry; the increase is considerably less for fraction III and but very slight for the coarser fractions.

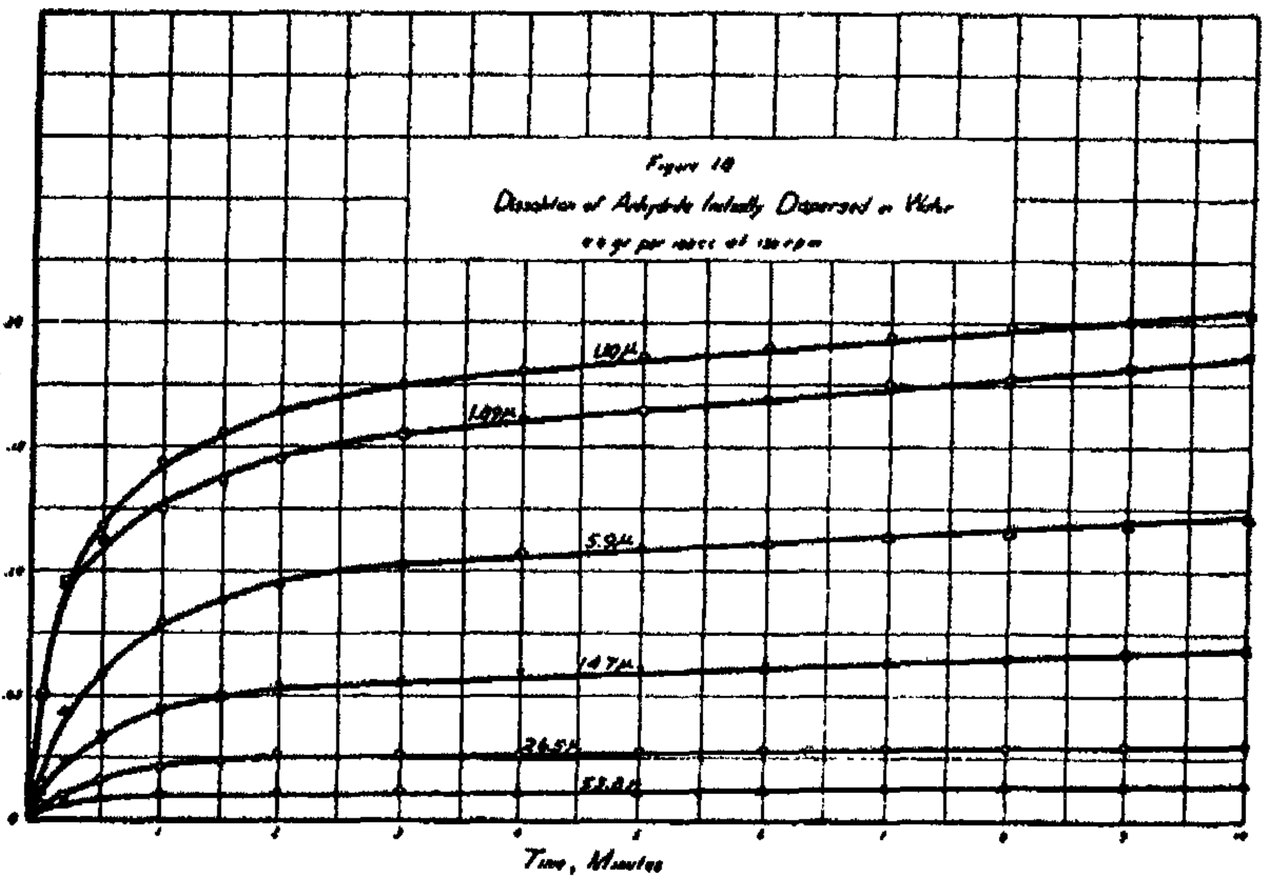


TABLE XI

Dissolution of 0.8 Gram Anhydrite, initially dispersed in Water, in 100 c.cm. of Water at 130 r.p.m.

	I	II	III	IV	V	VI	Fraction
			Surface Mean Diameter				
Time Min.	1.10	1.89	5.9	14.7	26.5	53.8	Microns
			Grams $CaSO_4 \times 10^2/100$ c.c.				
0.1	5.20	5.10	1.56	.95	.57	.00	
0.25	9.70	9.54	4.32	2.39	.98	.54	
0.50	11.77	11.17	5.94	3.33	1.56	.70	
1.00	14.30	12.50	8.00	4.40	2.17	.85	
1.5	15.62	13.65	8.81	5.00	2.42	.92	
2.0	16.46	14.50	9.49	5.33	2.58	.98	
3.0	17.50	15.50	10.30	5.67	2.61	1.02	
4.0	18.15	16.10	10.80	5.88	2.68	1.06	
5.0	18.76	16.53	11.00	6.06	2.76	1.09	
6.0	19.15	16.96	11.21	6.21	2.83	1.12	
7.0	19.40	17.50	11.40	6.40	2.91	1.16	
8.0	19.83	17.84	11.60	6.55	2.96	1.19	
9.0	20.05	18.17	11.82	6.80	3.00	1.22	
10.0	20.30	18.68	12.02	6.90	3.02	1.25	

Relative Rate of Solution versus Particle Size for Anhydrite dispersed

The method of determining the relative rate of solution of the different fractions is the same as that for the powder added dry. Table XII shows the concentration ordinates after 6 minutes of multiple weights of 0.8 gram of each of the fractions. It is seen for 1.6 grams of fractions IV and V in contrast to the result for 0.8 gram where the rates were practically the same, that the rate of solution with the powder dispersed is appreciably higher than for the same material added dry.

TABLE XII

Comparison of Concentration Ordinates for initially dispersed Anhydrite at 130 r.p.m.

Fraction	Surface Mean Diameter	Grams taken for Solution	Dissolved, gr. $CaSO_4 \times 10^{-2}$ in 100 c.c. after 6 min.
I	1.10	0.8	19.15
II	1.89	0.8	16.96
		1.6	19.00
III	5.9	0.8	11.21
		1.6	12.68
		2.4	13.65
IV	14.7	0.8	6.21
		1.6	8.92
V	26.5	0.8	2.83
		1.6	4.45
VI	53.8	0.8	1.12
		1.6	1.74

TABLE XIII

Relative Rate of Solution of Different Particle Sizes of Anhydrite, initially dispersed in Water, at 130 r.p.m.

Fraction	Surface Mean Diameter microns	Relative Surface in Pairs	Relative Rate in Pairs	Relative Specific Rate in Pairs	Dissolution Factor	Dissolution Factor Dry
I	1.10	1.72	2.28	1.32	9.94	.33
II	1.89	3.12	6.26	2.01	7.51	.69
III	5.9	2.49	2.92	1.17	3.75	8.30
IV	14.7	1.80	3.12	1.73	3.21	4.80
V	26.5	2.03	3.84	1.85	1.85	1.77
VI	53.8	1.00	1.00	1.00	1.00	1.00

The specific rate of solution of the fractions taken in pairs, and from this the dissolution factor, were calculated as above with results shown in Table XIII. In this table a value of unity has been chosen for the dissolution factor of fraction VI which is closely justified from the results of Table IX. In the last column of Table XIII the dissolution factor for the anhydrite added dry is recalculated for purpose of comparison to a basis of unity for fraction VI. In Fig. 19 is a plot of the dissolution factor versus particle size for the anhydrite initially dispersed and added dry.

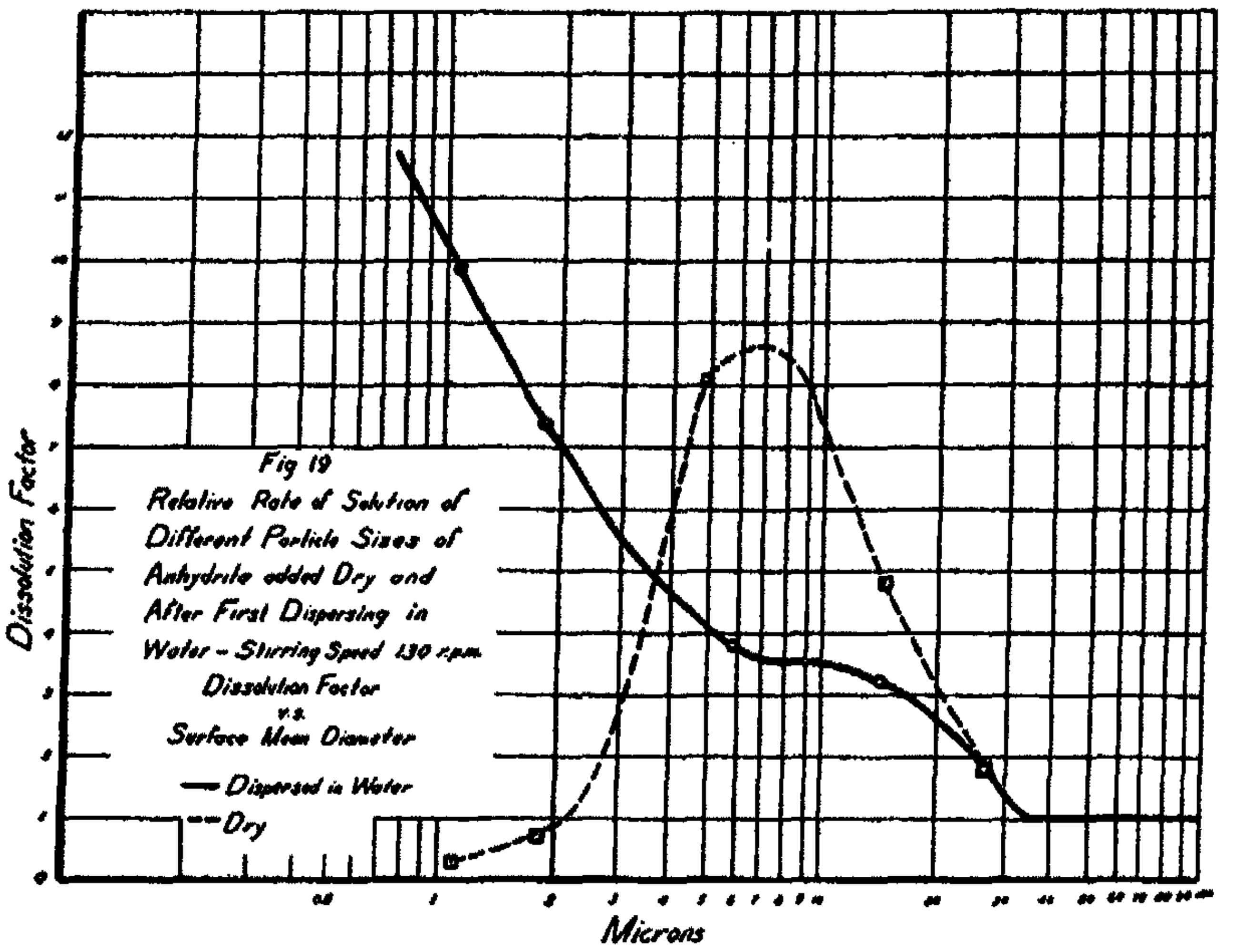


Fig 19
Relative Rate of Solution of Different Particle Sizes of Anhydrite added Dry and After First Dispersing in Water – Stirring Speed 130 r.p.m.
Dissolution Factor v.s. Surface Mean Diameter

It is seen that for fraction V the dissolution factor is closely the same in both cases. For smaller particles it is less for the powder dispersed until a flat inflection point is reached that lies near the particle size corresponding to the maximum for the powder added dry, that is, at 8 microns. With further decrease in particle size beyond the inflection point, the dissolution factor increases continuously from 3.6 to a value of 7.2 at 2 microns and 10.2 at 1 micron.

Physical Interaction of the Microscopic Grains

It has been seen that the mutual attraction of the particles below about 5 microns hindered the action of the solvent so that the rate of solution of the solute added dry was inhibited. Indeed, with the 1.10 micron fraction of anhydrite, initial dispersal with violent shaking in 2 c.c. of water was not sufficient to detach the "associated" grains; a higher dilution by the use of 3 c.c. was necessary. The differences in dissolution factor of anhydrite fractions III and IV dispersed and dry suggests that a physical interaction of the grains of some kind may also play a part for these less fine particles (5.90 and 14.7 microns). In particular it is to be noted that the difference in dissolution factor is due to the greater rate of solution, dispersed over dry, of 1.6 grams of each of the fractions IV and V (14.7 and 26.5 microns), although with 0.8 gram the rate was closely the same.

It has been seen that for all the fractions added dry, settling of the solute was complete in 5 seconds. Essentially then, solution for these fractions takes place from the sediment in contact with a stirred liquid. It is evident that the solvent penetrates to the interior of sediment and solution takes place therein. For if, on the contrary, the surface of the sediment alone dissolved, the rate of solution would be closely the same for all fractions of a given substance, especially in view of the results of Bruner and Tolloczko[25] and Brunner[6] that a rough pitted surface affected the rate of solution but little, that is, that the projected surface determined the rate. Secondly, it would be impossible to explain on any other basis than that solution takes place in the interior of the sediment, the fact that the concentration ordinate at a fixed time increases in the range of solute weights covered at the same rate as the increase in weight of solute taken for solution.

In view then, of the consideration that the solvent flows through the sediment, the structure of the latter, in so far as it may vary from fraction to fraction, will be an important variable in deciding the relative rate of solution. A loose structure will permit a more rapid flow of the solvent through the dissolving sediment than one densely packed; due to displacement and orientation of the particles[26] the contact between the solvent and individual grains also will be rendered more effective.

For coarse grains the specific volume of a settled powder is essentially independent of the particle size. On the other hand, for finer grains it is found that the sediment volume increases with decrease in particle size. For powders in air this has been found to be true for particles less than about 20 microns.[27] For a quartz powder in contact with an electrolyte, Buzágh[28] found that the sedimentation volume increased with decrease in particle size below about 100 microns. To see whether this was also true for the anhydrite fractions in question, the sedimentation volume was measured by shaking with 10 c.c. of water for 30 seconds and allowing to settle. In the case of fractions I and II, the volume was also determined after adding the powder dry to the water without shaking. Temperature was maintained constant in a forced-draft air bath at 22.0 ± .1°C. The measuring cylinder, graduated in 1/10 c.c., was 12.88 mm. in diameter, and was calibrated with mercury, correction being made for the meniscus. Readings were made with a magnifying lens at suitable time intervals.

The results which are the average of two or more measurements are shown in Table XIV.

---

[25] Bruner and Tolloczko: Z. physik. Chem., **35**, 283 (1900).

[26] Hatschek: J. Soc. Chem. Ind., **27**, 538 (1908).

[27] Roller: Ind. Eng. Chem., **22**, 1206 (1930).

[28] Buzágh: Kolloidchem. Beihefte, **32**, 114 (1930).

TABLE XIV

Sediment Volume of Anhydrite Fractions at 22°C.

Fraction	Surface Mean Diameter	Time, mins.				
		5	10	15	30	60
		Volume, c.c. per gram.				
VIII	250	.71	.70	.70	.70	.70
VII	157	.70	.70	.70	.70	.70
VI	53.8	.73	.73	.73	.73	.73
V	26.5	.80	.79	.79	.79	.79
IV	14.7	.88	.88	.88	.88	.88
III	5.9	1.46	1.14	1.07	.96	.96
II	1.89	9.34	8.32	7.21	4.16	3.40
I	1.10	9.43	8.04	6.88	5.55	4.83
II	1.89*	1.15	1.15	1.15	1.15	1.15
I	1.10*	1.35	1.35	1.35	1.35	1.35

* Added dry to water without shaking.

From this table sedimentation of the dispersed material is seen to be complete in 5 minutes for fractions IV to VII, in 15 minutes for fraction III, while for fractions I and II the volume is still decreasing after 60 minutes at the low rate of .02 c.c. per minute. For the same fractions I and II added dry, the end volume is reached in 5 minutes and is considerably less than for the material shaken up. Considering the end sedimentation volume, it is seen that this is constant above about 100 microns, but thereafter increases with decrease in particle size.

In explanation of this augmented effect below 100 microns (and also for the effect caused by a change in solvent or of electrolyte concentration) Ostwald and Haller[29] and Pawlow[30] assume that the particles are surrounded by a "solvate" layer that may vary in thickness. On the other hand, Ehrenberg[31] and Buzágh[28] incline to the view that increase in sediment volume is due to an increasingly loose structure, with contact of the grains at edges and corners resulting in ramifying aggregates. Usher[32] and McDowell and Usher[33] have recently obtained evidence that the latter interpretation is the correct one in contrast to the theory of the solvate layer.

An attempt was made to see what difference is effected in the structure of a sediment, as measured by the volume, by differences in the manner of adding the powder to the water. It was endeavored to simulate conditions that obtain in the actual rate of solution experiments with the solute added dry and initially dispersed. The final sedimentation volume was measured (a) with the powder added dry to the water in the measuring cylinder, (b) after shaking, and (c) after centrifuging. The results are shown in Table XV.

---

[29] Ostwald and Haller: Kolloidchem. Beihefte, 29, 354 (1929).

[30] Pawlow: Kolloid-Z., 42, 112 (1927).

[31] Ehrenberg: "Bodenkolloide," 83 (1918).

[32] Usher: Proc. Roy. Soc., 125A, 143 (1929).

[33] McDowell and Usher: Proc. Roy. Soc., 131A, 564 (1931).

TABLE XV

Sediment Volume of Anhydrite Fractions under Different Conditions at 23-25°C.

Fraction	Surface Mean Diameter	Volume, c.c. per gram Added Dry	Shaken Up	Centrifuged
III	5.9	.89	.96	.66
IV	14.7	.75	.89	.69
V	26.5	.72	.81	.66
VI	53.8	.71	.71	.66
VII	157	.70	.72	.71

It is seen that the sedimentation volume of the powder added dry is intermediate between the values obtained by shaking and by centrifuging. In the last instance, a densely packed structure obtains as is seen by the fact that the volume after centrifuging is nearly the same for all fractions. For the coarsest fraction, the sedimentation volume is closely the same, regardless of the manner of adding the powder. In actual rate of solution measurements, differences in the sedimentation structure due to adding the solute dry or dispersed will, of course, be less than indicated in Table XV because of the dispersing effect of the stirrer.

In order to secure more information concerning the structure of the sediment, experiments were made on the time of filtration of 10 c.c. of water through the different fractions. The filter was of G-3 Jena fritted glass 14 mm. in diameter. The temperature was 24.5 ± .3°C. and the pressure was maintained constant at 15 cm. of mercury by a regulator similar to that described by Cox.[34]

In the instance of fractions IV and V, there was a steady increase in resistance with each successive 10 c.c. pass. The results for different weights of each fraction which are the average of about 6 successive passes, are shown in Table XVI.

TABLE XVI

Filtration of Anhydrite Fractions at 24.5 ± .3°C. under a Head of 15 cms. Hg.

Fraction	Surface Mean Diameter	Weight Taken	Time of Outflow of 10 c.c. mins.
VII	157	0.5	51.6
		1.0	54.0
VI	53.8	0.5	77.2
		1.0	80.0
V	26.5	0.5	117
		1.0	142
		1.5	162
IV	14.7	0.5	301
		1.0	381

---

[34] Cox: Ind. Eng. Chem., Anal. Ed., 1, 7 (1929).

The resistance as measured by the time of outflow for 0.5 gram of powder, is due to both that of the powder itself and of the clogged filter. Consequently, it is the difference in resistance between 0.5 and 1.0 grams that corresponds to the resistance of the powder itself. The results show that this resistance increases rapidly with decrease in particle size below 53.8 microns.

It is to be noted that in the filtration experiments the final structure of the sediment was altered to a densely packed one by the pressure. If in the rate of solution measurements the flow of the solvent through the sediment corresponded to the filtration resistances of Table XVI, it is clear that the rate of solution would decrease rapidly with decrease in particle size instead of increasing as observed. It may be concluded, therefore, that the structure of the sediment as measured by the sediment volume of Tables XIV and XV is of fundamental importance in determining the relative rate of solution of the powder added dry.

This conclusion can be tested directly. It may reasonably be expected that, although the powder added dry has settled in 5 seconds, still for an appreciable time thereafter the physical interaction of the grains might alter so as to form a denser structure. If stirring of the solution be stopped now for a certain period, and then resumed, any increase in density of the structure would, during the quiescent period, in which the amount dissolved is negligible, be reflected in a decrease in the concentration at equal periods of stirring with respect to the normal uninterrupted procedure.

Eight-tenths gram of anhydrite fractions II, III, V, and VII were added dry to 100 c.c. of water in the usual manner. The normal procedure was varied, however, by stopping the stirring after 40 seconds for a period of about 6 minutes, and then resuming.

Because of other objectives that were contemplated, the measurements were carried out in a Pyrex beaker described above. Owing to the increased dimensions of the beaker the effectiveness of the stirring was decreased with a resultant decrease for all the fractions in the rate of solution with respect to that normally obtained. This was especially true for fraction III (5.9 microns) due to a large extent to the inability to effectively distribute the "lumped" fraction over the bottom of the beaker. In Table XVII, in which

TABLE XVII

Dissolution of 0.8 gr. Anhydrite added dry to 100 c.c. Water, Continuous and Interrupted Stirring

Fraction	Particle Size Fraction microns	Grams $CaSO_4 \times 10^2$/100 c.c. after 6 minutes of Stirring	
		Continuous Stirring	Interrupted Stirring
II	1.89	4.41	4.50
III	5.9	5.80	4.48
V	26.5	1.66	1.62
VII	157	.59	.72

the results obtained are recorded, it is seen that for fractions II and VII, corresponding to a permanently structured sediment, the concentration after 6 minutes of interrupted stirring is slightly greater, as would normally be expected, than for 6 minutes of continuous stirring. On the other hand, with fractions III and V, the converse is true well within the experimental error. The unusual result for these fractions is to be interpreted as due to the increasing density of the sediment structure during the 6-minute quiescent period. This effect results in a subsequent decrease in the rate of solution which more than compensates for the slight amount of solution during the period of nonstirring.

In light of the above evidence and conclusions, the difference in the dissolution factor of anhydrite fractions III and IV when dispersed and added dry, is due to a more loosely structured sediment of the 1.6 grams of solute of the comparison fractions IV and V when initially dispersed in water. Indeed it may be concluded that the physical interaction of the grains, varying with particle size below about 50 microns and with experimental conditions, is, for the powder added dry, the most important factor in determining the relative rate of solution as a function of size of grain.

Non-existence of Theoretical Nernst Film

It has been seen that all the fractions added dry dissolve as a sediment through which the solvent flows during stirring. This means that the solvent actively penetrates to a point near the surface of the grains, that is, to at least one-half the mean distance of separation of the particles. Assuming these to be cubes, the mean half-distance of separation may be calculated from the following easily derived equation:

$$(2)\ 3\tau/d + 6\,(\tau/d)^2 + 4(\tau/d)^3 = \rho V/2$$

where d is the length of a cube edge (average particle diameter), τ the mean distance of separation, ρ the density, and V the volume of the sediment per gram.

From the values of Table XIV calculations of the half-distance of separation of the grains have been made by the use of equation (2) with results shown in Table XVIII. It is seen that $\tau/2$ which is only 17.5 microns for the

TABLE XVIII

Mean Distance of Separation of Grains of Anhydrite

Fraction	Surface Mean Diameter	Sedimentation Volume V, c.c. per gram	Mean Distance τ, microns
VII	157	.70	35
VI	53.8	.73	12
V	26.5	.79	6.5
IV	14.7	.88	3.9
III	5.9	.96	1.6
II	1.89	1.15	.60
I	1.10	1.35	.39

coarsest fraction VII rapidly decreases to a value of .19 microns for fraction I. That the solvent actively penetrated the latter sediment is seen from the fact that increasing weights of this solute resulted in proportionate increases in the rate of solution. Consequently, the theoretical Nernst film, if it exists, must be smaller than 0.2 micron, a value that is less than 1/100 of that calculated from the Nernst diffusion film theory, 20 to 50 microns.

Spangenberg[35] found by observation under the microscope that the slightest disturbance of a saturated solution in contact with a crystal of NaCl was communicated within about 0.4 micron, the resolving power of the microscope, which is far within the 20 to 50 micron range of the Nernst film. Recent careful measurements by Bulkley[36] of flow through capillary tubes show that motion of the fluid exists at least as close as 0.03 micron from the surface for a flow as small as 1/400,000 c.c. per minute. Miyamoto, Kaya, and Nakata[37] found that a monomolecular film of palmitic and stearic acids barely affected the rate of oxidation of sodium sulphite solution by O_2, and concluded "that the thickness of the stationary film, if it exists, should be smaller than 23.7×10^{-8} cm."

In agreement with the result found in this work, independent and direct evidence strongly contradicts the existence of the theoretical Nernst diffusion film. Apparently then, the enhanced rate of solution with decrease in particle size that has been observed can in no way be attributed to a decrease in thickness of such a film with decrease in particle size.

Effect of Edges and Corners

There is increasing evidence that catalysis, solution and crystallization take place at "active centers" which may be "crystal defects," edges, and corners.[13,14,15,16,17,18] The number of edges per gram increases inversely as the square of the particle size, and the number of corners inversely as the cube.[19] Therefore, if the edges and corners alone were active, one should expect the rate of solution to be inversely proportional, not to the first power of the particle size as would ordinarily be expected, but to the second and third power, respectively. In general, however, the surface may be expected to play a part, and therefore the effect of edges and corners would be apparent only below a certain particle size and the exponent would then fall between 1 and 3.

From Tables IX, X and XIII in which are given the relative rate of solution of the fractions taken in pairs at 130 r.p.m. and also, from results previously obtained at 470 r.p.m.,[2] the exponent n in the equation:

$$(3)\ R_1/R_2 = (S_1/S_2)^n$$

has been calculated for the fractions taken in pairs. In equation (3) R_1/R_2 is the relative rate of solution, S_1/S_2 the relative surface per gram of two adjacent fractions.

---

[35] Spangenberg: Z. Krist., 59, 383 (1923).

[36] Bulkley: Bureau Standards, J. Res., 6, 89 (1931).

[37] Miyamoto, Kaya, and Nakata: Bull. Chem. Soc. Japan, 6, 133 (1931).

It is seen from Table XIX that for the fractions added dry the calculated values of n are quite variable, lying above 3 in two cases and below 0 for fractions I and II of anhydrite and II of gypsum at slow stirring. In view of all the considerations that have been advanced, the values of n for the solute added dry obviously depend essentially on the structure of the sediment and not on the effect of corners and edges.

Table XIX

Value of Exponent n for Fractions taken in Pairs

Fraction	Anhydrite Added dry 130 r.p.m.	Anhydrite Added dry 470 r.p.m.	Anhydrite Initially dispersed 130 r.p.m.	Gypsum Added dry 130 r.p.m.
I	− .36	1.10	1.51	.018
II	−1.18	1.95	1.62	− .60
III	1.60	3.13	1.17	.36
IV	2.70	2.10	1.93	1.86
V	1.81	1.03	1.90	3.52
VI	1.12			1.05
VII	.68			.54

However, for the solute initially dispersed in water the situation is different. Fractions I and II of anhydrite (1.10 and 1.89 microns) throughout the experiment remained suspended in the solvent. The slight settling effect of the first 10 minutes is quite similar for both fractions as seen from Table XIV. Fractions III and IV (5.9 and 14.7 microns) are still partially suspended in the solution after the first two or three minutes. On pouring the solution out of the beaker after several minutes of stirring, the solute flows out with it as though it were thoroughly suspended. On the other hand, fractions V and VI (26.5 and 53.8 microns) have completely settled in 1½ and ½ minutes, respectively; and on pouring out the solution, these grains in contrast to the particles of fractions I to IV tend to adhere to themselves and to the beaker in the manner of coarse sand. It is reasonable to conclude that for these coarser fractions the structure of the sediment strongly influences the relative rate of solution; on the other hand, for fractions I, II, III, and IV, (1.10 to 14.7 microns) initially dispersed in water, the physical interaction of the grains due to their effective separation is negligible or nil and the rate of solution corresponds to the activity of the individual particles.

This conclusion appears to be substantiated by the results shown in Fig. 19 for anhydrite dispersed. At 8 microns there is a flat inflection point at which the rate of change of the dissolution factor with particle size is nil; in other words, at this particular point the rate of solution is, by definition of the dissolution factor, strictly proportional to the surface exposed. This can be accounted for by the fact that owing to the effective dispersion of the fine grains corresponding to the inflection point, their physical interaction has vanished and no longer affects the rate of solution with decrease in particle size.

For coarser particles below 8 microns and up to 50 microns, the physical interaction, decreasing with diminution of particle size, results in an increase in the dissolution factor as observed.

For the particles less than 8 microns, there is again an increase in the dissolution factor. Since the physical interaction no longer plays a part here, the enhanced rate of solution must correspond solely to the effect of edges and corners.

The edges E, and corners C, per sq. cm. can be determined from the statistical count of Table I by equations similar to that of (1) for the surface mean diameter. We have

$$(4) \quad E = 2\Sigma d / \Sigma d^2$$

$$(5) \quad C = 1.33 \; 1/\Sigma d^2$$

In Table XX are given the results of calculation of n, E, and C. n is recalculated from Table XIII for fractions I, II, and III of anhydrite to a particle size of 8 microns as standard. It is seen that corresponding exclusively to the effect of edges and corners on the rate of solution, n is above unity for fraction III (5.9 microns) and substantially so for fractions II and I lying below 2 microns. The uncertainty in n can be calculated from the individual measurements and is ±.09, ±.06, and ±.11 for fractions III, II, and I, respectively.

TABLE XX

Value of Exponent n for Anhydrite, initially dispersed, Referred to 8 micron Particle as Standard

Fraction	Surface Mean Diameter microns	Edges per Unit Surface microns^{-1}	Corners per Unit Surface microns^{-2}	n
I	1.10	2.22	1.80	1.51
II	1.89	1.94	1.48	1.51
III	5.9	.40	.06	1.13
IV	8.0	.25	.02	1.00

Since n in Table XX is appreciably less than 2, the value corresponding to solution solely by way of the edges, and from the fact that the dissolution factor is close to unity for the coarse fractions VI, VII, and VIII, it appears that solution of the anhydrite takes place directly at the surface as well as by way of the edges.

However, to account for the observed appreciable effect of the edges (and corners), it is necessary to conclude that solution at the surface of the anhydrite takes place not uniformly but via the active centers. This conclusion comes about from the fact that even for a 1-micron particle the proportion of edge to surface atoms is slight, about 10^{-3}, and is thus insufficient to account for a value of n as high as 1.5; however, the proportion is quite appreciable with respect to the active centers since from the work of Smekal[14] the concentration of these is of about the same order.

Summary

1. A finely ground crystalline anhydrite and gypsum powder were separated into homogeneous particle size fractions between 1 and 250 microns surface mean diameter. The relative rate of solution of these fractions in water was determined by conductivity measurement at 20°C. at a stirring speed of 130 r.p.m.

The time concentration curves are of the same form for all the fractions. There is an initial high rate of solution that decreases rapidly in the first 2 or 3 minutes to a slow almost linear rate. For the finest fractions up to about 17 microns, added dry to the solvent, there is a slight induction period of 4 or 5 seconds.

2. With the solute added dry to the solvent at the slow stirring speed, the rate of solution of the fractions below 5 microns of both anhydrite and gypsum is unexpectedly low. This is attributed to difficulty of penetration by the solvent to the individual grains of the solute due to their initial strong mutual attraction. In accordance with the greater softness of gypsum, the effect for this substance is more pronounced than for the anhydrite. Increase in speed of stirring (from 130 to 470 r.p.m.) selectively promotes the rate of solution of the finest particles below 5 microns to a value approaching normal.

It is shown that the inertness of the finest particles when added dry at slow stirring is not due to any appreciable extent to entrained air.

3. When the anhydrite solute is first dispersed in 2 or 3 cc. of water before adding to the solvent, the rate of solution of the finest particles below 5 microns is enormously increased. This is true to a lesser extent for the 5.9 micron fraction; for the coarser fractions up to 50 microns the rate is almost the same for the powder dispersed and dry. However, when the quantity of solute is increased from 0.8 to 1.6 grams, the rate of solution is here also greater dispersed than dry.

4. With the solute added dry, the dissolution factor, or the relative specific rate of solution referred to the coarsest fraction as unity, increases from unity to a maximum with decrease in particle size. At 130 r.p.m., the maximum for anhydrite has a value of 8.6 at 7.0 microns, as against 17.6 at 2.8 microns with a stirring speed of 470 r.p.m. With gypsum at 130 r.p.m., the maximum is only 4.4 at 16.5 microns. With decrease in particle size below the maximum, the dissolution factor falls below the normal value unity both for anhydrite and gypsum, but to a greater degree for the latter, at the same slow stirring.

5. With the anhydrite initially dispersed in 2 or 3 c.c. of water, the dissolution factor at a stirring speed of 130 r.p.m. increases above unity with decrease in particle size below about 50 microns, passing through a flat inflection point with the value of 3.6 at particle size of 8 microns; thereafter, the dissolution factor increases with decrease in particle size, reaching a value of 7.2 at 2 microns and 10.2 at 1 micron.

6. For all the fractions added dry, solution takes place essentially from a settled sediment through which the solvent flows. Evidence based upon measurement of sedimentation volume, rate of filtration, and rate of solution with interrupted stirring, is presented to show that the structure of the sediment, that is, whether loosely aggregated or densely packed, is most important in determining the rate of solution. The structure of the sediment depends on particle size below 100 microns and on conditions of experiment.

7. Quite apart from considerations which may be mentioned against the general Nernst diffusion theory of heterogeneous reaction, it is shown that the Nernst diffusion film, if it exists, must be smaller than 0.2 micron, or less than 1/100 of the theoretical value 20 to 50 microns. Direct evidence from recent literature is adduced to show still further that any film which may exist approaches molecular dimensions. Consequently, the assumption of a diffusion film appears to be invalid, and it is not possible to account for the observed enhanced rate of solution on the basis of a decrease in thickness of such an adherent film with decrease in particle size below 50 microns.

8. The experimental results are examined in light of the theory that solution takes place from active centers which involve the edges and corners of a crystal. For the solute added dry the structure of the sediment overcomes all other effects in determining the rate of solution. For the solute (anhydrite) initially dispersed, it appears that the same situation holds for particles greater than corresponds to the inflection point at 8 microns. Between this particle size and 50 microns the enhanced rate of solution is due to increasing dispersity of the solute with decrease in particle size. At 8 microns, the physical interaction of the grains vanishes and the rate of solution is proportional to the surface exposed. Below 8 microns the enhanced rate of solution is to be attributed solely to the effect of edges and corners. Taking the rate of solution proportional to the nth power of the surface exposed and referring to an 8-micron particle as standard, n is 1.13 ± .09 at a surface mean diameter of 5.9 microns, 1.51 ± .06 at a mean diameter of 1.89 microns, and 1.51 ± .11 at a mean diameter of 1.10 microns. Since the exponent is substantially less than 2 which would correspond to solution by way of the edges alone, the anhydrite crystals dissolve also at the surface. This confirms the conclusion derived from the fact that the dissolution factor is close to unity for the coarsest fractions. However, in order to account for the appreciable effect due to the edges and corners for particles between 1 and 8 microns, it is necessary to conclude that solution of the anhydrite at the surface is not uniform but is determined by active centers.

THE SOLUBILITY OF UREA IN WATER*

BY LOUIS SHNIDMAN AND ARTHUR A. SUNIER

Introduction

Although the solubility of urea in water has been the subject of several researches,[1,2,3] the precision of measurement in most cases is poor, and judging from the procedures used, the accuracy of the results may well be questioned. One purpose of the present research was, therefore, to attempt to determine more precisely and accurately the solubility of urea in water. The data are also of some interest from the standpoint of a study of concentrated solutions—their ideality, non-ideality, and the like.

Materials

In work of this nature the materials used become of prime importance. Urea from two sources was used. First, the C. P. Grade of Baker's urea which was imported from Germany and made by the Synthetic Ammonia Carbon Dioxide Process[4] was used. It is interesting to note that at the present time apparently no urea is being made in the United States, all being imported from Germany. This sample of urea as received showed a melting point of 132.5°, but some solid insoluble material seemed to be present, so the urea was twice re-crystallized from distilled water. During the re-crystallization the temperature was never allowed to exceed 65°. The urea was then carefully dried at 55°C. in an electric oven for sixteen hours, after which the melting point was run. The melting point of the resulting crystals was 132.7°, which agrees exactly with the value of 132.7° recorded in the literature.[5]

Another sample of urea made from Calcium Cyanamid was used. This sample obtained through the courtesy of the Union Carbide Company, was made by them from Calcium Cyanamid in an experimental plant in 1925, and showed the following analysis:

	Dry Basis		
% Total Nitrogen	43.80		
Urea Nitrogen	40.40	Urea	86.62
Dicy Nitrogen	.18	Dicy	.27
Guanylurea Nitrogen	1.85	Guanylurea	3.37
Cyanamid Nitrogen	.18	Cyanamid	.27
Ammonia Nitrogen	.87	Ammonia	1.06
Insoluble Nitrogen	.13		
Combined H_2SO_4	5.52		
Moisture as received	7.35		

---

*Communication from the Chemical Laboratory of the University of Rochester.

This sample although impure was re-crystallized carefully four times from distilled water and twice from Baker's C. P. Methanol. During the re-crystallization, the temperature never exceeded 65°. The final crystals from the second methanol re-crystallization were dried in an electric oven at 52° for 24 hours. The melting point of the resulting crystals was 132.6° which agrees closely with the value recorded in the literature. The melting point was taken as the prime criterion for the purity of the substances used. Thus, two samples of urea from different sources, originally made by different methods, were obtained in a high state of purity.

Procedure and Apparatus

The synthetic method of Alexejew[6] was employed in making the solubility determinations. This method consisted in heating weighed quantities of solvent and solute in a sealed tube, shaken in a water bath, and noting the temperature at which the solid phase had nearly disappeared. In recent years other investigators[7,8,9] have found this method to be an accurate and a reliable means for determining the solubility of solids in various solvents. As pointed out by these investigators, care must be taken in attaining true equilibrium conditions at the solubility temperature; this can ordinarily be obtained through slow heating. The apparatus used has been described earlier.[9] A temperature rise of 0.01° per minute was used in some cases, though in many cases thermostating for a period of time was employed. Sunier[9] pointed out that with a rate of heating of 0.01° per minute, results well within 0.1° of the true solubility temperature were obtained for naphthalene—aliphatic alcohol systems. The authors feel that this same degree of accuracy would hold for the urea-water system.

In the preparation of the sealed tubes for a run, precautions were taken to insure the presence of small crystals. Other investigators[7,8,9] have shown that the size of the crystal is of importance in attaining true equilibrium conditions. The method was that ordinarily employed and consisted in rapidly heating the tube to a temperature where all the solute dissolved, and then cooling rapidly with vigorous shaking.

Thin-wall pyrex tubes of seven millimeters internal diameter and approximately fourteen centimeters long were used. The tubes were cleaned with sulphuric-chromic acid cleaning solution, rinsed with distilled water, and then heated over an open Bunsen burner to dull redness, placed in a desiccator, allowed to cool, and weighed. In these determinations a thermometer certified by the Bureau of Standards was employed. The thermometer could be read to ±0.01° with the aid of a magnifying glass. The temperatures recorded should be accurate to ±0.02°.

Statements are found in the literature[1,10,11] to the effect that care is necessary in heating solutions of urea because of the danger of decomposition at higher temperatures. In order to study this point more clearly, and at the same time check the accuracy of the results obtained at higher temperatures, a tube originally showing a corrected solubility temperature of 73.11° was heated to the temperature of boiling water (99°) with constant shaking for varying periods of time. The solubility temperature was re-determined after each period. The results are given in Table I, and are plotted in Fig. 1.

TABLE I

Effect of Heating at 99° on Solubility Temperature of Urea

Hrs. @ 99°	Solubility Temperature	Difference in degrees
0	73.11	—
1	73.08	−0.03
5	72.48	−0.63
10	71.36	−1.75
20	69.67	−3.44

As shown above after one hour heating and shaking at 99°, a change of 0.03° was noticed. This change is probably within the degree of accuracy of the method at that temperature. Hence, it is concluded that the solubility temperatures in the higher range are accurate and are not affected by any decomposition, because at no time was the tube subjected to its solubility temperature for more than one hour, and then considerably below 99°. If little or no decomposition took place at 99° after one hour, it was quite certain that the change or decomposition taking place at temperatures of 73° or below would be negligible for periods of one or two hours.

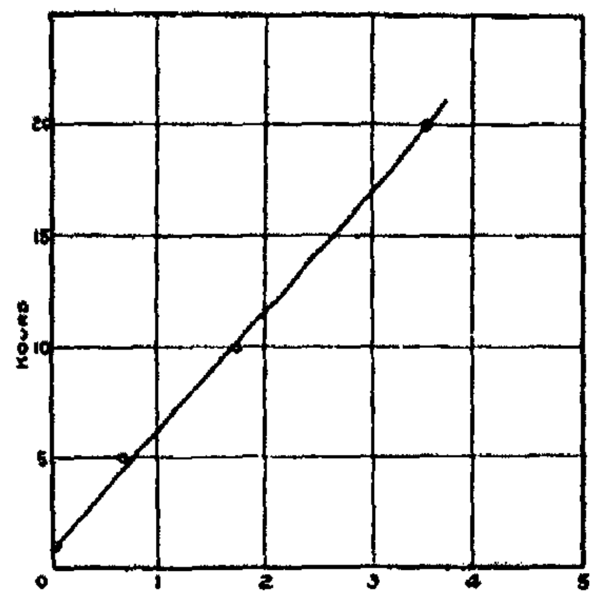


FIG. 1

Change in Solubility Temperature of Urea on Heating.

Fig. 1 shows clearly that the rate of decomposition after the first hour and during the next nineteen hours of heating and shaking at 99°, as indicated by its solubility temperature, is a straight line function. It is of course quite possible that the presence of the ammonium cyanate produced, affects the solubility temperature to some extent; hence the solubility temperatures do not give a true indication of the amount or rate of decomposition. Walker[10] heated a decinormal urea solution at 100° and found that the transformation of urea into ammonium cyanate had reached equilibrium after one hour. The tube used for the above heating at 99° was approximately a 57.5 normal urea. It may be that the more concentrated solution shows a slower rate of transformation, which would explain the progressive lowering of the solubility temperature, during the 20 hour heating period.

Results

The results of the various solubility determinations are presented in Tables II and III. Concentrations have been calculated and tabulated on both the mol fraction and weight per cent basis. The data was plotted on a large scale according to the method of Hildebrand and Jenks,[12] as the log N_2 vs. 1000/T. The solubilities at rounded temperatures were read off and are given in Table IV.

TABLE II

Solubility of Urea in Water

Urea made by Snythetic NH_3 + CO_2 Process (re-crystallized from water)

Grams Urea	Grams Solvent	Wgt. % Urea	Mol Fract. Urea	Solub. Temp.
1.5140	1.4486	51.10	0.2387	18.72
1.7891	1.4420	55.37	0.2712	26.83
1.8899	1.4951	55.83	0.2749	27.31
1.5119	1.0103	59.94	0.3099	35.42
2.3267	1.4955	60.87	0.3182	37.36
1.8298	1.0205	64.19	0.3498	43.94
2.8030	1.4832	65.39	0.3618	46.56
2.2347	0.9884	69.33	0.4041	54.77
2.1987	0.9250	70.38	0.4163	57.02
2.5702	0.9703	72.59	0.4428	61.76
2.3602	0.6823	77.57	0.5093	73.11

TABLE III

Solubility of Urea in Water

Urea made from Calcium Cyanamid—re-crystallized from water and methanol

Grams Urea	Grams Solvent	Wgt. % Urea	Mol Fract. Urea	Solub. Temp.
1.1217	1.0027	52.80	0.2513	21.59
1.7794	1.5176	53.97	0.2602	23.85
2.0496	1.5140	57.51	0.2888	30.38
1.5155	1.0114	59.97	0.3102	35.15
1.6631	0.9788	62.95	0.3377	41.11
1.8291	1.0148	64.31	0.3510	43.85
1.1159	0.4888	69.53	0.4065	54.97
2.2329	0.9520	70.10	0.4130	55.88
1.8579	0.7406	71.49	0.4294	59.13
1.3635	0.4879	73.64	0.4561	63.79
2.4081	0.7355	76.60	0.4956	70.49

TABLE IV

Solubility of Urea in Water at Rounded Temperatures
(expressed in Mol Fractions of Urea)

Temp. °C.	Synthetic Process N_2 Urea	Cynamid N_2 Urea	Mean N_2 Urea
20	0.243_5	0.244_7	0.244_1
25	0.264_2	0.265_5	0.264_9
30	0.285_5	0.286_8	0.286_2
35	0.308_0	0.309_3	0.308_6
40	0.330_8	0.332_2	0.331_6
45	0.355_4	0.356_9	0.356_1
50	0.380_2	0.381_6	0.380_9
55	0.406_0	0.407_9	0.406_9
60	0.433_2	0.434_9	0.434_0
65	0.460_9	0.462_7	0.461_8
70	0.490_5	0.492_0	0.491_4

Discussion of Results

The results of these determinations were compared with those published by earlier workers. Speyers,[1] many years ago, determined the solubility of urea in water. He used Kahlbaum's urea (no doubt made from cyanamid), re-crystallized from ethyl alcohol, and dried on a steam radiator to prevent decomposition. Ordinary distilled water was used in these determinations. He used a thermometer said to be accurate to a tenth of a degree, and kept the solution at a temperature to within a tenth of a degree for ten minutes, and then analyzed the filtrate by the Kjehldahl distillation method. He states that the filtration was carried on while the temperature was cooling slightly. Speyers' results were not very precise, and a study of his method of attaining equilibrium and analyzing his samples leads to conclusion that the results are not very accurate. Krummacher[2] determined the solubility of urea, re-crystallized from ethyl alcohol, at the three temperatures, viz. 5.5, 17.1, and 20.92°C. His results at the two higher temperatures are in essential agreement with the results presented in this paper. Comparison at the lower temperature is not possible, except by a considerable extrapolation of the present curve. Pinck and Kelley[3] more recently determined the solubility of urea in water and found that at higher temperatures there was a marked deviation from the results published by Speyers. Their method consisted in heating from three to four hundred cc. of solution in a water bath in the presence of solid urea at a temperature a few degrees above that at which the solubility was determined. When the solution was cooled to the desired temperature, and after being maintained at this point for about ten minutes, a sample of twenty-five to thirty-five grams was taken. The dissolved urea was determined by the urease method of Fox and Geldard.[13] These authors used a sample of synthetic urea purified by two re-crystallizations from water. Their procedure in obtaining equilibrium was not of extreme accuracy. Some of their results agree closely with the authors' determinations, but some of them, e.g. at the lower and higher temperatures, show some variations. The results of the above mentioned investigators are compared in graphic form with the authors' work in Fig. 2.

When Speyers' data are plotted according to the method of Hildebrand and Jenks,[12] no smooth or straight line curve results. When Pinck and Kelley's data are plotted in a similar manner, the curve also is not smooth. This deviation from the straight-line function was undoubtedly partly due to their method of obtaining equilibrium. The present data on the solubility of urea made by two independent methods, plotted according to the method of Hildebrand and Jenks, yield a smooth and straight line curve. The results on the two samples of urea are so close that they overlap in many cases.

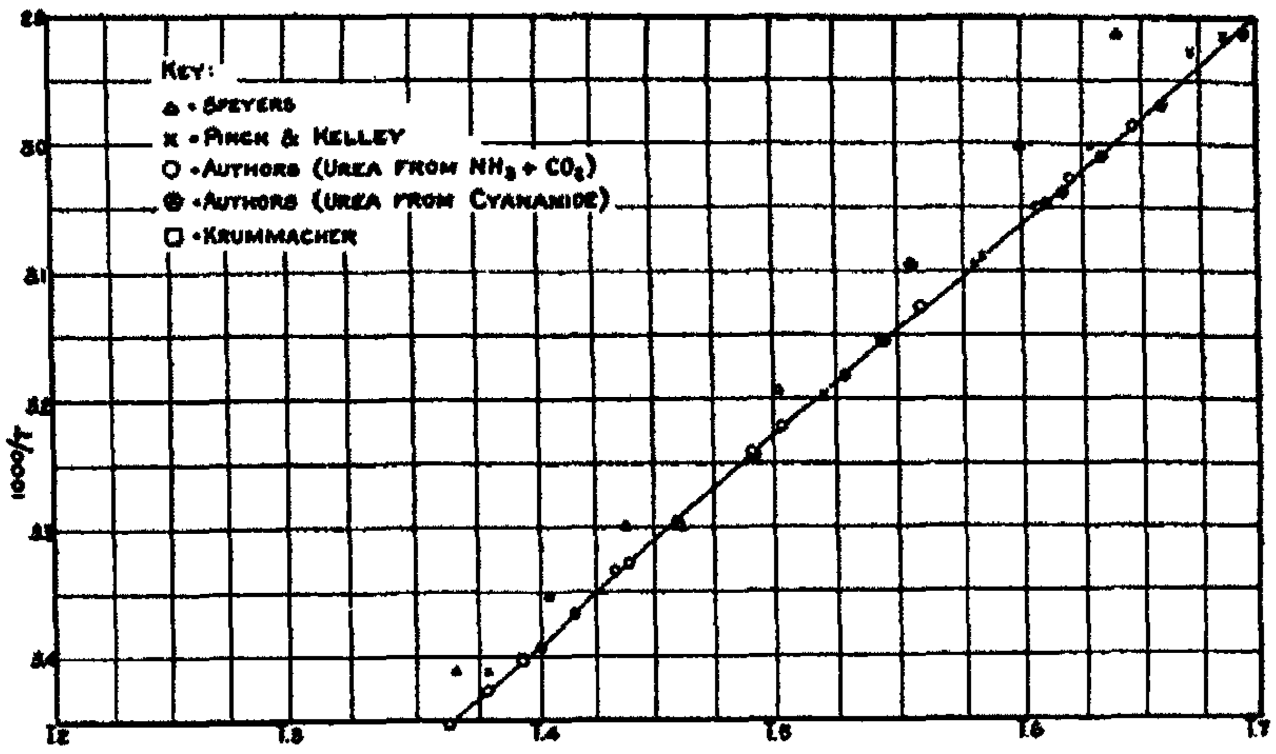


Fig. 2
Solubility of Urea in Water.

A study of Tables II and III shows the deviation obtained relative to the solubility of urea and water in two samples of urea made from different sources, and re-crystallized from water and methanol respectively. The fact that urea made by the synthetic method and urea made from calcium cyanamid shows such close agreement in regard to their solubility in water, leads to the conclusion that these determinations are more accurate than those of previously published work. This appears more plausible when it is recalled that the urea made by the synthetic process was re-crystallized from water, while that made from calcium cyanamid was re-crystallized from methanol. Hence, samples of urea made by two independent methods, and re-crystallized from water and methanol respectively, show close agreement as regards their solubility in water. These relations are brought out very clearly in Fig. 2. It is felt that the foregoing results are accurate to well within ±0.15° of the true solubility temperature; this figure representing the maximum deviation, whereas most of the determinations deviate much less. The mean deviation in the solubility temperature for the synthetic urea sample was 0.10°, while for urea from calcium cyanamid it was 0.07°. It is believed that the solubility results obtained with the sample of synthetic urea are nearer the true value, than those of urea from calcium cyanamid; first, because the former showed a slightly higher melting point, and secondly the product before re-crystallization was in a higher state of purity. However, in the final results (see Table IV) a mean value of the solubility of urea at rounded temperatures is presented. This mean value, representing the average of the solubilities of the respective samples of urea, was read off from the large plot, previously referred to. From this plot the equation of the mean straight line was determined and found to be $\log_{10}N = -609.8 (1/T) + 1.468$ and is valid over the temperature range 20° to 70° studied. It gives results to within one part per thousand of the values as obtained from the plot. Some nine preliminary determinations by Mr. E. Doell in this laboratory, using urea twice re-crystallized from absolute ethanol, has given results which lead to the same conclusion.

The fact that the log N vs. 1/T curve is a straight line, leads one to inquire whether or not ideal solutions are encountered in this range of concentration and temperature. When the curve is extrapolated to log N = 0, the intercept on the temperature axis gives a value of 142° whereas the melting point of pure urea is agreed to be 132.7°. This discrepancy rather definitely points to the fact that the solutions are non-ideal, perhaps yielding a reverse S form of curve discussed by Mortimer.[14] No data seems to be available concerning

TABLE V

Vapor Pressure of Urea Solutions at 60.28°
(Perman and Lovett's Data)

Mols Urea per Mol H_2O	Mol. Fract. Urea (Exp.)	Observed Vap. Press. (mm.)	Mol Fract. (Calc.)	% Diff. or Error
—	—	151.42	—	—
.0231	.0226	149.1	.0153	47.6
.0445	.0426	146.8	.0305	39.7
.0690	.0645	144.7	.0444	45.4
.0813	.0752	142.2	.0609	23.5
.1339	.1181	136.1	.1012	16.7
.1763	.1499	131.3	.1329	12.8
.2537	.2024	123.8	.1824	10.9
.3409	.2542	118.0	.2207	15.2
.4160	.2938	111.7	.2623	12.0
.4712	.3203	107.0	.2934	9.2
.5188	.3416	104.0	.3132	9.1
.6482	.3933	95.4	.3700	6.3
.8127	.4483	85.5	.4353	3.0

the latent heat of fusion of urea (no doubt because of the decomposition of urea at its melting point); hence a comparison of the experimental and ideal slope of the line is not possible. It may be said that when the slope, 609.8, is multiplied by 4.583, a value of approximately 2800 calories is obtained; if the solutions were ideal, this value would represent the molal latent heat of fusion of urea.

At least two sets of data are to be found in the literature dealing with the vapor pressures of urea solutions. That of Perman and Lovett[15] covers quite a range of concentrations at several temperatures. Since these authors did not present any calculations of deviations from Raoult's law (Bancroft[16] in a recent article mentions briefly the variation of these data from Raoult's law) calculations have been made using their data. The pertinent data and the results of the calculations at only one temperature—60.28° would appear to be of sufficient interest to be included in this paper.

In Table V columns one and three are taken directly from the paper of Perman and Lovett. In column two concentrations are recorded on the mol fraction basis. Column four gives the mol fractions calculated by substituting the proper values in the well known equation $(p_0 - p)/p_0 = x$ of Raoult. The difference between the experimental and calculated values of the mol fraction is seen to vary from nearly 50 per cent to 3 per cent. Similar calculations using Perman and Lovett's data at 40.02° where the mol fraction of urea ranged from 0.0595 to 0.4021 showed a deviation from Raoult's Law decreasing from nearly 40 per cent to 8 per cent; the data at 80.10° where the mol fraction of urea ranged from 0.0431 to 0.5547 showed deviations from Raoult's Law decreasing from nearly 180 per cent to 1 per cent. One peculiar point is worthy of mention, viz. the deviations are greatest in the most dilute solutions in all cases. This may in part be explained by the relatively small pressure differences encountered at the lower concentrations, but it is hardly possible that this explanation holds throughout the range of concentrations studied. It would appear that with solutions of most other substances studied, the deviations from Raoult's Law are greater in the more concentrated solutions. An example of this is found in the work of Berkeley, Hartley, and Burton[17] on the vapor pressures of sugar solutions. These workers have found that on increasing the mol fraction of sugar from 0.0175 to 0.1025, the deviation from Raoult's Law increases from 10 per cent to 37 per cent. Such results, along with others which are not presented at this time, lead one to the view that any attempt to express quantitatively the deviations from Raoult's Law for urea solutions should be postponed until further data are accumulated. The data of R. Fricke[18] on the vapor pressure of urea solutions were obtained at temperatures near zero degrees centigrade and are confined to only three concentrations at two different temperatures, and thus do not materially assist in deciding the question just touched upon. In connection with the work of Perman and Lovett, it may be well to mention further that some of the more concentrated solutions were super-saturated, a fact apparently known to the authors when the work was under way.

As a result of their study of the heat of solution and heat of dilution curves of urea solutions, Perman and Lovett[15] have suggested a new method of determining solubilities, viz. "If a number of points of the Heat of Solution curve were determined and afterwards a number on the Heat of Dilution curve, it is obvious that these curves would intersect at the saturation point and would indicate the solubility of the substance." The results so obtained for urea solutions differ by about 1.4 per cent by weight at 50°. It may be said that Perman and Lovett did not claim a high precision for the solubility determined in this way.

Summary

1. Samples of urea from two different sources have been carefully purified.

2. Some twenty-two determinations of the solubility of urea in water have been made using the synthetic method in the temperature interval 20° to 70°; the precision of measurement in these runs is much higher than any previously published; it is believed that this is true of the accuracy also. The data may be accurately represented by the following equation, $\log_{10}N = -609.8\,(1/T) + 1.468$.

3. Preliminary data are presented showing the effect of varying periods of heating on the solubility temperature.

Literature cited

[1] Speyers: Am. J. Sci., (4) **14**, 294 (1902).
[2] Krummacher: Z. Biol., **46**, 302 (1905).
[3] Pinck and Kelley: J. Am. Chem. Soc., **47**, 2170 (1925).
[4] Bosch and Merser: U. S. Patent—1,429,483 (Sept. 19, 1922).
[5] Inter. Crit. Tables, **1**, 177.
[6] Wied. Ann., **28**, 305 (1886).
[7] Ward: J. Phys. Chem., **30**, 1316 (1926).
[8] Sunier and Rosenblum: J. Phys. Chem., **32**, 1049 (1928).
[9] Sunier: J. Phys. Chem., **34**, 2582 (1930).
[10] Walker: J. Chem. Soc., **67**, 746 (1895).
[11] Thorpe: "Dictionary of Applied Chemistry," **7**, 271 (1927).
[12] Hildebrand and Jenks: J. Am. Chem. Soc., **42**, 2180 (1920).
[13] Fox and Geldard: Ind. Eng. Chem., **15**, 743 (1923).
[14] Mortimer: J. Am. Chem. Soc., **44**, 1416 (1922); **45**, 633 (1923).
[15] Perman and Lovett: Trans. Faraday Soc., **22**, 1 (1926).
[16] Bancroft: J. Phys. Chem., **35**, 3160 (1931).
[17] Phil. Trans. Roy. Soc., **218A**, 295 (1919).
[18] R. Fricke: Z. Elektrochemie, **35**, 631-40 (1929).

ADSORPTION OF THORIUM X BY FERRIC HYDROXIDE AT DIFFERENT pH

BY IW. KURBATOW

The Properties and the Methods of obtaining highly Emanating Preparations

Hydroxides of different elements containing radium or thorium X uniformly distributed throughout their entire mass are able to give off quantitatively emanation which is formed in the process of radioactive disintegration. Such compounds of air-dried hydroxides with radium received the name of highly emanating preparations in the science of radioactivity. The methods of their preparation and their properties have been systematically studied by O. Hahn and his co-workers in recent years. Their research resulted in important changes and in the simplification of the technical methods of obtaining emanation. By the use of these preparations it is now possible to obtain emanation, as for instance for medical purposes, in exactly measured quantities. At the same time a nearly quantitative utilization of the produced emanation is realized. The whole technical equipment has been very much simplified and to obtain emanation it is now necessary only to attach the gold emanation needle to the apparatus.

In spite of the practical importance of these compounds the method of their preparation remained purely empirical. The only theory which received general attention was proposed by O. Hahn[1] some five years ago.

The procedure followed in preparing highly emanating compounds consisted according to Hahn in pouring a barium-radium chloride solution containing ferric ions into a large excess of ammonia and ammonium carbonate or sulfate. The purpose of ammonium carbonate or sulfate was to obtain insoluble radium salts which are adsorbed on ferric hydroxide. The investigation of Hahn and Heidenheim led the authors to the following conclusion: "Insoluble salts of radium are quantitatively precipitated from the solution, even if their solubility product has not been exceeded, if the precipitation is carried out in presence of a large excess of ferric hydroxide."[2]

Erbacher and Kädig have given another method of separating the highly emanating substances. They first precipitate ferric hydroxide and add then radium salt solution. The whole is poured into an excess of ammonium carbonate. The authors noticed that in alkaline solutions radium was quanti-

---

[1] O. Hahn and Heidenheim: Ber., 59, 284 (1926).

[2] According to this point of view radium is precipitated as carbonate if ammonium carbonate is present, etc. Ferric hydroxide is considered to be only a carrier of the radium containing substance. See: Hahn and Müller: Z. Elektrochemie, 27, 189 (1923); Hahn: Ann., 440, 121 (1924); Hahn: Naturwissenschaften, 12, 1140 (1924); Hahn, Erbacher, Feichtinger: Ber., 59, 2014 (1926); Hahn and Z. Biltz: Z. physik. Chem., 126, 323; Biltz: 356 (1927); Hahn: Ann., 462, 174 (1928); Hahn: Naturwissenschaften, 15, 295 (1930).

tatively removed from the solution even before addition of ammonium carbonate. Nevertheless, they think that it is necessary to add some anions forming insoluble radium salts to prevent a subsequent desorption of radium from the ferric hydroxide.

Another theory can be proposed which is consistent with the preparation method, and is based on the colloidal properties of the precipitates. The hydroxides contain, as it is well known, varying quantities of anions (SO_4^{--}) in bound condition, depending on the pH of the solution. We may assume then that the adsorption of radium depends on the presence of these anions. The hydroxide resembles then a labile compound of changing composition corresponding to the pH of the solution in which it is present. According to this view it is natural to expect that radium would be uniformly distributed throughout the precipitate and would not be present in the form of submicroscopic crystals adhering to the hydroxide. This theory has received now a satisfactory experimental confirmation as will be seen from the following:

The Experimental Part

For the following experiments not radium but its isotope thorium X was chosen because a rapid determination of the radio-active content of the solution and of the precipitate by the emanation method is then possible.

It seemed to be desirable to establish first the fact whether the ions SO_4^{--} and HCO_3^- have any influence on the amount of radium precipitated on ferric hydroxide. A series of experiments with this purpose in view has been made and the results will be clear from the following examples.

Two solutions were prepared containing each: Fe^{+++}: 0.0797 gr., Th X : 2.84×10^{-3} gr.[3] and Cl^- and NO_3^- ions in 500 cc. The second of these solutions contained some SO_4^{--} ions in addition. Ferric hydroxide was precipitated from both solutions by adding ammonia. After a period of four hours samples of solution were withdrawn. No Th X could be detected showing that the whole of it was adsorbed on the precipitate. To the remainder of the solutions hydrochloric acid was added until ferric hydroxide became flocky while remaining still in the precipitate. After another four hours samples of the clear solution were again withdrawn and Th X determined. The following Table I shows the results:

TABLE I

Effect of SO_4^{--} on the Adsorption of Th X

Contents before the experiment in one cc. of solution	Th X (Th-units) after the experiment in one cc. of solution	Th X in % of total quantity (2.84×10^{-3} gr.)	
		in solution	in precipitate
1. solution			
5.68×10^{-6} Th X	2.92×10^{-6} gr.	51.4	48.6
2. solution (containing SO_4^{--})			
5.68×10^{-6} Th X	4.80×10^{-6} gr.	84.5	15.5

---

[3] Th X is given here and in the following in Th units which give grams of thorium in equilibrium with the present quantity of Th X. All experiments in the following were performed using portions of the same standard solution containing Th, $Msth_1$, Rdth and Th X in radioactive equilibrium.

It will be seen that the presence of SO_4^{--} does not increase the amount of Th X precipitated with ferric hydroxide. The following experiment shows whether the presence of SO_4^{--} has any influence on the free exchange of Th X between the precipitate and the solution or not.

A solution containing Fe^{+++} : 0.0793 gr.; Th X : 2.84×10^{-3} gr. Cl^-, NO_3^- and 0.1 normal SO_4^{--} ions in 500 cc. was made. Strong ammonia was added and 50 cc. of the solution analyzed for Th X. Found 1.2×10^{-6} gr. Th X per cc. or 21% of the total Th X in solution. The remaining solution was then neutralized with HCl and Th X again determined. Found: 5.15×10^{-6} gr. Th X per cc. or 92.7% of it in solution. Strong ammonia was added to the rest again and a determination of Th X made. No Th X could be found in solution. It is seen thus that the ion SO_4^{--} does not prevent free exchange of Th X between the precipitate and the solution.

In the same manner it has been established that the HCO_3^- ion does not prevent this exchange either. A solution containing Fe^{+++} 0.0793 gr. Th X 2.84×10^{-3} gr., Cl^-, NO_3^- in 500 cc. was made. It was boiled and the precipitation carried out with a large excess of ammonia. All reagents were carefully purified from traces of CO_2 and all work was carried out in a closed space free of CO_2. No Th X could be detected in 50 cc. of solution, showing that it was quantitatively precipitated with ferric hydroxide.

A solution identical with the preceding one was now made and precipitation made without adding an excess of ammonia. Found: 4.9×10^{-6} gr. Th X per cc. or 86.3% of it in solution. Another such solution was precipitated with a small amount of dilute ammonia to which 10% ammonium carbonate was added. Found 4.7×10^{-6} gr. per cc. or 82.8% Th X in solution. A large excess of ammonia was later added to this solution. No Th X could be detected in solution.

The preceding experiments show clearly that adsorption of Th X—and therefore of Ra—is determined by the alkalinity of the solution above. In the following experiments the dependence of Th X adsorption upon the pH of solutions was quantitatively studied. The experiments were carried out in the following manner. To a solution containing known quantities of ferric ion and Th X some ammonia was added. A sample of the solution was withdrawn and Th X and pH determined. More ammonia was added to the remainder and a sample again withdrawn. In such a manner from 3 to 6 determinations of Th X at varying pH could be made with one solution. The determination of Th X in sample solutions was made as follows. The sample was poured into a special glass vessel, acidulated with HCl and made up to a constant volume. Air was blown through the solution and then through the ionization chamber at constant rate. The ionization was measured with a unifilar electrometer. The apparatus was calibrated before and after each determination by determining the ionization produced by a standard solution of thorium in equilibrium with its disintegration products.

A sample determination:

1. Natural ionization before the experiment: 2.36 scale divisions per minute or 0.036 volts per minute (Electrometer sensitivity 65.0 divisions per volt).

2. Natural ionization after the experiment 2.19 scale divisions per minute or 0.034 volts per minute (Electrometer sensitivity 64.5 scale divisions per volt).

3. Ionization produced by the standard Th solution containing 1.57×10^{-3} gr. Th X (in Th units of course) 0.36 volts per minute (Mean of 0.372 and 0.348).

4. The unknown solution produced ionization equivalent to 0.042 volts per minute. It contains therefore:

$$\frac{1.57 \times 10^{-3} \times 0.042}{0.36} = 1.84 \times 10^{-6} \text{ gr. Th X}$$

The pH of solutions was determined with the aid of quinhydrone calomel electrodes. A potentiometer and a Hartmann and Braun mirror galvanometer were used. In the following Table II are given the results of these experiments.

TABLE II

The Dependence of Th X Adsorption on the pH of Solutions

t = 17° C.

pH	Th X used for the experiment		Th X found in the solution		% Th X in precipitation
	Total	in 1 cc.	in 1 cc.	% of total quantity	
Solution No. 6 contains: a) Th X—7.80×10^{-3} gr. b) Fe—0.0793 gr.					
5.09	7.8×10^{-3}	3.12^{-5}	2.97^{-5}	100.	——
6.48	5.34×10^{-3}	2.72×10^{-5}	2.40×10^{-5}	88.2	11.8
7.6	4.195×10^{-3}	1.70×10^{-5}	0.74×10^{-5}	33.17	66.83
Solution No. 7 contains: a) Th X—3.90×10^{-3} gr. b) Fe—0.0793 gr.					
4.24	3.9×10^{-3}	1.56×10^{-5}	1.52×10^{-5}	100.	——
4.37	3.12×10^{-3}	1.56×10^{-5}	1.73×10^{-5}	100.	——
5.00	1.46×10^{-3}	1.39×10^{-5}	1.43×10^{-5}	100.	——
7.20	1.95×10^{-3}	1.39×10^{-5}	0.70×10^{-5}	50.25	49.75
Solution No. 8 contains: a) Th X—7.8×10^{-3} gr. b) Fe—0.1586 gr.					
5.36	7.8×10^{-3}	3.12×10^{-5}	2.88×10^{-5}	92.5	7.5
7.68	4.51×10^{-3}	2.61×10^{-5}	0.60×10^{-5}	23.1	76.9
7.53	2.43×10^{-3}	1.64×10^{-5}	0.22×10^{-5}	13.15	86.85
8.25	1.98×10^{-3}	1.46×10^{-5}	——	——	100.0
Solution No. 9 contains: a) Th X—19.5×10^{-3} gr. b) Fe—0.1586 gr.					
4.7	19.5×10^{-3}	3.9×10^{-5}	4.010^{-5}	100.	——
5.99	15.6×10^{-3}	3.81×10^{-5}	3.80×10^{-5}	100.	——
5.99	12.55×10^{-3}	3.69×10^{-5}	3.70×10^{-5}	100.	——
6.23	9.60×10^{-3}	3.62×10^{-5}	3.40×10^{-5}	94.	6.
6.90	6.70×10^{-3}	3.40×10^{-5}	2.04×10^{-5}	60.	40.
7.54	4.68×10^{-3}	2.92×10^{-5}	0.42×10^{-5}	14.4	85.6

The last two columns of the table give the percentage of Th X in solution and in the precipitate. Since, however, the experiments were performed with different amounts of Th X and ferric hydroxide present, the following Table III gives the results recalculated for the case of a solution containing the same quantity of ferric hydroxide, 0.1586 gr.

TABLE III

Th X adsorbed at Different pH

pH	Th X in 1 cc. of solution	Th X in 0.1586 gr. of of ferric hydroxide
5.99	3.80×10^{-5}	——
6.23	3.4×10^{-5}	0.58×10^{-3}
6.48	2.4×10^{-5}	1.26×10^{-3}
6.90	2.04×10^{-5}	2.62×10^{-3}
7.20	0.70×10^{-5}	1.94×10^{-3}
7.54	0.42×10^{-5}	3.49×10^{-3}
7.60	0.74×10^{-5}	5.60×10^{-3}
7.68	0.60×10^{-5}	3.47×10^{-3}
7.53	0.22×10^{-5}	2.11×10^{-3}
8.25	——	3.80×10^{-3}

The precipitated ferric hydroxide contains Rdth from the standard Th X solution. The question arises whether Th X produced by Rdth is freely exchanged with the solution or whether it is retained in the precipitate. In the first case one should expect that, when a solution is maintained at constant pH, the amount of Th X in solution will not change with time, in the second case it should decrease due to its radioactive decay. A solution identical with solution No. 1 described on the previous pages and containing ferric hydroxide on the bottom was kept at pH 6-7 for a longer period of time. It contained at the beginning of the experiment 2.55×10^{-3} gr. Th X. The following results were obtained:

TABLE IV

The Change of Th X in Solution with Time

Time from the beginning of the experiment	Volume of the Solution	Th X in 1 cc. of solution (gr.)	Th X in the whole solution (gr.)	Calculated quantity of Th X (gr.)
45 hours	900 cc.	2.88×10^{-6}	2.59×10^{-3}	2.64×10^{-3}
167 hours	800 cc.	3.39×10^{-6}	2.71×10^{-3}	2.65×10^{-3}
A. 307 hours	700 cc.	1.84×10^{-6}	1.29×10^{-3}	2.67×10^{-3}
B. 307 hours	600 cc.	3.81×10^{-6}	2.28×10^{-3}	2.49×10^{-3}

Before taking the first and second samples of this experiment the solution was shaken. For the third sample it was not shaken while for the fourth it was warmed up and shaken. The calculation of Th X in solution (last column) was made assuming a free exchange between precipitate and solution. A typical calculation is given below for the 45 hour sample:

1. The quantity of Th X remaining in the solution considering the decay: 1.79×10^{-3} gr.
2. Th X produced by 2.84×10^{-3} gr. Rdth (45 hrs.) 0.85×10^{-3} gr.
3. The total Th X in solution: 2.64×10^{-3} gr.

The agreement of calculated and determined quantities shows that the concentration of Th X in solution is maintained by Th X rising from Rdth in the precipitate. Four solutions were now made containing equal quantities of ferric ion and Th X. They were precipitated with different amounts of ammonia. After thirteen and fifteen days two samples were taken from each solution (after shaking) and Th X and pH determined. The following Table V shows the results:

TABLE V

The Amount of Th X in Solution as a Function of Time and pH

No. of the solution	Th X (Th-units) used for the experiment	pH of the solution	Quantity of Th X (Th-units) found in the solution	Remarks
1	1.92×10^{-3} gr.	7.6	not found	pH and Th X measured after 13 days
2	1.92×10^{-3} gr.	7.62	not found	
3	1.92×10^{-3} gr.	5.42	1.71×10^{-3} gr.	pH and Th X measured after 15 days
4	1.92×10^{-3} gr.	4.6	1.82×10^{-3} gr.	

It will be seen that Th X is freely exchanged between the precipitate and the solution when the solution has a pH between 5 and 6 but that the exchange is absent when pH exceeds 7. These experiments were performed in absence of SO_4^{--} and HCO_3^- ions.

Discussion of the Results

The experiments described on the previous pages show quite conclusively that the opinion, that ferric hydroxide (and similarly other hyrdoxides) is simply a carrier of a distinct radioactive compound, is untenable. Instead it must be assumed that the precipitation of radium together with ferric hydroxide in alkaline media depends on the formation of a salt-like compound in which radium acts as a cation and ferric hydroxide as anion. This is established by the observations that the presence of neither SO_4^{--} nor HCO_3^- ions is necessary to produce highly emanating preparates. Thus the procedure of obtaining these is simplified still further. A more detailed study shows, that at pH higher than 7, Th X is firmly adsorbed by the hydroxide. At pH lower than 7 Th X originally adsorbed or produced by Rdth is freely exchanged with the solution. The exact point on the pH scale at which Th X (or radium) is adsorbed on ferric hydroxide or is desorbed from it can not be given, of course.

The experiments here described show also that in order to obtain the highly emanating preparates the solubility product of pure radium salt (or of the isomorphous Ba-Ra salts) should not be exceeded in the solution. This is contrary to the earlier views on the subject but is in accord with the observations of Erbacher and Kädig (loc. cit.) who found that by precipitating Ra and Ba salts with large amounts of ammonium chromate preparates of diminished emanating activity were obtained. By exceeding the solubility product of Ra salts they obtained these in the form of microscopic crystals instead of having Ra uniformly distributed throughout the mass of the hydroxide, a state which obtains when Ra is fixed on the ferric hydroxide in presence of ammonium chromate.

This work has been carried out in the Chemical Laboratory of the University of Moskau.

Summary

1. The properties and the methods of preparation of the highly emanating Ra preparates are described.

2. It is shown that the fixation of Th X (and Ra) on ferric hydroxide does not depend on the presence of some anions forming insoluble Ra salts but is entirely determined by the pH of the solution.

3. The structure of the highly emanating preparates is described.

TRANSMISSION SPECTRA OF DYES IN THE SOLID STATE[*]

BY W. C. HOLMES[1] AND A. R. PETERSON[2]

Practically no data are available in the literature on the transmission of light by dyes in the solid state. The method herein employed consisted in depositing a thin film of "air dried" dye upon a glass slide and interposing it at right angles to the path of one of the parallel beams of light of a visual spectrophotometer.

The dye films were obtained by the evaporation of aqueous or alcoholic solutions of the dyes. With many dyes it is difficult or impossible to obtain continuous films in this manner without resorting to the employment of gelatine or similar agents which it was desired to exclude. It was found possible to obtain deposits of a reasonably satisfactory character, however, with numerous azo, triphenylmethane, and xanthene dyes. In such instances the only difficulty involved was that of regulating the thickness of the dye film within limits wherein its light absorption could be measured advantageously.

Typical absorption measurements obtained with such films are recorded in Table I. The dyes investigated were representative samples of commercial grade which were, in nearly all instances, recrystallized before use. The numbers recorded with them are their list numbers in the Colour Index of the Society of Dyers and Colourists (Bradford, England, 1924). Aqueous solutions were employed in obtaining these films of azo dyes and alcoholic solutions in obtaining those of dyes of other classes. The tabulated values are Bunsen extinction coefficients.

Discussion

Although the spectra of solid dyes frequently differ considerably from the spectra of their dilute solutions, they exhibit no features which are exclusively characteristic of the solid state. The outstanding modifications in spectra which occur when dyes are dissolved are (1) a shifting in the spectral location of the absorption band, attended by (2) evidences of increasing molecular dispersion and, frequently, by (3) evidences of tautomeric alteration in the dye. The first of these phenomena, however, also occurs in passing from one solvent to another, and evidences of increasing dispersion and of tautomerism which are of the same type, if not of equal degree, are often observed upon the mere dilution of aqueous dye solutions.[3]

---

[*] Contribution No. 205 from the Color and Farm Waste Division, Bureau of Chemistry and Soils, U. S. Department of Agriculture, Washington, D. C.

[1] Senior Chemist, Color and Farm Waste Division, Bureau of Chemistry and Soils, U. S. Department of Agriculture, Washington, D. C.

[2] Research Associate, Commission on Standardization of Biological Stains.

[3] Holmes: Ind. Eng. Chem., 16, 35 (1924).

TABLE I

Extinction Coefficients (E) of Light transmitted by Dyes in the Solid State

Part 1—Azo Dyes

	Janus Green B	Dianil Blue R	Niagara Blue 3RD	Pontamine Blue AX	Niagara Blue RW	Pontamine Sky Blue 6BX	Pontamine Sky Blue 5BX
Colour Index No.	133	309	468	502	512	518	520
				E			
460 mμ	—	—	—	—	—	—	—
480 "	—	—	—	—	—	—	—
490 "	—	—	—	—	—	—	—
500 "	0.42	0.57	1.38	0.70	0.56	0.56	0.65
510 "	0.42	0.62	1.42	0.74	0.62	0.66	0.73
520 "	0.43	0.66	1.45	0.78	0.69	0.77	0.82
530 "	0.48	0.69	1.48	0.83	0.76	0.90	0.92
540 "	0.55	0.72	1.50	0.86	0.84	1.03	1.02
550 "	0.63	0.75	1.50	0.89	0.94	1.15	1.09
560 "	0.69	0.77	1.49	0.92	1.03	1.27	1.16
570 "	0.72	0.78	1.48	0.94	1.09	1.36	1.23
580 "	0.75	0.77	1.46	0.95	1.16	1.45	1.28
590 "	0.78	0.765	1.43	0.96	1.21	1.50	1.32
600 "	0.81	0.76	1.40	0.95	1.27	1.50	1.36
610 "	0.83	0.74	1.36	0.92	1.32	1.44	1.40
620 "	0.84	0.72	1.32	0.90	1.35	1.35	1.42
630 "	0.82	0.69	1.25	0.87	1.33	1.23	1.39
640 "	0.79	0.67	1.18	0.85	1.25	1.17	1.35
650 "	0.74	0.64	1.10	0.87	1.21	1.11	1.32
660 "	0.68	0.62	1.03	0.87	1.19	1.05	1.30
670 "	0.63	0.59	0.95	0.80	1.22	0.95	1.29
680 "	0.58	0.56	0.88	0.73	1.24	0.83	1.30
690 "	0.52	0.54	0.84	0.67	1.16	0.70	1.30
700 "	0.45	0.51	0.81	0.62	0.97	0.57	1.27

Part 2—Triphenylmethane Dyes

	Victoria Green	Brilliant Green	Alphazurine FG	Xylene Blue VS	Pararosaniline	Crystal Violet	Ethyl Violet	Acid Fuchsine
Colour Index No.	657	662	671	672	676	681	682	692
				E				
460 mμ	—	—	—	—	—	—	—	0.80
480 "	—	—	—	—	0.72	—	—	1.10
490 "	—	—	—	—	0.77	—	—	1.18
500 "	0.12	0.07	0.28	0.15	0.82	0.77	0.62	1.23
510 "	0.16	0.10	0.30	0.22	0.87	0.91	0.80	1.23
520 "	0.25	0.14	0.36	0.30	0.89	1.07	0.95	1.20
530 "	0.40	0.21	0.44	0.46	0.89	1.18	1.08	1.17
540 "	0.60	0.35	0.54	0.68	0.88	1.22	1.19	1.15
550 "	0.80	0.52	0.73	0.89	0.87	1.19	1.27	1.10
560 "	0.99	0.71	0.98	1.28	0.85	1.13	1.30	1.04

TABLE I (continued)

Extinction Coefficients (E) of Light transmitted by Dyes in the Solid State

	Victoria Green	Brilliant Green	Alphazurine FG	Xylene Blue VS	Pararosaniline	Crystal Violet	Ethyl Violet	Acid Fuchsine
Colour Index No.	657	662	671	672	676	681	682	692
				E				
570 "	1.13	0.86	1.29	1.53	0.83	1.06	1.30	0.96
580 "	1.23	0.98	1.60	1.77	0.81	0.97	1.27	0.84
590 "	1.29	1.06	1.77	1.95	0.75	0.90	1.19	0.70
600 "	1.31	1.11	1.89	2.07	0.67	0.83	1.15	0.58
610 "	1.29	1.09	1.93	2.10	0.61	0.78	1.12	0.46
620 "	1.24	1.06	1.96	2.12	0.54	0.73	1.08	0.35
630 "	1.22	1.06	2.02	2.12	0.46	0.68	1.00	—
640 "	1.22	1.07	2.03	2.19	0.40	0.63	0.88	—
650 "	1.20	1.03	2.02	2.29	0.35	0.56	0.72	—
660 "	1.16	0.96	1.95	2.36	0.32	0.48	0.56	—
670 "	1.05	0.86	1.80	2.32	0.30	0.38	0.41	—
680 "	0.90	0.75	1.29	2.26	0.29	0.28	0.27	—
690 "	0.65	0.61	0.69	2.07	—	0.21	—	—
700 "	0.41	0.58	0.37	1.90	—	0.16	—	—

Part 3—Xanthene Dyes

	Pontamine Violet C4B	Victoria Blue B	Pyronine G	Pyronine B	Rhodamine B	Rhodamine G	Rhodamine 3B	Violamine B
Colour Index No.	698	729	739	741	749	750	751	757
				E				
460 mμ	—	—	—	—	—	—	0.33	—
480 "	—	—	0.95	—	—	—	0.45	—
490 "	—	—	1.01	—	—	—	0.60	—
500 "	0.25	0.23	1.04	1.48	0.35	0.56	0.71	0.37
510 "	0.34	0.36	1.05	1.59	0.44	0.69	0.79	0.48
520 "	0.48	0.50	1.04	1.66	0.53	0.86	0.82	0.67
530 "	0.67	0.66	1.02	1.70	0.61	0.95	0.83	0.83
540 "	0.81	0.83	0.95	1.58	0.62	0.95	0.85	0.95
550 "	0.89	0.96	0.89	1.45	0.62	1.00	0.87	1.02
560 "	0.88	1.06	0.84	1.40	0.66	1.07	0.87	1.05
570 "	0.81	1.12	0.80	1.30	0.68	1.12	0.83	1.00
580 "	0.75	1.15	0.76	1.13	0.67	1.06	0.76	0.93
590 "	0.68	1.15	0.70	0.86	0.60	0.84	0.60	0.82
600 "	0.64	1.13	0.63	0.59	0.36	0.52	0.42	0.66
610 "	0.60	1.10	0.57	0.33	0.18	0.23	0.31	0.54
620 "	0.55	1.09	0.50	0.19	0.11	—	0.25	0.40
630 "	0.47	1.06	0.45	0.11	—	—	—	0.27
640 "	0.36	1.01	0.40	—	—	—	—	0.19
650 "	0.27	0.96	—	—	—	—	—	0.12

TABLE I (continued)

Extinction Coefficients (E) of Light transmitted by Dyes in the Solid State

	Ponta-mine Violet C4B	Victoria Blue B	Pyro-nine G	Pyro-nine B	Rhoda-mine B	Rhoda-mine G	Rhoda-mine 3B	Viola-mine B
Colour Index No.	698	729	739	741	749	750	751	757
				E				
660 "	0.18	0.91	—	—	—	—	—	0.07
670 "	0.13	0.83	—	—	—	—	—	—
680 "	0.10	0.73	—	—	—	—	—	—
690 "	—	0.62	—	—	—	—	—	—
700 "	—	0.51	—	—	—	—	—	—

Part 4—Xanthene Dyes

	Viola-mine RR	*Viola-mine G*	*Uranine*	Eosine	Ethyl Eosine	Eosine B	Erythro-sine	Phlox-ine B	Rose Bengal B
Colour Index No.	758	759	766	768	770	771	773	778	779
					E				
460 mμ	—	—	0.82	0.30	0.44	0.43	0.21	0.68	—
480 "	—	0.27	1.10	0.60	0.70	0.58	0.52	0.88	0.43
490 "	0.60	0.40	1.05	0.83	0.97	0.72	0.71	0.93	0.67
500 "	0.78	0.53	1.10	0.95	1.19	0.90	0.92	0.97	0.90
510 "	1.02	0.67	1.06	0.89	1.20	1.00	1.06	1.00	1.10
520 "	1.23	0.81	0.83	0.86	1.10	1.05	1.02	1.00	1.09
530 "	1.33	0.92	0.52	0.85	1.13	1.06	0.99	0.97	1.03
540 "	1.42	0.95	0.27	0.72	1.17	1.04	0.91	1.04	1.15
550 "	1.40	0.89	0.14	0.53	1.11	0.95	0.75	1.13	1.27
560 "	1.30	0.78	—	0.32	0.92	0.82	0.53	1.23	1.13
570 "	1.15	0.60	—	0.17	0.67	0.68	0.33	1.35	0.80
580 "	0.92	0.38	—	0.10	0.38	0.52	0.19	1.28	0.45
590 "	0.69	0.21	—	—	0.23	0.38	0.11	0.75	0.18
600 "	0.47	—	—	—	0.16	0.26	—	0.38	0.08
610 "	0.31	—	—	—	—	0.17	—	0.23	—
620 "	0.19	—	—	—	—	0.11	—	—	—
630 "	—	—	—	—	—	—	—	—	—
640 "	—	—	—	—	—	—	—	—	—
650 "	—	—	—	—	—	—	—	—	—
660 "	—	—	—	—	—	—	—	—	—
670 "	—	—	—	—	—	—	—	—	—
680 "	—	—	—	—	—	—	—	—	—
690 "	—	—	—	—	—	—	—	—	—
700 "	—	—	—	—	—	—	—	—	—

Fig. 1 affords a comparison of the absorption spectrum in the solid state with spectra of dilute alcoholic and aqueous solutions of several of the dyes investigated.

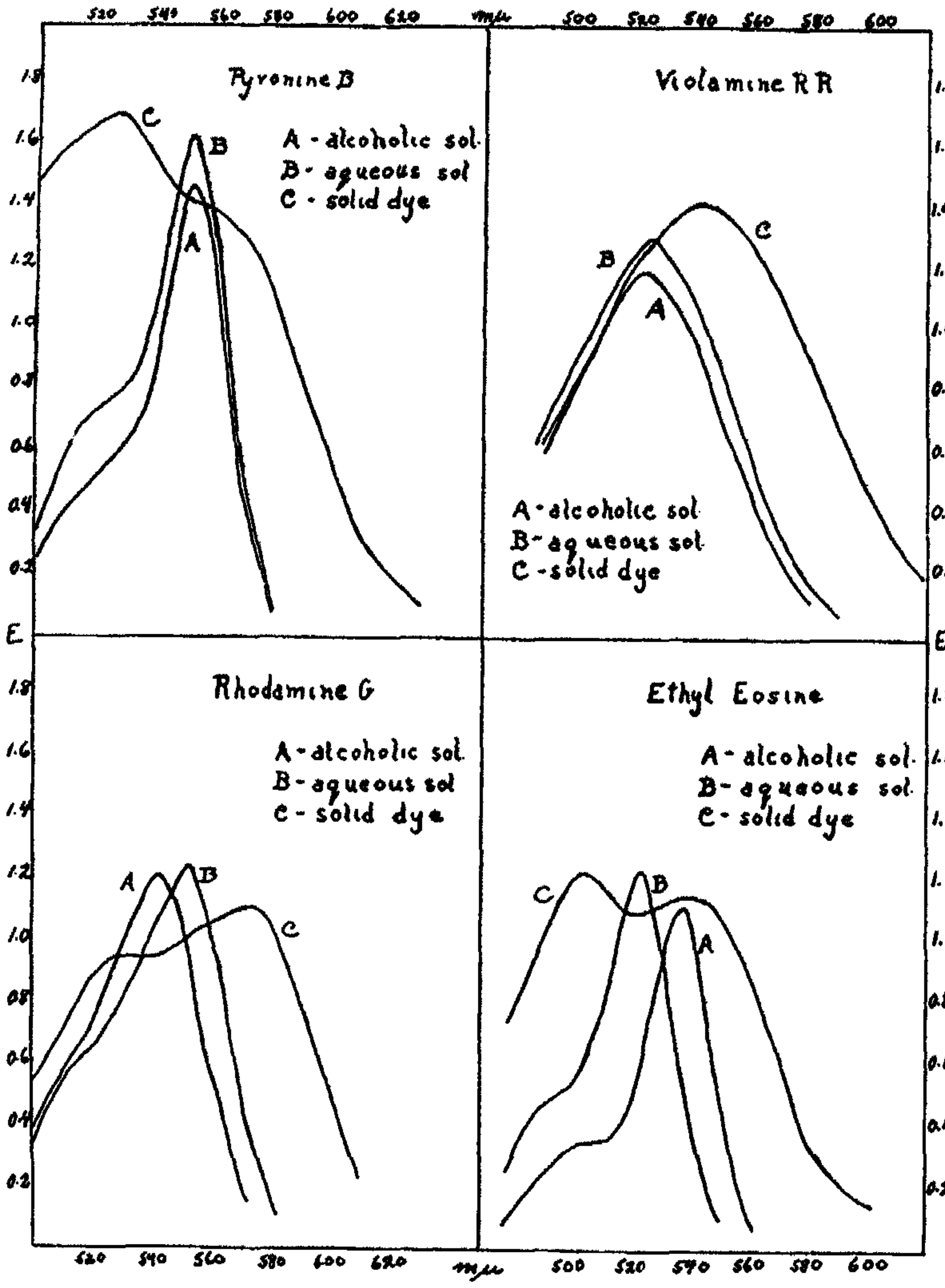


FIG. 1

A comparison of the spectra of solid dyes with the spectra of their aqueous and alcoholic solutions indicates that the effect of solution upon the hue of the dye is intrinsically hypsochromic. The practical effect, however, may frequently be the reverse. This anomaly arises from the fact that the hue of many dyes is a composite hue of two isomeric forms, and that the solution of such dyes is attended by an alteration in the equilibrium between the tautomers which exerts an effect upon the composite hue which is opposite in type and greater in degree than is the direct effect of solution. Thus, Crystal Violet exists in two tautomeric forms with decidedly different hues, of which the lighter predominates in the solid state. The hue of each dye form becomes lighter when the dye is dissolved, but solution is attended by such extensive conversion of the lighter dye form into the deeper that the hues of solutions are decidedly deeper than that of the dye. The general effect of solution, however, is to displace absorption bands in the direction of shorter wave length, and dye solutions are lighter in hue than are the dyes from which they are prepared when tautomerism does not exert a preponderant effect.

In general, the absorption bands of solid dyes are decidedly broader in proportion to their height than are those of their solutions. The depression of band maxima and the broadening of their slopes are criteria of increasing molecular aggregation[4] and would be anticipated in passing from solution to the solid state. In the instance of Brilliant Green, the phenomenon of increasing molecular aggregation was observable in the solid state. Freshly prepared dry films of dye absorbed light in the manner indicated by the tabulated measurements, but the absorption bands became distinctly broader and less well defined within a few hours.

Previous investigation of aqueous solutions of dyes has demonstrated that many dyes undergo tautomeric alterations of one type or another. The data of Table I are of interest because of the further evidence which they afford for that conclusion.

Numerous indications of tautomerism in aqueous solutions of azo dyes of diverse character have been noted,[3] and Brode[5] has recently established the tautomeric nature of even a very simple type of azo dye. The measurements with solid azo dyes indicate a type of tautomerism in disazo dyes prepared from dianisidine which appears characteristic for that dye type.

The type of tautomerism illustrated in the instance of Ethyl Eosine (Fig. 1) has been observed previously in fluoresceine and in its halogenated derivatives substituted within the phthalic anhydride residue.[3] The examination of solid dyes has now shown that it also occurs in the more important dyes of the same group in which substitution occurs within the resorcin residues. Similar results to those reported have also been obtained with several kindred dyes of laboratory preparation, and it may now be stated that all the dyes of the group which are substituted exclusively by halogens exist in two tautomeric forms. This tautomerism may be suppressed, however, by other types of substitution. Neither Eosine B (Table I) nor mercurochrome give evidence of tautomerism.

It appears very probable that tautomerism in this dye group must originate in changes in the character of the quinoid oxygen bonding. The most obvious explanation which might be suggested is that of tautomerism between an anhydrous dye form in which the oxygen is typically quinoid and a hydrated

---

[4] Pihlblad: Z. physik. Chem., 81, 417 (1912).

[5] Brode: J. Am. Chem. Soc., 51, 1204 (1929).

dye form in which it is replaced by two hydroxyl groups in the hemiquinoid arrangement. Although the typically quinoid structure has been assigned to the dyes of this group for many years, it has recently been shown that they retain the elements of a molecule of water with great tenacity and that their structure is probably hemiquinoid.[6,7] It is by no means clear, however, that actual tautomerism occurs between quinoid and hemiquinoid structure.

The previous study of dye solutions has demonstrated that aminated dyes of the triphenylmethane, xanthene and quinonimide classes undergo a striking tautomeric alteration with the dilution of their aqueous solutions.[3] This phenomenon has been observed with a very large number of such dyes, including many of those which are of great importance in scientific applications. In general a decided degree of tautomeric alteration could be noted with any considerable variation in the dye concentration of aqueous solutions. With basic and acid fuchsines and with diamino derivatives in the triphenylmethane dye group, however, the degree of tautomeric alteration observable was very small, and the violamines in the xanthene dye group appeared stable.

The recorded series of measurements on solid dyes indicate very clearly that basic and acid fuchsines, and that diamino derivatives of the triphenylmethane series in general, undergo decided degrees of tautomeric modifications, differing from other triphenylmethane dyes only in respect to the variation in conditions which is required to render them manifest. On the other hand, the measurements on violamines in the solid state give no indication whatever of the presence of more than one dye form.

It now appears, accordingly, that the violamines probably constitute the sole exception to the general rule that aminated triphenylmethane, xanthene and quinonimide dyes exist in two tautomeric forms. This fact seems significant. A hypothesis has been advanced which refers this type of tautomerism to valence rearrangements, occurring within the salt-forming amino group, which involve a tautomerism between trivalent and pentavalent bonding of the nitrogen atom.[8] The violamines are unique among the dye classes referred to in respect to the fact that they do not allow a pentavalent amino arrangement. They are structurally incapable, accordingly, of the type of tautomerism postulated and would be expected to prove stable on the basis of the hypothesis in question.

Summary

(1) Transmission spectra are recorded of thirty-two azo, triphenylmethane and xanthene dyes in the solid state.

(2) Solution is found to displace the absorption bands in the direction of shorter wave length.

(3) The data indicate a high degree of molecular aggregation in dry dyes.

(4) New evidence is afforded on the occurrence and degree of tautomerism in dyes.

---

[6] Gomberg and Tabern: J. Ind. Eng. Chem., 14, 1115 (1922).

[7] Holmes and Scanlan: J. Am. Chem. Soc., 49, 1594 (1927).

[8] Holmes: Stain Tech., 1, 116 (1926).

THE SURFACE CHEMISTRY OF HYDRATES. II

Decomposition without Lattice Rearrangement*

BY V. R. DAMERELL, F. HOVORKA AND W. E. WHITE

Introduction

According to classical theory, a hydrate or related substance will decompose below a certain vapor pressure or above a certain temperature, yielding a lower hydrate or anhydrous substance and water vapor. During this transition, the vapor pressure of the system will remain constant at a given temperature as long as any of the higher hydrate remains, since in phase rule terminology the system is univariant; also, the lattice structure will rearrange as the dehydration progresses, forming that of the lower hydrate or anhydrous substance. It is to be noted that most hydrates which behave experimentally in accordance with this theory have been studied at temperatures not very far below their transition temperatures.

In a recent article,[1] however, a finely divided trihydrate of alumina was described which appeared to break up at room temperature differently than in the manner described above. The composition of this hydrate was obtained by the approximation equation

$$\frac{w_1 - c}{w_s - c} = \frac{w'_1 - c}{w'_s - c} \qquad (1)$$

where w_1 and w_s represent the total number of molecules of water per molecule of alumina (adsorbed and chemically combined) contained by two samples of the substance over the same water vapor pressure source, the two samples having a different average particle size; w'_1 and w'_s represent the total number of molecules of water per molecule of alumina for the same two samples over a different water vapor pressure source; and c is the number of molecules of water of crystallization per molecule of alumina. Since the various values for w can be obtained experimentally, c is given by

$$c = \frac{w_1 w'_s - w_s w'_1}{w_1 + w'_s - w_s - w'_1} \qquad (2)$$

Calculations involving five precipitates of different average particle size showed c to be close to three.

The behaviour of this substance over phosphorus pentoxide indicated the possibility of water being lost from the surface without appreciable rearrangement of the remaining lattice structure. The work presented herein was undertaken, therefore, as an investigation of this type of decomposition and its relation to the constant vapor pressure decomposition of hydrates.

---

* Contribution from the Morley Chemical Laboratory of Western Reserve University.

[1] Cf. Damerell: J. Phys. Chem., 35, 1061 (1931).

Experimental

Preparation of alumina trihydrate.

This substance was prepared by precipitation of hydrous alumina from a solution of aluminum sulfate with ammonium hydroxide, followed by repeated washing at room temperature in the presence of small amounts of ammonia. The details of the preparation are given in an earlier publication,[2] and will not be repeated here. After about two months aging, the precipitate was separated into two portions of a different average size of particle by suspending in water and decanting after a partial settling, as described before. Two precipitates were obtained in this way, and will be designated hereafter as large particle and small particle precipitates. These were filtered off and dried for several days in the air.

This method of separation will be successful only when the disperse phase is composed of primary particles which vary in size, and it is conceivable, as Weiser[3] has pointed out, that the most rapidly settling portion may have been composed of aggregates of primary particles of about the same size having a specific surface that approached the sum of the specific surfaces of the slower settling primary particles. But an earlier experiment of Tartar and Damerell[4] indicates that there is a decided difference in the primary particle size. Aged hydrous alumina was prepared as described above from aluminum nitrate, and after being washed essentially free from nitrate and ammonia was centrifuged out once. The precipitate was shaken with distilled water, with which it formed a stable colloidal suspension of the settling type. Portions were taken from the top, middle and bottom of this suspension after it had been allowed to settle partially, and each was analyzed for alumina in the usual manner. From the analyses, a sol was made up from each containing just 0.85 grams of alumina per liter. A sufficient amount of basic aluminum chloride solution was now added to each portion so that the chlorine concentration became 0.355 grams per liter. Such mixtures always increased in acidity upon standing, probably due to a preferential ion adsorption. The hydrogen ion activities in the experiment in question after equilibrium was reached were as follows.

Grams of chlorine per liter from basic aluminum chloride	Portion of colloidal suspension taken	pH
0.355	top	3.825
0.355	middle	3.87
0.355	bottom	3.94
0.355	(distilled water)	4.03

This is considered as evidence for a different primary particle size.

---

[2] See reference 1, page 1063.

[3] Private communication.

[4] J. Phys. Chem., 36, May (1932).

Desiccation experiments.

It was decided to calculate values for c from equation (2) using only w values of less than three, and also to see if the composition of the trihydrate would reach a constant value after long exposure to phosphorus pentoxide. To accomplish this, two samples of the trihydrate, one from the large particle precipitate and the other from the small particle precipitate were put in weighing bottles and kept in a desiccator over phosphorus pentoxide for nearly six months. Each weighing bottle contained about a gram of the sample, sufficiently air-dried beforehand so that it did not adhere to the glass. The desiccator was kept in a constant temperature room having an observed temperature over the six months period of 24° ± 1°C. Numerous weighings were made, the procedure being to open the desiccators and immediately put the ground glass covers on the weighing bottles, which were then weighed as rapidly as possible. Care was taken to follow just the same procedure each time as regards order and method of weighing. As the results in Table I show, opening the desiccator every three days seriously slowed up the desiccation, so after constant weight was practically reached using this time interval, the desiccator was opened less and less frequently, being allowed to stand for two months before the final weighing. It is seen from Table I that constant composition was essentially reached when weighing was stopped. The samples were finally ignited for many hours in platinum crucibles, not only until constant weight was reached, but also until the alumina gained practically no weight when allowed to stand on the balance pan after weighing.

TABLE I

Change in composition of the hydrate with time over phosphorus pentoxide

Days between weighing	Composition of the large particle precipitate	Composition of the small particle precipitate
0	$Al_2O_3 . 3.534\ H_2O$	$Al_2O_3 .\ 3.207\ H_2O$
2	2.996	2.965
2	2.975	2.944
3	2.966	2.933
3	2.960	2.926
3	2.958	2.925
3	2.958	2.924
3	2.957	2.924
3	2.955	2.923
3	2.956	2.922
3	2.956	2.921
3	2.955	2.921
3	2.954	2.921
7	2.946	2.907
15	2.939	2.900
27	2.934	2.893
35	2.930	2.888
62	2.928	2.888

From the resulting water contents given in Table I, it is possible to calculate a great many values for c. Since the large particle and small particle samples must be in a comparable condition before the calculation can have any meaning, the first two values given in the table cannot be used, as the large particle precipitate was obviously in a more moist condition than the small particle precipitate at the start. It is seen by comparing the water lost each time that the two samples were in a similar state about the fourth day. In Table II are given several values for c, together with the values of w used in the calculations.

TABLE II

Calculations for c from equation (2)

w_s	w_l	w'_s	w'_l	c
2.923	2.955	2.888	2.928	3.1
2.926	2.960	2.888	2.928	3.2
2.922	2.956	2.893	2.934	3.1
2.933	2.966	2.893	2.934	3.1
2.944	2.975	2.888	2.928	3.1

Determination of the change in water content with vapor pressure.

It was decided to determine experimentally the composition-vapor pressure curve at 25°, and for this purpose a special apparatus, shown in Fig. 1, was built. A glass cylinder was fitted with a stopper (A) and glass tube (B), and another stopper containing the exterior part of a conical ground glass joint (C) was inserted in this tube as shown. The inner part of this joint (D) was pulled out at each end and fused around a platinum wire. The lower end of the platinum wire held a glass container in which was placed about ten grams of the small particle trihydrate precipitate. A hole was drilled in the floor of a balance just under the left hand pan support, and the upper end of the platinum wire went through this hole and ended in a loop by which it could be attached to the pan support. The drawing shows the wire and ground glass stopper as they were during weighings. At all other times the stopper was lowered into place, closing the apparatus. The glass cylinder was immersed in a thermostat, kept at 25° ± 0.1°C, and the desired hydrate or desiccant was placed in the bottom. When the time came to change the water vapor pressure

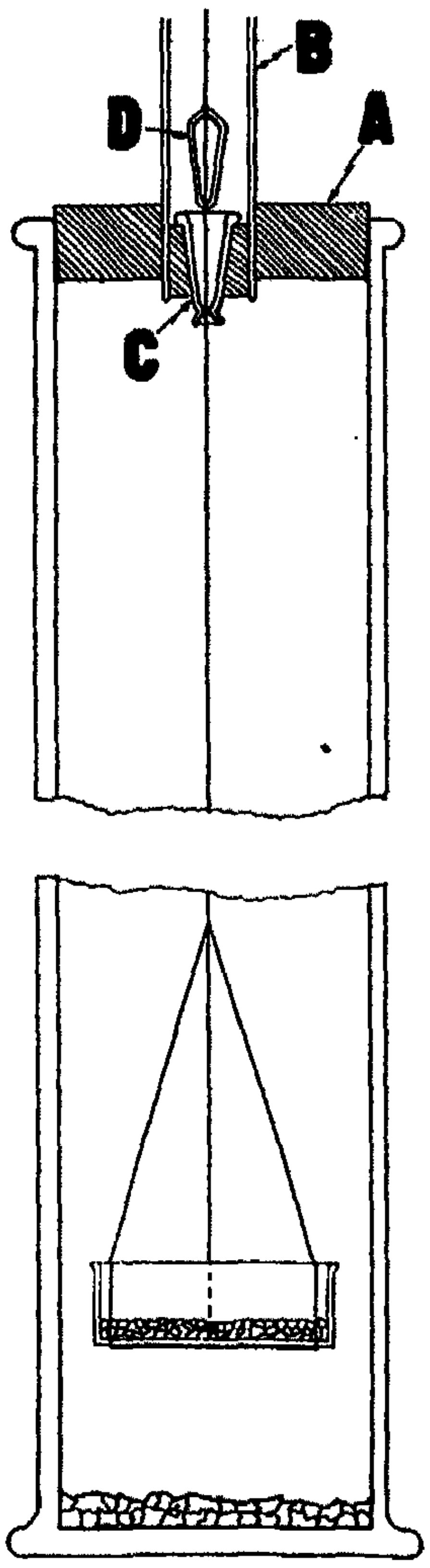


Fig. 1

TABLE III

Composition of alumina trihydrate over various hydrates at 25°C

Hours between weighing	Hydrate	Millimeters Vapor pressure	Composition
0	$H_2C_2O_4.1.75\ H_2O$	2.69	$Al_2O_3.2.973\ H_2O$
12	"	"	2.981
24	"	"	2.993
24	"	"	2.995
30	"	"	2.995
44	$NaOOCCH_3.2.3\ H_2O$	6.40	3.058
24	"	"	3.066
29	"	"	3.067
21	"	"	3.068
26	"	"	3.068
120	$CuSO_4.4.4\ H_2O$	7.80	3.066
24	"	"	3.066
24	"	"	3.066
96	$MgSO_4.6.75\ H_2O$	12.7	3.111
214	"	"	3.151
72	"	"	3.153
24	"	"	3.154
24	"	"	3.154
96	$Na_2HPO_4.4.0\ H_2O$	14.51	3.197
19	"	"	3.201
28	"	"	3.202
24	"	"	3.202
20	"	"	3.202
48	$Na_2CO_3.9.3\ H_2O$	18.01	3.257
95	"	"	3.276
119	"	"	3.328*
52	"	"	3.295
20	"	"	3.296
23	H_2O	23.52	3.312
144	"	"	3.751
288	"	"	4.079
390	"	"	4.320
88	"	"	4.417
	Final approximated value		5

* Thermostat overheated.

source, stopper (A) was loosened, the cylinder withdrawn, and another one substituted containing the new hydrate.

The trihydrate sample was first dried over phosphorus pentoxide for a few days, and was then allowed to stand over the hydrates listed in Table III in the order given. The vapor pressures of all these hydrates have been accurately determined. Many weighings were made over each hydrate, but to save space only enough of these are given to show the change of composition with time and the final composition over each hydrate. In obtaining the maximum water content the trihydrate was allowed to stand over water for six weeks, with frequent weighings. At the end of this time it was still gaining steadily, so an approximate composition of $Al_2O_3.5H_2O$ was used for this vapor pressure, since for the purpose of this work the upper portion of the vapor pressure curve did not need to be accurately known. The composition-vapor pressure curve is given in Fig. 2. The lower value, over phosphorus pentoxide, was taken from Table I. The vapor pressures of the various hydrates were those obtained by Wilson,[5] Carpenter and Jette,[6] and Baxter and Cooper.[7]

Change of composition with temperature.

The change of composition with increasing temperature was measured using an apparatus quite similar to that shown in Fig. 1. The thermostat was replaced by a thermo-regulated electric oven, and two glass tubes corresponding to (B) of Fig. 1 were used, being put through the top of the oven. A desiccator and metal cover were used in place of the glass cylinder and stopper (A) of Fig. 1. A thermometer and an air-inlet tube also went through this metal cover and through the top of the oven. The stoppers and ground glass joints corresponding to (D) of Fig. 1 were put at the top of the glass tubes, about 20 centimeters from the top of the oven, to avoid possible injury due to heat. The desiccator cover was not air tight, since there were small openings between the cover and the desiccator top, and around the various tubes. It was purposely left this way to provide outlets for the air-stream that was being passed in. This air-stream was dried at room temperature by passing it through two cylinders containing concentrated sulfuric acid and then a third containing barium oxide, which served as a powerful desiccant[8] and removed sulfuric acid spray. About a gram of the trihydrate compound was taken for each experiment, the sample container being smaller than the one shown in Fig. 1. Six of these samples were heated from 119° up to at least 250°, the change in composition of the one given in Table IV being typical. Weighings were made at intervals of 24 hours or longer. Enough of these are given in Table IV to show the change of composition with time at each temperature. In Fig. 3 are shown the curves obtained by plotting compositions at two different time intervals against temperature, using some of the results in Table IV. The upper curve represents the composition after 96 hours at the temperatures

---

[5] J. Am. Chem. Soc., 43, 704 (1921).

[6] J. Am. Chem. Soc., 45, 578 (1923).

[7] J. Am. Chem. Soc., 46, 923 (1924).

[8] Cf. Booth and McIntyre: Ind. Eng. Chem., Anal. Ed., 2, 12 (1930).

given. The lower curve shows the composition after 96 additional hours at the same temperatures. The composition at 119° after the second period of 96 hours was obtained by extrapolation from the data given in Table IV.

TABLE IV

Change of composition of the large particle trihydrate precipitate with increasing temperatures

Hours between weighing	Composition of large particle precipitate	Temperature in degrees Centigrade
72	$Al_2O_3 . 2.759\ H_2O$	119° ± 1°
24	2.756	"
24	2.757	"
24	2.678	164° ± 1.5°
72	2.650	"
96	2.629	"
48	2.627	"
24	2.626	"
72	2.545	184° ± 2°
24	2.530	"
75	2.481	"
21	2.463	"
72	2.377	"
167	2.201	"
167	2.030	"
143	1.852	"
52	0.419	270° ± 4°
22	0.415	"

X-ray data.

The substance indicated by its adsorption behaviour that it was probably composed of small crystals, since equation (2) would not be expected to hold for amorphous substances. To verify this, the X-ray diffraction pattern was obtained by the powder method. A water cooled Coolidge tube with a molybdenum target was used. The average wave length of the radiation was 0.710 Å. The glass tube containing the sample was a millimeter in diameter, and the distance from the center of this tube to the film was 20.04 centimeters. With a sample of the small particle precipitate, the lines shown in Fig. 4 were obtained, after a 48 hour exposure, using a current of 20 milliamperes and a potential of 32,000 volts.

Discussion of Results

The lines obtained in the diffraction pattern of the trihydrate were sharp, indicating a well defined crystalline structure. This pattern is similar to, but not identical with some of those given by Biltz and Lehrer.[9]

---

[9] Z. anorg. Chem., **172**, 305 (1928).

The results of the desiccation at room temperature can not be explained readily by assuming the ordinary type of hydrate decomposition, since equation (2) would not be expected to hold if a lower hydrate or anhydrous substance and water had been formed. Furthermore, the composition-time curve does not show the induction period that usually appears at the start when crystalline hydrates that have not been previously desiccated are allowed to decompose in the ordinary manner,[10] although Topley and Hume[11] have pointed out that this need not necessarily be present for very finely divided hydrates.

The evidence given here indicates a surface dehydration at room temperature in which the remaining lattice structure does not appreciably rearrange to form a new solid phase, but remains as a skin on the surface of the crystals, causing a slower and slower loss of water. Such a decomposition would cause the water content to approach a value of less than that required for perfect crystals, and the results in Table I indicate that this is the case. A practically constant composition of $Al_2O_3.2.888\ H_2O$ and $Al_2O_3.2.928H_2O$ was reached when samples of the small particle and large particle trihydrate precipitates were desiccated for six months over phosphorus pentoxide. In a decomposition of this type, when dehydration does not penetrate too deeply into the crystal, it should be possible to calculate values of c from equation (2), using values of w of less than three. As seen in Table II, values of c calculated in this way are in good agreement with those obtained earlier[1] using values of w greater than three.

This dehydrated lattice would be expected to undergo some change other than an actual rearrangement, due to the condition of strain produced. In view of the reversible manner in which water is taken up by these hydrates having a high transition temperature[12] after desiccation or even moderate heating, it is probable that this change is not great.

This type of decomposition would cause the system to be bivariant, since from the phase rule standpoint it is behaving like a solid solution. Thus the vapor pressure would be expected to vary with the composition at constant temperature, and from the curve shown in Fig. 2, this appears to be the case. If it be assumed that a monomolecular layer of water molecules in contact with each other is present on trihydrate crystals at a vapor pressure of about 7.5 millimeters, where the curve is most nearly flat, it is possible to calculate the surface per gram molecular weight of the trihydrate. Assuming that each water molecule occupies 9 Å^2 of the surface, this works out to be approximately 3.8×10^7 square centimeters. A precipitate composed of cubes of the order of 1×10^{-5} centimeters on the side would have a surface of this size.

The temperature-composition curve given in Fig. 3 shows roughly the relationship between surface dehydration without lattice rearrangement and the ordinary type of hydrate decomposition. It was found that when air

---

[10] Cf. Rae: J. Chem. Soc., **109**, 1230 (1916).

[11] Proc. Roy. Soc., **120A**, 217 (1928).

[12] Cf. Rothmund: Rec. Trav. chim., **44**, 332 (1925); Barnitt, Derr and Scripture: Ind. Eng. Chem., Anal. Ed., **2**, 357 (1930).

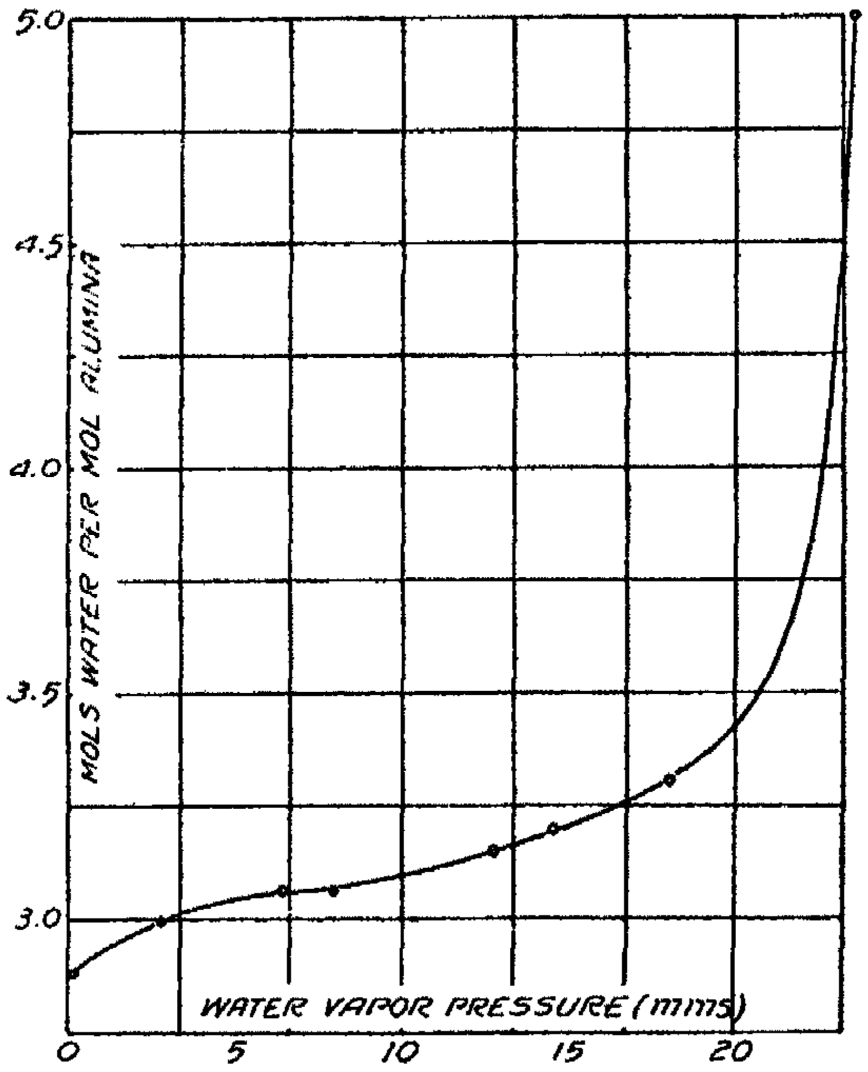

5.0
4.5
4.0
3.5
3.0
MOLS WATER PER MOL ALUMINA
WATER VAPOR PRESSURE (mms)
0
5
10
15
20

FIG. 2

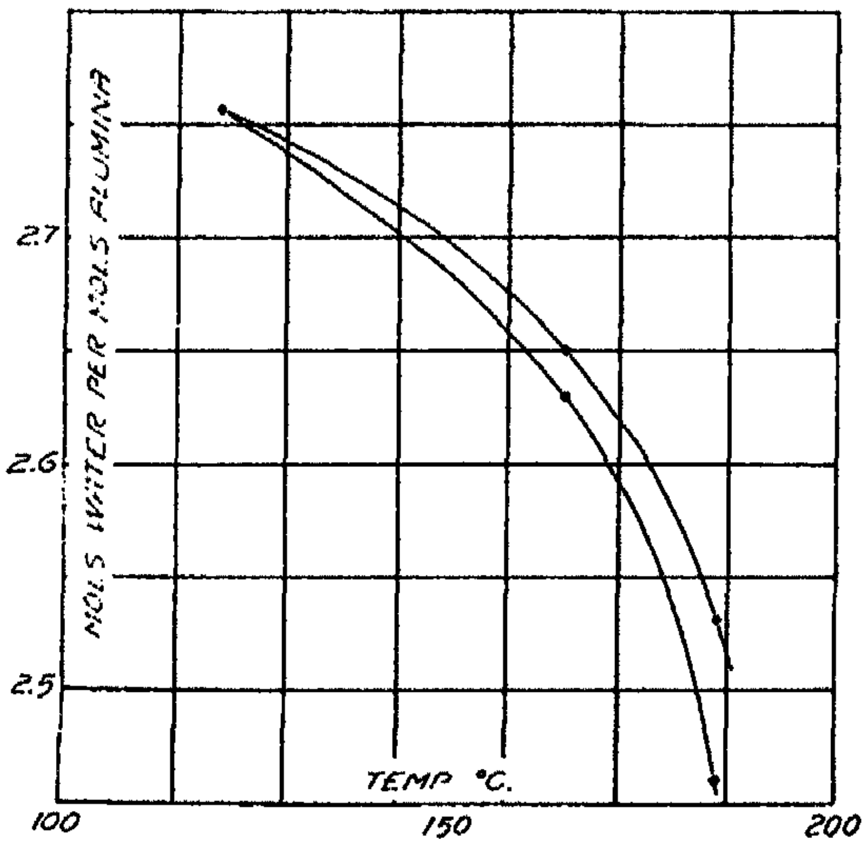

2.7
2.6
2.5
MOLS WATER PER MOLS ALUMINA
TEMP °C.
100
150
200

FIG. 3

having a low water vapor pressure was passed over the trihydrate at 119°, a constant composition was reached at least in 96 hours, as shown in Table IV. If the assumption be made that equilibrium was reached at all higher temperatures in ninety-six hours as far as decomposition without lattice rearrangement goes, then any weight change after this must have been due to the ordinary type of hydrate decomposition, with lattice rearrangement. The lower curve of Fig. 4, showing the composition at each temperature after 96 additional hours, is seen to diverge steadily from the upper curve as the temperature increases. The vertical thickness of this band defined by the two curves may thus be taken as an approximate measure of the rate of the ordinary type of hydrate decomposition at the various temperatures. It appears to be almost immeasurably slow at 119°, but much faster at 184°, as would be expected. This will only be an approximation, since the time which elapses between the start of surface dehydration and the start of lattice rearrange-

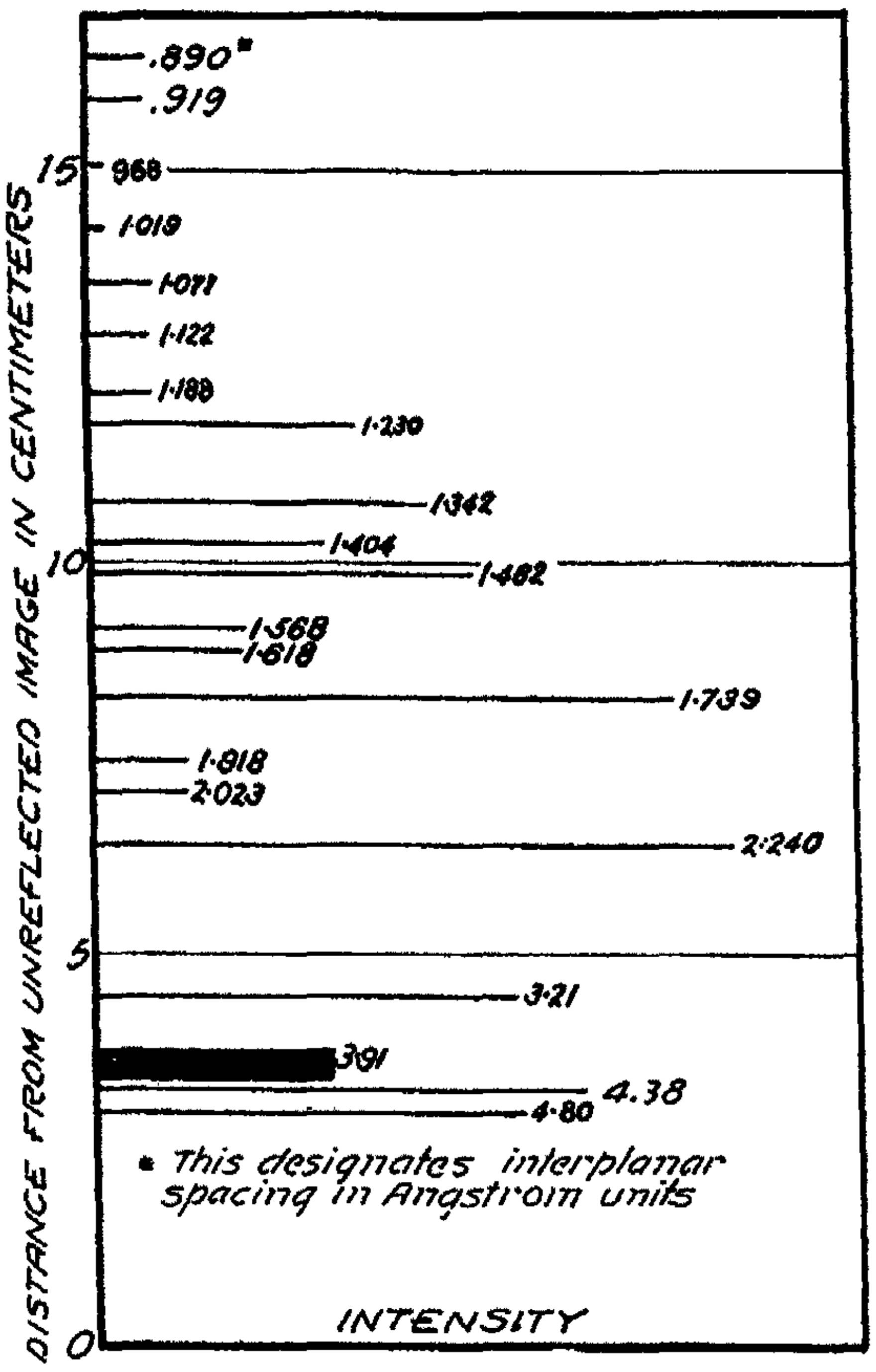


Fig. 4

ment is unknown, and since the rate at any temperature will depend on many factors, some of which were not constant in this experiment, such as composition.

Thus this trihydrate of alumina, and probably hydrates and related compounds in general, may be considered to have two vapor pressures. One is the pressure exerted by water as it evaporates from the surface of the crystal leaving behind a skeleton lattice structure. From Fig. 2 this is about 2.5 millimeters in the case of crystals of the trihydrate compound at 25°C. The other is the ordinary type of hydrate decomposition pressure depending on the presence of two solid phases. At room temperatures this must be a small fraction of a millimeter for the trihydrate compound. The two pressures probably approach each other as the temperature increases, becoming identical at the transition point, as shown in Fig. 5. The pressures along the upper curve cannot be measured by the ordinary methods used to measure vapor pressure, since they probably decrease as water leaves from deeper and deeper portions of the lattice. These pressures must be measured by some such method as described in this paper.

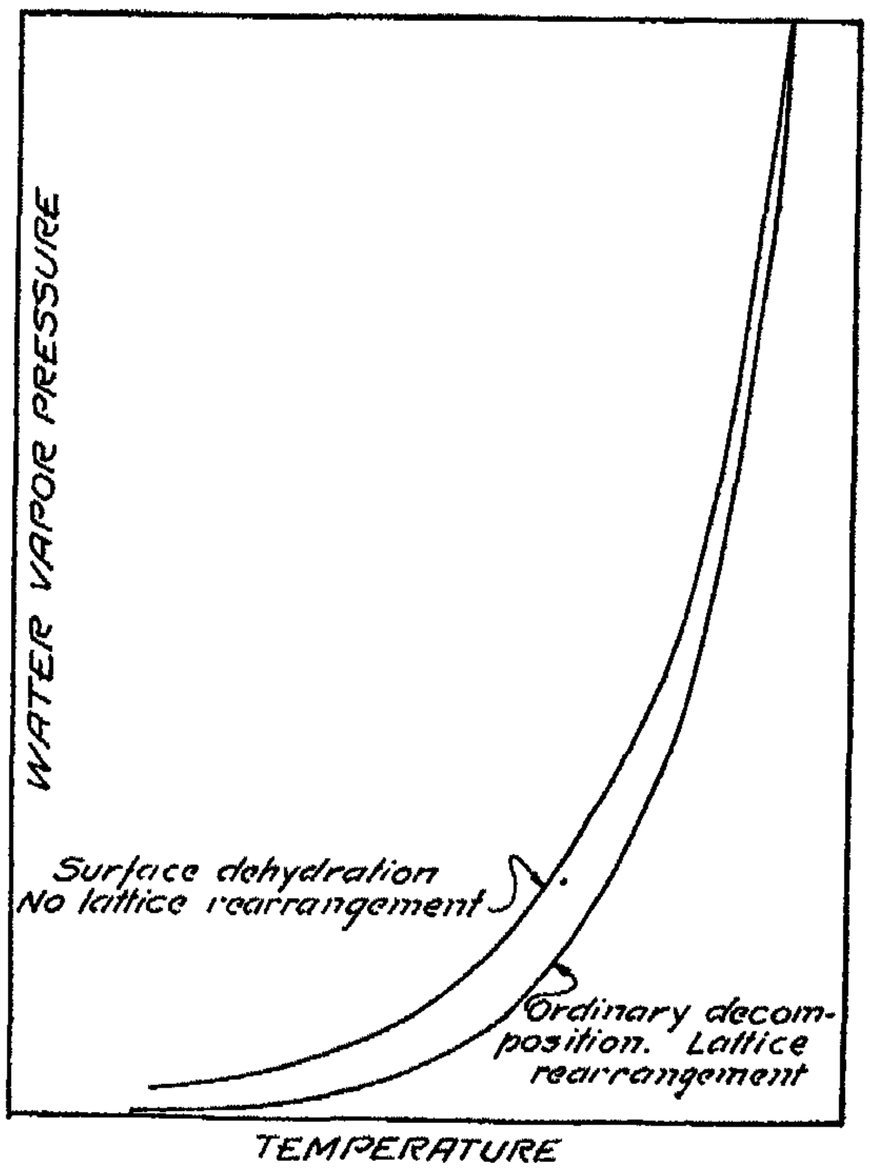


Fig. 5

This conception leads to a promising dehydration theory, which apparently embraces all classes of hydrate decompositions. In brief this theory is that the vapor pressure of perfect crystals of a hydrate, indicated at different temperatures by the upper curve of Fig. 5, diminishes as water molecules leave from the surface layers until the corresponding point on the lower curve is reached. At this point the outermost portion of the skeleton lattice structure will become unstable, a rearrangement starting at various points and spreading over the surface. The rate at which this rearrangement will penetrate into the crystal will be governed in most cases by the rate of formation of new skeleton lattice within the crystal. The term skeleton lattice is of course used in a relative sense, and does not necessarily imply the total absence of water. For hydrates near their transition point, such as the decahydrate of sodium sulfate at room temperatures, comparatively little water would be lost by surface dehydration before lattice rearrangement would begin. For hydrates at temperatures considerably below their transition temperature, such as hydrargillite, magnesium perchlorate trihydrate, the zeolites, and many others at room temperatures, the skeleton lattice must be a much more stable affair, and comparatively large amounts of water could be lost from the surface without lattice rearrangement taking place. This theory is being investigated at the present time, and will be reported on more fully at a later date.

The conception of a relatively rigid skeleton lattice in which water of crystallization has some freedom of movement is not new. Thus the decomposition of the zeolites has been explained in this manner.[13] Hüttig uses it to explain certain types of hydrate decomposition curves,[14] and Hackspill and Kieffer[15] employ it in their hydrate classification scheme. The possibility of this type of water loss from the surface has not been taken into account by Willstätter and his co-workers,[16] however, in their attempted identification of new hydrates in gels and small particle preparations. In working with alumina preparations two methods were used in obtaining the so-called hydrates: removal of surface water by washing with acetone and determination of the breaks in temperature-composition curves. Both of these methods are open to the same criticism, namely, failure to take into account possible loss of water by surface dehydration in preparations having an enormous surface. Thus in the acetone-drying experiments, any point on a curve similar to or even steeper than that shown in Fig. 2 might be reached, depending on the length of washing and the dryness of the acetone; only by chance could one arrive at the correct formula by this method. In drying preparations like these at increasing temperatures, the loss of water by surface dehydration might be very great, or the water adsorption might be very great, depending on the temperature and the water vapor pressure of the air used in the drying. Again, the correct formula could be obtained only by chance.

---

[13] See Weigel: Centr. Min. Geol., 1922, 164-78, 201-8; Chem. Abst., 17, 3151 (1923).

[14] Fortschr. Chem. Physik physik. Chem., 18, 5 (1924).

[15] Ann. Chim., (10) 14, 227 (1930).

[16] Ber., 56, 149, (1923); 57, 58 (1924); 58 2448, 2458 (1925); 64, 1697 (1931).

The authors wish to express their thanks to Professor Nusbaum of the Physics department of Case School of Applied Science for his assistance with the X-ray work, and to Professor H. B. Weiser of Rice Institute for valuable suggestions.

Summary

1. Evidence has been given showing that alumina trihydrate loses water at ordinary temperatures by a surface dehydration in which the remaining lattice structure does not appreciably rearrange.

2. A tentative dehydration theory has been advanced.

3. The methods employed by Willstätter and co-workers to identify hydrates have been criticised as giving doubtful results in the case of gels and precipitates of small particle size.

THE VELOCITY OF SOUND IN SOLUTIONS OF BENZENE AND N-BUTYL ALCOHOL IN N-HEPTANE*

BY E. BRIGHT WILSON, JR., AND WILLIAM T. RICHARDS

Introduction

The velocity of sound v in an elastic medium of density ρ is connected with its adiabatic compressibility β_s by the relation

$$v^2 = 1/\beta_s \rho$$

Measurements of the velocity of sound can, therefore, supply one of the coefficients necessary to define the thermodynamic properties of the medium. Owing to the work of Hubbard and Loomis,[1] the accuracy of such measurements in liquids has been greatly increased and it appears probable that interesting information may now be obtained in certain types of liquid systems. In order to explore the field of binary liquid mixtures the measurements reported below were undertaken. Smyth and Stoops[2] have carried out density and polarization determinations for n-heptane–n-butyl alcohol solutions finding that, although the density-composition curves are regular, the polarization shows irregular dependence on composition. These mixtures were, therefore, investigated in order to ascertain whether the behavior of their polarizabilities was to any extent mirrored in that of their adiabatic compressibilities. Benzene–n-heptane mixtures were also measured to give a comparison with a semi-ideal solution.

Experimental Part

Apparatus. The velocity of sound was determined by means of the sonic interferometer which has been devised by Hubbard and Loomis (loc. cit), a cell of the type described by Freyer, Hubbard and Andrews[3] being employed. The quartz crystal, which was entirely similar to that used by the investigators previously cited, was driven by a heterodyned oscillator of the Hubbard and Loomis design. An oscillator of the thermo-galvanometer type was found on the whole more troublesome to operate and no more accurate than the heterodyne. Measurements made at 500.00 k.c. and at 390.07 k.c. were indistinguishable within experimental error, and are hence quoted indiscriminately in the tables which summarize the results. This shows not only the expected independence of the velocity of sound with frequency over a small range, but also the more important freedom of the measurements from errors due to irregularities in the sound wave pattern.

---

* Contribution from the Frick Chemical Laboratory of Princeton University.

[1] Hubbard and Loomis: Phil. Mag., 5, 1177 (1928); Loomis and Hubbard: J. Opt. Soc. America, 17, 295 (1928).

[2] Smyth and Stoops: J. Am. Chem. Soc., 51, 3312 (1929).

[3] Freyer, Hubbard and Andrews: J. Am. Chem. Soc., 51, 759 (1929).

The cell in which measurements were made was immersed in a constant temperature bath held at 25.0°, 35.0° or 50.0°C. to 0.01°, 0.03° or 0.1°C., respectively. The temperatures were determined by means of Beckmann thermometers, which were calibrated by certified Bureau of Standards thermometers.

Materials. The n-heptane was obtained in a pure condition from the Ethyl Gasoline Corporation. It was distilled, refluxed over sodium wire, and finally redistilled, the fraction having a corrected boiling point of 97.0°C. being employed. The index of refraction of this sample for the D sodium lines was 1.38777 at 20°C.

The n-butyl alcohol was refluxed with fresh lime at 100°C. for 12 hours, and then at boiling for 1 hour. It was then left over fused potassium carbonate for a month and distilled. The fraction used had a corrected boiling point of 117.65–117.85°C. and a refractive index of 1.3994.

The benzene was a guaranteed C.P. brand. Since the benzene–n-heptane solutions were employed merely as a standard and since the velocity of sound in this benzene was in good agreement with that found by Freyer, Hubbard and Andrews, it was subjected to no further purification.

TABLE I

The Velocity of Sound in n-Heptane–Benzene Solutions

Temperature °C.		Mole fraction benzene			
		0	0.3040	0.5991	1.0000
25.0	v in m. sec^{-1}	1130	1154	1191	1302
35.0		1087	1109	1147	1254
50.0		1025	1043	1080	1187

TABLE II

Velocity of Sound and Related Properties in n-Butyl Alcohol–n-Heptane Mixtures

	M. F. Alcohol .2570			M. F. Alcohol .4843		
Temp.	v in m. sec.$^{-1}$	Density	β_s in bar^{-1} × 10^{10}	v in m. sec.$^{-1}$	Density	β_s in bar^{-1} × 10^{10}
25.00	1139	.7004	1.100	1155	.7252	1.034
35.0	1095	.6917	1.206	1113	.7161	1.127
50.0	1031	.6788	1.386	1053	.7034	1.282
	M. F. Alcohol .7457			M. F. Alcohol .8243		
25.00	1190	.7603	.929	1205	.7735	.890
35.0	1148	.7519	1.009	1167	.7656	.959
50.0	1088	.7392	1.143	1113	.7526	1.073
	n-Butyl Alcohol			n-Heptane		
25.00	1245	.8061	.800	1130	.6793	1.153
35.0	1205	.7987	.862	1087	.6708	1.262
50.0	1156	.7867	.951	1025	.6575	1.448

The solutions were made up by weight with suitable precautions against changes in composition due to evaporation. It is estimated that their composition was known to better than 0.04 mole per cent.

Measurements. Since the velocity of sound is obtained by simple multiplication from the readings of a micrometer screw, it is possible to give the results of the measurements in the form of self-explanatory tables. Velocities are expressed in meters per second.

Discussion

The measurements in pure benzene are in excellent agreement with those of Freyer, Hubbard and Andrews.[3] Those in n-heptane are consistently lower, indicating, perhaps, that the liquid here under consideration was slightly more dry than theirs. In any case the divergence is hardly greater than experimental error, and certainly cannot affect the present thermodynamic significance of the velocity of sound measured at these frequencies.

In both solutions the velocity of sound is a regular and very similar function of both temperature and composition. Whether each of the two obeys the law of ideal mixtures for this property cannot be determined until the remaining thermodynamic coefficients have been measured. It is already apparent, however, that factors which may gravely affect the regularity of polarization-composition-temperature relationships are without important influence on the velocity of sound. It follows by inference that the adiabatic compressibility may be a property of little interest in the study of binary mixtures, although many more instances are necessary before this can definitely be stated. If the specific heats of these solutions were known it would be possible to state whether any of the first thermodynamic coefficients showed parallel variation with that of the polarizability. Such parallelism, while not to be expected, would be of considerable descriptive interest if it were established.

We are indebted to Professor J. C. Hubbard for supervising the construction of the interferometer cell, and to Mr. A. L. Loomis for the loan of the quartz crystal.

Summary

The velocity of sound in solutions of benzene and n-butyl alcohol in n-heptane at 25, 35 and 50°C. has been measured over the entire concentration range. In both cases it is a regular function of temperature and composition.

Princeton, New Jersey.

THE LIQUID-VAPOR INTERFACE*

BY J. L. SHERESHEFSKY

While the structure of surfaces of solids and of insoluble films is fairly well established, the structure of liquid surfaces in contact with their own saturated vapor remains obscure to the present day. The Laplacian theory of surface tension assumes a uniform density of the liquid up to the vapor phase; on the other hand the theory of van der Waals involves the assumption of a continuous transition from liquid to vapor. Neither of the theories allows for an evaluation of the thickness of the transitional region except on the introduction of an arbitrary potential function.

The experimental evidence seems to be in favor of an abrupt change. Lord Rayleigh[1] found that the reflected light from a clean liquid surface is plane polarized, indicating a definite transition from liquid to vapor. Although Raman and Ramadas[2] found some ellipticity in the polarized light reflected from a clean surface of water, they agree with Rayleigh that the transition layer is about one molecule thick.

The conflict between the theory of van der Waals, which maintains the presence of a non-uniform capillary layer, and the experimental evidence may be more apparent than real. In a previous paper[3] the author has shown that the free surface energy of a liquid surface is the resultant of two effects, one due to the liquid surface proper, and the other due to the vapor phase in contact with this surface. It may therefore be that closely approaching the liquid surface there is an adsorbed phase of vapor which, while being more dense than the rest of the vapor phase, is yet not dense enough to constitute a continuation of the liquid phase. It is this adsorbed phase together with the unimolecular transition layer of the liquid phase that make up the capillary layer, which is giving rise to the various capillary phenomena.

Adsorption of Vapor at a Liquid-Vapor Interface

In a previous paper the author has shown that the surface tension of a liquid may be expressed by the equation

$$\sigma = \sigma_1 - \sigma_2 \qquad (1)$$

where σ is the surface tension measured, σ_1 the surface tension of the liquid surface proper, and σ_2 the surface tension of the vapor. From this it follows that the surface tension of a liquid in contact with undersaturated vapor would be higher, and in contact with supersaturated vapor would be lower than

---

* Contribution from the Chemical Laboratory of Howard University.

[1] Phil. Mag., 33, 1 (1922).

[2] Phil. Mag., 3, 220 (1927).

[3] J. Phys. Chem., 35, 1712 (1931).

ordinarily. In general, a liquid at any given temperature may exhibit various surface tensions depending on the degree of saturation of the vapor in contact with it. Mathematically we may express this by differentiating equation (1) with respect to σ_2

$$d\sigma = -d\sigma_2 \tag{2}$$

But since σ_2 was shown[1] to be given by the expression

$$\sigma_2 = \frac{\Delta T_c}{\rho_c^{1/3}\, M^{2/3}}(1 - T/T_c)^{0.9}\, \rho_2 \tag{3}$$

we obtain by differentiating with respect to ρ_2, the density of the vapor, the following differential equation

$$d\sigma = -\frac{\Delta T_c}{\rho_c^{1/3}\, M^{2/3}}(1 - T/T_c)^{0.9}\, d\rho_2 \tag{4}$$

where the change of surface tension of a liquid with the density of the vapor is given as a function of the critical constants and temperature.

Now since the change in the surface tension is negative, there must be a region contiguous with the liquid surface proper which is richer in vapor than the rest of the vapor phase. Therefore a liquid in contact with its saturated vapor may be represented as a system consisting of three phases, one liquid, one vapor, and one intermediate adsorbed phase.

To calculate the amount of vapor adsorbed in this intermediate phase we may apply Gibbs' adsorption equation. This system, since it has only one component, represents the simplest case to which Gibbs' equation may be applied. Up to the present it has been applied to systems having at least two components, and in order to evaluate the amounts adsorbed, approximating assumptions had to be made. Thus in calculating the adsorption of alcohol at the surface of an alcohol-water mixture Schofield and Rideal[2] used only an approximate equation of Gibbs

$$d\sigma = -\Gamma\, d\mu \tag{5}$$

instead of the full equation

$$d\sigma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 \tag{6}$$

where the subscripts (1) and (2) refer to the components of the system. In the case of a liquid in contact with its vapor no error is introduced by using equation (5), since there is only one component in the system.

Since μ, the thermodynamic potential, is given by the expression

$$\mu = \mu_0 + RT\log a \tag{7}$$

then at a given temperature

$$d\mu = RT\, d\log a \tag{8}$$

where a is the thermodynamic concentration of the vapor in the vapor phase, which may be substituted by the density of the vapor, ρ_2.

---

[1] Loc. cit.

[2] Proc. Roy. Soc., 109A, 61 (1925).

Combining (8) and (5), Gibbs' equation becomes

$$d\sigma = -\Gamma RT \, d \log \rho_2 \qquad (9)$$

which, when combined with equation (4) gives the final expression for the calculation of the adsorption in the capillary phase, namely

$$\Gamma = \frac{\Delta}{R} \cdot \frac{T_c}{T} \left(\frac{\rho_2}{\rho_c}\right)^{1/3} \left(\frac{\rho_2}{M}\right)^{2/3} (1 - T/T_c)^{0.9} \qquad (10)$$

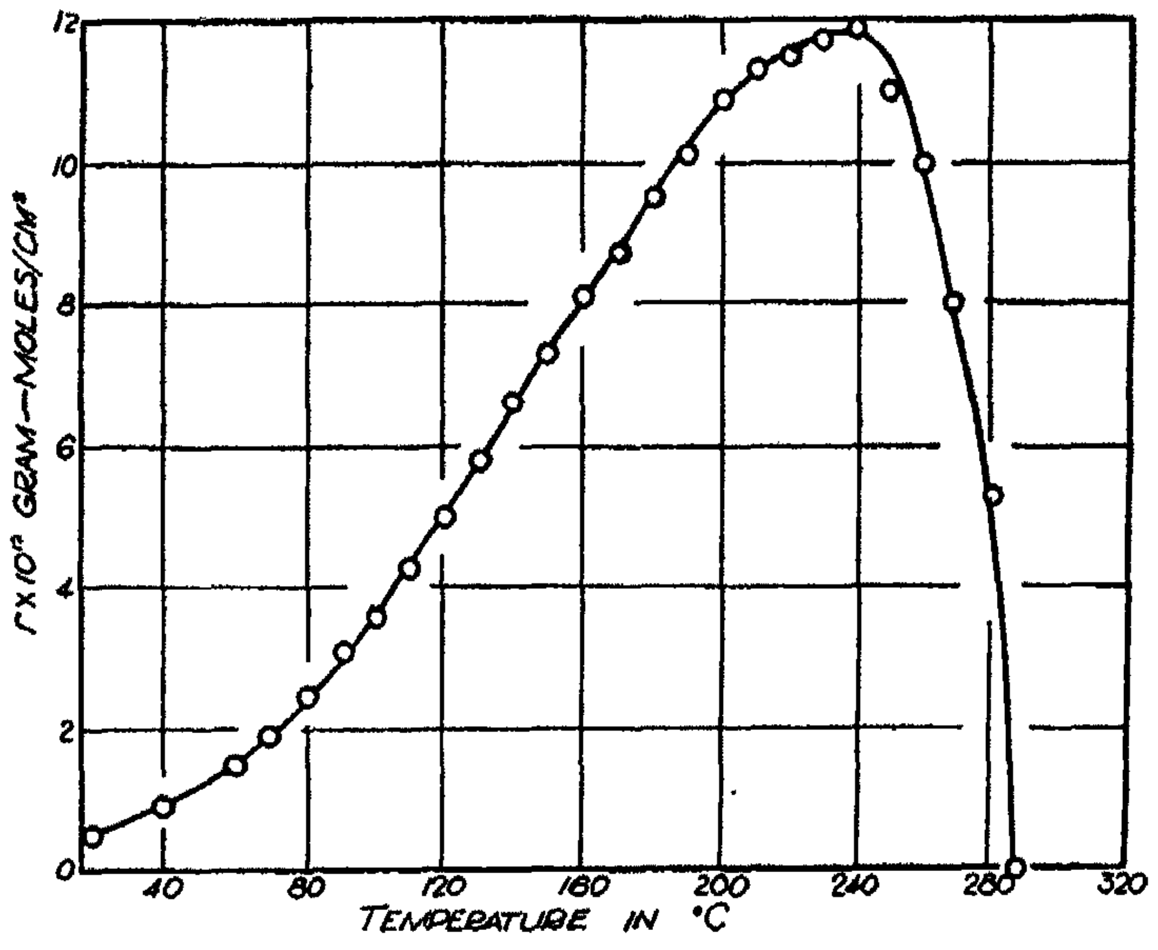


FIG. 1
Adsorption of Benzene Vapor at a Liquid Benzene Surface

It is rather of interest to point out that in combining equations (10) and (3) we obtain

$$\sigma_2 \, 1/\Gamma = RT \qquad (11)$$

which is the so-called equation of state of gaseous films, since σ_2 represents the surface tension lowering, and $1/\Gamma$ is the area occupied by a gram-molecule.

In Table I are given the results of calculations on the adsorption of benzene vapor. In the first column are given the temperatures, and in the second column the corresponding vapor densities, which were taken from the International Critical Tables. In the fourth column are given the amounts adsorbed in gram-mols per square cm. These values seem to be quite reasonable, since alcohol which causes a lowering of surface tension a hundredfold is adsorbed at the surface of an alcohol-water solution in the order of 1×10^{-10} gram-mols per square cm. Fig. 1 shows the variation of adsorption with temperature.

It is of interest to point out that the temperature at which adsorption is at a maximum corresponds to the temperature of maximum surface tension of the vapor. This was to be expected, since the maximum surface tension of the vapor corresponds to a maximum lowering of the surface tension of the liquid surface. This maximum point was shown by the author in a previous paper[1] of this series to be, for all vapors, at 0.9 of the critical temperature. Furthermore, a glance at equation (10) will show that at corresponding temperatures the adsorption of various vapors is proportional to $(\rho_2/M)^{2/3}$, or that $\Gamma(M/\rho_2)^{2/3}$, which may be called the molar adsorption, is the same for all vapors. The molar adsorption at various temperatures is given in the last column of Table I, and is represented graphically in Fig. 2.

TABLE I

Adsorption of Benzene Vapor at a Liquid Benzene Surface

$\Delta = 1.39$ Mol. Wt. = 78.05 $T_c = 561.5$ $\rho_c = .3045$

t°C	ρ_2	$1-T/T_c$	$\Gamma \times 10^{12}$ gram-mol./cm²	$\Gamma(M/\rho_2)^{2/3} \times 10^{9}$ gram-mol.
20	.0004	.478	.53	1.79
40	.0008	.443	.93	1.97
60	.0015	.407	1.51	2.11
70	.0020	.390	1.91	2.18
80	.0027	.372	2.43	2.26
90	.0036	.353	3.12	2.43
100	.0047	.337	3.50	2.35
110	.0060	.318	4.27	2.36
120	.0077	.302	5.04	2.37
130	.0096	.282	5.78	2.34
140	.0118	.265	6.61	2.33
150	.0144	.247	7.34	2.26
160	.0173	.228	8.05	2.18
170	.0209	.212	8.75	2.12
180	.0249	.193	9.55	2.04
190	.0298	.176	10.10	1.92
200	.0355	.157	10.80	1.83
210	.0421	.140	11.25	1.70
220	.0502	.122	11.50	1.54
230	.0598	.105	11.72	1.40
240	.0714	.086	11.90	1.26
250	.0855	.068	11.00	1.03
260	.1038	.052	10.00	.83
270	.1287	.033	8.08	.58
280	.1660	.016	5.23	.32
288.5	.3045	0	0	0

---

[1] J. Phys. Chem., 34, 1947 (1930).

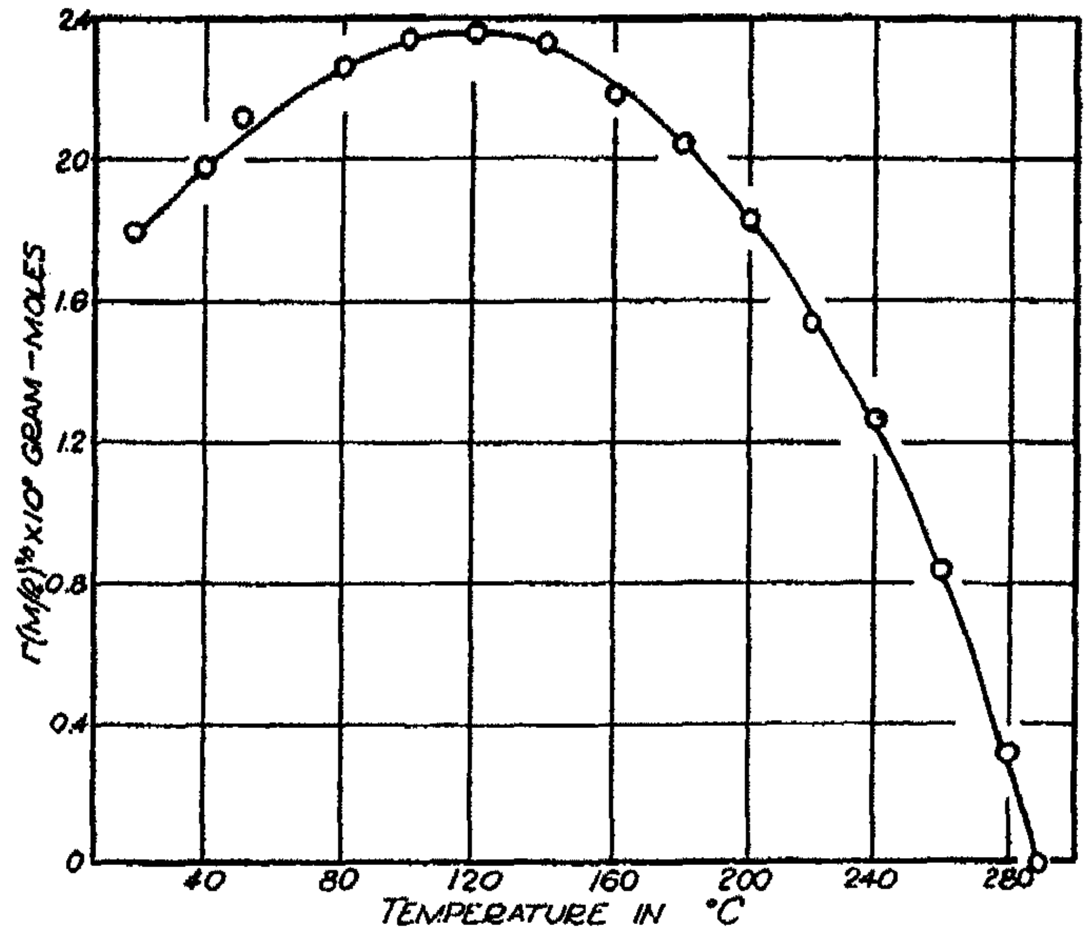


FIG. 2
Molar Adsorption of Benzene Vapor

The Thickness of the Adsorbed Phase

The adsorption of the vapor may be looked upon as due to an attractive force exerted by the molecules in the liquid surface. Since molecular forces diminish rapidly with distance, the concentration of the adsorbed phase is greater at a distance near the liquid surface, then it rapidly decreases until it approaches the concentration of the vapor phase. The distance from the vapor phase to the closest approach of the adsorbed molecules to the liquid surface may be termed as the thickness of the adsorbed layer. If c is the concentration of this phase, which we assume to be approximately uniform, and c_0 is the concentration of the vapor phase, the work done in bringing a molecule from the vapor phase to the adsorbed phase is given by the Maxwell-Boltzmann equation

$$c = c_0\, e^{\phi/\kappa T} \qquad (12)$$

where ϕ is the change in the potential energy of the molecule, T the temperature, and κ Boltzmann's constant. The energy change, θ, involved in the transference of a gram-molecule is given by

$$c = c_0 e^{\theta/RT} \qquad (13)$$

where R is the gas constant.

Since Γ is the number of moles adsorbed per unit surface and d is the thickness of the layer, the amount adsorbed per cubic centimeter is Γ/d and is given by

$$\Gamma/d = c - c_0 \qquad (14)$$

when c and c_0 are expressed in moles per cubic centimeter. Combining equations (13) and (14) we obtain

$$\Gamma/d = c_0 e^{\theta/RT} - c_0 \quad (15)$$

or

$$\Gamma/c_0 = d\, e^{\theta/RT} - d \quad (16)$$

which relates adsorption with the work of adsorption and the thickness of the capillary layer.

When θ is large d may be neglected, and the above equation becomes

$$\Gamma/c_0 = d\, e^{\theta/RT} \quad (17)$$

which in logarithmic form is

$$\frac{\theta}{RT} = \log_e \frac{\Gamma}{c_0} - \log_e d \quad (18)$$

or

$$\frac{.434\theta}{RT} = \log_{10} \frac{\Gamma}{c_0} - \log_{10} d \quad (19)$$

In the range of temperatures where θ and d are constant, plotting log Γ/c_0 against $1/T$ should give us a straight line whose slope is $.434\theta/R$ and whose intercept on the log Γ/c_0 axis is log d. Since Γ obtained in the preceding part is over a wide range of temperatures up to the critical, and since θ and d surely vary with the temperature of the liquid surface, a straight line could not be expected. However, at lower temperatures we may expect the values of θ and d to remain approximately constant. It is to this range of temperatures that equation (19) is applied.

Fig. 3 shows the curve obtained by plotting log Γ/c_0 as ordinate and $1/T$ as abscissa. Table II gives the calculated data for the plot. In the first column are given the values of Γ/c_0, which were obtained from

$$\Gamma/c_0 = \frac{\Gamma M}{\rho_2}$$

where ρ_2 is the vapor density and M is the molcular weight. Γ was taken from Table I. In the fifth and sixth columns are given the value of θ and the value of d.

As evident from the figure, the curve is practically a straight line from the melting point, which is for benzene 5.4°C, up to 70°C. The boiling point of benzene is about 80°C. It may be asserted, therefore, that under atmospheric pressure the work of adsorption and the thickness of the capillary layer are practically constant throughout the whole range of temperatures under which the substance is in the liquid state.

In spite of the various approximations introduced into the equation (19), the thickness d obtained is of the right order of magnitude. However, it is much less than the diameter of a benzene molecule as calculated from the density at 20°C. The thickness of the adsorbed layer is evidently not more than one molecule.

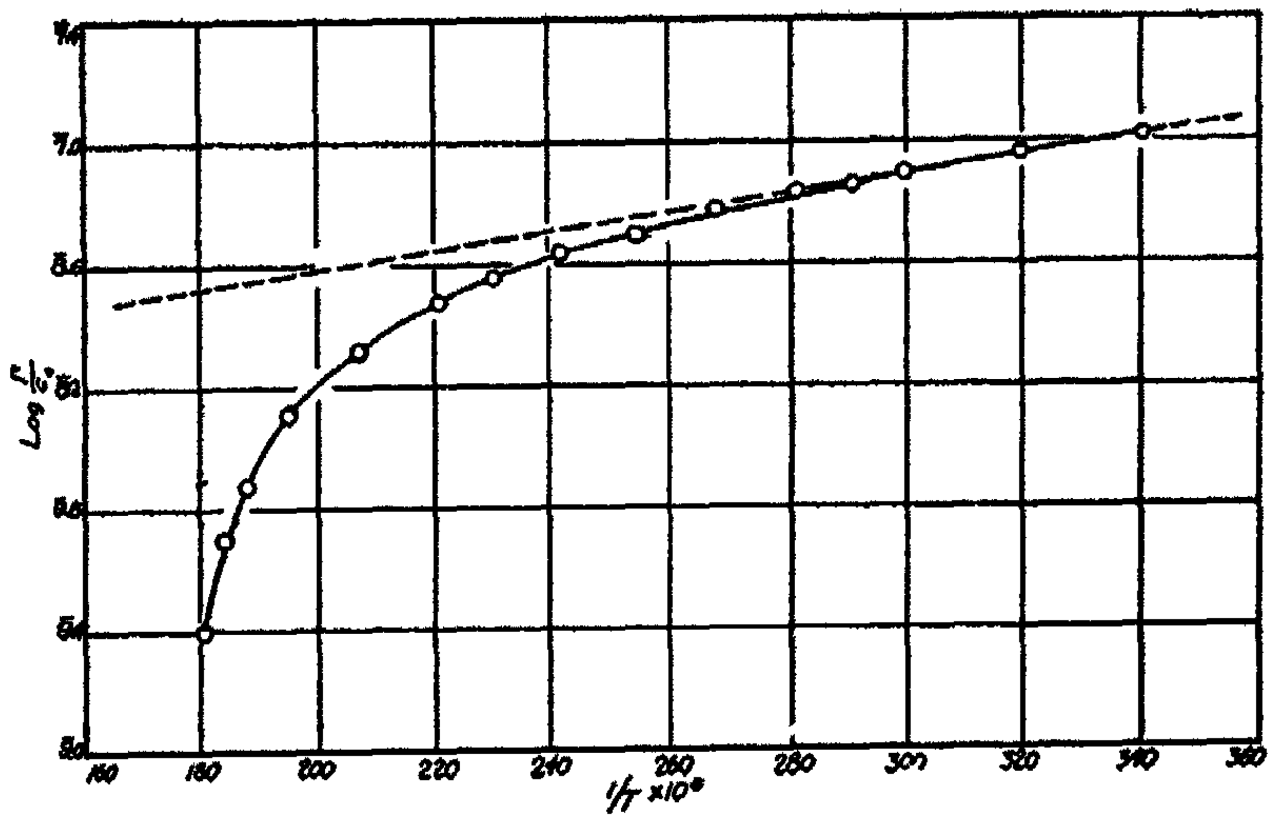


Fig 3
The Thickness of the Capillary Layer

Table II

The Thickness of the Capillary Layer

$(\Gamma/c_0)\times 10^9$	$\log(\Gamma/c_0)$	$\frac{1\times 10^6}{T}$	$.434\,\theta/R$	θ cal/mole	$d\times 10^8$cm
104	$\bar{7}.0170$	341	298	1365	1.0
90.7	$\bar{8}.9576$	320	298	1365	1.0
78.7	$\bar{8}.8960$	300	298	1365	1.0
74.0	$\bar{8}.8692$	291	298	1365	1.0
69.2	$\bar{8}.8401$	283	298	1365	1.0
67.6	$\bar{8}.8299$	276			
51.2	$\bar{8}.7093$	255			
43.7	$\bar{8}.6405$	242			
36.4	$\bar{8}.5611$	231			
29.9	$\bar{8}.4957$	221			
21.0	$\bar{8}.3222$	207			
13.1	$\bar{8}.1173$	195			
7.5	$\bar{9}.8751$	188			
4.9	$\bar{9}.6902$	184			
2.5	$\bar{9}.3979$	181			

TABLE III

The Density of the Adsorbed Phase

Temperature °C	Density of Vapor ρ_2	Density of Adsorbed Phase ρ	Density of Liquid ρ_1
20	4×10^{-4}	4.16×10^{-3}	.8790
40	8×10^{-4}	7.15×10^{-3}	.8576
60	15×10^{-4}	11.78×10^{-3}	.8367
70	20×10^{-4}	14.78×10^{-3}	.8248

In Table III are given the densities of benzene in the three co-existing phases. The density of the adsorbed phase was calculated by means of Boltzmann's equation

$$\rho = \rho_2 e^{\theta/RT}$$

in which θ was taken to equal 1365 calories per gram-molecule. A comparison of the densities in the three phases shows that, while the density of the condensed phase is from seven to ten times greater than the density of the vapor phase, the former is from sixty to two hundred times smaller than the density of the liquid. The transition from the liquid to the adsorbed phase may therefore be considered to be abrupt, and the light reflected from the liquid surface would be plane polarized, in accordance with the experiments cited above.

Summary

Evidence as to the thickness of the capillary layer of liquid surfaces is reviewed.

It is suggested that contiguous to a liquid surface there is an adsorbed layer of vapor.

An equation was derived whereby the amount of adsorbed vapor may be calculated.

It is shown that at corresponding temperature the "molar adsorption" is the same for all vapors.

The work of adsorption and the thickness of the capillary layer is calculated by applying the Maxwell-Boltzmann law.

Washington, D. C.,
January, 1932.

A TEMPERATURE CONTROL CLOSET FOR ADIABATIC CALORIMETRY*

BY B. CLIFFORD HENDRICKS AND WARREN H. STEINBACH, JR.

In a former communication[1] one of us and others reported a temperature control closet constructed of wallboard. This closet later proved quite unsatisfactory when work with it was attempted during summer months with atmospheric temperatures at levels ten or more degrees above the twenty degree level then in use in the calorimeter. Later, when it was decided to use a twenty-five degree temperature for the constants being determined, the wallboard arrangement was entirely inadequate for either summer or winter.

Help in remodeling the wallboard structure into something more permanent and dependable was not easily found. Publications[2,3] upon calorimetry refer to such controls but give no details either of construction or of operation. Isabe[4] describes a toluene-mercury thermo-regulator in circuit with a relay which is said to establish thermal constancy to 0.05°C. in an air chamber whose dimensions are not given. A more recent paper[5] describes a double walled room equipped with a temperature control which raises temperature by electric heating units, decreases it by water coils and equalizes it by electric fans.

For adiabatic work the atmospheric temperature does not need to be thermostated but rather must be under such control by the experimenter that increases or decreases in its value may be made at a rate known in advance of their use. In order to maintain a temperature varying, either positively or negatively, from that of the laboratory temperature, provision has to be made for: 1) heating, 2) cooling, 3) insulation from the room, and 4) the manipulation of all experimental equipment within it by outside controls. To meet these requirements, the closet shown in Fig. 1 was made and has been in use in this laboratory for the past two years.

The closet is constructed of soft wood and has the dimensions 185 by 70 by 65.5 cm. The bottom is raised 20 cm. above the floor. The earthen-ware jar, J, of 120 liters capacity, is installed in the lower half of the cabinet, by removing screws which hold panel doors in place. The upper half is provided with two hinged doors, one front and one back, with glass windows, W′, W″, through which all observations are made. During all experiments these doors

---

*Contribution from the Chemical Laboratory of the University of Nebraska.

[1] B. Clifford Hendricks, James H. Dorsey, Royce LeRoy, and A. G. Moseley, Jr.: J. Phys. Chem., 24, 418-426 (1930).

[2] Frederick Barry: J. Am. Chem. Soc., 42, 1915 (1920).

[3] W. P. White: "The Modern Calorimeter," 20, 45 (1928).

[4] Hajime Isabe: J. Chem. Soc. Japan, 43, 650-3 (1922).

[5] U. R. Evans: Chem. and Ind., 50, 66 (1931).

are kept closed, yet temporary changes in equipment within the closet may be quickly made by merely opening them.

Provision is made for stirring the contents of the calorimeter vessel, inserted at Ga, the calorimeter water jacket in J, and the air in the upper part of this closet, through fan F, by means of power through a system of pulleys, P, P′, S′, S″, S‴.

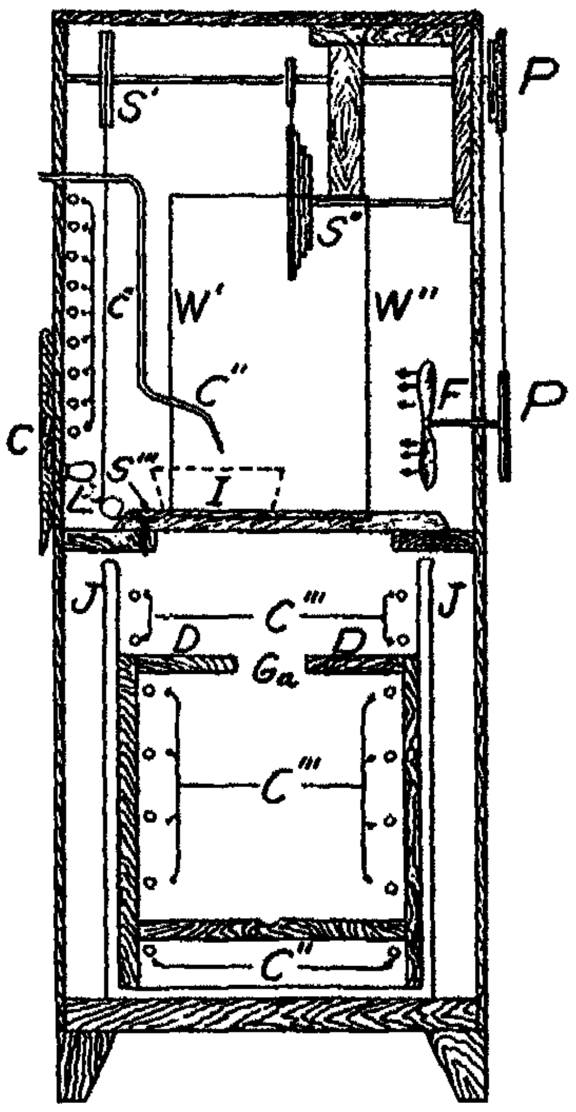


Fig. 1

In those experiments in which heat is evolved, giving an elevation of temperature above that of the 25 degree level of the bath, adiabatic work requires that bath, water jacket, and air closet temperatures must be brought upward at a rate comparable with the change taking place in the calorimeter. The range of this change, for which this apparatus was constructed, was assumed to never be greater than two degrees on the Centigrade scale. All tests here reported are made for that range.

The water jacket is equipped with a mercury-toluene thermo-regulator in series with a polarized relay. This thermo-regulator can be thrown into circuit with any one of the two 250-watt lamps or the two 250-watt knife heaters, each immersed in a different quadrant of the water jacket, and by test was found to maintain temperature constancy at Ga, Fig. 1., to 0.004 degrees C. By hand control any one of the four heaters raises the temperature of the water jacket above 25 degrees C. at a rate of 0.04 degrees per minute.

Temperature elevation of the air closet is accomplished by a lamp at L. Tests indicate that a 50-watt lamp in this position on a 110-volt circuit, raises the air temperature at the rate of 0.1 degrees C. per minute when the water-jacket temperature is 25 degrees C. and room temperature 24 degrees C. A more powerful or less powerful lamp shows correspondingly faster or slower rates of temperature change.

In heats of solution experiments, where heat is commonly absorbed, calorimeter temperatures drop below the water jacket level. Richards and co-workers[1] met such an emergency by the introducing of ice water into the water jacket. In case slower cooling is adequate ordinary hydrant water[2] has been put into the water jacket. The apparatus here presented uses neither

---

[1] T. W. Richards: Proc. Am. Acad., **38**, 434 (1920).

[2] B. Clifford Hendricks, James H. Dorsey, Royce LeRoy and A. G. Moseley, Jr.: J. Phys. Chem., **24**, 419 (1930).

of these cooling methods. Inside of the water jacket jar, J, arranged in spirals, with seven turns, are 1160 cm. of three-eighths inch copper tubing, C'''. This tubing is connected at one end through a closed-end manometer to the laboratory water and the other end projects into a sink. A compression faucet permits the adjustment of the water pressure of the entering water to almost any desired value. A series of tests[3] made it possible to prepare a calibration curve showing manometer pressure reading plotted against the rate of cooling. These values vary from a rate of 0.007 degrees C. per minute with a manometer pressure reading of five centimeters to a cooling rate of 0.186°C. per minute when the pressure reading is 18 cm. The entering tap water was at 15.5°C. during the tests. By reference to the calibration curve the experimenter can set the pressure through those coils to duplicate any rate of cooling desired between the limits named. The flow of water through the coils may be deflected from them by merely turning the two-way stop cock, C.

A similar control of the air temperature of the closet is sought by running water through coils, c'. However, these coils do not show any marked increase in speed of cooling as the pressure of the water through them is increased. After but a few minutes of water flow through them they become wet with condensed moisture. This condensation assumes, after a very short time, such proportions that it is necessary to provide drains to carry it away. It seems reasonable to assume that it is responsible for the reduced cooling when the water flow through the pipes is increased. Tests indicate that the coils may be depended upon to cool the air space of the closet at the rate of .13°C. per minute with the temperature one degree above the water jacket temperature and two degrees above room temperature. This rate of cooling can be improved by using compressed air through C'' over ice in Pan, I. For this procedure the drop was 0.26°C. per minute. By the addition of salt to the ice the cooling rate was increased to 0.62°C. per minute.

The closet is not air tight but with the doors shut it is not a difficult matter for the experimenter to hold the temperature of the air of the closet to within 0.2°C. of the desired value. While this is maintained by hand control, such control is justified since adiabatic work requires not constancy, but near-equivalence.

In order to introduce samples into the calorimeter after equivalence of its temperature, and the water jacket temperature has been achieved, an electromagnetic trip was devised. This releases a weight which forces a plunger to push the cap out of a sample tube within the calorimeter. The calorimeter's thermometer is tapped, to prevent mercury from sticking, by a rubber covered hammer of a mutilated electric bell. This is also operated by a switch upon the outside of the closet.

After having fixed the calorimeter in the bath with its sample tube loaded, the electro-magnetic trip and thermometer tapper adjusted, it is possible for the experimenter to start the stirring motor, vary the heating or cooling rate, illuminate the thermometers, release the sample, tap the thermometer, all by means of switches and without opening doors or even moving from his seat.

---

[3] The authors wish to credit Mr. R. V. Witter for making these tests.

CANCER RESEARCH

BY B. CRAWLEY

The twenty-ninth annual report of the Imperial Cancer Research Fund states that "though there are many examples of the greater viability of cancer cells as compared with the normal, there is no evidence as yet available of a single property in which they are more vulnerable," and again: "We are not yet in possession of such knowledge of the properties of the cancer cells as would ndicate clearly the direction in which a rational specific therapy of cancer should proceed." It is bitter to have to confess after thirty years' work that as we can't find what is wrong, we don't know how to set about putting it right.

What is to be done next? It is not of much use to go on collecting facts indefinitely without attempting to fit them into a general scheme of some sort. Although (as Dr. Dale has recently pointed out) biologists are traditionally shy of theories on account of the number of unknown and uncontrollable variables always present in their work, and cancer research workers in particular have learnt over and over again how misleading an imperfectly checked hypothesis can be, yet the sheer bulk of undigested observations is becoming so great that even "Chemical Abstracts" may presently fail to encompass it. It is time to sit down and think things over.

In a series of papers appearing in the "Journal of Physical Chemistry" from January 1931 onwards, Professor Bancroft has been amplifying and extending an old suggestion of Claude Bernard's on the nature of anaesthesia. His ideas may be very briefly summarised as follows. The successive cell states of (1) excitation, (2) anaesthesia or temporary inhibition of activity, and (3) death, are respectively characterised by (1) incipient reversible agglomeration (enlargement of the micelles) of the protein sols contained within the cell, (2) a more advanced but still reversible agglomeration, and (3) irreversible coagulation. His theory thus explains why a single chemical reagent, or even suitable radiation or mechanical shock, can under different conditions behave as (1) a stimulant, (2) a narcotic or antiseptic, and (3) a cell poison or disinfectant. The sedative action of bromides, their power of reducing irritability and of counteracting narcosis and anaphylactic shock, together with the catatonic nature of the symptoms produced by excessive use of bromides, he explains as due to the peptising action of the bromide ion on the negatively-charged cell proteins.

Taking Professor Bancroft's theory as a basis, let us suppose —as a working hypothesis—that the essential difference of malignant cells (and possibly of embryonic cells also) from the normal of the same species lies in *their protein sols being in a chronic state of excessive peptisation*, i.e. the micelles are smaller than those occurring in normal cell colloids.

If this hypothesis is correct, the causation of cancer by continued irritation may be explained as follows. After a period during which the cell colloids are maintained in a state of incipient agglomeration (stimulation), and at the same time are called upon to do heavy repair work, sooner or later they become protectively altered in such a way that the cells perform the abnormal repair work as a part of their customary and heritable duty (malignant growth) without requiring stimulation; in other words, increased peptisation has rendered the protein sols too stable to be appreciably agglomerated by stimuli which have a marked effect upon the sols of similar normal cells. The mechanism of the protective change may possibly be connected with the abnormally rapid breakdown of glucose in cancerous tissue,—for it is not unlikely (Nechkovitch; Archiv int. Physiol., **28**, 285) that glucose in normal tissue fulfils the physiological rôle of maintaining the cell colloids at their optimum dispersion. Then there is the question of susceptibility: why do some persons readily develop malignant growths in response to a given irritation, while others are either resistant for a much longer period or altogether immune? At present we can only reply in general terms that the cell proteins of susceptibles are for some reason unusually prone to incipient agglomeration as the result of irritation, so that they are more readily perverted into the protective peptisation characteristic of malignant growths. This suggests why cancer is largely a disease of later life; with advancing age the cell colloids always tend to become more readily agglomerated, as is evidenced by the easily excited emotions of the aged, by the habit of dozing and falling asleep on the slightest pretext, and by general sensitiveness toward shock.

The hypothesis of excessive peptisation, i.e. abnormal stability towards agglomerating agents, at once accounts for the observation that sarcoma cells exhibit a higher resistance than normal connective-tissue cells to the dyeing action of trypan blue, and may also explain why normal cells fail to form around the boundary of a malignant tumour an impervious coating such as limits the extent of a non-malignant growth. Treatment of malignant growths by intravenous injections of colloidal metals, though dangerous, has shown some positive results, as has also the use of certain bacillus toxins and of emulsions of embryonic tissue; the normal body tissues may be supposed to be stimulated by these agents into a sufficiently enhanced state of activity (incipient agglomeration) to put up a successful fight against the progress of the tumour. Excessive doses of metallic colloids, however, favour instead of retarding the malignant growth, because such a very strong stimulus carries the agglomeration of the normal cell proteins right through to the anaesthetised or inhibited stage, while producing only an exciting effect on the more stable cancer cells. The statement that, in every property which has been experimentally investigated, cancer cells are more resistant to attack than normal cells, becomes of small moment as soon as it is realized that investigation has been confined to one single property, namely the susceptibility of the colloids to agglomeration. Chemical poisons, heating, freezing and other destructive radiations all attain their lethal effects on cells by directly or indirectly bringing about irreversible coagulation of the cell proteins; and since malignant cells happen to resist coagulation more strongly than normal cells, it is easy to understand how a "cure" based on coagulating agents may well prove more fatal than the disease itself.

It remains to be seen what help the hypothesis can give us toward preventing or curing malignant growths. As regards prevention the answer is:

with our existing knowledge, not much. We know that mechanical and chemical irritants are liable to produce cancers, and the means of preventing such cases are self-evident. But cancers often develop without clear evidence of the nature of the primary irritant, so that while it is easy to blame civilized man's general mode of life it would be absurd to hope to exclude thereby every possible cause. Until a new experimental technique has been developed there is no hope of establishing with certainty the exact physicochemical changes which bring about the increased dispersion of malignant cell proteins. Phenomena of antiserum therapy and anaphylaxis, for instance, show that present physical and chemical methods cannot detect the difference between two proteins which are sufficiently dissimilar for one to cause rapid death (coagulation) in all cells of a given species to which it is applied, while the other is quite without effect,—so that, even if a specific cancer toxin existed and could be isolated, little light would be thrown thereby on the mechanism of the disease. Probably, too, there are at least as many separate strains of malignant cells as there are kinds of protein in the normal cells from which they are derived. A study of the chemical structure of extraneous substances which happen to agglomerate cell proteins—constituents of coal tar, for instance—is unlikely in any event to tell us more about the nature of the resulting injury than we might learn about a bruised shin by analysing the wood of the misplaced chair that caused the damage. The hope of attributing the general causation of cancer to a specific molecular structure is quite illusory.

The hypothesis of excessive peptization promises more immediate success in the treatment of existing cancers. There is evidence that a cell's activity can be inhibited not only by excessive agglomeration, but also by peptisation if the latter be carried to extremes; the cancer cell is already abnormally peptised to begin with, and a peptising agent can probably be found which, while increasing the dispersion of normal cell colloids to a certain extent but not enough to interfere seriously with their functions, will disperse the malignant cell colloids to the extreme point necessary for inhibition. Preliminary trials should be made of local treatment with the largest possible doses of negative-protein dispersing agents such as ephedrine, sodium thiocyanate or sodium bromide, mild general stimulants perhaps being administered at the same time to counteract the effect on the normal cells.

To characterize malignant cells by the abnormally dispersed condition of their protein is obviously only one step toward the solution of the cancer problem; the basic hypothesis will have to be added to again and again as we acquire more knowledge of the nature and mutual actions of the various external and internal cell secretions. But even in its present simple form the idea is able to unify a great number of observations, of which only a few have been mentioned in this note. Although we must admit that the cancer problem as a whole "will not yield to the sound of a trumpet," it is equally certain that it will not be solved by outworn technical methods such as the staining of cells before microscopic examination, nor by a habit of thought which is content to tabulate facts without correlating ideas.

Wendover,
Bucks.

PHASE RULE STUDIES ON THE PROTEINS. VI*

Non-Aqueous Solutions

BY WILDER D. BANCROFT AND S. LOUISA RIDGWAY**

Historical

When proteins were found to be amphoteric and to contain amino acids, it was assumed without question that true compounds were formed with the acids and bases which the proteins "bound." The later studies of colloid chemistry and adsorption suggested to some that the mechanism of the "binding" might be adsorption rather than compound formation. Van Slyke and Van Slyke[1] were among the first to mention this possibility. They worked in water solution with casein and such dilute acids that no casein dissolved. They measured the acid left over by a conductivity method. After citing twelve references supporting compound formation between acids and proteins; and after carefully going over their own data with reference to the three possibilities of compound formation, solution of acid in protein, and adsorption, they decided that in their case they had adsorption. T. B. Robertson[2] immediately replied to this article to support the theory of compound formation. For each of the criteria of adsorption set up in the first article, he gave examples of chemical reactions which would fulfill it. Van Slyke and Van Slyke[3] answered Robertson to the effect that their differences were partly a matter of the definition of adsorption, and that their criteria determining adsorption could apply equally well to compound formation which is incomplete, reversible, and occurs between changing proportions of the mass of reactants. They said that proteins might form compounds with acids under other conditions, but that they did not believe they did in their case. Robertson in later works[4] has continued to favor compound formation, and in the latest one cited says: "It is now admitted by all observers who have directed adequate attention to this question that the proteins accomplish the neutralization of acids and bases in stoichiometrical, that is, molecular or equivalent-molecular proportions."

In general, some stand is taken for one theory or the other by the various leaders of protein research and by many colloid chemists. Loeb[5] is one of the

---

* This work has been done under the programme now being carried out by Cornell University and supported in part by a grant from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

** Recipient of a grant in aid from the National Research Council.

[1] Am. Chem. J., 38, 383 (1907).

[2] J. Biol. Chem., 4, 35 (1908).

[3] J. Biol. Chem., 4, 259 (1908).

[4] "Die physikalische Chemie der Proteine" (1912); "The Physical Chemistry of the Proteins" (1918); Chapter in Alexander's "Colloid Chemistry", 2 (1926).

[5] "Proteins and the Theory of Colloidal Behavior" (1924).

strongest supporters of the compound theory. He studies proteins from the point of view that they are, at least partially, in true solution and follow the classical laws of stoichiometrical chemistry. He explains physical properties of proteins such as swelling, osmotic pressure, membrane potential, and viscosity on the basis of the Donnan membrane equilibrium, where the non-diffusible ion is a protein ion of a protein salt. This has been criticized by Donnan[1] who says that the Donnan theory rests only on the existence of equilibrium and the existence of certain restraints which restrict the free diffusion of one or more electrically charged or ionized constituents; and that protein with adsorbed acid or basic ions fulfills the second requirement as well as protein ions. Pauli[2] criticized Loeb from a different point of view, namely that there is no restriction of the movement of the particles of protein in solution. He has also been criticized in reviews on his book by Bancroft[3] and by Alexander[4] who feel that his experimental results point as much, or perhaps more, to adsorption than to compound formation.

Procter,[5] Procter and Wilson,[6] Wilson,[7] and Wilson and Wilson,[8] have developed a theory for the swelling of gelatine in dilute acid mathematically based on the Donnan membrane equilibrium and on the assumption that a highly ionized protein salt is formed. Their "chemical combination" would sound very much like adsorption to many chemists for it occurs on colloidal surfaces, is not stoichiometric, and is a function of the concentration of the acid present. They got formulae for both the concentration of the chemically bound electrolyte and the total quantity of electrolyte either combined with or present in the solution in contact with the colloid, as functions of the concentration of the electrolyte in solution. The curves for these functions are approximately the same as those obtained by the use of the ordinary empirical adsorption formula. Here again, Donnan[9] has criticized them in the same way he did Loeb—that proteins with adsorbed ions would give the same results as protein ions. Atkin[10] did work which he thought supported Procter and Wilson. Ghosh[11] confirmed the results of Procter and Wilson on the swelling of gelatine in acid. He derived an equation for the swelling of gelatine on the basis of the Donnan equilibrium, but he made fewer assumptions. He says that it is more likely that acid is adsorbed than combined.

Some of the other workers who in various ways support compound formation are Schmidt, Greenberg, et al.[12] from the University of California,

---

[1] Chem. Rev., 1, 87 (1924).

[2] Alexander: "Colloid Chemistry,", 2, 223 (1926).

[3] J. Phys. Chem., 26, 687 (1922).

[4] Chem. Met. Eng., 27, 368 (1922).

[5] J. Chem. Soc., 105, 313 (1914).

[6] J. Chem. Soc., 109, 307 (1916).

[7] J. Am. Chem. Soc., 38, 1982 (1916).

[8] J. Am. Chem. Soc., 40, 886 (1918).

[9] Chem. Rev., 1, 87 (1924).

[10] J. Soc. Leather Trades' Chem., 4, 248, 268 (1920).

[11] J. Chem. Soc., 711 (1928).

[12] J. Biol. Chem., 25, 63 (1916); J. Gen. Physiol., 7, 287, 303, 317 (1924-25); 8, 271 (1925-26); Univ. of Cal. Publications in Physiol., 5, 289, 307 (1926); 7, 9 (1927).

Hitchcock,[1] Lloyd and Mayes,[2] and Cohn.[3] Others besides those already mentioned who favor adsorption are Moeller,[4] de Izzaguirre,[5] Shukoff and Stschoukareff,[6] and Fanselow.[7] Tolman and his co-workers[8] have a theory of the swelling of proteins in acid and alkali which is based on adsorption. This adsorption they suppose is of a chemical nature and occurs in the case of acids on the free amino groups and in the case of alkalies probably on enolized —COHN— groups.

Gortner and his associates[9] believe that between pH 2.5 and 10.5 there is true compound formation, and that at a pH above or below these limits, there is true adsorption. They have performed numerous and careful experiments on which they base this belief.

In an effort to distinguish between the two possibilities of compound formation and adsorption, many experiments have been made. Although the supporter of each theory can see proof for his own theory in his experiments, very often his opponent can see proof for the opposite one in the same experiments. Frequently the opponents appear to be separated further than is actually the case by a disagreement in the definition of terms, but there still remain two distinct possibilities, either of which, or both, may take place in a given case. The criteria which distinguish between the two are not sufficiently clear-cut under most of the experimental conditions employed. Bancroft and Barnett,[10] and Belden[11] performed some experiments of such a nature that the results show definitely whether there has been compound formation or adsorption, or both, under the conditions of the experiment in any given case. They treated solid proteins with gaseous HCl and NH_3 in a special apparatus. If a compound formed, the pressure remained constant over the two solid phases as long as they both existed; if an adsorption complex formed, the pressure varied continuously. Casein, arachin, fibrin, gliadin, edestin, and gelatine were found to form compounds with HCl with subsequent adsorption of further acid on the compound formed. Zein simply adsorbed HCl. Casein, zein, arachin, fibrin, gliadin, and gelatine adsorbed NH_3 without any indication of compound formation. This method is obviously not applicable to caustic soda. People might claim that a strong base would react stoichiometrically with the proteins.

Introduction

The present work follows directly that of Bancroft, Barnett, and Belden. We have attempted to extend their method to apply to acids and bases, which

---

[1] J. Gen. Physiol., 4, 597, 733 (1921-22); 5, 383 (1922-23); 6, 95 (1923-24); 12, 495 (1928-29); 14, 99 (1930-31).

[2] Proc. Roy. Soc., 93B, 69 (1922).

[3] Physiol. Rev., 5, 349 (1925).

[4] Collegium, 319, 382 (1920).

[5] Kolloid-Z., 32, 47 (1923).

[6] J. Phys. Chem., 29, 285 (1925).

[7] Colloid Symp. Mon., 6, 237 (1928).

[8] J. Am. Chem. Soc., 40, 264 (1918); 41, 1503, 1511 (1919).

[9] Colloid Symp. Mon., 2, 209 (1925); J. Phys. Chem., 34, 1071 (1930).

[10] J. Phys. Chem., 34, 449, 753, 1217, 1930, 2433 (1930).

[11] J. Phys. Chem., 35, 2164 (1931).

are not necessarily gases. The acid or base is dissolved in some solvent, chemically inert to the system, which does not dissolve the protein or the product formed. Varying amounts of the acid or basic solution are added to known weights of the protein and sufficient solvent added to make the volume a convenient and definite one. When equilibrium has been reached, some of the supernatant liquid is pipetted off and the excess acid or base determined by titration. From these data the amount of acid or base taken up per gram of protein may be calculated. These values are plotted against the acidity or basicity of the supernatant liquids.

On the basis of the phase rule, we may predict the types of curves which will be obtained, and explain their significance. Suppose first that an adsorption complex forms and there is never more than one solid phase present. There are three components—protein, acid or base, and solvent. There are three phases—one solid, one liquid, one vapor. Then, since $F = C - P + 2$ (where F = the number of degrees of freedom, C = the number of components, and P = the number of phases), $3 - 3 + 2 = 2$. The temperature is fixed at room temperature, using up one degree of freedom. One variable is left—that of the concentration of the liquid phase. If a compound is formed instead of an adsorption complex, there are two solid phases until the protein is entirely used up, and therefore only one degree of freedom in that range. Since the temperature is fixed, there is no variable left. In the presence of two solid phases, then, the composition of the liquid must remain fixed. A smooth, continuously varying, curve indicates adsorption; one with a "flat" showing constant composition for the liquid phase indicates a compound. This method was used with success by Kawamura[1] on stearic and humic acids with NaOH in water.

Preliminary Experiments

Proteins are very complex bodies and there has been much controversy as to the character of their combination with acids and bases. In order to test thoroughly the method outlined above, it was first tried on some solid basic and acidic substances for which the results could be predicted accurately.

1. *Succinic Acid*—It is difficult to find a fairly simple carboxylic acid which is not quite appreciably soluble in any solvent which could be used with proteins. Succinic acid and isobutyl alcohol were chosen as the best available pair although at 25° the acid is soluble to the extent of nearly three percent in the alcohol. This is much greater than we should like for a test case, and affects considerably certain portions of the curve. The curve should show two flats corresponding to the mono- and di-sodium salts. There might or might not be adsorption on the latter.

Experimental work on the acid immediately presented a second difficulty. The di-sodium salt formed in such a way as to coat the solids in the system almost completely and to hinder greatly the attainment of equilibrium. The first experiment was carried out with sodium isobutylate in absolute isobutyl alcohol in an effort to cut down the water content of the system and therefore

---

[1] J. Phys. Chem., 30, 1364 (1926).

TABLE I

Summary of the Runs on Succinic Acid

No.	Substance treated	Base used	Solvent	Time of run	Special treatment*	Result
1.	Succinic acid	Sodium isobutylate	Absolute isobutyl alcohol	7 days	W 1 day	Equilibrium not reached
2.	"	NaOH	"	3 days	W 2 days	"
3.	"	"	"	7 days	W 5 days	Approximate flat for mono salt, then no equilibrium.
4.	NaH succinate	"	"	6 days	W 6 days	Equilibrium not reached
5.	"	"	"	1½ days	R 22½ hrs.	"
6.	Succinic acid	NaOH up to 1 equivalent	95% isobutyl alcohol	1 day	R 18 hrs.	Some ester formation and solution of rest
7.	NaH succinate	NaOH	"	5¼ days	R 5¼ days	Flat for di-sodium salt and complete adsorption on it
8.	"	"	"	4¼ days	R 2 days	"
9.	Succinic acid	"	"	11 days	S 140 hrs.	See Fig. 1. and Table II

* W = warm (at 50°-60° on top of an oven).
R = refluxed.
S = shaken in a mechanical shaker. See p. 1303.

the solubility of the succinic acid. From that first trial to the final attainment of the desired results, Table I shows the methods used and their measures of success.

It is obvious that the presence of a small amount of water hastens equilibrium, probably because of the greater solubility of the acid and its salts. The acid sodium succinate was used in order to facilitate the obtaining of the second flat, although it was later found to be unnecessary. It was made by adding standard NaOH to a weighed quantity of succinic acid, evaporating the water, and drying. Its purity was determined by finding the neutral equivalent.

Runs 6–8 in Table I, plotted on the same graph, give a curve of the sort that ought to be obtained, but which still leaves much to be desired. The conditions for the three runs were not the same; and there was considerable ester formation between the refluxing alcohol and the unused acid or acid salt. A final run (No. 9), using succinic acid with NaOH in 95% isobutyl alcohol, was made. It stood for eleven days and was shaken in a mechanical shaker about 140 hours of that time. Equilibrium, as indicated by activity to phenolphthalein, had been reached in numbers 1–9 in about four days, but time was given for the rest to come to equilibrium. Ester formation was separately determined to be about 5% in number 1 where it would be greatest. The results are given in Table II and Fig. 1.

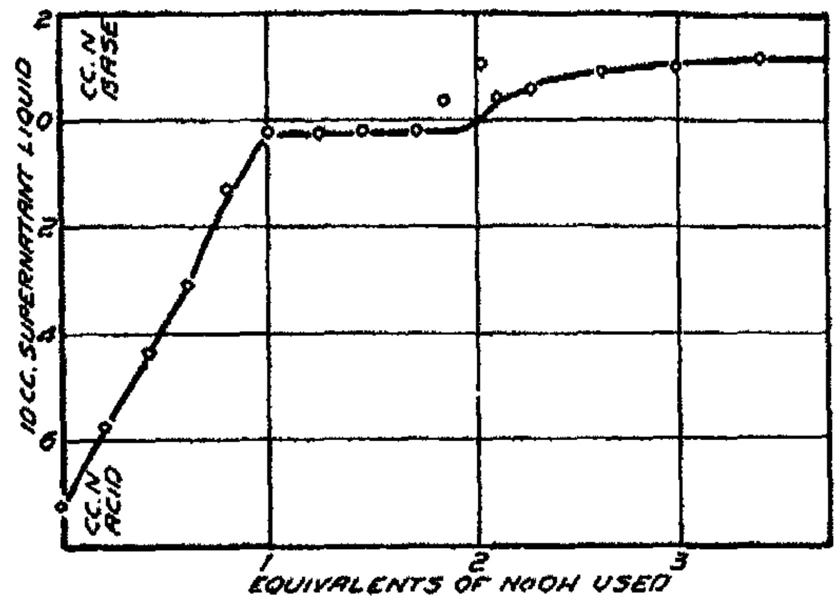


Fig. 1
Succinic Acid and NaOH in 95% Isobutyl Alcohol

Table II

Succinic Acid and NaOH in 95% Isobutyl Alcohol

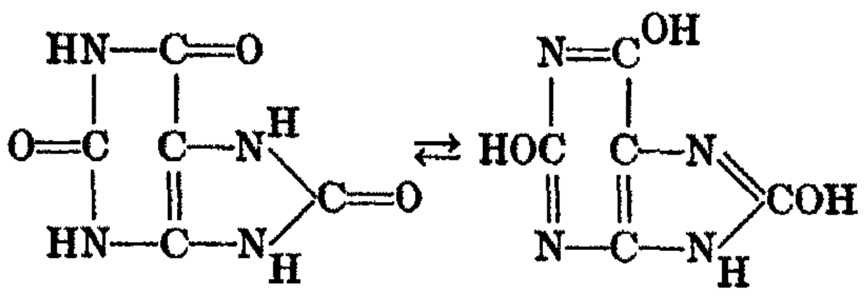
1 gm. succinic acid, which requires 16.94 cc. of N NaOH for complete neutralization, taken for each number

Length of run—11 days

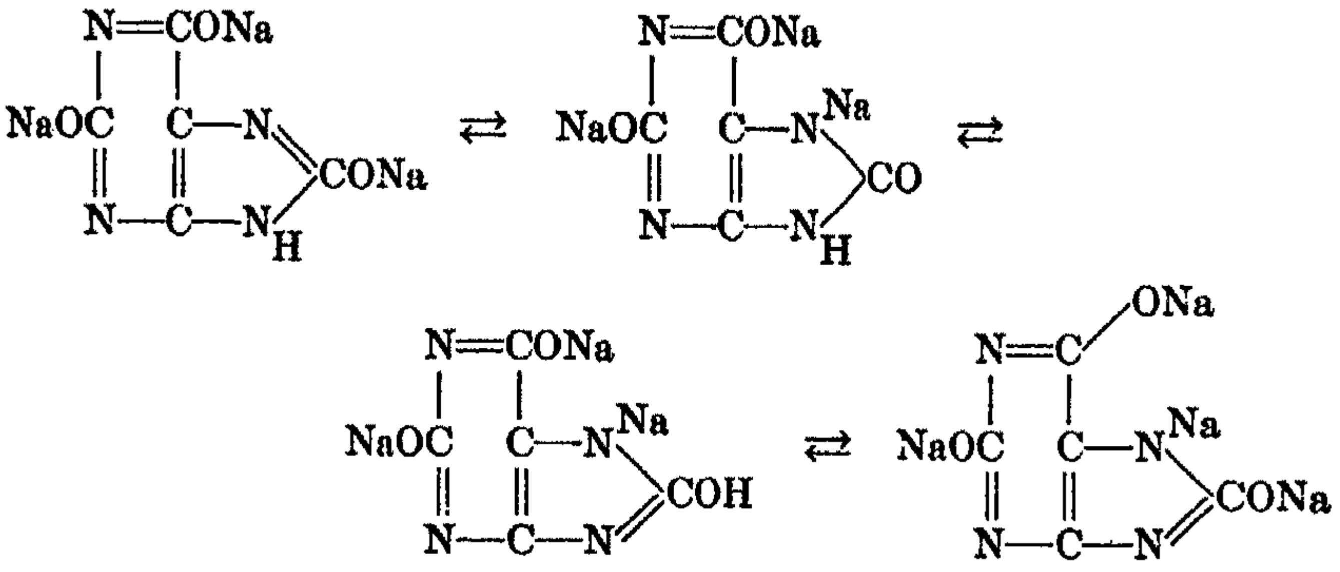
No.	a cc. N NaOH added	b Total vol. of liquid added cc.	c cc. N acid (or base) for 10 cc. sup. liq.	d cc. N base in super. liquid c × b/10	e cc. N base used a − d	f Equiv. of NaOH used e/8.47
1.	0.00	20	7.20 base	—	0.00	0.00
2.	1.80	20	5.77 "	—	1.80	0.21
3.	3.60	20	4.32 "	—	3.60	0.43
4.	4.95	20	3.11 "	—	4.95	0.59
5.	6.75	20	1.30 "	—	6.76	0.80
6.	8.56	20	0.24 "	—	8.56	1.01
7.	10.81	40	0.24 "	—	10.81	1.24
8.	12.61	40	0.24 "	—	12.61	1.46
9.	14.86	40	0.22 "	—	14.86	1.72
10.	17.11	40	0.34 acid	1.36	15.75	1.83
11.	18.97	40	0.32 "	1.27	17.69	2.09
12.	21.55	40	0.53 "	2.12	19.43	2.29
13.	23.42	60	1.04 "	6.26	17.16	2.03
14.	25.86	40	0.90 "	3.60	22.26	2.63
15.	29.31	40	0.99 "	3.94	25.37	3.00
16.	33.62	40	1.13 "	4.54	29.09	3.43

The curve has three distinct parts. From 0 to 1 equivalent, the curve is a measure of the acid in solution after all the NaOH present has been used. If there had been more acid in proportion to alcohol, there would have been a horizontal line extending some short distance from the vertical axis along which would lie points determined from systems in which both solid acid and sodium acid succinate were in contact with the liquid at equilibrium. Actually we had no such points. From 1 to almost 2 equivalents, there is the flat due to the formation of normal sodium succinate. The sloping portion just before 2 equivalents is due to the slight solubility of the acid salt in the alcohol. The rest of the curve shows adsorption of alkali on the normal salt. The amount of adsorption depends on conditions. In the first curve obtained, it was complete.

2. *Uric Acid*—Although uric acid is not a true carboxylic acid, it was used next because of its very low solubility in alcohol. Its formula is:—



and it owes its weak acid powers to the hydrogens in the $\geqq$COH groups of the enolic form. From the formula it may be seen that it is theoretically possible to replace three H atoms by metals. If the metal can shift to the N as does the H in forming the keto form, there is the possibility of the fourth H being replaced by metal, i.e.



If this is so, four flats may be obtained. Each may be separate, or if the alkali necessary to keep them from decomposing is practically the same, two or more may be along the same level. Uric acid is, however, generally known as a weak dibasic acid. The enolization of two groups may suppress further enolization.

The work done on uric acid was at first similar to that on succinic acid, and the same difficulty of obtaining equilibrium was encountered. The various runs on uric acid are summarized in Table III. In absolute alcohol (Runs 1–3), no compound formation was obtained although mono-sodium urate is a

TABLE III

Summary of the Runs on Uric Acid

No.	Substance treated	Base used	Solvent	Time of run	Special treatment*	Result
1.	Uric acid	sodium isobutylate	Absolute isobutyl alcohol	4 days	W 1 day	Apparent adsorption—rough curve
2.	"	NaOH	"	3 days	W 2 days	Apparent adsorption
3.	"	"	"	2 days	R 10½ hours	Scattered points approaching a flat to 2 equivalents
4.	"	"	99% isobutyl alcohol	"	"	Flat to 2 equivalents, then adsorption
5.	"	"	95% isobutyl alcohol	2 days	W 2 days	Flat to 2 equivalents, and a flat for the 3rd and one for the 4th equivalent
6, 7, 8.	"	"	"	3 days	W 2 days	
9.	Mono Na urate	"	Absolute isobutyl alcohol	3 days	W 3 days	Flat to 2 equivalents, then complete adsorption to 2.4 equivalents, and some little further adsorption
10.	"	"	"	4 days	W 2 days	
11.	"	"	"	5 days	W 2½ days	
12.	Uric acid	"	95% ethyl alcohol	18 days	S 50 hrs.	Flat up to 1.1 equivalents, then apparent adsorption
13.	"	"	"	6¼ days	W 5½ days S occasionally	Flat up to nearly 2 equivalents, then apparent adsorption
14.	"	"	"	37 days	W 35 days	Flat to 2 equivalents, then very little adsorption

* W = warm (at 50°-60° on top of an oven).
R = refluxed.
S = shaken in a mechanical shaker. See p. 1303.

definite and well-known compound. With the addition of a small amount of water (Runs 4–8), compound formation occurred. The question immediately came up as to whether there were true adsorption or a lack of equilibrium conditions in the anhydrous medium. The third run by approaching a flat, favors the latter view, although it may be argued that under the vigorous conditions of the experiment, any small amount of water in the alcohol (which was not specially treated) could be utilized. In order to test experimentally between adsorption and compound formation without equilibrium, further runs were made. If any curve represents equilibrium conditions it should be possible to reach it from either side. In this case mono-sodium urate put into absolute isobutyl alcohol containing less than equilibrium amounts of NaOH, should give up NaOH until equilibrium is reached. Accordingly mono-sodium urate was made. (This was done by adding the requisite amount of uric acid, evaporating to dryness, and air drying. It was acid to phenolphthalein, showing the absence of free NaOH, and alkaline to methyl red.) Runs 9–11 show that instead of reaching the apparent adsorption curve, there was still further compound formation.

However, Beilstein and Meyer and Jacobson[1] state that mono-sodium urate contains one molecule of water of crystallization. Certain compounds are known to exist only with molecules of solvation, as for example $KI_3 \cdot H_2O$ and $KI_7 \cdot H_2O$.[2] If the mono-sodium urate could not exist without this molecule of water, we would have a very logical explanation for adsorption in absolute alcohol and compound formation in alcohol containing water. When moisture determinations were run on the salt, which had been made in the usual way (drying at 110° and then evacuating to about 11 mm. of mercury) less than three percent of moisture was obtained. One molecule of water of crystallization would correspond to 9.47%. By heating to 140°–150° for three weeks, about 5% of moisture was driven off (or the compound may have slowly volatilized). Determination of the nitrogen by the Kjeldahl method was finally resorted to as the simplest and most accurate method. It gave a moisture content of 11.62%, and showed that if the salt could exist without water of crystallization, the water was at least very firmly bound. As a final test of this point, nearly anhydrous mono-sodium urate was put into absolute isobutyl alcohol. (Mono-sodium urate containing only 0.5% moisture was prepared by heating the moisture-containing salt to 140°–150° in an oil bath while simultaneously evacuating to less than 10 mm. of mercury for a period of about 15 hours.) The anhydrous salt lost no free NaOH in 15 days as indicated by neutrality of the supernatant liquid to phenolphthalein. It is, therefore, possible for the mono-sodium urate to exist in absolute isobutyl alcohol without water of crystallization. Equilibrium in the anhydrous alcohol is reached very slowly, and adsorption is simulated. This is an important warning.

After the formation of the mono-sodium salt, the formation of the di-sodium salt occurs with relative ease. In 95% isobutyl alcohol (Runs 5–8), there is then clear indication of the formation of the tri- and tetra-sodium

---

[1] "Lehrbuch der organischen Chemie," 2 III, 1307 (1920).

[2] Grace: J. Chem. Soc., **1931**, 594.

Table IV

Uric Acid and NaOH in 95% Isobutyl Alcohol

1 gm. uric acid, which requires 5.95 cc. of N NaOH to form the mono-sodium salt, used for each number

Length of run—3 days

Kept at 50°–60° for 2 days

No.	a cc. N NaOH added	b Total vol. of liquid added cc.	c cc. N acid (or base) for 10 cc. sup. liq.	d cc. N base in super. liquid c × b/10	e cc. N base used a − d	f Equiv. of NaOH used e/5.95
1.	0.00	20	0.01 base	0.00	0.00	0.00
2.	1.14	20	0.03 "	0.00	1.14	0.19
3.	2.28	20	0.04 "	0.00	2.28	0.39
4.	4.56	20	0.04 "	0.00	4.56	0.75
5.	5.70	20	0.05 "	0.00	5.70	0.97
6.	6.84	20	0.06 "	0.00	6.84	1.17
7.	9.13	20	0.00 "	0.00	9.13	1.54
8.	11.41	20	0.00 "	0.00	11.41	1.93
9.	13.69	20	0.01 acid	0.01	13.68	2.31
10.	15.17	20	0.15 "	0.29	4.88	2.50
11.	16.25	20	0.17 "	0.33	5.92	2.68
12.	17.33	20	0.15 "	0.29	17.04	2.86
13.	18.42	20	0.17 "	0.33	18.09	3.04
14.	20.58	20	0.25 "	0.51	20.08	3.37
15.	3.61	20	0.01 base	0.00	3.61	0.61
16.	8.50	20	0.00 "	0.00	8.50	1.43
17.	10.61	20	0.01 acid	0.01	10.60	1.78
18.	12.63	20	0.04 "	0.09	12.54	2.11
19.	17.13	20	0.21 "	0.42	16.72	2.81
20.	19.39	30	0.18 "	0.54	18.85	3.17
21.	21.24	30	0.26 "	0.77	20.48	3.44
22.	23.00	30	0.40 "	1.21	21.78	3.66
23.	2.18	20	0.10 base	0.00	2.18	0.37
24.	3.82	20	0.11 "	0.00	3.82	0.64
25.	6.00	20	0.01 "	0.00	6.00	1.01
26.	11.99	30	0.01 acid	0.04	11.96	2.01
27.	13.09	30	0.03 "	0.08	13.01	2.19
28.	14.18	30	0.05 "	0.16	14.01	2.36
29.	19.27	30	0.19 "	0.58	18.69	3.14
30.	23.00	30	0.30 "	0.90	22.09	3.71
31.	23.90	40	0.26 "	1.03	22.87	3.84
32.	25.97	40	0.30 "	1.20	24.77	4.16

salts. (See Table IV and Fig. 2) Each flat is extended somewhat beyond its theoretical limit by adsorption of alkali on it. The amount of alkali in equilibrium with each of them is nearly the same. In 95% ethyl alcohol (Runs 12-14), the formation of the di-sodium salt is very much slower than it is in 95% isobutyl alcohol. Run 14 (Table V and Fig. 2), showing only apparent adsorption on the di-sodium salt, would certainly have been taken as the equilibrium curve if the work in isobutyl alcohol had not been done first. But if the tri- and tetra-sodium salts are formed in one case, they must be in the other, unless we make the assumption that they exist only with molecules of one of the solvents as part of the compound. Uric acid was treated in isobutyl alcohol with NaOH, so as to contain about three equivalents of alkali. This was put into 95% ethyl alcohol containing such an amount of NaOH that it was less than that required by the curve for Run 14, and too much for that required by the curves from Runs 8–11. After standing at about 40° for three weeks, no change was appreciable in the composition of either the solid or liquid phases. But after refluxing for 22 ½ hours, the composition of the solid and liquid approached closely a point on the curve for isobutyl alcohol.

TABLE V

Uric Acid and NaOH in 95% Ethyl Alcohol

1 gm. uric acid, which requires 5.95 cc. of N NaOH to form the mono-sodium salt, used for each number

Length of run—37 days Kept at 40°–60° for 35 days

Total volume at liquid added—25 cc.

No.	a cc. N NaOH added	b cc. N acid (or base) for 10 cc. sup. liq.	c cc. N base in super. liquid b × 2.5	d cc. N base used a − c	e Equiv. of NaOH used d/5.95
1.	1.15	0.03 base	0.00	1.15	0.19
2.	3.45	0.03 "	0.00	3.45	0.58
3.	5.75	0.02 "	0.00	5.75	0.97
4.	6.90	0.01 "	0.00	6.90	1.16
5.	9.20	0.01 "	0.00	9.20	1.55
6.	10.35	0.00 "	0.00	10.35	1.74
7.	12.65	0.02 acid	0.04	12.61	2.12
8.	14.95	0.62 "	1.54	13.41	2.25
9.	16.10	0.50 "	1.25	14.85	2.50
10.	18.40	1.80 "	4.51	13.90	2.34
11.	19.55	2.22 "	5.54	14.01	2.35
12.	21.85	2.95 "	7.27	14.48	2.43
13.	23.00	2.97 "	7.42	15.58	2.62
14.	25.30	3.96 "	9.91	15.39	2.59
15.	26.45	4.57 "	11.43	15.02	2.52
16.	28.75	5.31 "	13.80	14.95	2.51

This gave a strong confirmation of the correctness of that curve and of the formation of the tri- and tetra-sodium salts. Equilibrium in 95% ethyl alcohol is reached very slowly indeed in the last part of the curve.

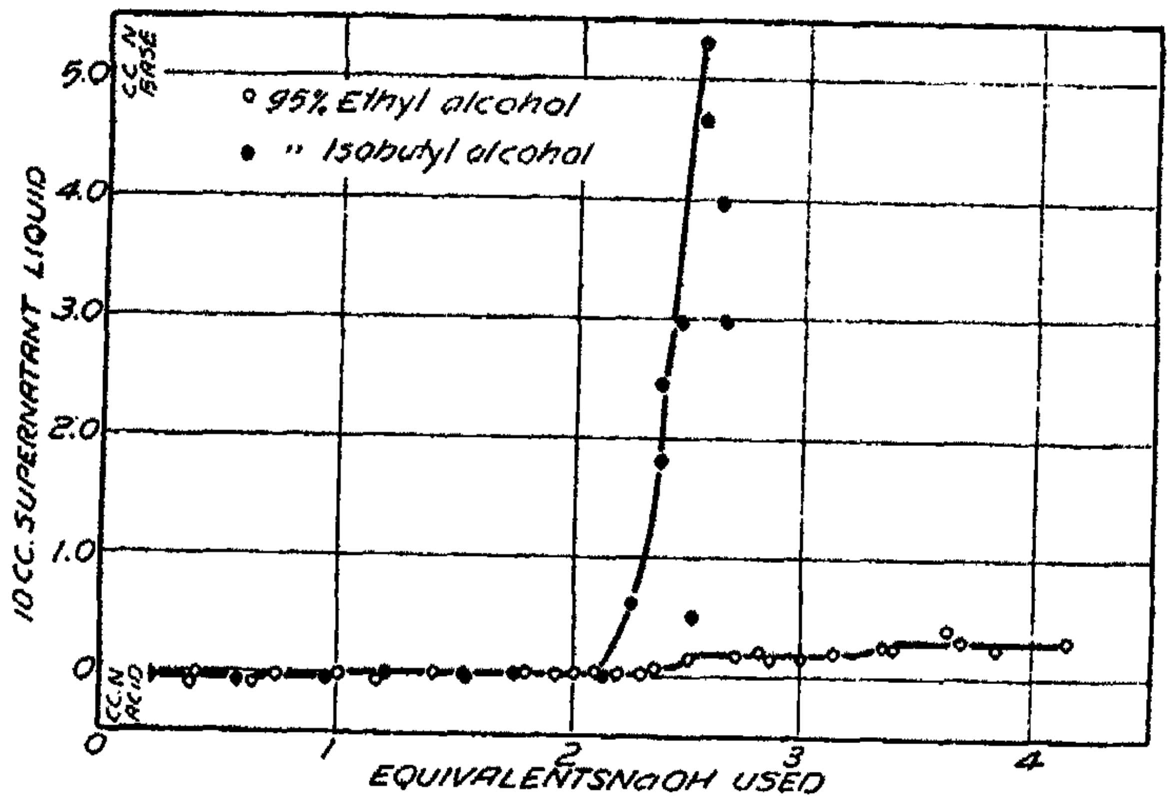
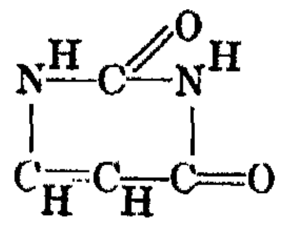


Fig. 2
Uric Acid and NaOH

3. *Uracil.*

Uracil has the formula



which shows its relation to uric acid. According to Levene and Bass,[1] it is a mono-basic acid. Either of the keto groups in the above formula may enolize to give the acidic properties, but enolization of one group inhibits that of the other. They say it does not react with acids. If the formula given above is the only one considered, it should not react with acids according to the criteria set forth by Bancroft and Barnett.[2] However they found that it did react with gaseous HCl at 20 mm. pressure.[3] They give four alternative formulae, each obtained by a shift of one hydrogen, which would account for this reaction.

When we treated uracil with NaOH in 95% ethyl alcohol, it formed the sodium salt quite readily. The salt was a voluminous precipitate and tended to cake, but alternate shaking and heating to 50°-60° obviated this difficulty and quickened the speed of the reaction. Data are given in Table VI and Fig. 3. With HCl there was no compound formation and very little adsorption even after three days of refluxing.

---

[1] "Nucleic Acids" (1931).

[2] J. Phys. Chem., 34, 753 (1930).

[3] J. Phys. Chem., 34, 1244 (1930).

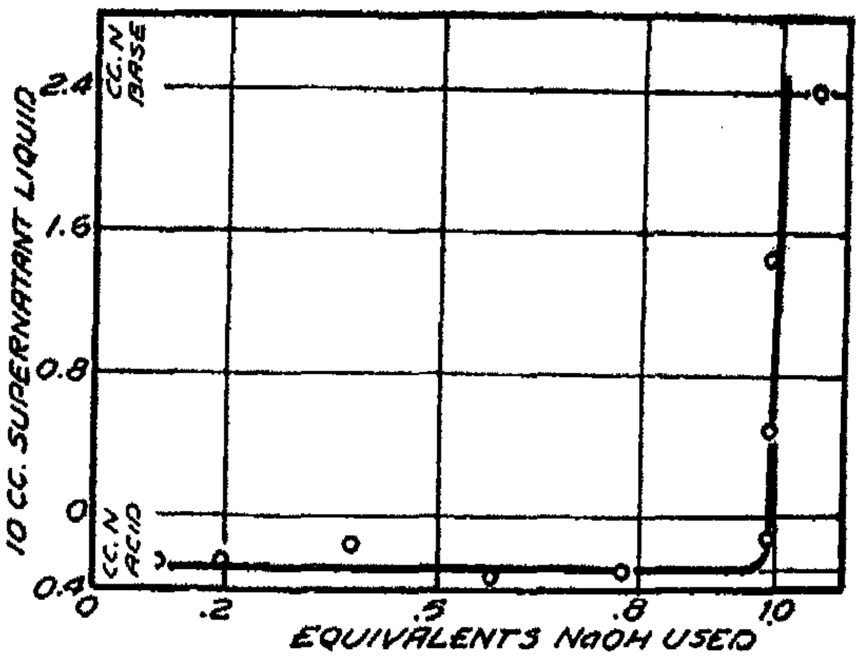


FIG. 3
Uracil and NaOH in 95% Ethyl Alcohol

TABLE VI

Uracil and NaOH in 95% Ethyl Alcohol

0.5602 gm. uracil, which theoretically reacts with 5 cc. N NaOH, used for each number

Volume in each number—20 cc.

Kept at 50°-60° for 4 days
Shaken occasionally

No.	a cc. N NaOH added	b cc. N acid (or base) for 10 cc. sup. liq.	c cc. N base in super. liquid b × 2	d cc. N base used a − c	e Equiv. of NaOH used d/5
1.	0.56	0.26 base	0.00	0.56	0.11
2.	1.01	0.26 "	0.00	1.01	0.20
3.	1.91	0.16 "	0.00	1.91	0.38
4.	2.91	0.33 "	0.00	2.91	0.58
5.	3.92	0.30 "	0.00	3.92	0.78
6.	4.93	0.10 "	0.00	4.93	0.99
7.	5.94	0.50 acid	0.99	4.95	0.99
8.	7.84	1.46 "	2.91	4.93	0.99
9.	10.09	2.39 "	4.78	5.31	1.06

3. *Alanine*—Alanine was chosen as typical of amino acids which would show a behavior more similar to the proteins than any simpler substances. It is insoluble in alcohol. When NaOH in 95% ethyl alcohol was added to the alanine, there was some peptization which became more apparent as the strength of the alkali increased and became complete when one equivalent or more of base had been added. The peptization of the product seemed to render the method useless for alanine, and to make it of doubtful value for proteins. Efforts were made to save the method. Various solvents such as

ether, benzene, carbon tetrachloride, and isobutyl alcohol were added in an unsuccessful attempt to precipitate the sodium salt of the alanine which was known to be present. Several tests were made which convinced us that the sodium salt was peptized rather than in true solution. For instance the sodium salt of the alanine, which was made in the same way as those of succinic and uric acids, was insoluble in alcohol. The sodium salt, put into apparent solution in alcohol by NaOH, was dialyzed against alcohol, and practically nothing went through the membrane. Then it was found that solid sodium alaninate did not interfere with the titration of NaOH by acid in alcoholic solution, using phenolphthalein as indicator. Since the peptized sodium alaninate is simply finely divided solid, it should not interfere with the titra-

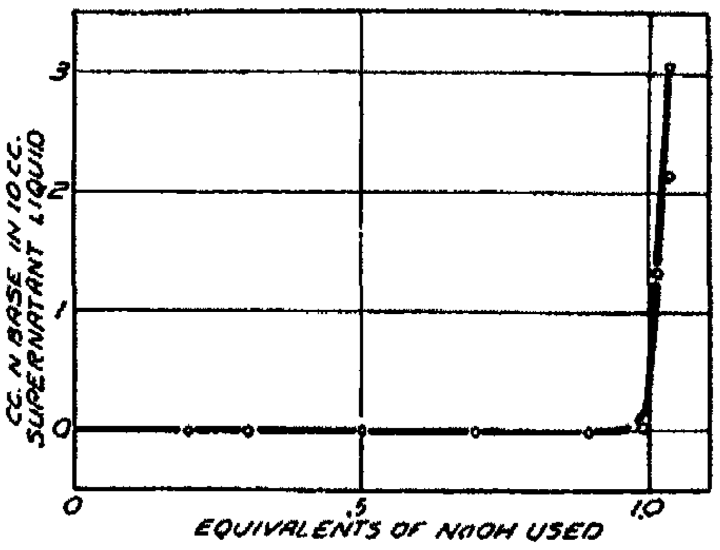


Fig. 4
Alanine and NaOH in 95% Ethyl Alcohol

Table VII

Alanine and NaOH in 95% Ethyl Alcohol

0.8906 gm. alanine, which theoretically reacts with 10 cc. N NaOH, used for each number

Total volume of liquid added was 22 cc. in each case

Length of run—3 days

No.	a cc. N NaOH added	b cc. N acid for 10 cc. sup. liq.	c cc. N base in super. liquid b × 2.2	d cc. N base used a − c	e Equiv. of NaOH used d/10
1.	2.00	0.00	0.00	2.00	0.20
2.	3.00	0.00	0.00	3.00	0.30
3.	5.00	0.00	0.00	5.00	0.50
4.	7.00	0.00	0.00	7.00	0.70
5.	9.00	0.00	0.00	9.00	0.90
6.	10.00	0.05	0.11	9.89	0.99
7.	13.00	1.34	2.94	10.06	1.01
8.	15.00	2.14	4.71	10.29	1.03
9.	17.00	3.05	6.71	10.29	1.03

tion of unused NaOH by acid. It was found to behave in the expected manner, and the method was therefore applicable if the supernatant liquid were titrated in alcoholic solution. The titration was found to be more satisfactory when thymolphthalein was used as indicator. The data in Table VII and the curve in Fig. 4 show the result of this modification of the method.

When alanine was treated with HCl in 95% ethyl alcohol, peptization occurred in the same way as with the NaOH. A very similar method was used to titrate the excess acid in the supernatant liquid. It was done in alcoholic solution using the acid change of thymol blue as indicator. The results are not as gratifying as those with NaOH and thymolphthalein, and the curve leaves some doubt of compound formation; but the break in the curve occurs at just about the theoretical point. This is shown in Table VIII and Fig. 5.

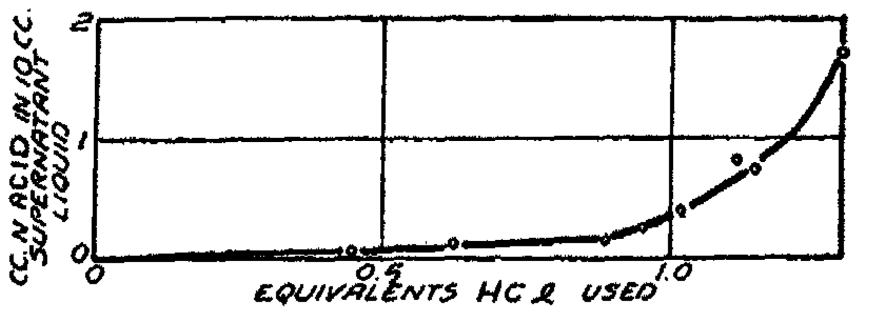


Fig. 5

Alanine and HCl in 95% Ethyl Alcohol

If a suspension of finely powdered alanine in alcohol is used, alcoholic base may be added directly and a direct titration of the amino acid with alkali may be made, using thymolphthalein as indicator. There must be constant shaking and a permanent blue must be reached. The titration takes from 20

Table VIII

Alanine and HCl in 95% Ethyl Alcohol

0.8906 gm. alanine, which theoretically reacts with 10 cc. N HCl, used for each number

Total volume of liquid added was 20 cc. in each case, except 7 which was 30 cc.
Length of run—4 days

No.	a cc. N HCl added	b cc. N base for 10 cc. sup. liq.	c cc. N acid in super. liquid b × 2	d cc. N acid used a − c	e Equiv. of HCl used d/10
1.	4.57	0.06	0.12	4.45	0.45
2.	6.39	0.12	0.23	6.16	0.62
3.	9.13	0.15	0.31	8.82	0.88
4.	10.04	0.25	0.50	9.54	0.95
5.	10.96	0.39	0.77	10.19	1.02
6.	12.78	0.81	1.61	11.17	1.12
7.	13.70	0.73	2.18	11.52	1.15
8.	16.43	1.72	3.45	12.99	1.30

to 30 minutes for a gram of alanine. This is similar to the alcoholic titration worked out by Foreman,[1] Willstätter and Waldschmidt-Leitz,[2] and Harris;[3] and which has been used by many others[4] in its original or a modified form. This titration was not known to us until after the work on alanine had been done. It seems to have been overlooked by many others besides ourselves, although it appears to be a common and useful tool among biochemists. We have found it indispensable.

It depends on the fact that in alcoholic solution, most weak acids, bases, and ampholytes are neutral to the rather high or low pH change of the indicators used. Salts, as they are formed during titration with strong acid or base, do not hydrolyze and therefore do not react with the indicator. After the end-point has been reached, any excess strong acid or base added will affect the indicator. If an appreciable amount of the acid or base is needed to bring a volume of alcohol equal to that in the titration flask to the end-point of the indicator, that amount must be subtracted as a blank from the results obtained. The use of this method of titration obviously limits us to the reactions of strong acids and bases with the substances we wish to examine.

The facts of the alcoholic titration are quite adequately and easily described in the foregoing paragraph, but the theory is not so readily explained. This is partly because experimental work supporting a theory of acidimetry depends on accurate measurements of hydrogen ion concentration. These are difficult to make in non-aqueous solutions and still involve certain assumptions which probably introduce errors. It is generally agreed, however, that the degree of dissociation is less in alcohol and most other non-aqueous solvents than in water, for it depends on the dielectric constant of the solvent. Walden[5] finds as an approximation that $D_1:D_2 = \sqrt[3]{v_1} : \sqrt[3]{v_2}$, where D_1 and D_2 are the dielectric constants of the solvents and v_1 and v_2 are the dilutions of a strong electrolyte when the amount of dissociation is equal. Dissociation constants have been determined conductometrically in alcohol by Hartwig[6] for formic, acetic and butyric acids, and by Goldschmidt[7] and his co-workers for quite a number of organic acids and bases. Constants were determined potentiometrically in alcohol by Michaelis and Mizutani[8] for acetic, propionic, lactic, salicylic, benzoic, phosphoric and carbonic acids, ammonia, glycine, and amino-benzoic acid. They are lower than in water.

Then an acid is weaker in alcohol than in water, and if other conditions are the same, it should have a smaller range of pH at the point where an

---

[1] Biochem. J., **14**, 451 (1920).

[2] Ber., **54B**, 2988 (1921); Z. physiol. Chem. **161**, 191 (1926).

[3] Proc. Roy. Soc., **95B**, 440, 500 (1923); **97B**, 364 (1925); **104B**, 412 (1929).

[4] Schidrowitz: Analyst, **28**, 233 (1903); Sutton: "Volumetric Analysis," 8th edit. p. 38 (1900), (This is the reference which gave Foreman his clue); Vorländer: Ann., **341**, 73, 75 (1905); Ber., **52B**, 309 (1919); Birckner: J. Biol. Chem., **38**, 245 (1919); Woodman: J. Agri. Science, **12**, 231 (1922); Bishop, Kittridge, and Hildebrand: J. Am. Chem. Soc., **44**, 135 (1922); Martens: Bull. Soc. chim. biol., **9**, 454 (1927).

[5] Z. physik. Chem., **54**, 228 (1905); **94**, 263 (1920).

[6] Wied. Ann., **33**, 58 (1888); **43**, 838 (1891).

[7] Z. physik. Chem., **89**, 129 (1914); **91**, 46 (1916); **99**, 116 (1921).

[8] Z. physik. Chem., **116**, 135 (1925).

equivalent amount of base has been added and should accordingly have a less distinct end-point. But there is very little alcoholysis (corresponding to hydrolysis) so the break in the titration curve at the equivalent point is very much sharper and the end-point is also much sharper. The amount of alcoholysis is low, for although the dissociation of the acid is less, that of the alcohol is very much less than that of water.[1] If the salt formed is soluble in the alcohol, the pH at which the break or vertical portion of the titration curve commences will be relatively high due to the depressing effect of the salt on the ionization of the acid. If the salt is absolutely insoluble, the vertical portion of the titration curve can not start above the pH of the neutral solvent; for only acid will be present until it is all used up, and by definition acid dissociates to give hydrogen ions. Then the titration curve of all acids forming insoluble salts with a given base will be the same above the pH of the neutral solvent. This of course is a limiting case and is never actually realized. It would however tend to lower the pH of an end-point. Similar reasoning applies to weak bases.

We have left out of our discussion the effect of the alcohol on the pH range of the indicator, for we do not know accurately what it is. Hildebrand[1] has shown that the relative pH ranges are the same for the majority of indicators, but that some are shifted (i.e. cyanine is more acid in alcohol).

Experimentally, we find these facts. Very weak acids, such as the phenols and certain inorganic acids—boric, hydrocyanic, etc.—can not be titrated in water solution. Neither can they be titrated in alcoholic solution, but a larger proportion of the equivalent alkali may be added before the indicator is affected. In the case of boric acid with thymolphthalein in alcohol, the end-point is quite good, so that probably a given percentage could be titrated consistently. The carboxylic acids with the exception of the amino acids, may be titrated satisfactorily in water with phenolphthalein. In alcohol, though the dissociation constants are less, and they are consequently weaker, they can still be titrated with phenolphthalein. Sodium carbonate, which is the salt of an acid of strength intermediate between the carboxylic acids and the phenols, is acid to thymolphthalein in alcohol. It gives phenolphthalein a faint pink color. It is strongly alkaline to both these indicators in water.

When we come to apply this reasoning to amino acids, we may assume, as has been done until recently, that they dissociate either as a weak acid or base to give hydrogen or hydroxyl ions, according to the equations:

$$H_2N\text{-}R\text{-}COOH \rightleftarrows H_2N\text{-}R\text{-}COO^- + H^+$$

$$H_2N\text{-}R\text{-}COOH + H_2O \rightleftarrows {}^+H_3N\text{-}R\text{-}COOH + OH^-.$$

Adding alcohol would make the end-point sharper for the reasons given above. Or we may follow Bjerrum's[2] generally adopted "zwitterion" theory according to which the amino acid is present in neutral solution to a greater or lesser extent as an internal salt, $^+H_3N\text{-}R\text{-}COO^-$. When NaOH is added, the Na^+

---

[1] Cf. Hildebrand: J. Am. Chem. Soc., **44**, 135 (1922).

[2] Z. physik. Chem., **104**, 147 (1923).

replaces the $-NH_3^+$ of the "zwitterion" to form $^+H_3N\text{-}R\text{-}COONa$; and when HCl is added, the Cl^- replaces $-COO^-$ to form $ClH_3N\text{-}R\text{-}COO^-$. In either case we are titrating a weak acid or base made still weaker by a substituted group of opposing tendency, and in either case titration will be made more satisfactory in alcohol. It is not necessary, then, to assume the "zwitterion" hypothesis.

Proteins

The general method was applied to the proteins just as outlined in the introduction. The work on alanine had led us to believe that there might be some peptization of the protein in acid or alkaline solution. With some proteins, this was practically complete, and with some it was negligible. A good idea of its amount could be obtained by titrating the $-COOH$ or $-NH_2$ groups in the supernatant liquid (by finding the amount of acid necessary to change the reaction from just blue to thymolphthalein to just red to thymol blue or vice versa).[1] However, the titrations were made directly on the undiluted supernatant liquid with acid or alkali in 95% ethyl alcohol in the same way as they were done for alanine. Consequently, we titrated only excess strong acid or base, and not any peptized protein, protein salt, adsorption complex, or any possible hydrolysis products or their salts. The results of using water solution for the titration of a peptized protein are shown graphically in Fig. 6, where they are compared with results of titration in alcohol. The end-points in the water solution were very indistinct.

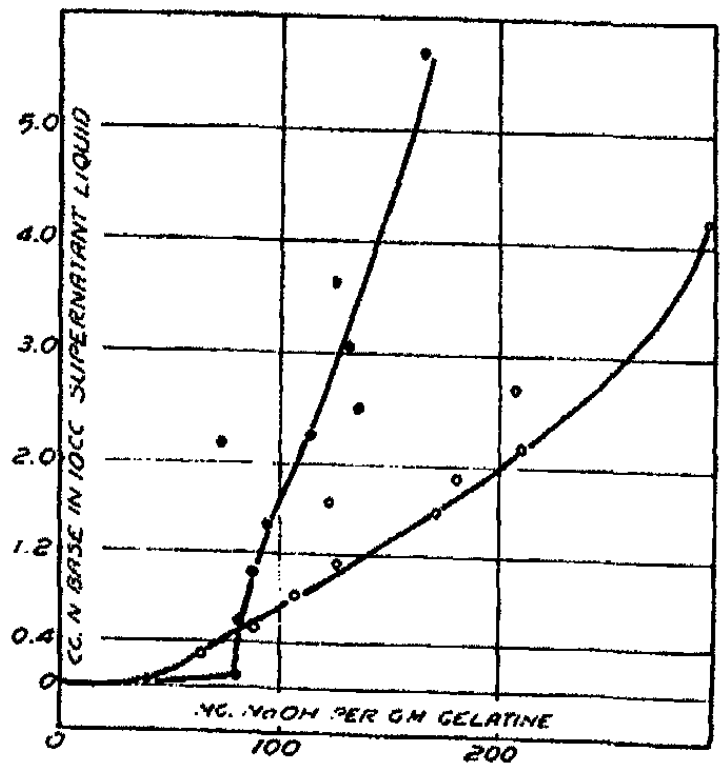


Fig. 6

● Titration in water
○ Titration in alcohol

---

[1] Cf. Harris: Proc. Roy. Soc., 95B, 500 (1923).

Robertson[1] and Hoffman and Gortner[2] make some objections to the use of indicators in determining the amount of acid or base bound by a protein, especially when it is in apparent solution. We feel that the alcoholic titration outlined meets most of these. The end-points are quite good in alcohol, especially with thymolphthalein. A second objection is that in colorimetric titrations, only the amount of acid or base bound at the particular pH of the indicator change is determined. *In the alcoholic solution, the pH of all* proteins and practically all of their possible products, is within the pH ranges of the indicators used. After equilibrium has been reached under any desired conditions, free acid or base *only* is titrated. The removal of the acid or base in most cases disturbs the equilibrium, and the system immediately starts to re-establish it. In alcohol, especially with proteins, we have found that this is a slow process, so that there would be no appreciable change in the one or two minutes required for titration. The third objection, that the indicators may change the protein, holds except when it is disproven in specific instances. We are confident that our indicators were perfectly satisfactory in this respect.

Equilibrium was slow with succinic and uric acids, and the work on uric acid showed that lack of equilibrium may appear to be adsorption. Consequently a time which may seem inordinately long was given for the proteins to reach equilibrium. Less time was allowed when peptization occurred as there could then be more intimate contact. Shaking was also employed to bring about equilibrium by keeping the solid and liquid phases thoroughly mixed. The shaking apparatus consisted of a large platform having places for 100 bottles, suspended from a frame by pliable iron strips. The platform was given a back and forth motion by an eccentric run by a motor. There were about 150 complete shakes a minute.

The long time of the runs made hydrolysis of the proteins seem quite probable, although the presence of alcohol was a factor opposing it. It was tested for in the following manner. The supernatant liquid of the number in each run which contained the largest amount of acid or base was titrated as usual. The liquid in the titration flask was returned quantitatively to the bottle. Sufficient further acid or base was then added to neutralize all the base or acid originally used. The bottle now contained salt and the original protein or its hydrolysis products in alcohol. The alcohol was pumped off. The material left was analyzed for amino nitrogen by the method of Van Slyke and Birchard.[3] A gram of the original protein was subjected to an identical analysis. The amino nitrogen content of the completely hydrolyzed protein was taken from the literature or calculated. It is obvious from its use in the following equation that it does not need to be very exact. Then if a is the percent of nitrogen as amino nitrogen in the original protein, b that of the material used in the run, and c that of the completely hydrolyzed material; $(b - a)/(c - a)$ is the fraction of hydrolysis which has taken place. These values are a maximum, for any error in the method would be due to further

---

[1] "The Physical Chemistry of the Proteins" (1918).

[2] Colloid Symp. Mon., **2**, 209 (1925).

[3] J. Biol. Chem., **16**, 539 (1913-14).

hydrolysis in its execution. With acids, the hydrolysis was uniformly low (not more than 2.5%) with the exception of that of zein in 85% acetone. In alkali, the hydrolysis of all the proteins except casein was much higher. It ranged from 10% to 40%. This method of determining hydrolysis is open to the objection that the increase in amino groups may not always parallel the amount of hydrolysis, but it is sufficiently accurate for our purpose.

Moisture determinations on the proteins were made by heating them to about 60° in a desiccator which was at the same time evacuated to low pressure. This treatment was carried out for about 25 hours. The results are given below, as the percent of the original weight which was lost in heating.

Casein	9.9%
Gelatine	11.4
Zein	3.7
Gliadin	5.5
Edestin	7.2

All data given for proteins has been calculated on the dry basis.

TABLE IX

Summary of the Runs on Proteins

No.	Protein	Source	Reacts with	Solvent	Length of run	Time of shaking
1.	Casein	Kahlbaum	HCl	95% ethyl alcohol	52 days	343 hrs.
2.	Casein	"	NaOH	"	"	317 hrs.
3.	Gelatine	Eastman	HCl	"	53 days	285 hrs.
4.	Gelatine	"	"	"	30 days	290 hrs.
5.	Gelatine	"	"	Absolute alcohol	48 days	385 hrs.
6.	Gelatine	"	NaOH	95% ethyl alcohol	14 days	— —
7.	Gelatine	"	"	"	"	— —
8.	Gelatine	"	"	"	25 days	270 hrs.
9.	Gelatine	"	"	" with 52% benzene	53 days	285 hrs.
10.	Zein	Conn. Agr. Expt. Sta.	HCl	95% ethyl alcohol	21 days	190 hrs.
11.	Zein	"	NaOH	"	35 days	350 hrs.
12.	Zein	"	HCl	85% acetone	35 days	450 hrs.
13.	Zein	"	NaOH	"	"	"
14.	Gliadin	Univ. of Minnesota	HCl	95% ethyl alcohol	30 days	345 hrs.
15.	Gliadin	"	NaOH	"	"	"
16.	Edestin	Eimer and Amend	HCl	"	31 days	330 hrs.
17.	Edestin	"	NaOH	"	"	"

TABLE IX

Summary of the Runs on Proteins

No.	Amount of peptization	App. amt. of hydrolysis	Compound formation	Mg. per gm. protein	Equiv. $\times 10^{-6}$	Combining weight
1.	None	0.8-0.9%	+	61	167	600
2.	Negligible	0.7%	+	75	187	535
3.	Considerable in high nos.	2.5%				
4.	"	"	+	25	68	1470
				might be considered to be		
5.	None	2.3%		31	86	1160
6.	Complete	40%				
7.	"	"	+	30	75	1330
8.	Some	17-18%				
9.	Considerable	37%	?	—	—	—
10.	Considerable	2%	—	—	—	—
11.	Complete	27%	+	28	70	1430
12.	Considerable	15%	—	—	—	—
13.	Considerable	20%	?	—	—	—
14.	None	1.4%	—	—	—	—
15.	Some	14%	+	25	62	1613
16.	Negligible	1.4%	+	45	124	806
17.	Negligible	11%	+	43	108	925

It will be well, before taking up the specific proteins, to consider briefly some of the difficulties encountered in interpreting the curves obtained. Theoretically there are none, but practically they are met. There is first the possibility of such complete adsorption that the amount of substance left in the supernatant liquid is too small to be detected experimentally. The curve then appears to show compound formation. Examples of this are the adsorption of dyes by charcoal, and some of our own work on succinic acid. Then a lack of equilibrium in compound formation, due to its slowness, may appear as an adsorption curve. This situation was met several times during the experiments on uric acid. Hydrolysis of the protein must profoundly affect the shape of the curve. In the proteins used, there is roughly from 15 to 70 times as much amino nitrogen in the completely hydrolyzed as in the unhydrolyzed material; so that even one per cent hydrolysis would mean at least a fifteen per cent increase in the amount of amino nitrogen. This makes the protein in the higher numbers of each run, where there is most hydrolysis, appear to take up more acid or especially more alkali, than is really the case. In the lower numbers of each run, particularly in acid, this is cut down to negligible proportions. Fortunately for us, it is these lower numbers which determine whether or not a compound is formed. The amount of adsorption on the original protein or on any compound formed, as determined from the upper part of the curve, is unreliable.

We do not claim that our results will be applicable to water solution. Too often results have been compared which have been obtained under radically different experimental conditions. It would take a vast amount of work to harmonize them. Our results are simply those under the conditions of our experiments. Some agree well with values obtained in water solution. We will give the results of other workers for the different proteins. Many times, they give the maximum amount bound, while we give that present in the compound.

In order to facilitate comparisons between the different proteins, all the results on them are given in Table IX.

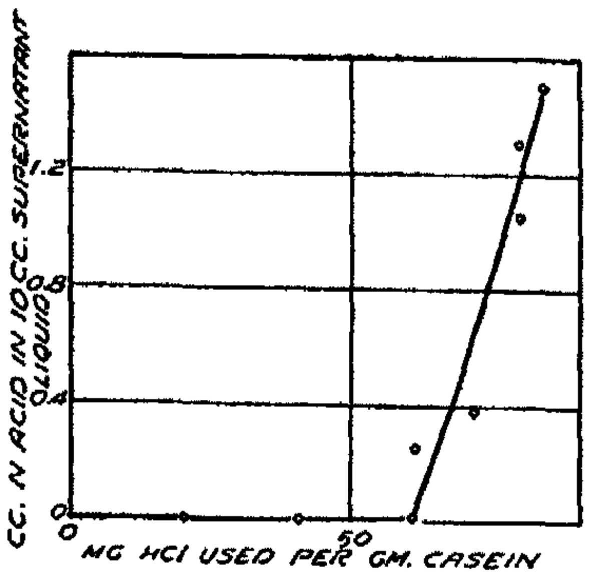


Fig. 7
Casein and HCl in 95% Ethyl Alcohol

1. *Casein*—The casein was a technical product purchased from Kahlbaum and used without further purification. The runs in both acid and alkali seemed perfectly normal in every way. In acid, the appearance of the casein did not change during the run. In alkali, it became somewhat yellow and swollen, but there was apparently no peptization. The hydrolysis of the casein in each case was less than one percent.

Casein formed a hydrochloride (Table X and Fig. 7), as Bancroft and Barnett[1] found, and there was then adsorption to a slight extent on the compound. It contained 61 mg. HCl per gm. of casein or 167×10^{-5} equivalents. This gives casein a combining weight with the acid of about 600. Bancroft and Barnett's compound contained 234×10^{-5} equivalents. Other results reported are:

90×10^{-5} equivalents at a pH of 2.5 and 600×10^{-5} equivalents at the maximum acid concentration by Hoffman and Gortner[2]

85×10^{-5} equivalents at a pH of 2.5 by Sandstrom[3]

33×10^{-5} equivalents when acid is "saturated" with protein by Robertson[4]

60×10^{-5} equivalents at neutrality to phenolphthalein by Bracewell[5]

59×10^{-5} equivalents by Hitchcock[6]

72×10^{-5} equivalents by Loeb[7] as recalculated by Cohn.[8]

---

[1] J. Phys. Chem., 34, 449 (1930).
[2] Colloid Symp. Mon., 2, 209 (1925).
[3] J. Phys. Chem., 34, 1071 (1930).
[4] J. Phys. Chem., 13, 469 (1909).
[5] J. Am. Chem. Soc., 41, 1511 (1919).
[6] J. Gen. Physiol., 5, 383 (1922-1923).
[7] J. Gen. Physiol. 3, 547 (1920-1921).
[8] Physiol. Rev., 5, 349 (1925).

TABLE X

Casein and HCl in 95% Ethyl Alcohol

1 gm. casein, equivalent to .901 gm. dry casein, used in each number
Volume of each number—20 cc. Length of run—52 days

No.	a cc. N HCl added	b cc. N base for 10 cc. supernat. liquid	c cc. N acid in super. liquid b $\times$ 2	d cc. N acid used per gm. casein equiv. $\times 10^{-3}$ $(a - c)/.901$	e mg. HCl per gm. casein d $\times$ 36.46
1.	0.50	0.00	0.00	0.56	20.5
2.	1.01	0.00	0.00	1.13	41.0
3.	1.52	0.01	0.01	1.67	61.0
4.	2.03	0.25	0.51	1.69	61.5
5.	2.54	0.38	0.76	1.97	71.7
6.	4.05	1.05	2.09	2.18	79.3
7.	4.56	1.30	2.60	2.18	79.4
8.	5.07	1.50	3.01	2.29	83.5

TABLE XI

Casein and NaOH in 95% Ethyl Alcohol

1 gm. casein, equivalent to .901 gm. dry casein, used in each number
Volume of each number—20 cc. Length of run—52 days

No.	a cc. N NaOH added	b cc. N acid for 10 cc. supernat. liquid	c cc. N base in super. liquid b $\times$ 2	d cc. N base used per gm. casein equiv. $\times 10^{-3}$ $(a - c)/.901$	e mg. NaOH per gm. casein d $\times$ 40.008
1.	0.50	0.00	0.00	0.56	22.2
2.	1.00	0.00	0.00	1.11	44.4
3.	1.50	0.00	0.00	1.66	66.6
4.	2.00	0.00	0.01	2.21	88.4
5.	2.50	0.01	0.01	2.76	110.4
6.	3.00	0.05	0.10	3.21	128.6
7.	3.50	0.23	0.46	3.37	134.9
8.	4.00	0.19	0.38	4.02	160.9
9.	4.50	0.38	0.75	4.16	166.3
10.	5.00	0.49	0.97	4.47	178.9
11.	10.00	2.02	4.05	6.62	264.7

Casein also formed a compound with NaOH (Table XI and Fig. 8) as was expected from its acidic character and much previous work done on it. There was considerable adsorption on this. It contained about 75 mg. NaOH per gm. casein or 187×10^{-5} equivalents, and gives casein a combining weight with strong base of 535. This is much more base than is contained in the "caseinates" often mentioned. This result may be compared with others reported:

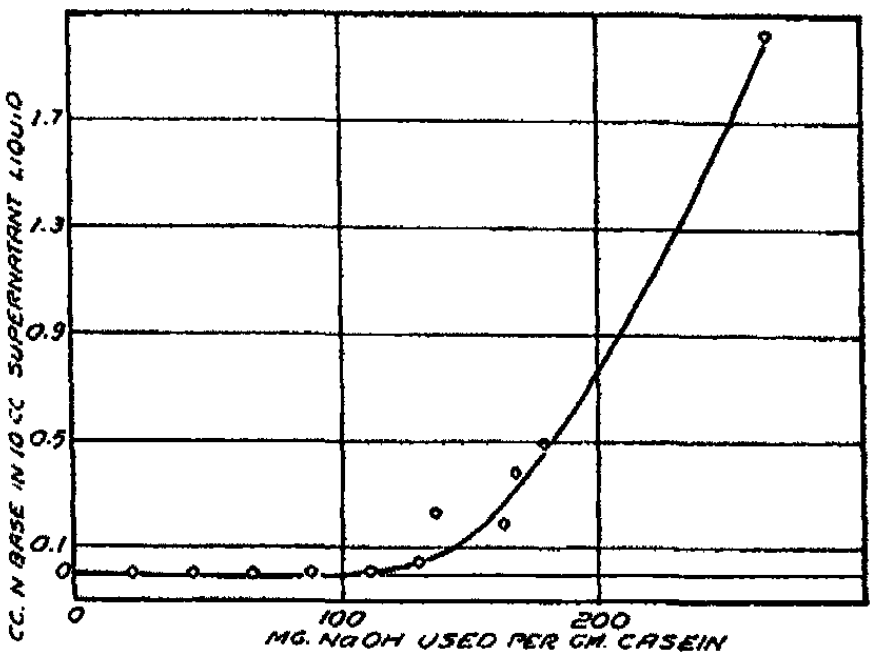


FIG. 8
Casein and NaOH in 95% Ethyl Alcohol

11×10^{-5} equivalents when base is "saturated" with protein by Robertson[1] and L. L. Van Slyke and Bosworth[2]

$50\text{-}55 \times 10^{-5}$ equivalents at neutrality to litmus by Robertson,[3] L. L. Van Slyke and Hart,[4] and Söldner[5]

90×10^{-5} equivalents at neutrality to phenolphthalein by L. L. Van Slyke and Hart,[4] Söldner,[5] Bosworth and L. L. VanSlyke,[6] Laqueur and Sackur,[7] and Courant[8]

11.2, 21.4, 58.4 and 87.2×10^{-5} equivalents in Mg. compounds of casein by L. L. Van Slyke and Winter[9]

90×10^{-5} equivalents at a pH of 10.2, 155×10^{-5} at a pH of 10.5, and a maximum of 1400×10^{-5} by Hoffman and Gortner[10]

---

[1] J. Phys. Chem., 13, 469 (1909).
[2] J. Biol. Chem., 14, 211 (1913).
[3] J. Phys. Chem., 14, 528 (1910).
[4] Am. Chem. J., 33, 461 (1905).
[5] Z. angew. Chem., 1895, 370.
[6] J. Biol. Chem., 14, 207 (1913).
[7] Beiträge Z. chem. Physiol., 3, 193 (1902).
[8] Archiv ges. Physiol., 50, 109 (1891).
[9] J. Biol. Chem., 17, 287 (1914).
[10] Colloid Symp. Mon., 2, 209 (1925).

146 × 10^{-5} equivalents at a pH of 10.5 by Sandstrom[1]

136-40 × 10^{-5} equivalents "under some conditions" by Cohn[2]

155-60 × 10^{-5} equivalents by Greenberg and Schmidt[3] and by Cohn and Berggren[4] if casein is not "nach Hammarsten"

180 × 10^{-5} equivalents by Robertson[5] and Cohn and Berggren[4]

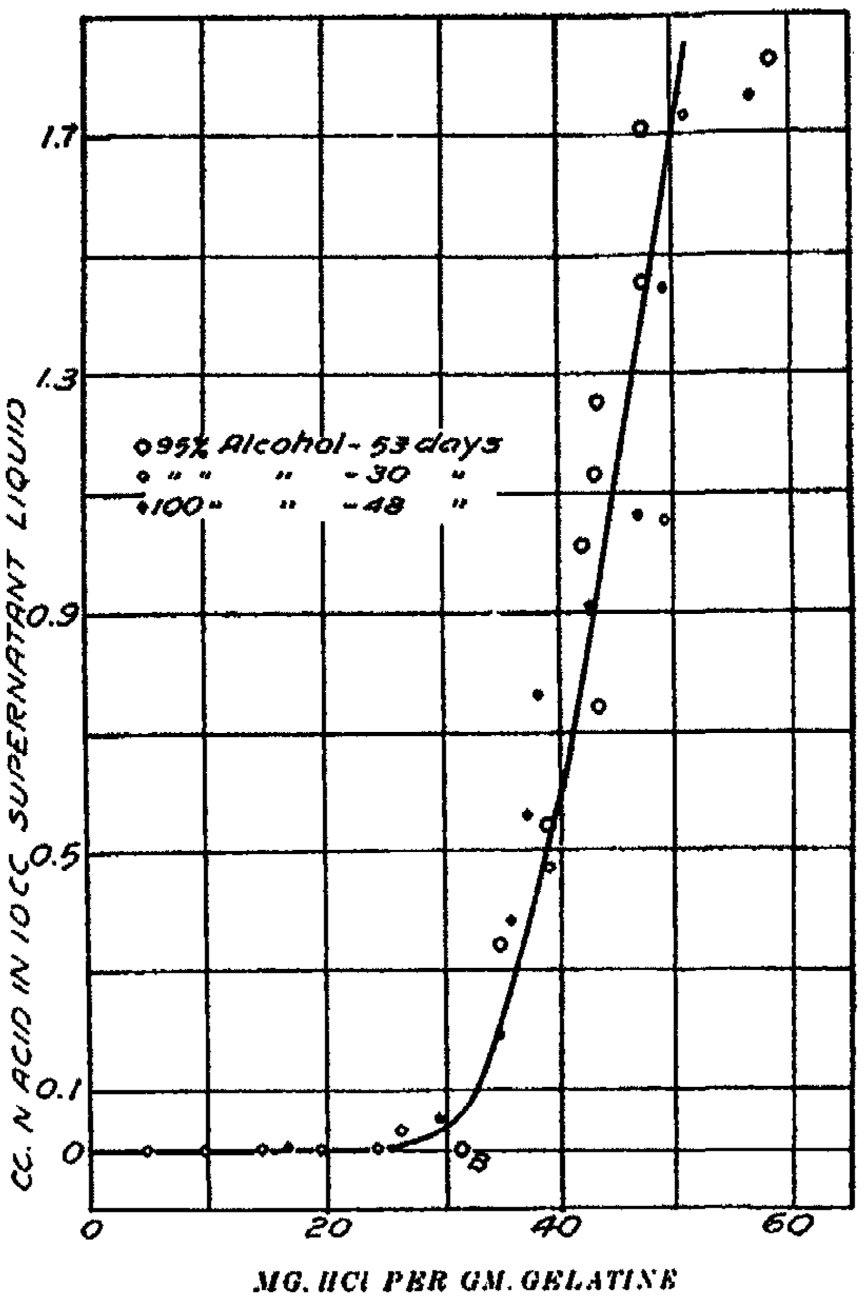


FIG. 9
Gelatine and HCl in 95% Ethyl Alcohol

2. *Gelatine*—The gelatine was from the Eastman Kodak Company, and was not further treated. It was from pig-skin, had a pH of 5.0, and was in the form of a powder.

Three runs with HCl were made. (See Tables XII-XIV and Fig. 9.) Both 95% and absolute ethyl alcohol were used. In the 95% alcohol, there

---

[1] J. Phys. Chem., 34, 1071 (1930).

[2] Physiol. Rev., (2) 5, 349 (1925).

[3] J. Gen. Physiol., 7, 317 (1924-5).

[4] J. Gen. Physiol., 7, 45 (1924-5).

[5] J. Phys. Chem., 14, 528 (1910).

was considerable peptization in the higher numbers. In the absolute alcohol, there was practically none. Hydrolysis of the gelatine was less than 2.5% in each. The time of the runs was from a month to two months. The results of all of them fall very nicely on the same curve, showing that equilibrium is reached in the time allowed. A compound was formed and a little adsorption took place on it. It contained 25 mg. HCl per gm. of gelatine or 68×10^{-5} equivalents, and gelatine therefore has a combining weight of 1470 for strong acid. If point B on the curve is taken to represent the composition of the hydrochloride (and this does not seem unreasonable), 86×10^{-5} equivalents are bound. This value agrees better with those obtained by other workers. Some of these are:

Table XII

Gelatine and HCl in 95% Ethyl Alcohol

1 gm. gelatine, equivalent to .886 gm. dry gelatine, used in each number
Volume of each number—20 cc. Length of run—53 days

No.	a cc. N HCl added	b cc. N base for 10 cc. supernat. liquid	c cc. N acid in super. liquid b × 2	d cc. N acid used per gm. gelatine equiv. $\times 10^{-3}$ (a − c)/.886	e mg. HCl per gm. gelatine d × 36.46
1.	0.76	0.00	0.00	0.86	31.3
2.	1.52	0.34	0.68	0.95	34.8
3.	2.03	0.54	1.08	1.07	39.0
4.	2.54	0.74	1.49	1.18	43.2
5.	3.04	1.01	2.03	1.15	41.8
6.	3.30	1.13	2.25	1.18	43.0
7.	3.55	1.25	2.50	1.18	43.2
8.	4.06	1.45	2.91	1.30	47.4
9.	4.56	1.71	3.41	1.30	47.4
10.	5.07	1.82	3.65	1.61	58.5

Table XIII

Gelatine and HCl in 95% Ethyl Alcohol

A continuation of Table XIII, except that the length of the run is 30 days

1.	0.00	0.00	0.00	0.00	00.0
2.	0.12	0.00	0.00	0.13	04.9
3.	0.24	0.00	0.00	0.27	09.7
4.	0.35	0.00	0.00	0.40	14.6
5.	0.47	0 00	0.00	0.53	19.4
6.	0.59	0.00	0.00	0.66	24.2
7.	0.71	0.03	0.07	0.72	26.3
8.	1.88	0.47	0.93	1.08	39.1
9.	3.29	1.05	2.10	1.35	49.3
10.	4.71	1.73	3.46	1.41	51.3

TABLE XIV

Gelatine and HCl in Absolute Ethyl Alcohol

1 gm. gelatine, equivalent to .886 gm. dry gelatine, used in each number
Volume of each number—20 cc. Length of run—48 days

No.	a cc. N HCl added	b cc. N base for 10 cc. supernat. liquid	c cc. N acid in super. liquid b × 2	d cc. N acid used per gm. gelatine equiv. $\times 10^{-3}$ (a − c)/.886	e mg. HCl per gm. gelatine d × 36.46
1.	0.41	0.002	0.004	0.46	16.6
2.	0.81	0.05	0.10	0.81	29.5
3.	1.22	0.19	0.38	0.95	34.6
4.	1.63	0.38	0.76	0.98	35.8
5.	2.03	0.56	1.13	1.03	37.4
6.	2.44	0.76	1.51	1.05	38.2
7.	2.85	0.91	1.81	1.17	42.5
8.	3.25	1.06	2.12	1.28	46.8
9.	4.07	1.44	2.87	1.35	49.2
10.	4.88	1.76	3.52	1.53	55.9

80×10^{-5} equivalents by Bugarszky and Liebermann[1] as recalculated by Cohn[2]
85×10^{-5} equivalents by Atkin and Douglas[3]
89×10^{-5} equivalents by A. E. Stearn[4]
92×10^{-5} equivalents from viscosity measurements by Bacon[5]
94×10^{-5} equivalents as the best value of many determinations by Loeb and by Hitchcock[6]
104×10^{-5} equivalents (of acid dye) by Chapman, Greenberg, and Schmidt[7]
113×10^{-5} equivalents by Wintgen and his associates[8]
130×10^{-5} equivalents by Procter and Wilson[9]
150×10^{-5} equivalents by Manabe and Matula[10]
300×10^{-5} equivalents by Lloyd and Mayes[11]
300×10^{-5} equivalents by Belden[12] using solid protein and gaseous HCl.

---

[1] Pflüger's Archiv, **72**, 51 (1898).
[2] Physiol. Rev., **5**, 349 (1925).
[3] J. Soc. Leather Trades' Chem., **8**, 359, 528 (1924).
[4] J. Gen. Physiol., **11**, 377 (1927-28).
[5] Ferguson and Bacon: J. Am. Chem. Soc., **49**, 1921, 1934 (1927); Bacon: J. Phys. Chem., **33**, 1843 (1929).
[6] J. Gen. Physiol., **4**, 733 (1921-22); **6**, 95, 201 (1923-24); **12**, 495 (1928-29).
[7] J. Biol. Chem., **72**, 707 (1927).
[8] *Wintgen and Krüger: Kolloid-Z.*, **28**, *81 (1921); Wintgen and Vogel:* **30**, *45 (1922).*
[9] J. Chem. Soc., **109**, 307 (1916).
[10] Biochem. Z., **52**, 369 (1913).
[11] Proc. Roy. Soc., **93B**, 69 (1922).
[12] J. Phys. Chem., **35**, 2164 (1931).

In an attempt to duplicate the work of Belden who obtained a much higher value for the amount of acid bound by gelatine, the run in absolute alcohol was made. It was thought that perhaps the presence of water hindered the binding of the acid, but as previously noted, the result was the same as in 95% ethyl alcohol. In a further effort to duplicate Belden's results much stronger HCl (up to 4 N) in absolute alcohol was used. Even this relatively high concentration of HCl caused no more compound formation. There are some indications that alcohol is adsorbed by the protein, and for the present we must postulate this as the most likely explanation of the different results.

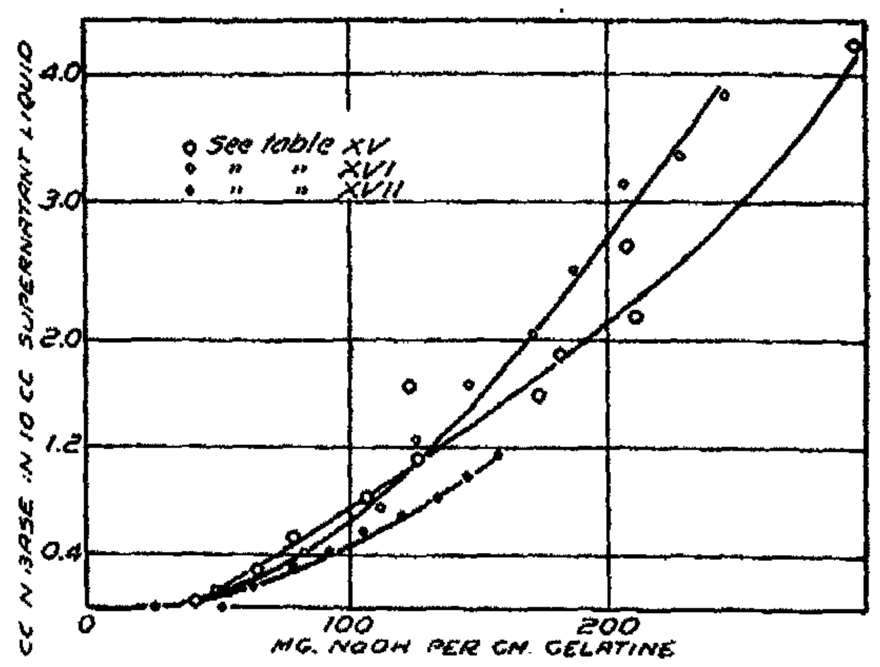


Fig. 10

Gelatine and NaOH in 95% Ethyl Alcohol

Three runs with NaOH in 95% ethyl alcohol were made. (See Tables XV-XVII and Fig. 10.) Peptization was considerable and became nearly complete in the more alkaline numbers. Two of the runs contained a large excess of alkali. Hydrolysis of the gelatine in the most alkaline numbers of these was about 40%, and was 17-18% in the most alkaline number of the third. The first two runs lasted two weeks and the other lasted nearly four. One of the first two was on a different sample of gelatine. The curves for all three coincide fairly well in the lower ranges, but the third soon shows the result of greater hydrolysis due to its longer standing. There is indication of the formation of a compound, but it is hard to judge accurately the amount of base bound in it due to the high hydrolysis. It contains about 30 mg. NaOH or 75×10^{-5} equivalents per gm. of gelatine, thus giving it a combining weight with strong alkalies of 1330. Another run with NaOH was made using about a 50% mixture of benzene and 95% ethyl alcohol as solvent. In all numbers of this run, all the NaOH was used up. This must be due to hydrolysis, which was very high—36%—even though the concentration of the alkali was no higher than usual, or we would be faced with the necessity of explaining a compound containing more than 530×10^{-5} equivalents of NaOH.

TABLE XV

Gelatine and NaOH in 95% Ethyl Alcohol

1 gm. gelatine, equivalent to .886 gm. dry gelatine, used in each number

Volume of each number—20 cc. Length of run—14 days

No.	a cc. N NaOH added	b cc. N acid for 10 cc. supernat. liquid	c cc. N base in super. liquid b × 2	d cc. N base used per gm. gelatine equiv. $\times 10^{-3}$ (a − c)/.886	e mg. NaOH per gm. gelatine d × 40.008
1.	0.00	0.00	0.00	0.00	00.0
2.	1.00	0.04	0.09	1.03	41.2
3.	2.00	0.28	0.55	1.63	65.2
4.	3.00	0.52	1.03	2.22	89.0
5.	4.00	0.82	1.65	2.66	106.1
6.	5.00	1.11	2.22	3.14	125.4
7.	6.01	1.65	3.30	3.05	121.9
8.	7.01	1.59	3.17	4.32	172.9
9.	8.01	1.89	3.77	4.78	180.9
10.	9.01	2.17	4.34	5.26	210.5
11.	10.01	2.70	5.40	5.20	207.8
12.	15.01	4.21	8.43	7.43	296.8

TABLE XVI

Gelatine and NaOH in 95% Ethyl Alcohol

The same as Table XVI except on slightly different sample of gelatine

1.	1.31	0.12	0.24	1.23	49.1
2.	2.62	0.40	0.80	2.06	82.2
3.	3.93	0.74	1.47	2.77	110.9
4.	5.24	1.24	2.47	3.12	125.0
5.	6.55	1.67	3.34	3.62	144.8
6.	7.86	2.04	4.09	4.27	170.3
7.	9.17	2.52	5.04	4.66	186.5
8.	10.48	2.96	5.91	5.16	206.3
9.	11.79	3.37	6.75	5.69	227.6
10.	13.10	3.83	7.65	6.15	246.0

TABLE XVII

Gelatine and NaOH in 95% Ethyl Alcohol

1 gm. gelatine, equivalent to .886 gm. dry gelatine, used in each number

Volume of each number—20 cc. Length of run—25 days

	a	b	c	d	e
No.	cc. N NaOH added	cc. N acid for 10 cc. supernat. liquid	cc. N base in super. liquid b $\times$ 2	cc. N base used per gm. gelatine equiv. $\times 10^{-3}$ (a − c)/.886	mg. NaOH per gm. gelatine d $\times$ 40.008
1.	0.58	0.00	0.00	0.65	26.0
2.	1.15	0.00	0.00	1.30	51.9
3.	1.73	0.16	0.32	1.58	63.3
4.	2.30	0.29	0.57	1.95	78.1
5.	2.88	0.42	0.84	2.30	91.8
6.	3.45	0.57	1.14	2.61	104.2
7.	4.03	0.69	1.39	3.00	119.1
8.	4.60	0.82	1.64	3.34	133.6
9.	5.18	0.99	1.98	3.60	144.1
10.	5.75	1.14	2.28	3.91	156.6

Some results recorded for gelatine and NaOH are:

56-7 $\times 10^{-5}$ equivalents by Loeb and by Hitchcock[1] as recalculated by Cohn[2]

60$\times 10^{-5}$ equivalents at a pH of 11 by Greenberg and Schmidt[3]

70-1 $\times 10^{-5}$ equivalents (of basic dye) by A. E. Stearn[4] and Rawlins and Schmidt[5]

74 $\times 10^{-5}$ equivalents by A. E. Stearn[6]

85 $\times 10^{-5}$ equivalents by Atkin and Douglas[7]

130 $\times 10^{-5}$ equivalents by Procter and Wilson[8]

2000 $\times 10^{-5}$ equivalents by Lloyd and Mayes[9]

3. *Zein*—The zein was very kindly sent to this department by Mr. H. B. Vickery of the Connecticut Agricultural Experiment Station.

With HCl in 95% ethyl alcohol, zein showed no compound formation, but considerable adsorption. (See Table XVIII and Fig. 11.) This result was also obtained by Bancroft and Barnett.[10] It is to be expected from the fact that zein is acidic, since it contains dicarboxylic amino acids and no free amino groups. Hoffman and Gortner[11] who say that it combines with

---

[1] J. Gen. Physiol., **6**, 457 (1923-24).

[2] Physiol. Rev., **5**, 349 (1925).

[3] Proc. Soc. Exp. Biol. Med., **21**, 281 (1923-24).

[4] J. Biol. Chem., **91**, 325 (1931).

[5] J. Biol. Chem., **82**, 709 (1929).

[6] J. Gen. Physiol., **11**, 377 (1927-28).

[7] J. Soc. Leather Trades' Chem., **8**, 359, 528 (1924).

[8] J. Chem. Soc., **109**, 307 (1916).

[9] Proc. Roy. Soc., **93B**, 69 (1922).

[10] J. Phys. Chem., **34**, 449 (1930).

[11] Colloid Symp. Mon., **2**, 209 (1925).

20×10^{-6} equivalents of HCl at a pH of 2.5 and a maximum of 65×10^{-6} equivalents, are the only authors who have mentioned a compound with acid. There was very considerable solution of the zein. It is a prolamine which is soluble in solutions with a higher percentage of alcohol than most of them. The hydrolysis of the zein was about two percent.

With NaOH in 95% ethyl alcohol, there was complete solution or peptization and *25-30% hydrolysis of the zein.* Although the upper part of the curve is undoubtedly displaced far to the right, the first few points where hydrolysis was very much less, show that a compound was formed. (See

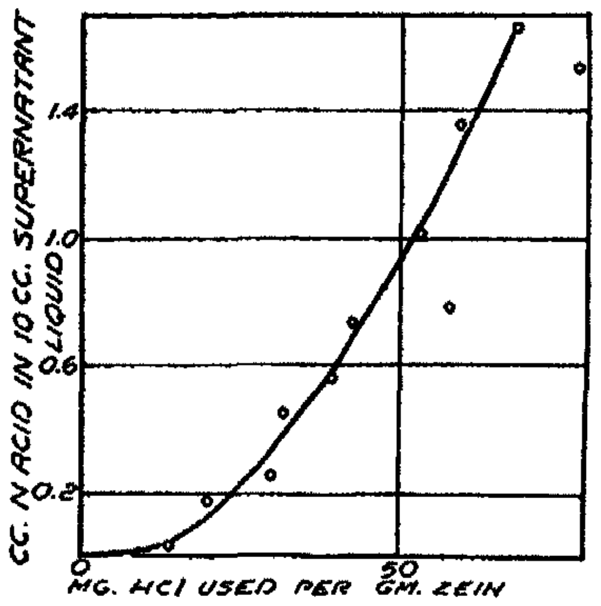


Fig. 11
Zein and HCl in 95% Ethyl Alcohol

Table XVIII

Zein and HCl in 95% Ethyl Alcohol

1 gm. zein, equivalent to .963 gm. dry zein, used in each number
Volume of each number—20 cc. Length of run—21 days

No.	a cc. N HCl added	b cc. N base for 10 cc. supernat. liquid	c cc. N acid in super. liquid b × 2	d cc. N acid used per gm. zein equiv. $\times 10^{-3}$ (a − c)/.963	e mg. HCl per gm. zein d × 36.46
1.	0.43	0.03	0.07	0.37	13.6
2.	0.86	0.17	0.34	0.54	19.6
3.	1.28	0.25	0.51	0.81	29.3
4.	1.71	0.44	0.88	0.86	31.5
5.	2.14	0.56	1.12	1.06	38.7
6.	2.57	0.73	1.45	1.15	42.1
7.	3.08	0.78	1.55	1.58	57.7
8.	3.42	1.01	2.03	1.45	52.7
9.	4.28	1.35	2.70	1.63	59.5
10.	5.13	1.53	3.05	2.16	78.6
11.	5.13	1.66	3.33	1.87	68.3

Table XIX and Fig. 12.) It contained approximately 28 mg. NaOH per gm. of zein, or 70 × 10^{-5} equivalents, and gives zein a combining weight with NaOH of 1430. Cohn, Berggren, and Hendry[1] found less NaOH bound—30 × 10^{-5} equivalents. Hoffman and Gortner[2] report 20 × 10^{-5} equivalents bound at pH values of 10.2 and 10.5, and a maximum binding of 1400 × 10^{-5} equivalents.

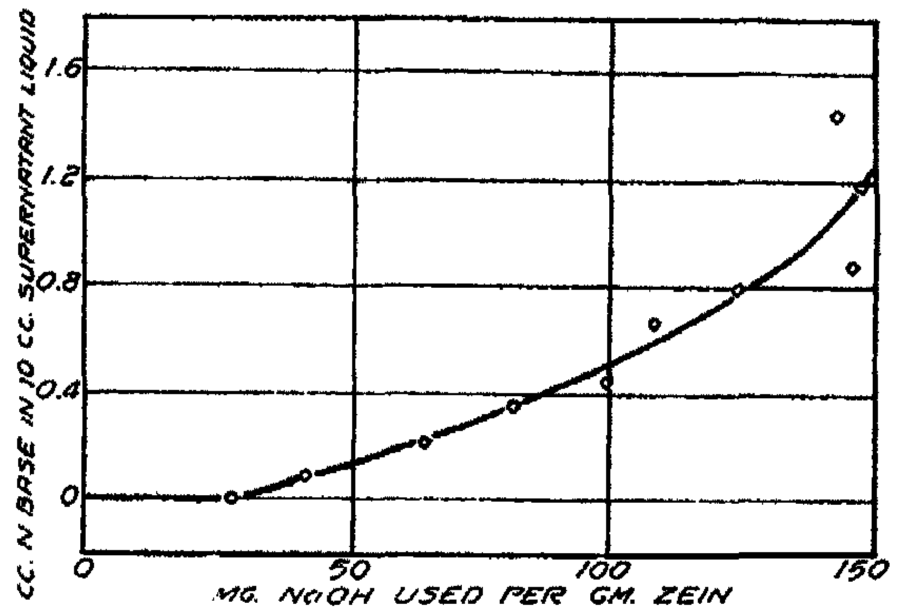


Fig. 12
Zein and NaOH in 95% Ethyl Alcohol

Table XIX

Zein and NaOH in 95% Ethyl Alcohol

1 gm. zein, equivalent to .963 gm. dry zein, used in each number
Volume of each number—20 cc. Length of run—35 days

No.	a cc. N NaOH added	b cc. N acid for 10 cc. supernat. liquid	c cc. N base in super. liquid b × 2	d cc. N base used per gm. zein equiv. × 10^{-3} (a − c)/.963	e mg. NaOH per gm. zein d × 40.008
1.	0.66	0.00	0.00	0.68	27.2
2.	1.31	0.09	0.19	1.17	46.6
3.	1.97	0.21	0.42	1.60	64.0
4.	2.62	0.33	0.66	2.04	81.5
5.	3.28	0.44	0.88	2.49	99.5
6.	3.93	0.66	1.32	2.71	108.5
7.	4.59	0.79	1.59	3.11	124.5
8.	5.24	0.87	1.73	3.64	145.7
9.	5.90	1.18	2.35	3.67	147.1
10.	6.55	1.41	2.82	3.86	154.8
11.	6.33	1.44	2.88	3.58	143.0

---

[1] J. Gen. Physiol., 7, 81 (1924-5).
[2] Colloid Symp. Mon., 2, 209 (1925).

Because zein went into solution almost completely in the 95% ethyl alcohol, runs were tried in 85% acetone. This seemed to be an ideal solvent for Foreman[1] says that it may be substituted for 95% alcohol in titrating amino and carboxyl groyps, and Galeotti and Giampalmo[2] say that zein is insoluble in water-acetone mixtures. But there was still considerable peptization of the zein in the acid and alkaline acetone. The hydrolysis of the zein was 15% in acid and 20% in alkali. The run with NaOH got very dark brown, so that the end-points were very poor; and the run with HCl had poor end-points, although the solutions were clear. With HCl the first part of the curve was the same as the one in 95% alcohol. Then the increased hydrolysis of the zein in acetone became apparent in a break in the curve which veered far to the right. With alkali, apparently much more was taken up in the form of a compound than in alcohol. We are inclined to doubt this. These runs in acetone were far from satisfactory.

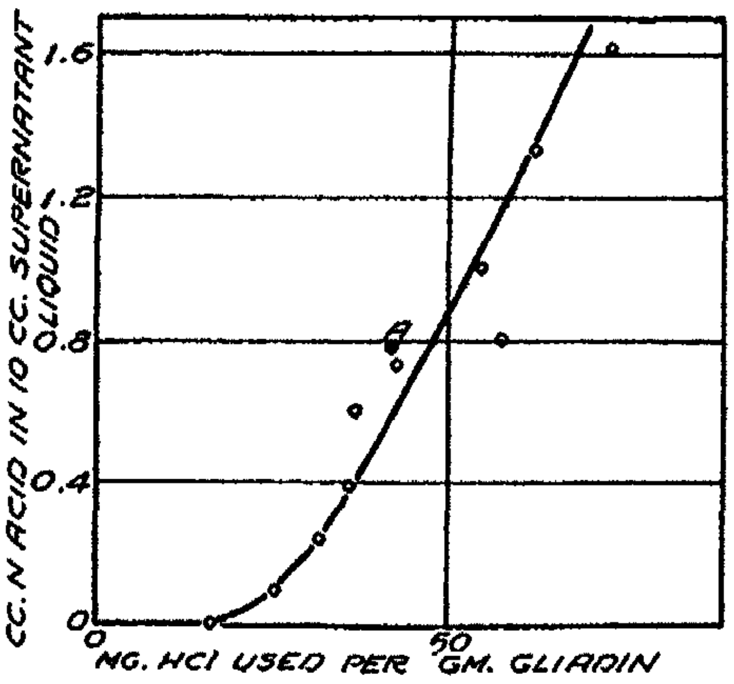


Fig. 13
Gliadin and HCl in 95% Ethyl Alcohol

4. *Gliadin*—The gliadin was a gift to this department from Professor R. A. Gortner of the University of Minnesota.

With HCl in 95% ethyl alcohol, gliadin did not peptize and hydrolyzed to the extent of about 1.4%. Contrary to expectations, it showed absolutely no indication of compound formation. (See Table XX and Fig. 13.) Bancroft and Barnett[3] obtained a curve with three flats and therefore showing three compounds, or at least three different pressures of HCl necessary for the formation of one or more compounds. In order to show whether our curve represented the true result under the conditions of our experiment, or whether it was lack of equilibrium, we made gliadin hydrochloride by the method of Bancoft and Barnett. This was put into 95% ethyl alcohol. It lost HCl until it reached a point (A-Fig. 13) on our curve, which must, therefore, be correct.

---

[1] Biochem. J., 14, 451 (1920).
[2] Kolloid-Z., 3, 118 (1908).
[3] J. Phys. Chem., 34, 449 (1930).

TABLE XX

Gliadin and HCl in 95% Ethyl Alcohol

1 gm. gliadin, equivalent to .946 gm. dry gliadin, used in each number
Volume in each number—20 cc. Length of run—30 days

No.	a cc. N HCl added	b cc. N base for 10 cc. supernat. liquid	c cc. N acid in super. liquid b × 2	d cc. N acid used per gm. gliadin equiv. × 10^{-3} (a − c)/.946	e mg. HCl per gm. gliadin d × 36.46
1.	0.43	0.003	0.007	0.44	16.2
2.	0.86	0.10	0.20	0.69	25.3
3.	1.28	0.24	0.48	0.86	31.4
4.	1.71	0.39	0.79	0.98	35.7
5.	2.14	0.60	1.20	0.99	36.3
6.	2.57	0.73	1.46	1.17	42.5
7.	3.08	0.80	1.60	1.57	57.2
8.	3.42	1.00	2.00	1.51	54.9
9.	4.28	1.33	2.66	1.71	62.2
10.	5.13	1.61	3.23	2.01	73.3

Compounds of gliadin with acid have been reported to contain:

28 × 10^{-5} equivalents by Bracewell[1]

34 × 10^{-5} equivalents by Cohn[2]

40 × 10^{-5} equivalents at pH 2.5 by Hoffman and Gortner[3] and to bind a maximum of 600 × 10^{-5} equivalents

184, 288, and 387 × 10^{-5} equivalents in three compounds by Bancroft and Barnett.[4]

With NaOH in 95% ethyl alcohol, there was some peptization and 14% hydrolysis of the gliadin. A compound (see Table XXI and Fig. 14) was formed which had 25 mg. or 62 × 10^{-5} equivalents of base per gm. gliadin. The combining weight with NaOH is then 1600. Some values given for the binding of alkali by gliadin are:

20 × 10^{-5} equivalents by Woodman[5]

30 × 10^{-5} equivalents by Greenberg and Schmidt[6] and Cohn[2]

20 × 10^{-5} equivalents at pH values of 10.2 and 10.5 and a maximum of 1300 × 10^{-5} equivalents by Hoffman and Gortner.[7]

---

[1] J. Am. Chem. Soc., 41, 1511 (1919).
[2] Physiol. Rev., 5, 349 (1925).
[3] Colloid Symp. Mon., 2, 209 (1925).
[4] J. Phys. Chem., 34, 449 (1930).
[5] J. Agri. Science, 12, 231 (1922).
[6] Proc. Soc. Expt. Biol. Med., 21, 281 (1924).
[7] Colloid Symp. Mon., 2, 209 (1925).

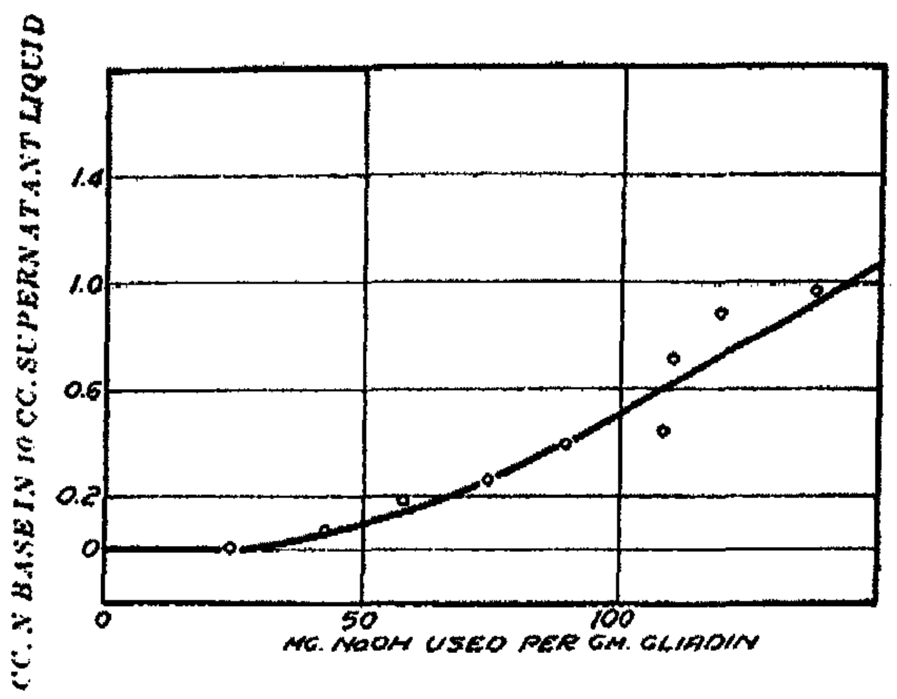


Fig. 14
Gliadin and NaOH in 95% Ethyl Alcohol

Table XXI

Gliadin and NaOH in 95% Ethyl Alcohol

1 gm. gliadin, equivalent to .946 gm. dry gliadin, used in each number
Volume in each number—20 cc. Length of run—30 days

No.	a cc. N NaOH added	b cc. N acid for 10 cc. supernat. liquid	c cc. N base in super. liquid $b \times 2$	d cc. N base used per gm. gliadin equiv. $\times 10^{-3}$ $(a - c)/.946$	e mg. NaOH per gm. gliadin $d \times 40.008$
1.	0.58	0.00	0.00	0.61	24.3
2.	1.15	0.07	0.15	1.06	42.5
3.	1.73	0.18	0.37	1.44	57.5
4.	2.30	0.28	0.55	1.85	74.0
5.	2.88	0.39	0.78	2.22	88.8
6.	3.45	0.44	0.88	2.72	108.7
7.	4.03	0.71	1.41	2.76	110.6
8.	4.60	0.88	1.77	3.00	119.9
9.	5.18	0.96	1.92	3.44	137.7
10.	5.75	0.97	1.93	4.04	161.7

5. *Edestin*—Edestin was purchased from Eimer and Amend and used as it was bought.

With HCl in 95% ethyl alcohol, there was no peptization and about 1.4% hydrolysis of the edestin. A compound (see Table XXII and Fig. 15) was formed with 45 mg. or 124×10^{-5} equivalents of HCl per gm. of edestin; or edestin has a combining weight of 810. Other values for the binding of acid by edestin are:

18×10^{-5} equivalents as the amount of strong monobasic acid required to dissolve 1 gm. edestin by Hardy[1]

14×10^{-5} equivalents necessary to "saturate" acid with edestin by Osborne[2b]

115×10^{-5} equivalents at pH 2.5 by Sandstrom[3]

127×10^{-5} equivalents by Cohn[4] as the best value recalculated from Hitchcock,[5a, b] Kodama,[6] and Osborne.[2a]

130×10^{-5} equivalents using tropaeolin as indicator by Osborne.[2a]

134×10^{-5} equivalents as his best value by Hitchcock.[5a, b, c]

250×10^{-5} equivalents by Bancroft and Barnett.[7]

TABLE XXII

Edestin and HCl in 95% Ethyl Alcohol

1 gm. edestin, equivalent to .928 gm. dry edestin, used in each number
Volume in each number—20 cc. Length of run—31 days

No.	a cc. N HCl added	b cc. N base for 10 cc. supernat. liquid	c cc. N acid in super. liquid $b \times 2$	d cc. N acid used per gm. edestin equiv. $\times 10^{-3}$ $(a - c)/.928$	e mg. HCl per gm. edestin $d \times 36.46$
1.	0.43	0.00	0.00	0.46	16.8
2.	0.86	0.00	0.00	0.92	33.6
3.	1.28	0.04	0.08	1.27	46.2
4.	1.71	0.23	0.46	1.35	49.1
5.	2.14	0.39	0.79	1.46	53.1
6.	2.57	0.55	1.10	1.58	57.6
7.	3.08	0.80	1.60	1.60	58.2
8.	3.42	1.00	2.00	1.53	55.9
9.	4.28	1.36	2.73	1.67	60.8
10.	5.13	1.76	3.53	1.73	63.0

---

[1] J. Physiol., 33, 251 (1905).

[2] (a) J. Am. Chem. Soc., 21, 486 (1899); (b) 24, 39 (1902).

[3] J. Phys. Chem., 34, 1071 (1930).

[4] Physiol. Rev., 5, 349 (1925).

[5] (a) J. Gen. Physiol., 4, 597 (1921-22); (b) 5, 383 (1922-3); (c) 14, 99 (1930-31).

[6] J. Biochem. (Japan), 1, 419 (1922).

[7] J. Phys. Chem., 34, 449 (1930).

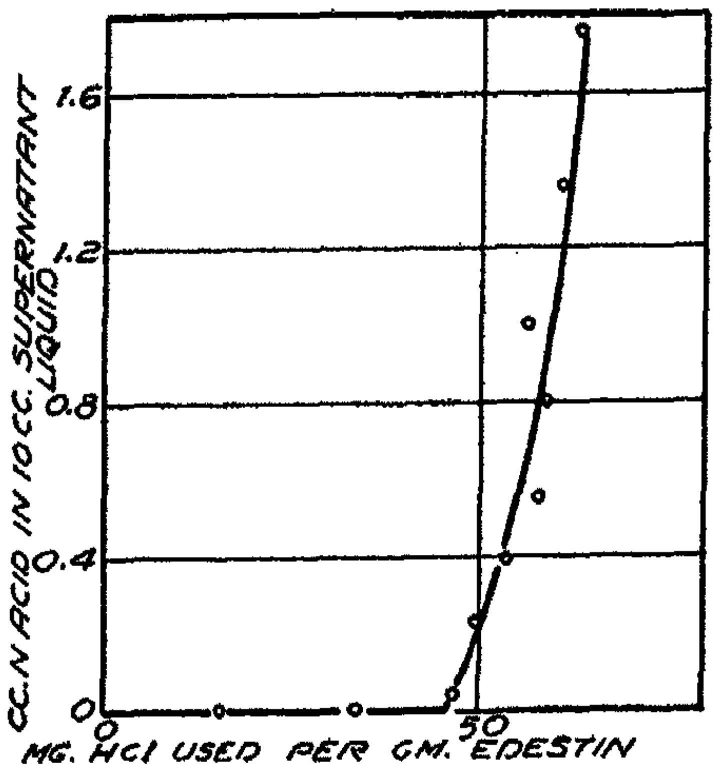


Fig. 15
Edestin and HCl in 95% Ethyl Alcohol

Table XXIII

Edestin and NaOH *in* 95% Ethyl Alcohol

1 gm. edestin, equivalent to .928 gm. dry edestin, used in each number
Volume in each number—20 cc. Length of run—31 days

No.	a cc. N NaOH added	b cc. N acid for 10 cc. supernat. liquid	c cc. N base in super. liquid $b \times 2$	d cc. N base used per gm. edestin equiv. $\times 10^{-3}$ $(a - c)/.928$	e mg. NaOH per gm. edestin $d \times 40.008$
1.	0.58	0.00	0.00	0.62	24.8
2.	1.15	0.02	0.04	1.19	47.7
3.	1.73	0.12	0.24	1.60	64.0
4.	2.30	0.23	0.45	1.99	79.7
5.	2.88	0.34	0.68	2.37	94.6
6.	3.45	0.31	0.63	3.04	121.7
7.	4.03	0.63	1.25	2.99	119.6
8.	4.60	0.74	1.48	3.36	134.6
9.	5.18	0.93	1.87	3.56	142.5
10.	5.75	1.11	2.22	3.80	152.0

With NaOH in 95% ethyl alcohol, there was no peptization. There was 11% hydrolysis of the edestin. A compound was formed (see Table XXIII and Fig. 16) on which the hydrolysis made the curve appear to represent a large amount of adsorption. The compound had 43 mg. or 108×10^{-5}

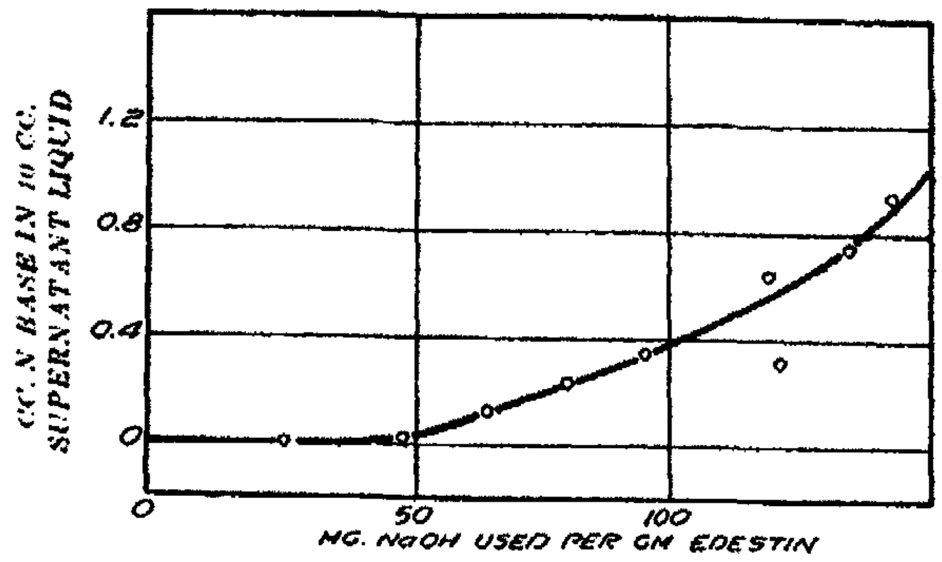


FIG. 16
Edestin and NaOH in 95% Ethyl Alcohol

equivalents of NaOH per gm. edestin, and therefore gives the protein a combining weight of 925. Other values for edestin and alkali are:

10×10^{-5} equivalents as necessary to dissolve edestin by Hardy[1]

7×10^{-5} equivalents to "saturate" alkali with edestin by Osborne[2]

36×10^{-5} equivalents at pH 10.5 by Sandstrom[3]

75×10^{-5} equivalents by Kodama[4] as recalculated by Cohn[5]

90×10^{-5} equivalents by Hitchcock[6] as recalculated by Cohn[5]

Summary

1. The phase rule method of studying proteins, developed by Bancroft and Barnett, has been extended to apply to acids and bases dissolved in a solvent, chemically inert to the system, which does not dissolve the protein or its product with acid or base.

2. The method of titrating excess strong acid or base in alcoholic solution in the presence of weak acids or bases, using thymolphthalein and thymol blue, has been applied to peptized proteins and their hydrolysis products.

3. Succinic acid, used as a test of the method, was found to form a mono- and a di-sodium salt.

4. Uric acid formed a mono- and a di-sodium salt; and in the presence of excess alkali, formed a tri- and a tetra-sodium salt. These formed much more readily in 95% isobutyl than in 95% ethyl alcohol. The presence of a small percent of water in the alcohol hastened the formation of the compounds but was not necessary to it.

---

[1] J. Physiol., 33, 251 (1905).
[2] J. Am. Chem. Soc., 24, 39 (1902).
[3] J. Phys. Chem., 34, 1071 (1930).
[4] J. Biochem. (Japan), 1, 419 (1922).
[5] Physiol. Rev., 5, 349 (1925).
[6] J. Gen. Physiol., 4, 597 (1921-22).

5. Uracil formed a compound with one equivalent of NaOH in 95% ethyl alcohol. With HCl, no compound formed, and there was very little adsorption.

6. Alanine formed a compound with one equivalent of NaOH and another with one equivalent of HCl.

7. Casein, gelatine, and edestin showed compound formation with HCl in ethyl alcohol. Zein and gliadin showed only adsorption with HCl.

8. Casein, gelatine, zein, gliadin, and edestin showed possible compound formation with NaOH in ethyl alcohol plus marked adsorption, or adsorption alone with the adsorption practically complete at the lower concentrations.

9. In general, less HCl was taken up from contact with an alcoholic solution than from contact with gaseous HCl.

Cornell University.

EXTINCTION COEFFICIENTS OF THE SILICIC ACID GEL-FORMING MIXTURES

BY MATA PRASAD, S. M. MEHTA AND J. B. DESAI

Lord Rayleigh has derived mathematically an expression according to which I, the intensity of light scattered by a colloidal solution at right angles to the incident beam is proportional to n, the number of particles per unit volume and to the square of v, the volume of the particle i.e.

$$I = \frac{Knv^2}{\lambda}$$

where K is a constant and λ will be constant if the same source of light is used.

Since c, the concentration of the colloid is given by $nv\rho$, where ρ is the density of the colloidal matter,

$$I = \frac{kcv}{\rho}$$

That is, at constant concentration the intensity of the scattered light is proportional to the volume of the particles. This expression does not apply to concentrated sols and to the sols in which the particles are not optically isotropic.

Mie[1] has studied the absorption and scattering of light by colloidal solutions containing particles of various dimensions and has concluded that at constant concentration the intensity of the diffused light increases with the size of the particles and is proportional to their volume.

Krishnamurti[2] has emphasized the importance of the study of the optical properties of colloidal solutions as they reveal their structure without disturbing their internal equilibrium. He has studied the scattering of light by agar sols and gels and has found that the micelles in the gels are much bigger than those in the sols.

In the present investigation the scattering of light from the silicic acid gel-forming mixtures has been studied during the process of gel-formation. The intensity of scattered light has been determined from the measurements of the extinction coefficients of these mixtures and the results obtained have been utilised in elucidating the changes in size and number of the colloidal particles which take place in these mixtures during the gel-formation.

Experimental

The extinction coefficients were measured by means of Nutting's photometer used in conjunction with the Hilger wave-length spectrometer.

---

[1] Ann. Physik, 25, 377 (1908).

[2] Proc. Roy. Soc., 122 A, 76 (1929).

Light from a 50 c.p. point-o-lite lamp was divided into two beams by a pair of prisms placed at a distance of 19 cms from the lamp. The two beams of light were incident on the two apertures of the Nutting's photometer after emerging from which they fell on the slit of the spectrometer and were refranged into three consecutive spectral bands of light. The different parts of the apparatus were accurately aligned with each other to avoid diffraction bands from obliterating the field of vision.

The nicol of the photometer was then adjusted so that the logarithmic scale on the disc of the photometer read zero when an empty rectangular glass cell, used to hold the gel-forming mixture, was interposed in the path of one of the beams. This was done with a view to eliminate any initial absorption due to the glass cell.

The gel-forming mixture was placed in the cell and the equality of the intensity of the three spectra in the green region ($\lambda = 5430\ \mu\mu$) was restored by turning the disc of the photometer. The rotation read on the logarithmic scale, is equal to log I_0/I where I_0 is the original intensity of the beam and I that of the beam transmitted through the mixture. Values of the extinction coefficient were obtained by dividing log I_0/I by t, the thickness of the gel-forming mixture.

Solution of sodium silicate was prepared by keeping a large quantity of Merck's extra pure dry sodium silicate ($Na_2O.2.5SiO_2$) in contact with redistilled water for three days. It was then twice filtered and kept in a well stoppered Jena glass flask. It was found that this solution underwent no change in concentration for about six months. The strength of the solution was determined by analysis and has been expressed in grams of silica per 100 c.c. of the solution.

Solution of acidic ammonium acetate which was first used for the preparation of gels[11] was prepared by dissolving a large quantity of Kahlbaum's extra pure ammonium acetate in redistilled water with the addition of a little acid to it. On analysis this solution was found to contain 39.99% free acetic acid. Solutions of acetic acid used later were prepared from Merck's extra pure product.

Equal volumes of solutions of sodium silicate and of acidic ammonium acetate or of acetic acid were thoroughly mixed in a test tube and transferred to the cell, which was thoroughly cleaned and dried beforehand. The stopwatch was started simultaneously with the mixing of the solutions and readings on the logarithmic scale of the photometer were taken at definite intervals after mixing.

The results obtained are given in the following tables and one set of the curves between the extinction coefficient and time is shown in Fig. 1. The reaction of these mixtures towards litmus has been tested and the pH values of some of them have also been measured by the colorimetric method.

---

[11] Cf. Prasad and Hattiangadi: J. Indian Chem. Soc., 6, 653 (1929).

TABLE I

Silica Content 3%

Time	Concentration of ammonium acetate			
	3%	4% Alkaline	5%	6% Acidic
1′ 0″	0.009993	0.1089	0.1579	0.03996
1′30″	0.04396	0.1659	0.1859	0.08794
3′ 0″	0.1140	0.1899	0.1859	0.1599
6′ 0″	0.1599	0.1899		0.1698
10′ 0″	0.1739			0.1819
15′ 0″	0.1819			0.1819
20′ 0″	0.1819			

	7%	8% Acidic	10%
1′ 0″	0	0.003996	0
3′ 0″	0.003996	0.007995	0
9′ 0″	0.04396	0.009995	0.001998
13′ 0″	0.084	0.01399	0.005995
23′ 0″	0.1379	0.01998	0.007995
38′ 0″	0.1539	0.05597	0.01199
56′ 0″	0.1539	0.09792	0.01799
70′ 0″		0.1219	0.03396
90′ 0″		0.1359	0.06195
104′ 0″		0.1419	0.07995
120′ 0″		0.1419	0.092

TABLE II

Silica Content 4%

Time	Concentration of ammonium acetate				Time	Concentration of ammonium acetate	
	3% Alkaline	4% Alkaline	9% Acidic	10% Acidic		15% Acidic	20% Acidic
1′ 0″	0.01998	0.1739	0.01199	0.01199	1′ 0″	0	0
2′ 0″	0.07394	0.1819	0.03396	0.03396	2′ 0″	0.01199	0
2′45″	0.1279	0.1958	0.07995	0.05995	8′ 0″	0.01399	0.001998
7′ 0″	0.1759	0.1958	0.1579	0.1079	25′ 0″	0.01998	0.005995
8′ 0″	0.1819		0.1599	0.1199	45′ 0″	0.02798	0.009993
13′ 0″	0.1819		0.1719	0.1479	60′ 0″	0.05795	0.01799
14′ 0″			0.1739	0.1539	72′ 0″	0.06995	0.02202
21′ 0″			0.1739	0.1819	96′ 0″	0.09994	0.04796
22′ 0″				0.1859	114′ 0″	0.1159	0.07396
26′ 0″				0.1859	120′ 0″	0.1219	0.07794

TABLE III

Silica Content 3%

Time	Concentration of acetic acid			
	0.331 N	0.34 N	0.36 N	0.397 N
	Alkaline		Acidic	
1′ 0″	0	0.01998	0	0
4′ 0″	0.007995	0.02598	0.03198	0.001998
14′ 0″	0.04197	0.06395	0.08392	0.007995
24′ 0″	0.07396	0.09393	0.1339	0.01079
35′ 0″	0.1020	0.1159	0.1419	0.02598
41′ 0″	0.1059	0.1239	0.1419	0.03198
54′ 0″	0.1239	0.1319		0.04796
73′ 0″	0.1299	0.1319		0.07595
79′ 0″	0.1319			0.08596
99′ 0″	0.1319			0.1099
109′ 0″				0.1140
115′ 0″				0.1140

TABLE IV

Silica Content 4%

Time	Concentration of acetic acid			
	0.373 N pH (9)	0.397 N (8.1)	0.55 N (5−3)	0.60 N (5.2)
1′ 0″	0.009993	0.04796	0.01399	0.01399
11′ 0″	0.02798	0.09993	0.01399	0.01599
28′ 0″	0.05196	0.1559	0.02598	0.01998
42′ 0″	0.06998	0.1719	0.04596	0.02598
48′ 0″	0.07596	0.1739	0.05597	0.03198
62′ 0″	0.09194	0.1739	0.07995	0.04197
85′ 0″	0.1119		0.1159	0.06395
98′ 0″	0.1219		0.1298	0.07595
106′ 0″	0.1239		0.1359	0.08392
118′ 0″	0.1239		0.1399	0.09194
120′ 0″			0.1399	0.09592

TABLE V

Silica Content 5%

Time	Concentration of acetic acid			
	0.45 N pH (9.15)	0.50 N (7.5)	0.67 N (5.3)	8.70 N (5.2)
1′ 0″	0.03198	0.1119	0.01399	0.01399
4′ 0″	0.03597	0.1819	0.02997	0.01799
6′ 0″	0.03597	0.1998	0.03797	0.02198
16′ 0″	0.04098	0.1998	0.08794	0.03597
29′ 0″	0.05196		0.1459	0.07794
43′ 0″	0.06395		0.1639	0.1199
48′ 0″	0.07194		0.1679	0.1299
68′ 0″	0.09194		0.1679	0.1539
92′ 0″	0.1099			0.1659
103′ 0″	0.1159			0.1679
110′ 0″	0.1219			0.1679
115′ 0″	0.1239			0.1679
120′ 0″	0.1259			

Discussion of Results

It will be seen from the curves (Fig. 1) that in each case the extinction coefficient of the gel-forming mixture increases with time at first slowly, then rather rapidly and finally more slowly until it reaches an almost constant value, when the curves run parallel to the time-axis. This indicates that the value of log. I or I continuously decreases, that is, the intensity of the scattered light increases with time. These curves, therefore, represent the manner in which the size of the particles of the gel increases during the process of gel formation.

The extinction coefficients of the various gel-forming mixtures have been measured from the time of mixing the gel forming constituents until the mixtures set to a gel. Prasad and Hattiangadi[1] have shown that when the gel forming constituents are mixed, a sol of silicic acid is first formed and the gel is formed from the coagulation of the sol. These observations, therefore, include those of the sols in the beginning and of the gels in the end. The higher values of the extinction coefficient in gels than in the corresponding sols definitely show that the particles in the gel are bigger in size than in the sol. Also the continuous nature of the curves indicates that in the gel forming mixtures the formation of the colloidal particles, their growth in size and increase in hydration and the final coalescence of these hydrated particles, resulting in the formation of definite structures, are continuous processes.

From study of different properties of soap sols and gels McBain[2] concludes that the colloidal particles in the sol and the gel state are identical in

---

[1] J. Indian Chem. Soc., 6, 893 (1929).

[2] J. Chem. Soc., 117, 1506 (1920).

nature and amount: gels differ from sols only in possessing elastic properties. This view is, however, not supported by the conclusions mentioned above, according to which the formation of the bigger particles by the union of the smaller ones appears to be a necessary factor in the sol gel transformation.

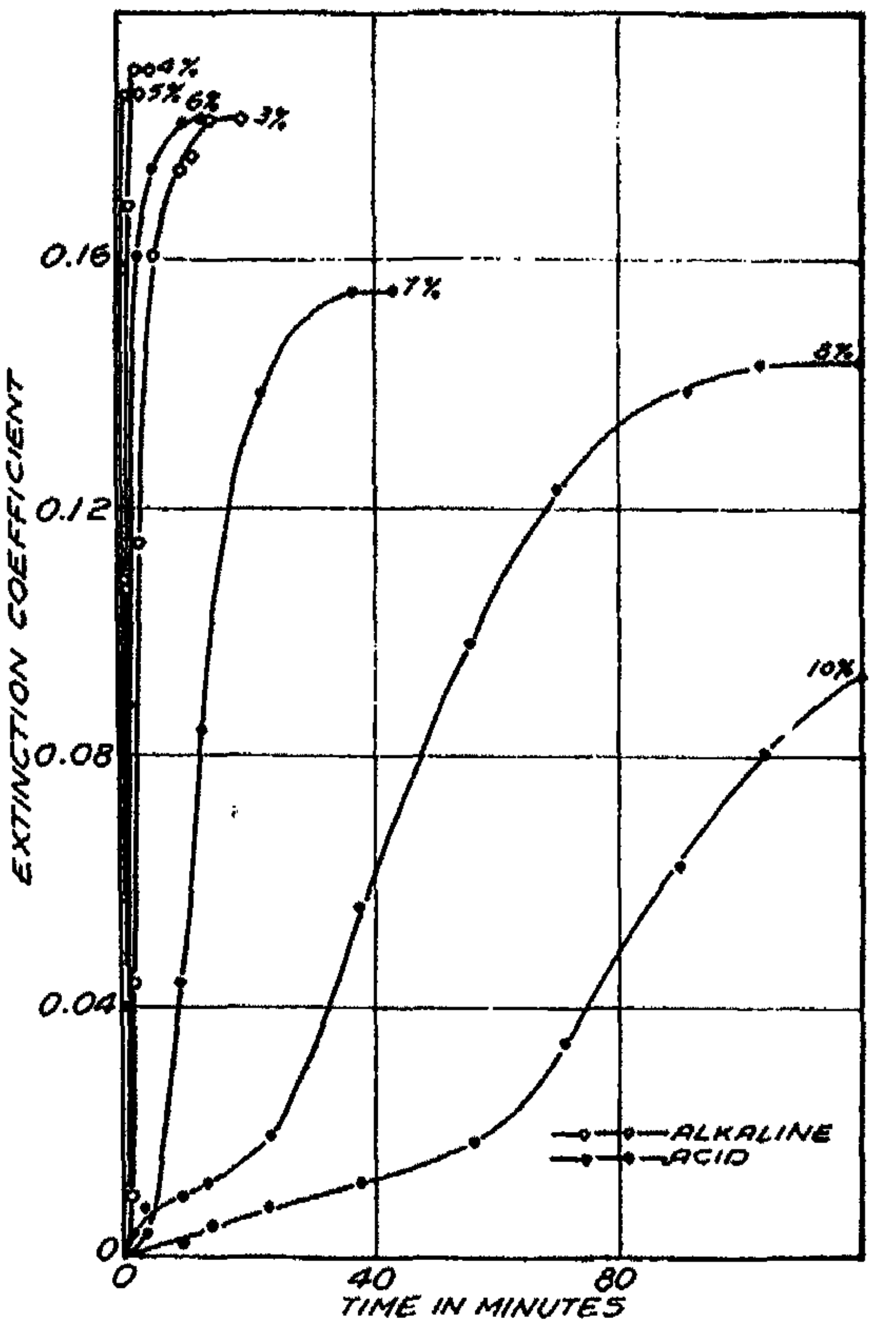


Fig. 1

Silica Content: 3% (with ammonium acetate)

Krishnamurti[1] has also come to the same conclusion from the study of the agar sols and gels.

Further it will be seen from Tables VI and VII that at the time of setting the extinction coefficients of alkaline gels are higher than those of the acidic ones, that is, the light scattered by the former gels is greater than that by the latter. Considering the gels containing the same concentration of silica it appears that the particles formed in the alkaline gels are bigger in size than those formed in the acidic ones and hence the alkaline gels appear more opalescent than the acidic ones.[2]

---

[1] Loc cit.

[2] Cf. Prasad and Hattiangadi: loc. cit. p. 653.

TABLE VI

Extinction coefficient at the time of setting

Concentration of ammonium acetate	Silica content 3%	4%
4%	0.1899 (alk)	0.1958 (alk)
5%	0.1859 "	—
6%	0.1819 "	—
7%	0.1539 (acidic)	—
8%	0.1419 "	—
9%	—	0.1739 (acidic)
10%	—	0.1859 "

TABLE VII

Extinction coefficient at the time of setting

Concentration of acetic acid	Silica content 3%	4%	5%
0.331 N	0.1319 (alk)	—	—
0.34 N	0.1319 "	—	—
0.36 N	0.1419 "	—	—
0.373 N	—	—	—
0.397 N	0.1140 (acidic)	0.1739 (alk)	—
0.50 N	—	—	0.1998 (alk)
0.55 N	—	0.1399 (acidic)	—
0.67 N	—	—	0.1679 (acidic)
0.70 N	—	—	0.1679 "

The conclusion regarding the size of the particles in alkaline and acidic gels is supported by the observation of Linder and Picton[1] who found no Tyndall cone in the dialysed sol of silicic acid in the presence of large concentration of hydrochloric acid.

It is also known that when hydrochloric acid is added to isoelectric gelatin, it gets positively charged and has a greater tendency to disintegrate than the iso-electric gelatin. Prasad and Hattiangadi[2] have shown that the silicic acid particles in the acidic mixtures are positively charged. Lösenbeck[3] has shown that the density of the positive charge in the silicic acid is much greater than the negative charge. The fineness of the particles in the acid mixture may, therefore, be due to the greater disintegration of the positively charged silicic acid in these mixtures.

It will be seen from the curves shown in Fig. 1 that they ultimately run parallel to the time-axis. This indicates that the changes involved in the

---

[1] J. Chem. Soc., **61**, 154 (1892).

[2] Loc. cit. p. 893.

[3] Kolloidchem. Beihefte, **16**, 27 (1922).

setting of the gel have reached a final stage. These measurements can, therefore, be used to determine the time of setting of gels.

The time of setting of silicic acid gels has been measured by Fleming[1] by the criterion that the set gel does not flow out of the container. Fells and Firth[2] have used the criterion of the pressure required to blow a bubble through the gel forming mixture. Prasad and Hattiangadi[3] have calculated the time of setting from the intensity of light transmitted by the gel forming mixture at different intervals during gel formation. The times of setting from the present investigation are given below.

TABLE VIII

(A) Silica Content 3%

	Alkaline			Acidic			
Concentration of ammonium acetate	3%	4%	5%	6%	7%	8%	10%
Time of setting	15′ 0″	3′ 0″	1′ 30″	10′ 0″	38′ 0″	116′ 0″	More than two hours
Concentration of acetic acid	0.33N		0.34N	0.36N		0.39N	
Time of setting	79′ 0″		55′ 0″	33′ 0″		109′ 0″	

(B) Silica Content 4%

	Alkaline		Acidic		
Concentration of ammonium acetate	3%	4%	9%	10%	15%
Time of setting	8′ 0″	2′ 45″	14′ 0″	22′ 0″	More than two hours
Concentration of acetic acid	0.37 N	0.40 N	0.55 N		0.60 N
pH value	9	8.1	5.3		5.2
Time of setting	106′ 0″	48′ 0″	118′ 0″		More than two hours

(C) Silica Content 5%

Concentration of acetic acid	0.45 N	0.50 N	0.67 N	0.70 N
pH value	9.15	7.5	5.3	5.2
Time of setting	More than two hours	6′ 0″	48′ 0″	110′ 0″

---

[1] Z. Physik, 41, 427 (1902).

[2] Trans. Faraday Soc., 23, 625 (1927).

[3] Loc. cit. p. 653.

The relative effect of the silica content, on the time of setting, is shown in the following table:

TABLE IX

(1)	Concentration of ammonium acetate	3%		4%	
	Silica content	3%	4%	3%	4%
	Reaction	Alkaline		Alkaline	
	Time of setting	15′ 0″	8′ 0″	3′ 0″	3′.45″
(2)	pH value	5.3		5.2	
	Silica content	4%	5%	4%	5%
	Time of setting	118′ 0″	48′ 0″	More than two hours	110′ 0″

The time of setting of the gel, therefore, depends upon (i) the concentration of silica and (ii) the H ion concentration of the mixture: it decreases as the concentration of silica is increased, while, with an increase in the H ion concentration the time of setting at first decreases and then begins to increase.[1]

The mixtures having pH 6-8 set in minimum time. No extinction coefficient readings could be taken with mixtures within this range as they set in a very short time but the determination of the time of setting by Fleming's method confirmed the results of previous workers, that the mixtures setting in minimum time are either slightly alkaline or neutral.

Considering that the process of gel formation is one of coagulation of the sol[2] it would be interesting to examine the applicability of Smoluchowski's theory of kinetics of coagulation[3] to the case of silicic acid gel formation. The conditions of the theory require that the coagulation curves must be similar in shape and related to one another. This is indicated by the similarity of the curves shown in Fig. 1. If then a particular value of the extinction coefficient is shown by various mixtures at times t, t_2, t_3, $\Sigma\eta$ which represents the same stage of coalescence, has a fixed value and

$$\frac{t_1}{T_1} = \frac{t_2}{T_2} = \frac{t_3}{T_3}$$

$$\text{or } t_1 : t_2 : t_3 \,.\,.\,.\,.\,.\, t_n = T_1 : T_2 : T_3 \,.\,.\,.\,.\,.\, T_n$$

where T_1, T_2, T_3 . . . . . T_n are constants. The ratio of T_1, T_2, T_3 must, therefore, be a fixed ratio independent of the absolute values of the extinction coefficients. These values are taken from the curves drawn for Tables I to V and are given in the following tables.

---

[1] Cf. Prasad and Hattiangadi: loc. cit.

[2] Cf. Arisz: Kolloidchem. Beihefte, 7, 18 (1915); Prasad and Hattiangadi: loc. cit., p. 893; Dhar and Prakash: J. Indian Chem. Soc., 6, 391 (1929).

[3] Physik. Z., 17, 557 (1916); Z. physik. Chem., 92, 129 (1917).

TABLE X

Silica Content 3%

	Time in minutes with following concentrations of ammonium acetate							Ratios						
Ext. coeff.	3% t_1	4% t_2	5% t_3	6% t_4	7% t_5	8% t_6	10% t_7	$\frac{T_1}{T_3}$	$\frac{T_2}{T_3}$	T_3	$\frac{T_4}{T_3}$	$\frac{T_5}{T_3}$	$\frac{T_6}{T_3}$	$\frac{T_7}{T_3}$
0.04	1.45	0.5	0.45	1.0	8.5	32.5	74	3.22	1.1	1	2.22	18.88	72.2	164.4
0.06	1.8	0.6	0.55	1.25	10.6	40.0	88	3.27	1.09	1	2.24	19.27	72.22	160.0
0.07	2.0	0.7	0.6	1.35	11.5	44.0	96	3.3	1.17	1	2.25	19.7	73.34	160.0
0.09	2.45	0.8	0.75	1.5	13.6	53.0	116	3.26	1.07	1	2.0	18.14	70.66	154.67
0.10	2.63	0.9	0.8	1.6	14.75	57.0	—	3.29	1.13	1	2.0	18.44	71.25	—
0.11	2.9	1.0	0.85	1.7	16.0	62.0	—	3.41	1.18	1	2.0	18.82	72.94	—
0.12	3.2	1.05	0.90	1.75	17.75	68.0	—	3.55	1.17	1	1.94	19.7	75.56	—

TABLE XI

Silica Content 4%

	Time in minutes with the following concentrations of ammonium acetate						Ratios					
Ext. coeff.	3% t_1	4% t_2	9% t_3	10% t_4	15% t_5	20% t_6	$\frac{T_1}{T_2}$	T_2	$\frac{T_3}{T_2}$	$\frac{T_4}{T_2}$	$\frac{T_5}{T_2}$	$\frac{T_6}{T_2}$
0.03	1.25	0.25	1.8	1.8	48	80	5.0	1	7.2	7.2	192	320
0.04	1.5	0.3	2.2	2.25	57	90	5.0	1	7.34	7.5	190	300
0.05	1.75	0.35	2.25	2.5	63	97	5.0	1	6.43	7.14	180	277.14
0.06	1.9	0.4	2.5	2.75	67	104	4.75	1	6.25	6.88	167.5	260
0.07	2.0	0.45	2.6	3.0	72	111	4.45	1	5.78	6.67	160	246.67
0.08	2.1	0.5	2.75	3.5	78	—	4.2	1	5.5	7.0	156	—
0.09	2.2	0.5	2.9	4.25	85	—	4.4	1	5.8	8.5	170	—

TABLE XII

Silica Content 3%

Ext. coeff.	Time in minutes with the following concentrations of acetic acid: 0.33 N t_1	0.34 N t_2	0.36 N t_3	0.397 N t_4	Ratios: $\frac{T_1}{T_3}$	$\frac{T_2}{T_3}$	T_3	$\frac{T_4}{T_3}$
0.04	12.5	9.0	0.8	47.5	1.56	1.13	1	5.94
0.05	15.5	11.0	9.5	55.5	1.63	1.16	1	5.84
0.06	19.0	13.0	10.5	62.5	1.81	1.24	1	5.95
0.07	22.5	15.5	12.0	69.5	1.88	1.29	1	5.79
0.08	26.0	18.5	13.0	75.5	2.0	1.42	1	5.81
0.09	31.0	22.0	14.0	81.5	2.21	1.57	1	5.82
0.10	36.0	26.0	16.5	88.0	2.12	1.58	1	5.34

TABLE XIII

Silica Content 4%

Ext. coeff.	Time in minutes with the following concentrations of acetic acid: 0.373 N t_1	0.397 N t_2	0.55 N t_3	0.60 N t_4	Ratios: $\frac{T_1}{T_2}$	T_2	$\frac{T_3}{T_2}$	$\frac{T_4}{T_2}$
0.06	34	6	50	81	5.67	1	8.34	13.5
0.07	42	7	56	91	6.0	1	8.0	13.0
0.08	51	8	61.5	101	6.38	1	7.69	12.63
0.09	61	9	67	113	6.78	1	7.45	12.56
0.10	71	11	74	—	6.45	1	6.73	—
0.11	81	12.5	80	—	6.48	1	6.4	—
0.12	95	15	87	—	6.34	1	5.8	—

TABLE XIV

Silica Content 5%

Ext. coeff.	Time in minutes with the following concentrations of acetic acid			
	0.45 N t_1	0.50 N t_2	0.67 N t_3	0.70 N t_4
0.05	29.0	0.20	9.5	20.0
0.06	40.0	0.25	12.0	24.0
0.07	48.0	0.30	13.0	27.0
0.08	56.0	0.40	15.0	29.5
0.09	66.0	0.55	16.0	32.0

Ratios			
$\frac{T_1}{T_2}$	T_2	$\frac{T_3}{T_2}$	$\frac{T_4}{T_2}$
145	1	47.5	100
160	1	48.0	96
160	1	43.34	90
140	1	37.5	73.75
120	1	29.09	58.18

It will be seen from these tables that in most of the cases the range of variation in the values of T is small. This shows that the ratios of the values of T are almost independent of the time or the stage of gelation. It appears that within a certain range of extinction coefficients shown in the tables the gelation of silicic acid approximates to the case of an ideal coagulation assumed by Smoluchowski. It should however be noted that for very low or very high values of extinction coefficients the variations in the ratios are too great to be negligible.

Prasad and Hattiangadi[1] have pointed out that the colloidal particles of silicic acid are first formed after the gel-forming constituents are mixed. Krishnamurti[2] has followed the changes in the intensity of the Tyndall light with time during the hydrolysis of methyl silicate and has found that the primary particles first formed, grow into bigger aggregates. The continuity of the time-extinction coefficient curves, however, indicates that the formation of colloidal particles and their coagulation are taking place simultaneously. But it is reasonable to assume that in the beginning the rate of formation of the colloidal particles will be much greater than their coagulation. The discrepancy in the preliminary stage thus appears to be due to the simultaneous formation of colloidal particles.

In the later stage of gel-formation the discrepancy may be due to the high degree of hydration of the particles on account of which their collisions may not be perfectly inelastic and the assumptions of Smoluchowski's theory are not satisfied.

---

[1] Loc. cit. p. 893.

[2] Nature, 124, 690-691 (1929).

Summary

(1) The extinction coefficients of various mixtures forming gels of silicic acid have been measured by means of Hilger Nutting's spectro-photometer. It has been shown that at constant concentration the micelles in gels are bigger than those in sols. Also, at constant concentration the micelles in alkaline gels are bigger than in the acidic ones.

(2) The time of setting of the gels has been calculated from the curves in which extinction coefficients are plotted against time.

(3) Application of Smoluchowski's theory of kinetics of coagulation of a colloidal solution by electrolytes has been extended to the case of gelation.

Physical and Inorganic Chemistry Laboratories,
Royal Institute of Science,
Bombay.

NEW BOOKS

Colloid Chemistry Theoretical and Applied. *Edited by Jerome Alexander. Vol. III. 23 × 17 cm; pp. 655. New York: Chemical Catalog Company, 1931. Price: $10.50.* In the preface the author says: "There is a wealth of wisdom in 'cooking recipes,' despite the fact that this term is sometimes used as an acme of scientific scorn. Time out of mind cooks have beaten the whites of eggs separately from the yolks, and secured light cake by carefully folding in the beaten leavening froth of the whites into the batter containing the yolks. The modern physical chemist finds that the lipoid or fatty matter in the yolks makes the foam bubbles of the beaten whole egg so unstable that if you beat up the whole egg 'your cake is all dough.' Furthermore, the use of oils or fats as 'foam killers' has long been 'rule-of-thumb' practice in many industries, and has also been frequently made use of by sea-captains. In fact, 'to throw oil on the troubled waters' has become proverbial.

"The upshot of these remarks is that scientists must consider the existence of a long-standing practice as presumptive evidence that there is *something* valuable in or about it and that exploration in that neighborhood, with impartial separation of gangue, should yield some nuggets of truth. Geologists frequently learn a great deal about the strata of certain regions by a careful examination of mineral grains in ant hills," p. 3.

"As to the arrangement of papers in Vols. III and IV, which conclude the series, the first group consists of subjects of interest to many industries, and comprises eleven papers on *general principles* and six papers dealing with *mechanical* or more specialized matters. The large second group (twenty-five papers) may, for want of a better name, be termed *telluric*; for it deals with matters which are of the earth, earthy, beginning with geology and mineralogy, and running to metals, petroleum, asphalt and agriculture," p. 5.

The papers and authors are: Cohesion and Adhesion by J. W. McBain and Jerome Alexander; Some Practical Results of X-ray Researches on Colloids by G. L. Clark; Wetting of Solids by F. E. Bartell; Spontaneous Dispersion of Small Liquid Particles by N. Rashevsky; The Influence of Elasticity and Permeability on the Swelling of Two-Phase Systems by Karl von Terzaghi; On the Rubber-like and Liquid-Crystalline States of Matter, in Connection with the Classification of Crystals and Molecules according to their Vectorial Fields by P. P. von Weimarn; Surface and Catalysis by E. F. Armstrong; Contact Catalysis by H. S. Taylor; Adsorption by Silica Gel, Theory and Applications by E. B. Miller; Colloid Factors in Water Supply by W. D. Turner and D. D. Jackson; Crushing and Fine Grinding of Quartz by Louis Navias; Colloid Mills and Comminution Chemistry by August Chwala; Suspensoids and their Electrical Precipitation by W. W. Strong; The Super-Centrifuge in Industry by E. M. James; Notes on Filtration with Special References to Metafiltration by J. A. Pickard; the Flotation Process by G. H. Buchanan; Chemical Warfare by Jerome Alexander; Colloid Chemistry and Geology by R. E. Liesegang; Colloidal Minerals by Cornelius Doelter; Colloids in Glass by Alexander Silverman; Some Colloidal Properties of Sodium Silicate Solutions by William Stericker; Porcelain and Allied Ceramic Bodies by Louis Navias; Ceramic Refractories as Disperse Systems by E. W. Washburn; The Colloidal Nature and Properties of Cements and Mortars by A. B. Searle; The Colloidal State in Metals and Alloys by Jerome Alexander; Colloidal Conditions in Metal Crystals by W. Guertler; Colloidal Systems in Metallography by Carl Benedicks; The Well-known Five Structures in Steel by Kôtarô Honda; The Rôle of Surface Energy on the Equilibria of Iron and Iron Carbide by Yap, Chu-phay; The Properties of Thin Films on Metals by U. R. Evans; The Colloids and the Corrosion of Iron by J. N. Friend; Colloid Chemistry and Petroleum by A. E. Dunstan; Colloid Chemistry of Petroleum by J. C. Morrell and Gustav Egloff; Colloid Chemistry and Petroleum by L. Gurwitsch; The Free Carbon of Coal Tar by J. M. Weiss and C. R. Downs; Asphalt by E. J. Nellensteyn; Deflocculated Graphite by E. G. Acheson; Colloid Fuel by L. W. Bates; Soil Colloids by J. di Gleria and Fr. Zucker; The Colloidal Chemistry of the Soil by Richard Bradfield; Rapid Colloidal and

Mechanical Analysis of Soils by G. J. Bouyoucos and M. M. McCool; The Colloid Chemistry of Wheat, Wheat Flour, and Wheat Flour Products by R. A. Gortner.

"That thin films are very much stronger than an adhesive *en masse* is established by Crow's results for soft solder and our much more striking instance of a wax-free shellac. Joints made with this shellac, which is fairly soft and quite pliable, actually withstood a pull of nearly 4000 lb. per sq. in. when a thin film was used between nickel surfaces. We have found that optically plane surfaces prepared at the National Physical Laboratory yield stronger joints than those which have not been prepared with such precision. An examination of the broken joint served to show how exceedingly thin was the film between those highly polished surfaces. The amount of adhesive attached to the metal was just sufficient to dim the lustre. Incidentally the results of the tests carried out with a shellac-creosote cement between optically plane surfaces of mild-steel and nickel prove beyond doubt that surface roughness plays but a negligible part in determining the strength of a 'specific' joint for here we have the smoothest possible surfaces yielding stronger joints than those prepared in the ordinary way and which are therefore comparatively very rough, "p. 22.

"Krishnamurti has found for samples of sugar, benzene, and naphthalene charcoals and carbon obtained by charring ash-free gelatin with molten sodium, together with colloidal graphite prepared by exploding graphite acid in a vacuum, that all showed the small angle scattering in a marked manner. The patterns showed two rings in addition to the central scattering, the first and prominent ring corresponding to the (002) reflection of graphite, having a spacing of about 3.8 A.U. as compared to 3.4 A.U. of graphite. The outer ring was fainter and broader and showed a spacing of 2.12 A.U. comparable to the (111) spacing of graphite (2.06 A.U.). The observations accord with the idea that in the amorphous state the carbon atoms join together in clusters, forming highly anisotropic units, essentially two dimensional, the thickness being about 1/3 the length or breadth. Assuming that the central scattering is due to the dimensions in the plane of the particle, and the first ring to its thickness, a rough calculation gives about 60 atoms of carbon per unit. This picture of the carbon particle agrees with chemical evidence, mainly its oxidation to mellitic acid and adsorptive properties," p. 33.

"Following the discovery of Krishnamurti that diffraction patterns of aqueous solutions of cane sugar, levulose and glucose were distinguished by intense scattering at small angles due to the dissolved molecules, it was then possible to undertake the study of colloidal solutions for which the state of molecular aggregation has been the subject of much speculation. The molecular weight of dextrin calculated from the extent of "amorphous" scattering by means of the Bragg formula $n\lambda = 2d \sin \theta$ comes out 600, and for gelatin, 3,000, which are not improbable values. The solution of sodium oleate produced a ring due to the presence of big groups or micelles of sodium oleate in the solution. The extent of the gaseous scattering gave the dimension for the sodium oleate molecule, agreeing with that calculated from molecular weight and density. An excess of scattering directly adjoining the central spot, is due to big groups of ionic micelles described by McBain. Aqueous solutions of starch, tannic acid and gum arabic showed a further scattering at small angles to the primary beam, due to the dissolved molecules or micelles. The molecular weights calculated from the extents of the coronas were 6,200, 3,134, and 2,810, respectively. Thus, a starch molecule contains about 10 dextrin molecules united together, and a tannin micelle contains 10 simple molecules of the formula $C_{14}H_{10}O_9$. The great importance of these studies is at once apparent, when it is considered that extremely valuable information should be obtained from biological fluids including blood, filtrable virus, etc. In all these cases of amorphous solids, liquids and solutions, the X-ray patterns are characteristic in showing the presence of one or more diffraction bands, even though these may be ill defined. The purely amorphous scattering where no maxima are present, evidently can exist only in the case of ideal gases. All of these newer investigations are in agreement with the contention by the writer that such a material as amorphous carbon represents an intermediate state designated as a paracrystalline, through which the atoms of carbon have to pass before obtaining the orderly arrangement underlying the graphite structure," p. 34.

"There has been a very considerable disagreement concerning the structures of gutta percha and balata which are like rubber, polymers of isoprene. The discrepancies have at last been explained in the work of Kopff and von Susich and of Stillwell and Clark. These two substances produce diffraction patterns different from rubber, but probably like each other. There are two modifications, the α which is stable below 60°C. and β produced by heating above 60°, giving different patterns in the unstretched state. The β-modification also produces a fiber pattern, since the specimens must be warmed before stretching. Stillwell and Clark have found balata in ordinary commercial form to differ from ordinary gutta percha, in the same way that von Susich's β-modification differs from β-gutta percha," p. 37.

"A plausible mechanism for muscular action can be deduced in terms of inner molecular forces. Rubber contracts because of double bonds in the long hydrocarbon chains which cause a spring-like coiling. In muscle protein there are many free basic and acid groups in the chains, since glutaminic acid and arginine and lysine may be derived. At the isoelectric point COO^- and NH_3^+ ions may attract and pull the chain into a close spiral," p. 39.

"If wetting be defined as 'that phenomenon which occurs when a solid phase and a liquid phase come in contact in any manner, so as to form a solid-liquid interface,' the ground for controversy relative to wetting and non-wetting has been removed. There remains only the question of degree of wetting of the solid by the liquid. If it be further specified that degree of wetting means the amount of change in free surface energy which occurs (or the work done by the system) when the solid and liquid are brought together, all confusion can be avoided," p. 41.

"Carbon pigments are used as a *filler for rubber*. Carbon gives an exceptionally high adhesion against the organic constituents of the rubber; this is desirable as it results in a product of high elasticity and good wearing qualities. Over one hundred million pounds of carbon black are used per year in the rubber industry alone. Large quantities of carbon pigments are used also in *printing inks*, in *stove polishes*, and in *shoe polishes*. In each of these preparations the liquids used must give a high degree of wetting with the pigment. In printing inks the liquid medium must possess a fairly low surface tension in order to give a smooth flow over the surface with a minimum tendency for the ink to pull up into drops; on the other hand 'spreading wetting' (the magnitude of which is increased as surface tension of liquid is decreased) against the paper cannot be too high, otherwise a sharp imprint will not be obtained," p. 54.

"Three different groups of facts lead, therefore, to the assumption that gelatine has a sponge or net-like structure," p. 86. "A system possessing the high elasticity of rubber must have the following structure: (1) The *primary* structure elements of such a system must possess the form of spirally curled fibrils; (2) the interfibril dispersion medium must be extremely viscous (plastic) and permit the fibrils, after the stretching out of the system, to become curled when the system has been released from tension," p. 96.

"It is the specific nature of the catalyst which determines what the chemical change shall be. More closely studied from this point of view has been the reaction of carbon monoxide with one, two or three molecules of hydrogen, producing formaldehyde, methyl alcohol or methane respectively. Any desired one of these three products can be made with the practical exclusion of the others, provided that a suitable temperature and catalyst is selected. A copper catalyst at 300° to 400°C. favors the formation of formaldehyde; to produce methyl alcohol a reduced basic zinc chromate is necessary at 300° to 350°C., whilst for methane the best catalyst is nickel at 150° to 200°C. The reactions are carried out at fairly high pressures," p. 103.

"The linearity of the time-hydrogen-adsorption curve in cases of hydrogenation in liquid media is held to be evidence of interaction of the organic compound rather than the hydrogen with nickel, because the rate of absorption varies during the course of hydrogenation of many unsaturated substances containing two ethylenic linkages at or near the point at which the material becomes semi-hydrogenated, and chemical analysis has shown in such cases that the reduction has been 'selective,' that is the two centres of unsaturation are reduced in number to one before any proportion of the singly unsaturated product is completely hydrogenated. Consequently, the slope of the time-absorption line is definitely correlated with the organic compound present. It is desirable to emphasize this most striking feature whilst at the same time bearing in mind that hydrogen undoubtedly also becomes associated with the nickel," p. 105.

"The extent of the surface which is active varies with the nature of the reaction catalyzed. There is unequivocal evidence that, in certain reactions, every atom in the surface is active. In others the evidence is equally definite that only a small fraction of the surface is active. In the former case the reaction is relatively insensitive to poisons, in the latter case extremely sensitive. Hence arises the possibility of progressive poisoning in which, on a given catalyst, different reactions are successively stopped by increasing amount of poison. The study by Vavon and Huson of a colloidal platinum on which the hydrogenation of propyl ketone, piperonal, and nitrobenzene were successively suppressed by addition of increasing quantities of sulfide poisons is a good example of such behavior," p. 108.

"When we turn from elementary catalysts such as the metals to catalysts composed of compound materials with ionic lattices such as oxides, halides, sulfates, etc., the surfaces in question contain an additional factor of variability. Such ionic lattices may be regarded as dual catalysts, the surface being composed of metal ion and negative ion. To each type of ion may be ascribed a definite and specific catalytic activity. Examination of the catalytic behavior of the oxides suggests that, on the metal ion, processes of hydrogenation and dehydrogenation occur, whereas, on the oxide ion, the processes are essentially hydration and dehydration. With a given process, the extent of the two alternative changes will be determined by the relative extent of adsorption of reactant on the two ions, on the relative frequency of the two ions in the surface and on their specific individual catalytic activities. These several factors (extent of adsorption, frequency of ions in the surface and catalytic activity) will be determined by the degree of saturation of the lattice ions, and by the extent to which the ions are already covered by poisons (salts, water, ammonia, etc.). With this concept, the variation in dehydration-dehydrogenation ratio of various oxide catalysts in, for example, formic acid decomposition

$$\begin{aligned} \mathrm{HCOOH} &= \mathrm{H_2} + \mathrm{CO_2} \\ \mathrm{HCOOH} &= \mathrm{H_2O} + \mathrm{CO} \end{aligned}$$

and ethyl alcohol decomposition

$$\begin{aligned} \mathrm{C_2H_5OH} &= \mathrm{CH_3CHO} + \mathrm{H_2} \\ \mathrm{C_2H_5OH} &= \mathrm{C_2H_4} + \mathrm{H_2O}, \end{aligned}$$

receives a more satisfactory interpretation than has hitherto been suggested for such reactions," p. 109.

"Probably the most important application of silica gel so far developed commercially is in the so-called contact sulfuric acid process. As a carrier for platinum it is ideal. It is chemically inert to sulfuric acid at high temperatures, stands up under continuous high temperature conditions, is resistant to mechanical action and offers an enormous surface upon which to distribute the platinum. Besides possessing these qualities silica gel mass has also proven insensitive to the usual negative effect of arsenic poisoning," p. 133.

"Micro-organisms often give trouble in reservoirs which at certain seasons may become literally hotbeds for the growth of various types of microscopic forms, which will contribute colloidal impurities to the water. The combined influences of warmth, sunlight, and quiet are all contributing factors which may sometimes be very difficult to alter. In certain regions reservoirs must be covered wherever possible to exclude sunlight, and thus inhibit microscopic growths. In Bermuda, for instance, where the climate is temperate, but the sun is hot, raw water cannot be stored in the sunlight for even forty-eight hours without becoming green from the prolific growth of chlorophyceae. All storage tanks in the region are, therefore, constructed with covers to keep out the light," p. 137.

"Red water occasionally gives trouble in certain water pipes, particularly, the system within private properties, and especially the hot water systems. This rusty discoloration is due to colloidal ferric iron in the water and is usually traceable to the effect of dissolved air or oxygen on the walls of the iron pipe. The effect is noticed more frequently with soft water and obviously more so with hot water. In New York City the water is so soft that incrustation in water heaters takes place very slowly, or not at all. Here it is, therefore, not uncommon to find the water in hot water pipe lines running brick red from the iron contamination originating within the heater system," p. 138.

"Reaction of the negative colloidal color with the positive nucleus of the coagulating agent (copperas or alum) gives flocculation precipitation and decolorization, but as pointed out by Whipple colored waters having the negative property increased by addition of CO_2 can be better decolorized by alum coagulation. This is in conformity with the experience of Jackson, who found that the highly colored water in the Everglades region of Florida could be successfully decolorized, first, by adjustment of the hydrogen ion concentration by addition of so active an agent as sulfur dioxide, followed by the customary addition of alum coagulant," p. 150.

"The traces of certain impurities which may give trouble are sometimes astonishingly small. This is well illustrated by an experience of the large rayon plant near Buffalo. Here it was definitely established that the discoloration in the top skeins of piles of fiber through which they were running wash water was due to a trace of copper in the water which gave trouble in concentrations as low as one part in 40,000,000," p. 153.

"Where no solvents are present, from solid non-gels there are formed only turbidities, provided that there are used as peptizers only substances which are polar and relatively slightly active. Solvates, on the other hand, form sols, but require as peptizers very active molecules having the power to form true compounds which can fasten themselves to the particle surface. The slightly active polar substances which serve as peptizers for solid non-gels, are incapable of orienting themselves on solvates," p. 188.

"The sedimentation of *Bacillus acidophilus* from broth culture furnishes an interesting example of the ability of the centrifuge to remove finely divided solids. The bacilli, which vary in length from 1μ to 3μ, and have a diameter of approximately 0.5μ are formed in the broth culture under carefully controlled conditions. When the concentration of the bacilli has reached fifteen hundred million per cubic centimeter, the broth is ready for centrifugal treatment. It is fed through a battery of super-centrifuges at the extremely low rate of 10 gallons per hour, and the effluent, whose bacterial count has been reduced to twenty-five million per cubic centimeter is wasted. When the centrifugal rotors are opened, the bacilli are found adhering to the wall of the bowl in a putty-like mass. From this form they are worked up into a special preparation, providing extremely high bacterial concentration," p. 210.

The tonnage of ore treated in the United States alone by the flotation process amounted "in 1929 to sixty million tons. At one metallurgical operation alone forty thousand tons of ore are treated daily," p. 225.

"The so-called 'Sea of Darkness' in the Atlantic Ocean between Cape Verde Island and the Canaries, probably owes its origin to dust storms from the Sahara Desert, especially between January and April. According to Hellman and Meimardus, a cyclonic storm central over Tunis about March 8-10, 1901, deposited about 150 million tons of dust on the African coast, and further great but incalculable amounts in the Mediterranean Sea. So high did the dust rise, that about one-third of the 1,800,00 tons deposited in Europe fell north of the Alps. E. R. Miller and A. W. Winchell traced a storm of dust-colored snow from Dubuque, Ia., to Chelsea, Vt., over an area of 100,000 square miles; the dust, apparently originating in the deserts of Arizona and New Mexico, must have been carried at high altitudes for over 1,000 miles before being brought down. The daily papers reported on December 19th, 1930, that a terrific storm swept over northern Algeria following a serious seven months drought; and on December 22nd the papers reported that a terrible fog (visibility 3 feet) had paralyzed London. Just prior to this (Nov. 27, 1930) a terrific sand-storm and hurricane blew over French Morocco, carrying a heavy deposit of yellow sand to the streets and foliage of Barcelona the next night. On the morning of Nov. 29th, a 'Mud-rain' fell in Paris, along the English Channel and the coast of Brittany. [See Jerome Alexander: Science, 63, 96 (1931)]," p. 260.

"The ascidian *Phallusia* has a vanadium-containing blood; manganese occurs in mussels; copper in most molluscs," p. 275.

"As a matter of fact, comparatively little is known about the chemical reactions of the sodium silicates in aqueous solutions. . . . If results are reported without specifying the silicate, many questions remain. As an example of the possible contradictions, the reaction with calcium carbonate studied by Carter, may be cited. He found that $Na_2O.2SiO_2$ would react with $CaCO_3$; but that neither $Na_2O.1.6SiO_2$ nor $Na_2O.3.3SiO_2$ showed any evidence of reacting within a period of a week," p. 295.

"Refractory materials are known to have extraordinarily high latent heats of fusion and consequently also very high heats of sublimation," p. 352. It seems to the reviewer that the vapor pressure should increase rapidly with the temperature if the heat of sublimation is very high and that consequently refractories should sublime at relatively low temperatures, in which case they would not be refractories.

"It seems to the present writer [Alexander] that there is no good reason to doubt the existence of Fe_3C, especially when the steel is semi-solid or solid, for there exists a condition of kinetic or dynamic equilibrium in which this compound is being continually formed and broken up, so that while a certain percent of free carbon atoms may exist at any one moment, there is probably an enormously larger percentage of Fe_3C. Viewed from the standpoint of a kinetic equilibrium, all difficulty regarding the diffusion of Fe_3C disappear," p. 429.

"Cold bauxite, which has been ignited and cooled in a vacuum desiccator was found to have lost its power of adsorbing sulfur derivatives from kerosene. When freshly heated (to 200°C.) its activity in this direction was regained. Heat appears to be evolved during active adsorption, thus a 20°C. rise in temperature was observed during the passage of 100 cc. of kerosene through 50 grams of bauxite," p. 494.

"It is estimated that in 1930 three hundred million barrels of the world's total crude oil production was produced in emulsion form, and required some form of treatment before it could be marketed," p. 504.

"From the economic point of view colloidal fuel possesses many advantages over fuel oil or coal alone. First, the fire hazard of colloidal fuel is less than that of oil or coal. The specific gravity of a composite using over about 15 percent of coal is greater than unity. If on fire, the flames may be quenched in and by water, and, in storage, fire may be prevented by a water seal. This fact is of cardinal importance as other liquid fuels are lighter than water and cannot be so safeguarded. Trials of a water seal have shown that certain grades of the fuel may be so stored for even a year without jeopardizing their operative character. Sprinkler systems of fire protection do not lose their utility as they do in plants using oil fuel. The insurance advantage and increased safety of ships and plants due to this fireproofing capacity is obvious," p. 557.

"The great interest practical soil chemists have shown in base exchange phenomena in the last few years is due largely to the fact that an understanding of these reactions promises to throw much light on several of the most important problems in soil management. Such studies as indicated above have served to greatly clarify some of the problems connected with the acid soils of the humid region. The proportion of exchangeable hydrogen in the colloidal fraction, or the "degree of unsaturation with bases" as it is commonly called, is one of the best measures we have of the degree of acidity of a soil," p. 587.

Wilder D. Bancroft

Essentials of Quantitative Chemical Analysis. *By Wilfred W. Scott. 23 × 15 cm; pp. viii + 219. Easton: The Chemical Publishing Co., 1931. Price: $2.75.* This is a new and enlarged edition of Scott's "Inorganic Quantitative Chemical Analysis," 1926. The text contains a comprehensive list of experiments of general educational value for students in introductory quantitative analysis. The arrangement is much the same as the previous addition although several procedures have been entirely rewritten and a number of new methods have been introduced.

The notes and theoretical discussions accompanying the experiments have been increased over those of the previous edition. Numerous references for outside reading and a list of study questions in the addenda of the text are also included.

M. L. Nichols.

Handbuch der allgemeinen Chemie. *Edited by Paul Walden and Carl Drucker. Vol. VIII. Part I. Elektromotorische Kräfte. By R. Kremann and Robert Müller. 25 × 17 cm: pp. xvi + 891. Leipzig: Akademische Verlagsgesellschaft, 1930. Price: 81 marks; bound, 85 marks.* This volume covers the whole field of electromotive forces, not differentiating between aqueous and non-aqueous solutions. The chapters are entitled: introduction; measurements of electromotive forces; conversion of chemical energy into electrical energy by means of galvanic (voltaic) cells and the temperature coefficient of such cells; Nernst's osmotic theory of the galvanic production of current; solution cells; concentration cells; amalgam cells; galvanic cells of the Daniell type; effect of pressure on reversible galvanic cells—gravity cells; determination of single potential differences at phase boundaries in galvanic cells; potential differences at other phase boundaries than those between metals and solutions; electrolytic solution pressure; single potential in cells; potentials of alloys; oxidation-reduction cells; normal potentials of electrode reactions; formation of metals and alloys by precipitation.

"The current in a cell of the Daniell type is due to the fact that the less noble metal (zinc) dissolves, sending positive ions into the solution, and becoming charged negatively itself, while simultaneously equivalent amounts of the ions of the nobler metal (copper) are precipitated on the copper electrode, thereby charging this positively. The equalization of the potential differences takes place in the external circuit with production of electrical work," p. 4.

On p. 13 the authors say that Helmholtz later developed independently the Gibbs formula. This is not true at all. Gibbs developed a theory to show that the electrical energy of a reversible cell is not necessarily equal to the heat of reaction. When Helmholtz deduced the equation for the relation between electromotive force, temperature coefficient, and heat effect, Gibbs showed that the same equation could be deduced from the Gibbs theory. Gibbs did not deduce it and there is nothing to show that he would have deduced it if Helmholtz had not done so.

On p. 20 and elsewhere throughout the book the authors write the formula of mercurour chloride as HgCl, although they cite Ogg's work, p. 99, showing that the mercury ion is Hg_2. Eight pages are given, p. 38, to the application of Nernst's heat theorem to voltaic cells. A good compilation is given, p. 111, of the data on concentration cells in non-aqueous solvents. On p. 132 there is a warning as to errors in electrometric titration caused by adsorption. The authors do not seem to know, p. 136, that there is always retrograde solubility with rising temperature whenever a binary compound is stable at its melting-point. It is difficult to tell, p. 144, what the authors' attitude is towards Spencer's measurements on amalgam cells. On p. 213 is given the deduction by Gans of the effect of pressure on electromotive force when the transference number varies.

"Arrhenius showed that air can act as an electrolyte. If one brings a zinc wire and a platinum wire into a tube pumped out to a pressure of 0.1-2.0 cm, and if one makes the air a conductor by means of cathode rays, a current is obtained between the metals flowing in the direction that it would if the metals were dipped in air; the electromotive force averaged about 0.86 volt," p. 221.

It is recognized, p. 248, that the maximum-surface-tension method does not give the true single-potential difference because of adsorption; but nobody seems to have determined the absolute maximum-surface-tension of mercury in any of these solutions. If the value in sulphate solutions were very close to the true surface tension, the error would be very small. If it were very large, the error would be correspondingly large and there might even be an agreement between this method and that of Billiter. The theory of Frunkin, p. 256, does not appear to come out with anything positive. The authors throw out Billiter's work, p. 276, because the potential difference of silver against a solution is a function of other things besides silver ions; but the potential difference of a hydrogen electrode is a function of chloride, bromide, and iodide ions.

There is a very good account of Haber's work on phase boundary potentials, p. 281; of membrane cells, p. 291; and of the Donnan equilibrium, p. 299. On the other hand, they quote with approval, p. 325, Luther's statement that the potential difference between a metal and a saturated solution of a salt of the metal is independent of the nature of the solvent. The discussion of the change of the solution pressure with the solvent, p. 326, is rather exceptionally poor. From a table for heats of ionization of metals, p. 351, the authors draw the conclusion that all metals which form ions readily have positive heats of ionization, while others have negative heats of ionization. Tin seems to be an exception.

In the discussion of the hydrogen-lead peroxide cell, p. 362, the authors point out that a much larger current can be drawn without polarization with palladium electrodes than with platinum electrodes. Apparently the rate of conversion of molecular into atomic hydrogen is much lower with platinum than with palladium. Also the oxygen polarization of the platinum electrode poisons the latter. Addition of colloidal platinum to a solution, p. 439, makes it possible to use smooth platinum electrodes. Strong poisons for metals, p. 441, are naphthoquinoline, strychnine, brucine, narcotine, and quinine. Less strong are nicotine, veratrine, cocaine, and cinchonine.

Amalgamated aluminum in N/10 $AlCl_3$ gives a potential difference of 1.66 volts against the normal calomel electrode. Since aluminum cannot be precipitated from an aqueous solution, the aluminum electrode is theoretically irreversible and its electromotive force is consequently not a function of the concentration of aluminum ions. This is not true for a fused mixture of aluminum and potassium bromides, p. 476. Aluminum dissolved much more rapidly in hydrochloric acid than in equimolecular hydrobromic or hydriodic acid, p. 477. The authors draw the apparently unwarranted conclusion that the rate of attack is proportional to the concentration of the undissociated acid.

Since iron takes up hydrogen readily and also oxidizes readily in water, its potential is hard to determine. The authors consider $\epsilon_h = -0.46$ as representing the equilibrium potential, p. 541. The intermittent action of acids on chromium is believed to be due to iron in the metal, p. 557. With pure iron in chromic acid, periodic fluctuations of 0.4 volts can be obtained, 558.

While sulphur may form quadrivalent cations, as indicated by the conductivity of liquid sulphur dioxide, it is not legitimate to postulate this from the fact that sulphur is set free at the cathode in the electrolysis of concentrated sulphuric acid, p. 573. That sulphur comes from the interaction of sulphurous acid with hydrogen sulphide.

If one superposes an alternating current on a direct current one can get evolution of hydrogen and oxygen below the point of reversible equilibrium for the oxyhydrogen gas cell. On increasing the alternating current relatively to the direct current, Grube and Dulk found a break in N NaOH at 1.24-1.26 volts which is very close to the theoretical value of 1.237 volts, p. 589. The experiments of Tartar and Wellmann show that soluble substances, possibly hydrogen peroxide, are also a factor, p. 590.

If platinum is precipitated electrolytically on porous charcoal, a film is obtained through which hydrogen passes with great ease and permits a current of twenty milliamperes per square centimeter, p. 613. Butler, Hugh and Hey find that constant potentials as non-attackable electrodes are reached by platinum, palladium, iridium, osmium, gold, rhodium, and ruthenium in about an hour, while molybdenum, tungsten, nickel, silver, and mercury are not certain to give constant potentials at all, p. 663.

The treatment of the effect of hydrogen ions on the potential difference due to oxidizing and reducing agents is perfunctory and unsatisfactory, p. 669.

There are a number of interesting facts on p. 697. A ferrous-ferric salt solution can be prepared which will precipitate silver and not copper. Addition of sodium fluoride causes the precipitation of metallic copper. An alkaline stannite solution precipitates metallic cadmium. There is a distinct over-voltage for hydrogen in vanadous chloride solutions, which can be overcome by platinum metal.

Sixteen pages are given to the quinhydrone electrode, p. 713. It is not clear why cane sugar should affect the readings but it does, p. 723. On pp. 786-790 there is a fairly complete table of electromotive force measurements depending on oxidation or reduction.

The book is a marvellously good one as a collection of facts. The authors are worshippers of the letter, however, and no one will turn to them for inspiration.

Wilder D. Bancroft

CATALYSTS FOR THE OXIDATION OF CARBON MONOXIDE—I

BY C. J. ENGELDER AND L. E. MILLER*‡

This paper is a record of the results of experiments carried out on the catalytic oxidation of carbon monoxide by titania and mixtures of titania with various metallic oxides. The investigation had for its main purpose the study of a number of metallic oxides with titania, with the hope of finding a mixture that would be catalytically active toward the oxidation of carbon monoxide to carbon dioxide at room temperatures and in the presence of water vapor.

Titania has been a favorite catalyst in this laboratory for a number of years. Rudisill and Engelder[1] investigated various factors influencing the catalytic activity of titania in the decomposition of ethyl alcohol. Wescott and Engelder[2] studied the catalytic decomposition of formic acid over titania. On the basis of its activity towards ethyl alcohol and formic acid titania merited special consideration in the reaction, $2CO + O_2 \rightarrow 2CO_2$, in the present research.

Much of the previous work upon the catalytic oxidation of carbon monoxide has been centered upon the study of manganese dioxide, cupric oxide, and mixtures of these oxides. The story of the development of hopcalite for the oxidation of carbon monoxide is well known. Lamb, Bray, and Frazer and their associates[3] conducted most of the investigations which culminated in the production of this well known catalyst. Much of the later work on the catalytic oxidation of carbon monoxide upon the various factors influencing the catalytic activity of hopcalite and its constituent oxides, has been reported by these same investigators.

Bone and his co-workers[4] studied the combustion of carbon monoxide with oxygen over nickel, copper, and their oxides. Other interesting contributions on the subject of carbon monoxide oxidation have been made by Benton and Williams[5] who studied the catalytic oxidation of carbon monoxide in con-

---

* Part of a dissertation presented by L. E. Miller to the Graduate School of the University of Pittsburgh in partial fulfillment of the requirements of the Ph.D. degree.

‡ Contribution No. 230 from the Chemistry Department of the University of Pittsburgh.

[1] W. A. Rudisill and C. J. Engelder: Catalytic Activation of Titania, J. Phys. Chem., 30, 106-113 (1926).

[2] B. B. Wescott and C. J. Engelder: The Catalytic Decomposition of Formic Acid, J. Phys. Chem., 30, 476-479 (1926).

[3] A. B. Lamb, W. C. Bray and J. C. W. Frazer: The Removal of Carbon Monoxide from the Air, J. Ind. Eng. Chem., 12, 213-221 (1920).

[4] W. A. Bone and G. W. Andrew: Studies in Catalytic Combustion. II. The Union of Carbon Monoxide and Oxygen in Contact with Nickel, Copper, and their Oxides, Proc. Roy. Soc., 110-A, 16-34 (1926).

[5] A. F. Benton and T. L. Williams: The Catalytic Oxidation of Carbon Monoxide in Contact with Quartz Glass, J. Phys. Chem., 30, 1487-1496 (1926).

tact with quartz glass. Taylor and Jones[6] made observations on the velocity of carbon monoxide-oxygen combination over copper and copper oxide.

Experimental Method

For the purpose of testing the activity of the various catalysts whose action was studied in this investigation, a definite method was adopted. It consisted in passing carbon monoxide-air mixtures over a sample of the finely ground catalysts contained in the tube of an electrically heated furnace. Analyses were made of the influent and effluent gases for carbon monoxide and carbon dioxide. In all cases one gram of the catalyst was used. The gas mixture which usually contained 10-12 per cent carbon monoxide was maintained at a uniform rate of flow of 50-60 cc. per minute. The duration of a test was usually two hours.

Apparatus. The apparatus for the experimental work consisted of an electrically heated tube furnace as described by Nelson and Engelder[7] in their experiments on the thermal decomposition of formic acid. The temperature was automatically regulated by a Leeds and Northrup temperature controller. The catalyst was contained in a porcelain boat placed in the center of the furnace. The carbon monoxide-air mixture which was contained in a 20-liter carboy was forced over the catalyst by displacing the gas mixture with water from an aspirating bottle. The effluent gases were collected over salt water in a second 20-liter carboy.

The carbon monoxide was prepared by dropping formic acid on hot sulfuric acid. It was freed from sulfur trioxide, sulfur dioxide, carbon dioxide, and formic acid fumes by passing it through a canister containing activated charcoal and soda-lime.

Analysis of Gas Mixtures. The analysis of the gas mixtures was made in the apparatus of Hempel. Carbon dioxide was absorbed in a fifty per cent KOH solution. Oxygen was taken up in alkaline pyrogallol and carbon monoxide in acid cuprous chloride solution.

Preparation of the Catalysts. In order to promote uniformity and to avoid any uncertainty due to the manner of preparation, the catalysts were prepared according to a uniform plan. In general the titania catalysts were prepared according to the method described by Rudisill and Engelder[8] in their experiments on the catalytic activation of titania. Titanium hydroxide was precipitated from a solution of titanium potassium oxalate by ammonium hydroxide. The precipitate was dissolved in dilute sulfuric acid and reprecipitated again with ammonium hydroxide. The precipitate was washed several times by decantation until free from sulfates. It was filtered by suction, and then dried at 150°C. in a drying oven. In the case of titania

---

[6] H. S. Taylor and H. A. Jones: The Reduction of Copper Oxide by Carbon Monoxide and the Catalytic Oxidation of Carbon Monoxide in presence of Copper and Copper Oxide, J. Phys. Chem., 27, 623-651 (1923).

[7] W. L. Nelson and C. J. Engelder: The Thermal Decomposition of Formic Acid, J. Phys. Chem., 30, 470-476 (1926).

[8] W. A. Rudisill and C. J. Engelder: loc. cit.

with the various metallic oxides the hydroxides were precipitated simultaneously from the solutions which would yield the oxides in the proportions by weight desired. So far as was possible the C.P. nitrate salts were used. In certain instances the sulfates were employed for the starting material.

The mixed oxide catalysts were given the same treatment as the titania catalysts. They were dried for about twelve hours and activated by ignition at a temperature of 300°C. for two hours preceding their use.

Experiments with Titania

In Table I are given the results of some representative experiments with titania. These will illustrate the activity of titania toward the catalytic oxidation of carbon monoxide. Titania was not found to be active at temperatures much below 300°C. Experiments carried out at 150°C. showed that with the best titania catalysts only 10-12 per cent of the carbon monoxide was oxidized. From an inspection of the table it may be observed that the titania catalysts were more active at the end of a four-hour run than at the end of a two-hour run. Experiment 2 in the table illustrates the unlimited activity of the titania catalysts.

Table I

Experiments with Titania

All catalysts received the same preliminary treatment. Temperature of ignition, 300°C. One gram of catalyst used. Rate of flow, 50-60 cc. per minute. Duration of run, two hours. CO-air mixture saturated with H_2O. CO, 10-12 per cent. Temperature of furnace, 300°C.

Experiment	Percentage of Oxidation at 300°C.				
	2 hrs.	4 hrs.	6 hrs.	8 hrs.	10 hrs.
1	70.4	75.2	—	—	—
2	74.5	84.9	88.2	85.9	86.3
3	58.9	67.7	—	—	—
4	74.1	79.6	—	—	—
5	55.3	71.6	—	—	—

The difficulty in obtaining identical results for catalysts prepared according to a uniform plan illustrates what differences there must be in the catalytic surfaces of different samples of catalysts from the same preparation.

In order to study the effect of the method of preparation of the titania catalysts on their catalytic activities, a titania catalyst was prepared by employing potassium hydroxide for the precipitant. The various steps in the method of preparation with the exception of the precipitant were exactly the same as that described for the titania catalysts prepared by precipitation with ammonium hydroxide. The results from the two following experiments (Table II) show in general how the titania catalysts prepared by ammonium hydroxide were the more active.

TABLE II

Experiments to show the Activity of Titania prepared by Different Precipitants

Rate of flow, two liters per hour. One gram of catalyst used. Duration of run, two hours. CO-air mixture, dry. CO, 10-12 per cent.

Catalyst	Percentage of Oxidation at 300°C.	
	2 hrs.	4 hrs.
TiO_2 (precipitated with NH_4OH)	92.5	95.8
TiO_2 (precipitated with KOH)	76.9	71.8

While considerable experimental work was done in order to develop a uniform method of procedure, it was observed that such fumes as H_2S and vapors from gasoline, naphthas, and oils had a very marked detrimental effect upon the activity of the catalysts when they were present in the same laboratory in which the catalysts were being prepared. A laboratory remote from any of these disturbing factors was finally selected for the preparation of the catalysts.

Experiments with Titania and Various Metallic Oxides

Although titania in itself proved to be a very good catalyst for the oxidation of carbon monoxide at 300°C. and very poor at a temperature of 150°C., it was thought that the addition of other oxides to titania might have a promoting action. Accordingly preliminary experiments were made with mixed catalysts of 99 per cent titania and 1 per cent of various oxides. The following oxides were tried: UO_2, Fe_2O_3, NiO, Cr_2O_3, Co_2O_3, CeO_2, CuO, SnO_2, MnO_2, ZnO, ThO_2, Bi_2O_3, HgO, Al_2O_3, Ag_2O, MgO, and CdO. From this list the first seven were selected for further study. Experiments were made at 300°C. and 150°C. with mixtures from 1 per cent up to 80 per cent with titania. The results of this extended study are recorded in Tables III and IV.

The best catalysts were obtained from mixtures of the metallic oxides with titania approximating a 50:50 ratio of mixed oxides. The results for ceria, which was only moderately active at 300°C., with titania illustrate the superiority of mixtures in this proportion as may be observed from Table III. In Table IV the combination of titania with ferric oxide shows again the superior activity of mixtures in this ratio. The results for mixtures of titania with nickel oxide and titania with copper oxide in Tables III and IV show that very active catalysts were obtained at these temperatures. Experiments at lower temperatures showed that catalysts in the ratio of 60 per cent titania and 40 per cent copper oxide were more active than when combined in any other proportion.

Titania and ferric oxide are both fairly active catalysts for the oxidation of carbon monoxide at 300°C. Mixtures of titania with ferric oxide produced catalysts that were quite active at 150°C., a temperature much below that

TABLE III

Experiments with Mixtures of Titania and Various Metallic Oxides at 300°C.

Oxide used	Percentage of Metallic Oxides present with Titania										
	1	5	10	20	30	40	50	60	70	80	100
	Percentage of Oxidation at 300°C.										
UO_2	13.4	74.8	59.3	—	17.4	—	17.2	—	—	0.0	0.0
Fe_2O_3	43.4	59.4	86.5	98.4	97.8	100.0	100.0	100.0	100.0	100.0	98.4
NiO	58.1	—	61.6	89.5	92.3	96.4	100.0	100.0	100.0	100.0	98.3
Cr_2O_3	6.1	—	—	—	—	100.0	—	93.4	—	—	92.1
CeO_2	43.2	—	—	—	—	100.0	—	100.0	—	—	37.3
CuO	100.0	—	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	93.3

TABLE IV

Experiments with Mixtures of Titania and Various Metallic Oxides at 150°C.

Oxide Used	Percentage of Metallic Oxides present with Titania										
	1	5	10	20	30	40	50	60	70	80	100
	Percentage of Oxidation at 150°C.										
UO_2	—	10.0	0.0	—	0.0	—	0.0	—	—	—	—
Fe_2O_3	0.0	5.8	6.0	7.7	36.5	51.6	78.8	86.4	81.1	10.6	45.6
NiO	0.0	—	0.0	0.0	12.5	9.5	90.9	100.0	100.0	100.0	91.9
Cr_2O_3	0.0	—	—	—	—	0.0	—	—	—	—	10.7
Co_2O_3	—	—	0.0	—	—	100.0	—	100.0	—	—	100.0
CeO_2	0.0	—	—	—	—	24.2	—	25.2	—	—	0.0
CuO	53.1	—	100.0	100.0	91.8	100.0	100.0	100.0	—	100.0	78.3

at which these oxides are catalytically active. Pease and Taylor[9] gave the term "co-activation" for such cases of increase in the catalytic activity of mixed oxides as is shown by the mixture of titania with ferric oxide.

Bone and Andrew[10] investigated the action of nickel and nickel oxide in the catalytic combustion of carbon monoxide. They found that at 150°C. nickel oxide became fairly active catalytically without any appreciable reduction of the nickel oxide. From the results obtained from experiments with mixtures of titania with nickel in the present study it was found that very active catalysts were obtained by the addition of from 20 per cent to 50 per cent titania.

Much work has been reported in the literature upon the adsorption of carbon monoxide by copper and copper oxide, and the catalytic activity of copper oxide toward the oxidation of carbon monoxide. Bone and Andrew in their experiments with copper and copper oxide in the catalytic combustion of carbon monoxide found that copper oxide was an active catalyst at 170°C.

The results from experiments of mixtures of titania with copper oxide at 300°C. and 150°C. may be seen in Tables III and IV. The addition of 1 per cent of copper oxide to titania produced a very active catalyst. Mixtures of titania with copper oxide were found to be very good catalysts at temperatures slightly above room temperature. The data in Table V are the results from experiments carried out at a temperature of 50-60°C. It may be observed that the mixture of 60 per cent titania with 40 per cent copper oxide exhibited the greatest activity.

TABLE V

Experiments with Titania and Copper Oxide at 50-60°C.

CO-air mixture, dry. CO, 10-12 per cent. One gram of catalyst used. Duration of run, two hours. Temperature of ignition, 300°C.

Catalyst	Percentage of Oxidation
TiO_2 90% + CuO 10%	0.0
TiO_2 80% + CuO 20%	87.0
TiO_2 70% + CuO 30%	14.9
TiO_2 60% + CuO 40%	98.6
TiO_2 50% + CuO 50%	93.1
TiO_2 40% + CuO 60%	92.7
TiO_2 20% + CuO 80%	79.6

Effect of Water Vapor upon Titania-Copper Oxide Catalysts. It has been pointed out by previous workers on the catalytic oxidation of carbon monoxide that water vapor has the effect of cutting down the reaction velocity. This was found to be true in the present investigation when working at a temperature of 50°C. It is quite evident from an inspection of Table VI that water

---

[9] R. N. Pease and H. S. Taylor: Promoter Action in Catalysis, J. Phys. Chem., 24, 241-265 (1920).

[10] W. A. Bone and G. W. Andrew: loc cit.

vapor has a marked retarding effect upon the catalytic activity of titania-copper oxide catalysts at 50°C. This effect was removed by working at a higher temperature. The same catalyst which previously had shown little or no activity at 50°C. in the presence of water vapor oxidized completely a carbon monoxide-air mixture saturated with water vapor when the temperature was raised to 150°C. and continued with 100 per cent efficiency after ten to twelve hours' use with a gas mixture saturated with water vapor.

Table VI

Experiments to show the Effect of Water Vapor upon Titania-Copper Oxide Catalysts

Experiment	Catalyst	Percentage of Oxidation at 50-60°C. 2 hrs.	4 hrs.
	CO-Air Mixture Dry		
1	TiO_2 40% + CuO 60%	80.0	82.5
2	TiO_2 60% + CuO 40%	85.1	100.0
3	TiO_2 60% + CuO 40%	92.7	100.0
	CO-air Mixture saturated with Water Vapor		
4	TiO_2 40% + CuO 60%	76.7	0.0
5	TiO_2 60% + CuO 40%	69.0	0.0
6	TiO_2 40% + CuO 60%	72.0	0.0
7	TiO_2 60% + CuO 40%	73.4	10.9

Discussion of Results

In all, between 250 and 275 experiments were carried out in the apparatus described, following a uniform procedure. The results of the experiments with the separate oxides, nickel oxide, cobalt oxide, cupric oxide, and hopcalite were in good agreement with those obtained by previous investigators. The results of the study of the retarding effect of water vapor show certainly that the inhibiting effect of water vapor may be attributed to the adsorption of the water vapor upon the catalytic surface. The results with titania mixed with the various metallic oxides emphasize the superiority of mixed oxides in the catalytic oxidation of carbon monoxide and serve again to illustrate the "mixture effect." It would be difficult and hazardous to explain just what part titania has in a mixture such as has been described for titania-copper oxide. It is probable that the surface of the copper oxide has been greatly activated. The net result of such a mixture has been a catalyst with high activity toward the catalytic oxidation of carbon monoxide.

Summary

A qualitative study has been made of the catalytic activity for the oxidation of carbon monoxide by titania and mixtures of titania with a number of

metallic oxides.[11] The important points brought out in this investigation are summed up as follows:

1. Titania has been shown to be a moderately good catalyst for the oxidation of carbon monoxide at a temperature of about 300°C. The inhibiting effect of small amounts of H_2S and other laboratory fumes on the preparation of the catalyst has been pointed out.

2. Preliminary experiments with titania in mixtures with chromium oxide, cerium oxide, and uranium oxide indicated little advantage over that of titania alone.

3. Mixtures of titania with ferric oxide function as catalysts for the oxidation of carbon monoxide at temperatures much below that at which these oxides are singly catalytically active.

4. Nickel oxide has been shown to exhibit greater catalytic activity by the addition of titania.

5. The results of experiments of mixtures of titania with copper oxide in this investigation show that very active catalysts for the oxidation of carbon monoxide can be obtained. They show undiminished activity at a temperature of 150°C. in the presence of water vapor after twelve hours of continuous use.

6. The inhibiting effect of water vapor upon the titania-copper oxide catalysts has been studied. At temperatures of about 50°C. there is a very marked retarding effect.

7. A comparison of the results obtained from catalysts prepared by different precipitants has been made.

---

[11] Letters patent have been applied for in the U. S. Patent Office to cover the preparation and use of this catalyst.

CATALYSTS FOR THE OXIDATION OF CARBON MONOXIDE—II

BY C. J. ENGELDER AND MANUEL BLUMER*†

Continuation of the work upon the catalytic oxidation of carbon monoxide begun in this laboratory by Miller led to further results which are here reported. Further examination of Miller's titania-copper oxide catalyst showed it to be unsatisfactory for use at high temperatures and the search for a better catalyst resulted in the one described below.

Lamb, Bray, and Frazer,[1] and their associates in their development of the catalyst called Hopcalite, which consists of a mixture of manganese dioxide and cupric oxide, conducted most of the investigations which culminated in the production of this well known catalyst. The same investigators performed much of the later work which dealt with the various factors influencing the catalytic activity of Hopcalite.

Bone and his co-workers[2] studied the combustion of carbon monoxide with oxygen using nickel, copper, and their oxides as catalysts. Other interesting contributions on this subject have been made by Benton[3] who studied the adsorption of carbon monoxide by oxide catalysts. The effect of water vapor upon the catalytic activity of oxide catalysts was investigated by Merrill and Scalione.[4] Lamb and Vail[5] also studied the effect of moisture upon Hopcalite.

Oxides of manganese, cobalt, and nickel, were found to be active at low temperatures when purified by an electro-endosmosis method developed by Bennet.[6] A two-component catalyst containing ferric and chromium oxides was shown by Frazer[7] to be active at elevated temperatures.

---

* This paper contains part of a dissertation submitted by Manuel Blumer to the Graduate School of the University of Pittsburgh in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

† Contribution No. 231 from the Chemistry Department of the University of Pittsburgh.

[1] A. B. Lamb, W. C. Bray and J. C. W. Frazer: "The Removal of Carbon Monoxide from the Air," J. Ind. Eng. Chem., 12, 213-221 (1920).

[2] W. A. Bone and G. W. Andrew: "Studies in Catalytic Combustion, II. The Union of Carbon Monoxide and Oxygen in Contact with Nickel, Copper, and their Oxides," Proc. Roy. Soc., 110-A, 16-34 (1926).

[3] A. F. Benton: "Adsorption of Gases by Oxide Catalysts," J. Am. Chem. Soc., 45, 887-900 (1923).

[4] D. R. Merrill and C. C. Scalione: "The Catalytic Oxidation of Carbon Monoxide at Ordinary Temperatures," J. Am. Chem. Soc., 43, 1982-2002 (1921).

[5] A. B. Lamb and W. E. Vail: "The Effect of Water and Carbon Dioxide on the Catalytic Oxidation of Carbon Monoxide and of Hydrogen by Oxygen," J. Am. Chem. Soc., 47, 123-142 (1925).

[6] O. G. Bennet: "Catalysts for Low Temperature Oxidation of Carbon Monoxide," Thesis, Johns Hopkins University (1930).

[7] J. C. W. Frazer: "Method of eliminating Combustible Constituents from the Products of Combustion of an Internal Combustion Engine," U. S. P. 1,789,812, Jan. 20, 1931.

Preparation of Catalyst. Single oxide catalysts were prepared by precipitation as hydroxides from aqueous solutions, ammonium hydroxide being used wherever possible. The precipitates were washed free from electrolytes, filtered by suction and dried at 100°C. After crushing to 12-20 mesh they were activated at 300°C. for 1 hour in an air stream containing 10 per cent carbon monoxide. Two-component catalysts were in general precipitated simultaneously by the use of appropriate reagents and treated in the manner just described.

Method of testing Catalyst. The oxide catalysts included in Table I were tested by passing a carbon monoxide-air stream, containing 10 per cent carbon monoxide by volume, at 2 liters per hour over 1 gram of catalyst contained in a glass tube inserted into an electrically heated furnace. The gas stream was dried by passing it through concentrated sulfuric acid, calcium chloride, and phosphorous pentoxide. The effluent gas was analyzed for carbon dioxide and carbon monoxide.

TABLE I

Per Cent Oxidation of Carbon Monoxide by Oxide Catalysts

Catalyst	Per Cent Oxidation at Temperatures					
	400	300	200	100	50	0°C.
	Single-Oxide Catalysts					
WO_3	—	0	0	0	—	—
BeO	—	3.4	0	0	—	—
HgO	—	Dec.	0	—	—	—
ZrO_2	—	51.0	0	0	0	—
CuO	—	56.0	33.0	—	—	—
V_2O_5	—	60.0	0	0	0	—
Ag_2O	—	76.0	0	—	—	—
NiO	—	89.0	98.0	91.0	20.0	—
ZnO	—	100.	25.0	0	—	—
TiO_2	—	95.0	—	—	—	—
MnO_2	—	100.	100.	85.0	71.0	—
Cr_2O_3	—	100.	34.0	0	—	—
Fe_2O_3	—	100.	100.	26.8	0	—
Co_2O_3	—	89.0	76.0	78.0	78.0	—
	Two-Component-Oxide Catalysts					
$Fe_2O_3 - MnO_2$	67.0	100	100	100	100	50.0
$Fe_2O_3 - NiO$	—	100	82.5	4.0	0	—
$Fe_2O_3 - Co_2O_3$	100	100	95.0	100	100	85
$Fe_2O_3 - V_2O_5$	—	100	15.0	0	0	—
$Co_2O_3 - MnO_2$	100	95.0	100	100	100	0
$Co_2O_3 - NiO$	100	100	100	100	81.5	0
$Co_2O_3 - V_2O_5$	—	100	100	80.5	45.0	—
$MnO_2 - NiO$	100	95.0	100	100	100	—
$NiO - V_2O_5$	—	100	100	62.0	0	—

The activity of the catalysts, tested at various temperatures, using a gas mixture containing 10 per cent carbon monoxide by volume, at 2 liters per hour, is given in Table I. All the two-component catalysts listed in this table contained equal parts by weight of the two constituents.

Of the single oxides tested, many exhibited a high degree of activity at the higher temperatures, the activity generally decreasing very rapidly as the temperature was lowered. The five most promising oxides were used in the preparation of the two-component catalysts.

The two-component catalysts proved to be highly active over a large temperature range. The catalyst containing cobaltic and ferric oxides being chosen as the most promising of the series, further efforts were concentrated upon this catalyst.*

The proportions of cobaltic oxide and ferric oxide were varied in a series of catalysts, the results being given in Table II. The catalyst containing 30 per cent Co_2O_3 and 70 per cent Fe_2O_3 was the most active at low temperatures, oxidizing 95 per cent of the carbon monoxide at 0°C.

TABLE II

Activity of Catalysts containing Varying Proportions of Cobaltic Oxide and Ferric Oxide

No.	Per Cent Co_2O_3	Per Cent Fe_2O_3	Per Cent Oxidation at Temperatures 400	300	200	100	50	0°C.
1	10	90	100	100	89.0	16.2	0	—
2	30	70	100	100	94.0	94.0	94.0	95.0
3	50	50	100	100	95.0	100	100	85.0
4	70	30	100	100	100	100	100	89.0
5	90	10	100	100	100	100	100	74.0

Air containing 10 per cent carbon monoxide by volume, and saturated with water vapor at room temperature, was passed over the freshly activated catalyst (30 : 70 $Co_2O_3 - Fe_2O_3$) for a period of 10 hours, no drying agent being used, with no decrease in the activity of the catalyst. The heat of reaction when carbon monoxide is oxidized to carbon dioxide maintains the catalyst at a temperature sufficiently high to prevent water adsorption.

Activity of Catalyst using Modified Bureau of Mines Test. 1. At 0°C. using ½ per cent carbon monoxide by volume.—The catalyst containing 30 per cent cobaltic oxide and 70 per cent ferric oxide was used in all the following experiments. A glass tube 3 cm. in diameter and 25 cm. long, to the bottom of which a glass spiral, made of 125 cm. of 5 mm. tubing was attached, was used as the catalyst container. The drying agent and catalyst being placed inside the large tube, the entire apparatus was placed in crushed ice to maintain a temperature of 0°C. Air saturated with water vapor containing ½ per cent by volume of carbon monoxide, was passed at 250 liters per hour through the

---

* Letters patent have been applied for in the U. S. Patent Office to cover the preparation and use of this catalyst.

spiral to cool it to 0°C., then through the catalyst tube. A carbon monoxide indicator, described by Katz[8] and his co-workers was used to indicate carbon monoxide in the effluent gas.

As Table III shows, the catalyst completely oxidized the carbon monoxide as long as the drying agent delivered dry gas. Doubling the quantity of drying agent doubled the time during which the catalyst was active. Upon reactivation, the catalyst regained its former activity.

Table III

Activity of Catalyst at 0°C.

Rate of flow—250 liters per hour

Concentration of CO—½ per cent by volume

Test No.	Wt. of Catalyst (grams)	Per Cent Conversion at End of			
		1 hour	2 hours	3 hours	4 hours
1	17.0	99.5	99.0	99.0	95.0
2	17.0	100.	100.	98.3	97.0
3	15.0	99.5	95.0	—	—
4	13.0	98.0	95.0	—	—
5	8.5	97.0	—	—	—

2. At room temperature using 1 per cent CO by volume.—A series of tests using gas of 50 per cent relative humidity at room temperature and containing 1 per cent carbon monoxide by volume were made using the same general procedure as in the 0°C. tests. These tests emphasize the sensitivity of the catalyst used to small amounts of water vapor, the life of the catalyst depending upon the quantity and quality of drying agents used.

The results obtained by these tests are included in Table IV.

Table IV

Activity of Catalyst at Room Temperature

Rate of flow—250 liters per hour

Concentration of CO—1 per cent by volume

Test No.	Wt. of Catalyst (grams)	Per cent conversion at end of		
		0.5 hour	1.0 hour	1.5 hours
1	17.0	100	97.0	88.5
2	17.0	97.5	88.5	85.0
3	17.0	99.0	98.0	95.0
4	17.0	98.0	97.0	93.0
5	17.0	99.0	98.0	95.0
6	17.0	97.0	95.0	—
7	17.0	98.0	95.0	—

---

[8] S. H. Katz, D. A. Reynolds, H. W. Frevert and J. J. Bloomfield: "A Carbon Monoxide Recorder and Alarm," Dept. Commerce, Paper 355 (1926).

It was found that a catalyst which had decreased in activity to 95 per cent had adsorbed 0.17 g. of water, which was 1 per cent of its weight, and became completely inactive when 2.5 per cent of its weight of water had been adsorbed. This explains the longer life at 0°C., as air of 50 per cent relative humidity at 20°C. contains approximately 4 times more water vapor than saturated air at 0°C. As the same quantity of drying agent was used, the catalyst life at room temperature should be approximately one-fourth that of 0°C. Using a large excess of drying agent, the catalyst maintained its initial activity for a period of 8 hours, at which time the drying agent was exhausted.

3. *Catalyst Activity using High CO Concentrations.*—As previously mentioned, with relatively high concentrations of carbon monoxide, the heat liberated by the oxidation of the carbon monoxide on the catalyst granules is sufficiently high to prevent water adsorption. It was found that when air at 20°C., of 50 per cent relative humidity, containing 3 per cent of carbon monoxide, was passed over the catalyst, its temperature was raised to approximately 250°C., and suffered no loss in activity at the end of eleven hours, although no drying agent was used.

Higher carbon monoxide concentrations were used, up to 20 per cent, the catalyst temperature increasing to 890°C. with the latter concentration, with no decrease in activity. At elevated temperatures it was possible to increase the gas flow to 50 liters per gram of catalyst and still obtain complete oxidation of the carbon monoxide.

4. *Supported Catalysts.*—Supported catalysts were prepared by adding the inert material, usually in the form of 12 to 14 mesh granules, to an aqueous solution of the nitrates of cobalt and iron in the proper proportion, and evaporating the solution to dryness. The impregnated granules were activated by maintaining the granules at 175°C. for 10 hours. Asbestos fiber, steel chips, pumice granules, and crushed fire brick were used as catalyst supports.

Tests at high temperatures (500-600°C.), using the catalytic pumice granules, showed that one gram of oxide catalyst coated upon 50 cc. of pumice granules was capable of completely oxidizing the carbon monoxide in a 3 per cent gas stream flowing at 250 liters per hour.

Catalyst coated upon asbestos fiber was equally active, but had a much higher resistance to gas flow.

Fire brick granules had a tendency to react with the oxide catalyst, at high temperatures, reducing its activity within a few hours.

Metallic supports, such as iron chips or screens, oxidized at the temperature used in the tests; the iron oxides formed peeled off, thus removing the catalytic surface.

Summary

1. A study has been made of a large number of oxides which function as catalysts for the oxidation of carbon monoxide.

2. The activity of single oxide catalysts, especially manganese dioxide, ferric oxide, cobaltic oxide, and nickelous oxide, were in good agreement with results obtained by previous investigators.

3. A catalyst containing 30 per cent cobaltic oxide and 70 per cent ferric oxide was found to have a high degree of activity at temperatures ranging from 0°C. to 200°C., using a thoroughly dried gaseous mixture containing ½ to 2 per cent carbon monoxide. In the above temperature range it was rapidly poisoned by water vapor, one per cent of the catalyst weight of water being sufficient to decrease its activity to 95 per cent, 2.5 per cent of water rendering it completely inactive.

4. The adsorption of water vapor, which caused a decrease in catalytic activity, was reversible, reactivation at 300°C. for 1 to 2 hours restored its previous activity.

5. When the concentration of carbon monoxide was 3 per cent or higher, no drying agent was required, as the heat of reaction was sufficient to prevent water adsorption from a gaseous mixture of 50 per cent relative humidity at room temperature.

6. At elevated temperatures, ranging from 200° to 850°C., complete oxidation was obtained using rates of gas flow as high as 50 liters per hour per gram of catalyst, the gas containing up to 20 per cent carbon monoxide.

7. Catalytic material coated upon asbestos fiber and pumice granules exhibited high activity at elevated temperatures.

CRITICAL CONSTANTS AND VAPOR PRESSURE OF BORON TRIFLUORIDE

BY HAROLD SIMMONS BOOTH AND JAMES M. CARTER

In view of the fact that a careful search of the literature failed to reveal any determination of the critical constants and vapor pressure of boron trifluoride, it seemed advisable to determine these constants.

Preparation of Boron Trifluoride

Boron trifluoride was prepared essentially as done by Germann and Booth.[1] Crystal boric acid from Asia Minor ore (kindly supplied by the Pacific Coast Borax Company) was dehydrated by fusion. The powdered fused boric oxide was then dissolved in hot concentrated sulphuric acid. When cold this was mixed with powdered fluorspar in a large porcelain mortar. The heat of reaction was sufficient to cause the evolution of most of the silicon fluoride. When this ceased and before the mass set, it was poured into a generating flask connected to the apparatus by a universal conical joint. The flask was then heated with a free soot flame and the gas passed through a reflux condenser (to separate volatile liquids), through a wash bottle containing boric oxide dissolved in sulphuric acid to remove hydrogen fluoride, and condensed by means of liquid air in the gas-fractionating tube.[2] The boron fluoride was then fractionally distilled rejecting the first and last portions until clear and free from apparent impurities. Usually six distillations were sufficient for this purpose but several more were made.

Preparation of Samples

Sample I was boron trifluoride thus purified and stored for six months before use. This gas was transferred to a separate fractionating apparatus, condensed with liquid air, and fractionated eight times more with generous discarding of the first and last fractions. Both the apparatuses for handling boron trifluoride were previously dried by rinsing twelve times with air which had passed slowly through tubes filled with broken stick potassium hydroxide, calcium chloride and then barium oxide.[3] Experience has shown this is ample rinsing.

The Cailletet tube, which had previously been sealed on to the apparatus with an intervening stopcock close to the tube and carefully dried at the same time as the apparatus, was rinsed with small amounts of the middle fractions of boron trifluoride at each distillation with thorough evacuation before the next rinsing, to insure removal of adsorbed air. The middle part of the middle fraction of the ninth distillation was used for a final rinse and then the

---

[1] Germann and Booth: J. Phys. Chem., 30, 369 (1926).

[2] For details of such an apparatus see J. Phys. Chem., 30, 369 (1926) and J. Chem. Ed., 7, 1259 (1930).

[3] "Barium Oxide as a Desiccant," H. S. Booth and L. H. McIntyre: Ind. Eng. Chem., Anal. Ed., 2, 12 (1930).

Cailletet tube was filled from this middle part of the middle fraction to within one or two centimeters of atmospheric pressure. The stopcock of the Cailletet tube was then closed and the space intervening between it and the fractionating apparatus carefully rinsed twelve times with carbon dioxide-free dry air before breaking off the Cailletet tube.

Sample II was prepared in the same way save in two respects: First, the mixture in the generator was heated by a water bath while evacuating the system to insure elimination of silicon tetrafluoride before heating with a soot flame to the temperature of boron trifluoride generation; and second, only one day elapsed between the generation and the first fractionation, and the final fractionation and filling of the Cailletet tube. Immediately after filling, the Cailletet tube was removed from the apparatus, and the stopcock broken off under mercury, to avoid any contamination by grease.

Keeping the open end of the tube under mercury, it was placed in the steel container attached to the pump and manometer.[1] It was found that the gas had no corrosive effect on mercury, even at high pressures, and over considerable periods of time. It was also found, as is usual with absolutely dry fluorides, that the glass was not attacked. What was more surprising, however, was that the stirrer used to accelerate equilibrium,[2] consisting of a small chromium-plated iron rod, was not attacked.

Measurement of Pressure and Temperature

The manometer used was one of the absolute type, manufactured by Schaffer and Budenburg. The size of the piston had been measured with micrometer calipers at various points, and the weights compared with a standard kilogram. In addition it had been compared with a closed Amagat type manometer, and found to agree to within the limits of experimental error, (slightly less than 0.1 atm.). The range of the Schaffer and Budenburg manometer used was such that it did not operate satisfactorily at pressures below ten atmospheres.

Temperatures were measured by means of a P.T.R. Anschütz thermometer, which was subsequently checked against a resistance thermometer calibrated by the Bureau of Standards. The P.T.R. thermometer could be read to .02°C. One point, at −50°, was measured on a liquid in glass thermometer, and is slightly more doubtful than the others. It was thought that the thermometer contained alcohol, but the readings below −45° were erratic unless the thermometer had been cooled from room temperature to the temperature of test immediately before reading. The one reading retained fulfilled this condition; others taken after the thermometer had been cold for some time, were discarded.

Experimental Procedure

After placing the thermostat around the experimental tube, the temperature was held constant, and the gas compressed. When a temperature had

---

[1] The Cailletet apparatus was the same as that used by the authors in determining the Critical Constants of Carbon Dioxide-Oxygen Mixtures, J. Phys. Chem., 34, 2801, 2813 (1930).

[2] Kuenen: Arch. néerl., 26, 394 (1892); Z. physik. Chem., 11, 38 (1893).

been reached at which the gas could be liquefied, the pressure was adjusted until the liquid and gas phases were equal in volume. The temperature was then raised very slowly, and the temperature at which the liquid disappeared was noted. The mixture was stirred vigorously, as equilibrium is only obtained very slowly otherwise. After the critical point had been passed, the pressure was maintained at the same value, and the temperature was gradually lowered, until the meniscus reappeared in the tube.

The critical pressure could be determined extremely accurately by this method. If the pressure chosen was too low, the meniscus moved down the bulb as the temperature was increased, and disappeared at the bottom, while if the pressure was too high it moved upward and disappeared at the top. The limits between which it remained near the middle of the tube were quite narrow, and varied by not more than 0.05 atm.

In determining the vapor pressures at lower temperatures, the pressure taken was that which made the volume of gas and liquid equal. Here again, the pressure limits from all gas to all liquid were extremely narrow. The slightest addition of weight to the manometer was sufficient to send the meniscus from the bottom to the top of the bulb.

The critical opalescence was clearly observed. Especially on cooling, the opalescence was marked, as the gas appeared to be supersaturated. If it was not stirred it remained heavy and foggy, and no noticeable liquid separated until the critical temperature had been passed. On stirring, however, the liquid phase separated immediately.

It was noticed that near the lowest temperatures reached (− 50°C.), the liquid appeared quite viscous. The stirrer tended to stick to the walls of the bulb unless it was kept in motion continuously. This probably indicates association of the liquid boron trifluoride at this pressure and temperature. At the boiling point, boron trifluoride is not viscous and is probably little associated.

Results

The results of the determinations of the critical constants and the vapor pressures are given below. Two gas samples were used, which had been purified separately, and several runs were made on each. In the case of Sample II the critical point and vapor pressure curve were redetermined after the gas had stood in the Cailletet apparatus in contact with glass and mercury for a week (Oberservations IIb). No change was found. The observations (cor.) of the critical temperatures and pressures are shown in Table I. The data for the vapor pressures are given in Table II.

The average of the determinations of the critical temperature was found to be $t_c = -12.25$°C. Variation ± 0.03°. Critical pressure $p_c = 49.2$ atm. (I.C.T. normal) Variation ± 0.1 atm.

The equation for the vapor pressure curve was found to conform to $\log_{10} P = 5.1009 - 0.8896 \cdot 1000/T$. According to the International Critical Tables, Volume 3, p. 232, boron trifluoride has a vapor pressure of 1 atmosphere at − 101°C. The vapor pressure at − 101°C. was calculated by this equation to be 0.8484 atmospheres. Obviously this comparison of the observed and calculated vapor pressures at the boiling point shows that the equation is satisfactory for low pressure data as well as those it was made to fit.

Calculation of Heat of Vaporization

The vapor pressure equation:

$$\log_{10}P_{\text{atm}} = 5.1009 - \frac{0.8896}{T} \cdot 1000,$$

may be differentiated to give

$$\frac{d(\log_{10}P)}{dT} = + \frac{889.6}{T^2}$$

Table I

Critical Constants of Boron Trifluoride

Temperature determinations Sample	t_c	Pressure determinations P
I	− 12.25°C.	49.0 atm. (I.C.T.
I	− 12.25	49.2 normal)
I	− 12.20	
II	− 12.25	49.1
II	− 12.20	49.3
I	− 12.30	
IIb	− 12.30	49.2
Av.	− 12.25°C. ± .03°	49.16 = 49.2 atm. ± .1 atm.

Table II

Vapor Pressure of Boron Trifluoride

t°	P atm.	Sample
−12.25	49.0	I
20.12	38.5	I
39.20	20.5	II
12.25	49.2	I, II
12.20	49.1	I, II
49.25	13.8	II
38.50	22.5	II
30.11	28.5	II
20.22	38.7	II
39.25	19.8	IIb
35.08	23.2	IIb
35.00	23.8	IIb
35.19	23.8	IIb
29.96	27.9	IIb
29.76	28.2	IIb
19.92	38.6	IIb
19.95	38.6	IIb
14.65	45.4	IIb
14.60	45.5	IIb

which may be compared with the approximate Clapeyron equation:

$$\frac{d(\log_e P)}{dT} = \frac{H_{vap}}{RT^2}$$

It is seen that $H_{vap} = 889.6R \cdot \log_e 10$
or $H_{vap} = 4057$ cal./mol.
$= 59.93$ cal./gm.

This value may be expected to be reasonably correct at a temperature where the assumptions of negligible liquid volume, and perfect gas behavior for the vapor may be reasonably close to the facts. This will probably be the case near the normal boiling point.

Summary

1. As a result of seven determinations it has been found that the critical temperature of boron trifluoride is − 12.25°C. ± 0.03°, and the critical pressure 49.2 atmospheres (I.C.T. normal) ± 0.1 atmosphere.

2. The vapor pressures have been determined from the critical pressure down to 10 atmospheres. The equation for the vapor pressure was found to be $\log_{10}P = 5.1009 - 0.8896 \cdot 1000/T$.

3. Dry boron trifluoride was found to have no corrosive effect on mercury, chromium plating, or glass even at high pressure and over considerable periods of time.

4. The heat of vaporization of boron trifluoride was calculated to be 4057 cal./mol.

5. It was noticed that near the lowest temperature reached, − 49.25°C., at a vapor pressure of 13.8 atmospheres the boron trifluoride became noticeably viscous, probably indicating some association.

Morley Chemical Laboratory,
Western Reserve University,
Cleveland, Ohio.

A STUDY OF THE MAGNITUDE OF THE CROWDING EFFECT IN CURRENT FLOW THROUGH SMALL TUBES AND SLITS*

BY H. L. WHITE, L. C. VAN ATTA AND E. A. VAN ATTA

In 1929 McBain, Peaker and King[1] reported that for 0.001 N aqueous solution of KCl at 25° the extra conductance in the neighborhood of optically polished glass corresponded to a specific surface conductance of 4.3×10^{-8} mhos. This value was determined by measuring the resistance of a cell filled with solution and containing a removable narrow glass slit of known dimensions. According to these authors three factors operate to make the observed resistance of cell plus slit filled with dilute salt solution different from the calculated resistance of the slit alone, the calculation being based on the specific resistance of the solution and the measured dimensions of the slit. The first of these factors is obviously the resistance of the cell alone. The second factor is the enhanced conductance at or near the glass-water interface, i.e. the surface conductance, appreciable only at low concentrations. The third factor is the "pinch" effect, "operating in all concentrations, and due to bending of the lines of current flow through the slit, and equivalent to a series resistance." The second factor operates to make the observed resistance less than the calculated, the third to make it greater. The present paper is an experimental and theoretical consideration of the third factor or pinch effect.

In order to confine ourselves to the pinch effect we shall consider in this paper only those experiments of McBain, Peaker and King in which concentrated (1.0 N or 0.1 N KCl) solutions were used. At these concentrations these authors assumed the surface conductance would be a negligible fraction of the normal or volume conductance and we shall prove in this paper that this assumption is correct. To consider a representative case, they find that with 1.0 N KCl the resistance of cell plus slit no. 5 is 204.45 ohms. The calculated resistance of the slit is 162.79 ohms, which leaves a cell resistance of 41.66 ohms. But when the resistance of the cell alone is determined it is found to be only 14.14 ohms. This means that the effective resistance of the cell has been increased by 27.52 ohms due to the presence of the slit, apart from the actual resistance of the slit. This increase is called the pinch effect. The sum of pinch effect and of resistance of cell alone is termed the "effective resistance." The effective resistance of a given cell plus slit should be proportional only to the specific resistance of the solution used. If then it is determined with a concentrated solution it can be calculated for a dilute solution. This calculated figure is subtracted from the observed resistance of cell plus slit for dilute solution to give the resistance of the slit alone. The figure so obtained is compared with the calculated resistance of the slit for the dilute solution and

---

* The Department of Physiology and the Department of Physics, Washington University, St. Louis.

found always to be lower. The increase in specific conductance in the slit may be as much as 53 per cent above normal for a 0.0125 mm. slit and 0.001 N KCl and is ascribed to surface conductance.

The results of McBain, Peaker and King with regard to pinch effect will be considered more in detail after a theoretical consideration of the expected magnitude of the effect. Because of certain inconsistencies in the results, to be discussed later, it is desirable to use, for a study of the influence of surface conductance on the measured resistance, an apparatus in which pinch effect is negligible.

In place of slits we have used pyrex capillaries ranging from 0.008 to 0.096 mm. bore. These offer several advantages over the slits. First, the technical difficulties which McBain, Peaker and King experienced in preparing and preserving their material are avoided. We had considerable trouble while we were drawing our own capillaries but our difficulties of preparation were practically eliminated by the cooperation of the Corning Glass Works in supplying us with tubing of outside diameter from 6 to 7 mm. and inside ranging in small steps from 0.005 to 0.100 mm. A second advantage is that the resistance of the cell or holder plus connections is a negligible fraction of the whole, less than 1 part in 10,000; this eliminates one of the factors. Third, there is no danger that cracks will develop. Fourth, higher values of the surface to volume ratio are attainable. And fifth, it will be shown that pinch effect is entirely negligible. The electrical connections to the capillary, its preliminary treatment, the procedure of filling it with solution, method of resistance determinations, etc., are described in the following paper.

In the present work direct current has been used. This avoids a number of complications, but raises the question as to whether the results have been affected by polarization. There is ample evidence that polarization is not a disturbing factor. In the first place the sum of the resistances of two parts of a broken capillary equals that of the whole. Further proof has been obtained directly from the electrometer which shows no deflection when a capillary is thrown into its circuit immediately after the capillary has had a constant EMF impressed upon it for several minutes. This is true for resistances as high as 10^{11} ohms.

The dimensions of seven capillaries of from 0.0080 to 0.0964 mm. bore were measured. Lengths of the order of 25 mm. were measured to 0.1 mm. with a micrometer caliper, diameters were measured at each end with a screw micrometer eye-piece and either a 16 or a 3 mm. objective. Several measurements at each cross section were made by two independent observers. The mean value of these measurements is probably less than 1 per cent from the true value for the larger capillaries and not more than 2 per cent for the small. The cross section is usually not completely circular but the eccentricity is small; in all these capillaries the area of the elliptical cross section differs by considerably less than 1 per cent from the calculated circular area, using the arithmetic mean of the major and minor axes as the diameter. The cross sectional areas of each end are of almost the same value; their average has been taken as mean cross sectional area. Thus it is possible to measure the resistance of a column of solution of known concentration, and also to calculate this resistance from a knowledge of capillary dimensions and specific resistance. Such measurements have been carried out and in every case the observed resistance agreed with the calculated, as is seen in Table I. The specific resistance at 25° of 1.0 N KCl is taken as 8.95, of 0.1 N KCl as 77.8 ohms; the observed resistances have been reduced to 25°. The measurements on 57a, 57b, 58, 58a and 58b with 1.0 N KCl were with a Wheatstone bridge, the others by the condenser rate of charge method. Each figure represents the average of a number of closely agreeing determinations.

TABLE I

Cap No.	Mean diameter by microscopic measurement mm.	length cm.	Calculated resistance with 1.0 N KCl ohms	Observed resistance with 1.0 N KCl ohms	Calculated resistance with 0.1 N KCl ohms	Observed resistance with 0.1 N KCl ohms
56	0.0078	1.40	2.63×10^7	2.50×10^7		
57	0.0398	4.45	3.21×10^6	3.27×10^6		
57a	0.0396	1.97	1.43×10^6	1.44×10^6	1.245×10^7	1.26×10^7
57b	0.0398	2.48	1.79×10^6	1.805×10^6	1.56×10^7	1.59×10^7
58	0.0964	4.77	5.85×10^5	5.87×10^5		
58a	0.0964	1.90	2.33×10^5	2.36×10^5	2.02×10^6	2.05×10^6
58b	0.0964	2.84	3.49×10^5	3.40×10^5	3.04×10^6	3.08×10^6

These results mean either that both surface conductance and pinch effect are absent or that they just cancel each other. That the latter is not the case is evident from the following consideration. Surface conductance becomes less prominent as capillary diameter increases, while pinch effect becomes more prominent; this latter statement will be proved in the theoretical discussion. Therefore these two factors, if present to an appreciable extent, could cancel each other only at a certain capillary diameter; the observed resistance of capillaries of diameters greater than this should be greater than the calculated and vice versa. Since no resultant effect appears at any diameter it follows that neither is present.

Another proof of absence of pinch effect follows. If pinch effect is present it will be manifested at each end of a capillary; the sum of the effects at each end may be called the pinch effect for that capillary. If now the capillary is broken into two pieces the sum of the two resistances should exceed the original resistance by one pinch effect, whether or not surface conductance exists and independent of any accurate measurements of capillary diameter. If it is shown that the sum of the two resistances equals the original, pinch effect is negligible. This is shown in Table I. Capillaries 57a and 57b are the two fragments into which 57 was broken; 58a and 58b are from 58. It will be seen that the sum of the observed resistances with 1.0 N KCl of 57a and 57b practically equals the resistance of 57; the same is true for the fragments of 58.

In view of McBain, Peaker and King's findings it is surprising that in our work repeated determinations consistently show the observed resistance to agree with the calculated. It is possible to predict a pinch effect from theoretical considerations, and to calculate the magnitude of such an effect for the capillaries used in the present experiment. This problem has been treated theoretically by Lord Rayleigh.[2,3]

In general, the measured resistance of a tube or slit terminating in a semi-infinite conductor of the same material may be written

$$R = R_1 + 2R_2 \qquad (1)$$

where R_1 = the resistance within the tube
R_2 = additional resistance at either end due to crowding of lines of flow (pinch effect).

The resistance within the tube is given by

$$R_1 = \rho\, l/A \qquad (2)$$

where ρ = specific resistance of the medium
l = length of tube
A = cross sectional area of tube.

The additional resistance at either end may be expressed in terms of C, the electrostatic capacity of an isolated disc identical in shape and area with the cross-section of the tube

$$R_2 = \rho/2\pi C \qquad (3)$$

Hence the fractional error introduced by pinch effect into the measurement of R_1 is, by (2) and (3)

$$E = 2R_2/R_1 = A/\pi l C \qquad (4)$$

For the particular case of a circular tube $C = (2/\pi)\sqrt{A/\pi}$ so that

$$E_{(\text{circle})} = \sqrt{\pi A}/2l = \pi d/4l \qquad (5)$$

where d = diameter of the circular tube. Using (5), it is possible to calculate the magnitude of the error for certain numerical cases.

Capillary No. 56: $d = .0078$ mm. $= .00078$ cm., $l = 1.40$ cm.

$E = \pi \times .00078/4 \times 1.40 = .00044 = .044\%$ error

Capillary No. 58: $d = .0964$ mm. $= .00964$ cm., $l = 4.77$ cm.

$E = \pi \times .00964/4 \times 4.77 = .0016 = .16\%$ error.

The conclusion from the above calculations is that there is no theoretical ground for expecting a measurable pinch effect in the capillaries used in the present experiment, since the experimental errors range from 0.5 to 2 per cent. This substantiates the experimental findings.

McBain, Peaker and King used slits differing considerably from the circular tubes treated above, so that a further development is necessary to find the theoretically predicted order of magnitude of the error due to pinch effect in their work. This is given by the general equation (4) above

$$E = A/\pi l C$$

where, in this case, C is the electrostatic capacity of a disc having the shape and dimensions of a cross-section of the slit.

The exact calculation of C for a rectangular disc is impossible but an approximation can be made by considering the case of an ellipse with equal area and with major and minor axes in the same ratio, a/b, as the sides of the rectangle. This proves to be a close approximation because of the fact that C is not sensitive to small changes in the shape of the disc. The ratio of the capacity of an elliptical disc to that of a circular disc *of the same area* is given by Rayleigh as

$$\frac{C_{(\text{ellipse})}}{C_{(\text{circle})}} = \frac{E_{(\text{circle})}}{E_{(\text{ellipse})}} = \frac{\pi}{2}\sqrt{\frac{a}{b}}\,\frac{1}{F(e)} \qquad (6)$$

where $e = \sqrt{1 - (\frac{b}{a})^2}$ = eccentricity of the ellipse,

$$\text{and } F(e) = \int_0^{\pi/2} \frac{d\phi}{\sqrt{1 - e^2 \sin^2\phi}}.$$

Combining (5) and (6), we have

$$E_{(\text{ellipse})} = \frac{1}{l}\sqrt{\frac{b}{a}\cdot\frac{A}{\pi}}\cdot F(e) = \frac{b}{2l}\cdot F(e) \qquad (7)$$

F(e), the complete elliptic function of the first kind, may be looked up in tables.[4,5] Consider the application of equation (7) to a numerical example.

Slit A: $l = 0.1$ cm. $a = 1.0$ cm. $b = .001$ cm.
$F(e) = \ln(4a/b) = 8.3$
$E = bF(e)/2l = .042 = 4.2\%$ error.

We are now in a position to consider the results of McBain, Peaker and King. The data for three slits with 1.0 N KCl are summarized in Table II.

TABLE II

slit no.	b width (cm.)	a length (cm.)	l thick. (cm.)	calc. slit resis. (ohms)	observed pinch effect (ohms)	observed pinch effect (per cent)	calc. pinch effect (per cent)
5	.00567	1.002	0.1033	162.79	27.52	16.9	18.0
6	.00125	1.001	0.1058	757.08	186.18	24.6	4.8
10	.00125	1.001	0.5014	3587.8	647.16	18.4	1.0

The last column gives the pinch effect as calculated from equation (7). These calculated values represent an upper limit for the pinch effect since the assumption that the slit opens into a semi-infinite fluid is not at all realized, especially when auxiliary slits are introduced. As a result of this fact the experimental values should be somewhat lower than the theoretical. Both the observed and calculated values indicate that pinch effect cannot be neglected in the case of these slits. There agreement ends, for the calculated pinch effect is in general much lower than the observed. Furthermore, the dependence of pinch effect on the dimensions of the slit predicted by theory is not found in the observed values. For example the pinch effect in ohms should be the same for slits 6 and 10, since they are identical in cross-section. Also the pinch effect in per cent should be smaller for slit 6 than for slit 5, since in this connection a decrease in width is equivalent to an increase in thickness. The conclusion is that the observed values are not to be explained as due to pinch effect.

A search for other causes for the increased resistance is not fruitful. Since pinch resistance = observed resistance of cell plus slit − calculated resistance of slit − observed resistance of cell, it follows that an erroneously high value for the first or low values for the second and third members on the right side of the equation would give rise to an apparent pinch resistance. It is inconceivable that errors of 25 per cent could arise in determination of either cell resistance or slit dimensions. As to sources of error in observed resistance of slit plus cell, cracks in the system need not be considered, as they would make the reading too low. The capacity of the cell, since the dielectric constant of glass is less than that of water, is less when the slit is added to the cell; this decrease in capacity, since it decreases the shunt across the resistance, would increase the impedance of the system. Calculation shows, however, that this factor is too small to introduce an appreciable error; even if the cell capacity were reduced from an estimated 5×10^{-10} farads to zero the impedance where the resistance is 100 ohms would be changed less than one part in 10,000,000 and with 1,000 ohms less than 1 in 100,000. On the basis of our own failure to find a pinch effect and on theoretical considerations we believe that McBain, Peaker and King's findings on pinch effect are due to some systematic error.

Summary

Whatever the explanation for the anomalous resistance in the case of slits, the difficulty is avoided by the use of tubular capillaries. The several advantages of capillaries have been mentioned above:

1. Negligible pinch effect
2. Negligible cell resistance
3. Large attainable ratio of surface to volume
4. Absence of many technical difficulties.

Three independent proofs are advanced that there is no significant pinch effect with capillaries of from 0.008 to 0.100 mm. bore. The first proof is that the observed resistance of the capillary filled with 1.0 N or 0.1 N KCl equals the calculated, where the calculation is based upon microscopic measurements of capillary dimensions and upon the specific resistance of the solutions. The second proof is that the sum of the resistances of the two fragments into which a capillary is broken equals the original resistance. The third proof is theoretical. On the basis of the experimentally and theoretically demonstrated absence of a significant pinch effect in small capillaries, of a theoretical treatment of the case of an ellipse of great eccentricity approximating a rectangular slit, and of relations between asserted pinch effect and width of slit in McBain, Peaker and King's work which conflict with theory, we believe that their observed increases of resistance with concentrated solutions are not due to a pinch effect but to some systematic error yet undetected.

Bibliography and Footnotes

[1] J. Am. Chem. Soc., 51, 3294 (1929).

[2] "Theory of Sound," 2 (1896).

[3] J. H. Jeans: "The Mathematical Theory of Electricity and Magnetism," 356 (1925).

[4] J. B. Dale: "Five Figure Tables of Mathematical Functions" (1904).

[5] When e is very close to unity, as in the case of a much-elongated ellipse, tables cannot be relied upon for values of F(e). As shown by Andrew Gray,[6] a rapidly converging series is obtained by the transformation $k = \sqrt{1-e^2} = b/a$. For values beyond the range of the tables high accuracy is obtained by using only the first term of the resulting series, i.e.,

$$F(e) = G(k) = \ln (4/k) = \ln (4a/b).$$

The writers are indebted to G. G. Harvey who pointed out the possibility of such a transformation.

[6] "Gyrostatics and Rotational Motion" (1918).

SURFACE CONDUCTANCE AT GLASS-SALT SOLUTION INTERFACES*

BY H. L. WHITE, FRANK URBAN AND E. A. VAN ATTA

McBain, Peaker and King[1] reported in 1929 on the increase of specific conductance of dilute KCl solutions in narrow polished glass slits. This was ascribed to surface conductance at or near the glass-solution interface, the excess of conductance becoming greater as the ratio of surface to volume increased and as the dilution became greater. The ratio of surface area in sq. cm. to volume in cc. in their narrowest slits, excluding slit S and slit 2, rejected because of breakage or cracks, was 1600 to 1; their most dilute solution was 0.001 N. The found at 25°C. a mean specific surface conductance with 0.001 N KCl of 4.3×10^{-8} mhos, with 0.002 N KCl of 5.3×10^{-8} mhos, and with 0.01 N KCl of 9.3×10^{-8} mhos, specific surface conductance being defined as that of 1 cm. square of surface. The values obtained with the various slits, from which the means were calculated, varied with 0.001 N KCl from 3.0 to 5.3×10^{-8} mhos, with 0.002 N KCl from 2.8 to 6.3×10^{-8} mhos, and with 0.01 N KCl from 1.8 to 19×10^{-8} mhos. The rapid increase in the experimental error as the solution becomes less dilute is obvious. In 1930 McBain and Peaker[2] reported that the specific surface conductance at the interface between KCl solutions and unpolished pyrex glass was 13×10^{-8} mhos with 0.001 N KCl and 20.7×10^{-8} mhos with 0.01 N KCl. The ratio of macroscopic surface area to volume with this apparatus was much lower, 93 to 1, than with the slits. The authors suggest that the higher conductances at the unpolished surfaces could be explained by the assumption that the actual surface area of ordinary pyrex tubing is 2¼ times greater than that determined by macroscopic measurements. Actually the factor would be about 3 to bring the 2 sets of data on 0.001 N KCl into agreement. We reported at the 1931 Colloid Symposium[3] on determinations of stream potentials in pyrex capillaries of various sizes which suggested that either McBain and coworkers' values for surface conductance were many times too high or that the stream potential equation $E = \frac{\zeta P D}{4\pi\eta\kappa}$ is invalid. The argument follows.

We made our stream potential determinations on pyrex capillaries of from 0.110 to 0.005 mm. inside diameter, using 0.0005 N KCl. We can estimate that the extrapolated value for the specific surface conductance with pyrex glass and 0.0005 N KCl according to McBain and Peaker would be not less than 1×10^{-7} mhos. Taking the specific volume resistance of 0.0005 N KCl at 25°C. as 1.35×10^{4} ohms, we calculate that the normal

---

* The Department of Physiology and the Department of Biological Chemistry, Washington University, St. Louis.

or volume resistance of a column of 0.0005 N KCl in a 0.005 mm. capillary at 25°C. is 6.88×10^{10} ohms per cm. The surface resistance of such a capillary would be, taking 1×10^7 ohms as its specific surface resistance, $1 \times 10^7/3.1416 \times 5 \times 10^{-4}$ or 6.38×10^9 ohms per cm. The observed resistance of a 0.005 mm. pyrex capillary filled with 0.0005 N KCl should then be, if McBain and Peaker's figures for specific surface conductance are correct, 5.82×10^9 ohms per cm., since the observed resistance is the resultant of the normal or volume resistance and of the surface resistance in parallel. That is, the observed resistance of this system would be 8.4 per cent of the normal or calculated resistance. This means that the conductance (resultant of volume and surface conductances) in the capillary should be 12 times the normal and since the conductance factor, κ, in the stream potential equation is in the denominator, the stream potential with a 0.005 mm. capillary should be, other factors being kept constant, only 8.4 per cent of that in a large capillary, say 0.10 mm., where surface conductance is relatively insignificant. The facts were, however, that the stream potential of a 0.005 mm. capillary was 75 to 85 per cent of that in a large capillary or about 10 times as great as would be predicted from McBain and Peaker's data. If our stream potential figures were correct they could be explained by any one of the following conditions, that McBain and coworkers' figures for surface conductance were much too high, that our glass was different from theirs, that the stream potential equation does not hold, or that some other factor or factors in the equation were changed in the small capillaries so as almost to compensate for the increased conductance if it exists. The answer depends upon the results of determinations of conductance in our capillaries under the conditions of our stream potential experiments.

In the above-cited paper we reported preliminary attempts to determine the resistance of our capillaries by determining the ratio of the potential drops across the capillary and across a known high resistance, using either a known impressed e.m.f. or the stream potential as the source of e.m.f. These measurements were not quantitatively satisfactory because our known resistances were not high enough to give a large fraction of the total potential drop. They were introduced merely to show that the "spontaneous" fluctuations in stream potential were not due to variations in conductance.

The present paper is a report of conductance measurements on pyrex capillaries of from 0.10 to 0.005 mm. bore filled with 0.0005, 0.1 or 1.0 N KCl. Since the ratio of macroscopic surface to volume in our 0.005 mm. capillaries is 8000 to 1 and our solution is twice as dilute as the most dilute used by McBain, the conditions in our experiments for bringing surface conductance into prominence should be much more favorable.

Apparatus and methods. Our first resistance measurements, as noted above, were inaccurate because of lack of suitable resistors and because of our failure to give adequate consideration to the potentials of the electrodes themselves. Considerable time was spent in attempting to make stable nonpolarizable resistances sufficiently high for our purposes. Carbon lines on paper imbedded in paraffin were satisfactory up to about 10^8 ohms but above that they could not be used, apparently because of polarization. Greater accuracy was attained on using a series of metallic sputtered resistors (5×10^8 to 1×10^{11} ohms) prepared by Dr. L. C. Van Atta[4] and lent us by him. These resistors give constant values and do not polarize. We eventually abandoned the potential drop ratio method because of practical difficulties which attended the method even after satisfactory standard high resistances were available.

Our next method was to measure the rate of discharge of a condenser through the unknown high resistance, which is given by the equation

$$R = \frac{t}{2.303C \log V_o/V_t}$$

where R is the resistance in ohms, t the time of discharge in seconds, C the capacity of the condenser in farads, V_o and V_t the voltages on the condenser immediately after charging and after time t, respectively. The condenser was a Leeds & Northrup standard mica, 0.1 mf. being used with the dilute solution, 1 mf. with the concentrated. The ratio V_o/V_t was taken as the ratio d_o/d_t, the ballistic deflections of galvanometer on condenser discharge; the galvanometer had a current sensitivity of 8×10^{-11} amp., a period of 12 seconds, coil resistance of 575 ohms and C.D.R. of 26,000 ohms; as used it was damped with 22,000 ohms. The calibration curve, i.e., deflection against impressed voltage, was frequently redetermined. The resistance of the condenser varied between 2.5 and 3×10^{11} ohms for 0.1 mf.; a correction was made for condenser resistance, the unknown being determined on the basis that the observed resistance was the resultant of the condenser and unknown resistances in parallel. This method was satisfactory provided the calomel electrodes serving as leads from the capillary were exactly isoelectric. Since this was not always the case and since we could not modify the equation to allow for this extraneous source of e.m.f. during the discharge we next turned to the other alternative, determining the rate of condenser charge through the unknown resistance. The e.m.f. of the unknown resistance, arising in the calomel electrodes, can be allowed for in this case. The charging e.m.f. can be either the stream potential of the capillary or an impressed e.m.f.; in either case the observed resistance of the capillary is the same. The resistance is expressed by the equation $R = \frac{-t}{2.203C \log (1 - V_t/V_f)}$, where V_t and V_f are the voltage at time t and the final or charging voltage, respectively. Here also the observed resistance is the resultant of unknown and condenser resistances in parallel. Since, however, the condenser is charged to only a fraction of the charging voltage, its leak becomes of much less importance than in the condenser discharge method. With the rate of charge method the error due to condenser leak is kept at a minimum because with low unknown resistances, i.e., below 5×10^9 ohms, the condenser resistance is so much higher than the unknown that its leak is negligible, while with high unknown the voltage at time t is usually only 20 to 35 per cent of the charging voltage so that relatively little opportunity for leak has existed. However, it has seemed worth while to calculate the error due to condenser leak; when this has been less than 0.2 per cent it has been disregarded. The equation $R = \frac{-t}{2.303\ KC \log (1 - V_t/KV_f)}$ has been derived independently and follows from equation 5, $q = \frac{rEC}{R+r}\left(1 - e^{-\frac{R+r}{RrC}t}\right)$, in the appendix of a paper by Bishop.[5] In our equation K is the correction factor $R_c/(R+R_c)$ where R_c is condenser resistance and R is the unknown resistance as first determined. A second approximation can be made by substituting for R in the correction factor the corrected R as found on the first approximation, but in any of our experiments the difference between the first and second approximations is hardly appreciable. In most of the determinations the first approximation introduces a correction of considerably less than 1/2 per cent; in only one case is it more than 3 per cent.

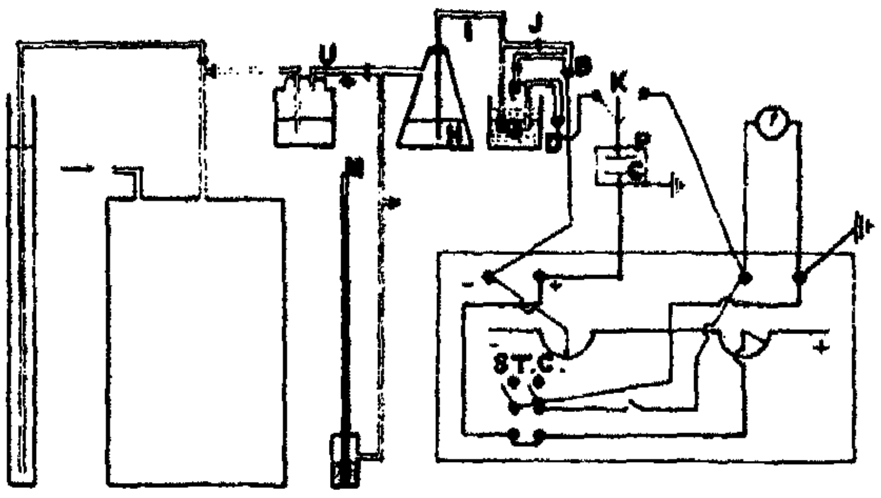


FIG. 1

The final arrangement of apparatus is shown in Fig. 1; the potentiometric system has been modified from Bishop's arrangement[6] by substitution of a SPDT quick acting highly insulated switch for the tap key. With this one can determine either stream potential or resistance; the latter can be determined by utilizing either the stream potential or an impressed e.m.f. from the potentiometer.

The condenser C, the switch K, and that side of the high resistance source of unknown e.m.f. which is connected with the condenser are thoroughly insulated, the other side of the source of unknown e.m.f. is grounded at the galvanometer. Adequate insulation of the upper end of the capillary was uncertain because of the possibility of a leak to the flask H through the rubber tubing U; it was, however, a simple matter to insulate the lower end of the capillary, i.e., the beaker G and the electrode D. The condition was then fixed that the lead D would be connected with the condenser and since in the stream potential measurements this was always positive the battery current was reversed from the polarity marked on the box and was as indicated in the figure. The condenser C has been placed alternately upon a hard rubber table and upon a grounded sheet of galvanized iron P with no change in extent of charge from a known source of voltage; the insulation of the condenser box is apparently adequate. When the potentiometer is set at zero and the electrodes are isoelectric there is no galvanometer deflection on the condenser discharge.

The steps of a resistance determination, using an impressed e.m.f., are as follows. The capillary holder I is put into the flask H which contains, in all of the experiments reported in this paper, 0.0005 N, 0.1 N or 1.0 N KCl. By proper manipulation of stopcocks a positive pressure of a few cm. Hg is applied and the tube F flushed out, cock J closed and tube F dipped into the beaker G, giving a low resistance circuit for the determination of electrode potentials. Calomel electrodes B and D are made up with 0.0005, 0.1 or 1.0 N KCl; they are usually 0 to 4 mv., occasionally as far as 10 mv. apart. The resistance of electrodes and connections exclusive of capillary is only 1.5 to 2.5 × 10^4 ohms with 0.0005 N KCl, i.e., practically zero as compared with the capillary resistances of 10^9 to 10^{11} ohms. The same proportion of course obtains with the concentrated solutions. This is of great importance as it enables us to disregard the resistance of the connections, which McBain could not do. The heights of the columns of solution in the right and the left arms of the capillary holder are next measured and their difference taken. This difference represents the negative pressure in the glass which will suck solution from the beaker up into the capillary. Since some evaporation from the beaker cannot be avoided, although it is freshly filled for each experiment, we next adjust the positive pressure, as indicated by the mercury manometer M, so that it just overtops the negative pressure, leaving a net positive pressure of 1 or 2 mm. Hg in the flask. This adjustment of pressure was occasionally checked as follows. If we have a net positive pressure of a few millimeters of mercury we can calculate the resultant stream potential, with 0.0005 N KCl, as about 1.5 mv. per mm. The algebraic sum of this and of the electrode potentials as determined through the low resistance circuit gives the potential which should exist across the capillary. When this is measured it always agrees with the calculated value.

Knowing the potential difference of electrodes exclusive of an impressed e.m.f. we next impress from the potentiometer an appropriate voltage, the total e.m.f. being the algebraic sum of the pre-existing and the impressed e.m.f. From 1000 to 1500 mv. with 0.1 mf. condenser were used with 0.0005 N KCl; from 100 to 200 mv. with 1 mf. with 0.1 or 1.0 N KCl. With some of the larger capillaries and 1.0 N KCl the measurements were made with a Wheatstone bridge. The charging time with the switch K to the left was taken with a stop watch, the ballistic throw of the galvanometer being observed when the condenser was discharged by throwing the switch to the right at time t. In no case was the time short enough that its measurement introduced an appreciable error. From 4 to 8 consecutive determinations were made on a capillary and their average taken as the resistance for that experiment; the variation of the corrected values of these consecutive determinations was practically always less than 1/2 per cent and never more than 1 per cent.

The observed values were corrected to a temperature of 25°C. by the equation $R_{25} = \frac{R_t}{1 - 0.022\,(t - 25)}$. Within the comparatively narrow range of temperatures in these experiments the correction factor 0.022 remains almost constant. The beaker G was at room temperature, a thermometer was immersed in the beaker at the same depth as and close to the capillary and was read every few minutes. The capillary was completely immersed; the column of fluid in the capillary will almost instantly come to the temperature of the beaker; there is, indeed, no reason why the temperatures should differ to any significant extent.

A single figure for the resistance values given in Table I represents the average of a series of consecutive determinations, each determination being corrected for temperature and for condenser leak, when the latter is of significance. Other figures for the same capillary represent averages of similar series made at different times. After the final arrangement of apparatus had been perfected the results were surprisingly reproducible; no observed data have been rejected in the compilation of these tables except in a few instances where obvious sources of error, as partial obstruction of the capillary or an error in dilution of the solution, had entered. In these cases the source of error was proved by other objective means as by microscopic examination of the capillary or refractometric examination of the solution.

TABLE I

Cap. No.	Length cm.	Diam. (calc.) micra	Observed resistance with 1.0 N KCl ohms	Observed resistance with 0.1 N KCl ohms	Observed resistance with 0.0005 N KCl ohms	Calculated resistance with 0.0005 N KCl ohms	$\frac{\text{Observed}}{\text{Calculated}}$ with 0.0005 N KCl
60	1.8	5.10		6.83×10^8	8.88×10^{10}	1.18×10^{11}	.752
				6.82×10^8	8.65×10^{10}		
					9.07×10^{10}		
61	.76	5.34		2.66×10^8	3.63×10^{10}	4.59×10^{10}	.798
				2.63×10^8	3.69×10^{10}		
				2.65×10^8	3.66×10^{10}		
64	1.25	5.64		3.92×10^8	5.60×10^{10}	6.75×10^{10}	.819
				3.87×10^8	5.43×10^{10}		
					5.59×10^{10}		
					5.64×10^{10}		
					5.37×10^{10}		
63	.75	5.76		2.26×10^8	3.39×10^{10}	3.93×10^{10}	.85
				2.27×10^8	3.30×10^{10}		
					3.33×10^{10}		
60a	.94	5.48		3.06×10^8	4.38×10^{10}	5.36×10^{10}	.823
				3.11×10^8	4.46×10^{10}		
				3.11×10^8	4.39×10^{10}		

TABLE I (Continued)

Cap. No.	Length cm.	Diam. (calc.) micra	Observed resistance with 1.0 N KCl ohms	Observed resistance with 0.1 N KCl ohms	Observed resistance with 0.0005 N KCl ohms	Calculated resistance with 0.0005 N KCl ohms	$\frac{\text{Observed}}{\text{Calculated}}$ with 0.0005 N KCl
56	1.40	8.0	2.49×10^7 2.50×10^7		3.20×10^{10} 3.22×10^{10} 3.33×10^{10} 3.47×10^{10} 3.35×10^{10}	3.76×10^{10}	.88
66	.54	11.4		4.13×10^7 4.12×10^7	6.70×10^9 6.70×10^9 6.75×10^9 6.59×10^9 6.76×10^9 6.59×10^9 6.64×10^9	7.16×10^9	.933
65	.89	12.0		6.12×10^7 6.14×10^7	9.65×10^9 9.93×10^9 9.97×10^9 9.76×10^9 9.74×10^9 1.01×10^{10}	1.06×10^{10}	.926
30	1.60	25.6	2.77×10^6 2.73×10^6 2.76×10^6	2.41×10^7 2.41×10^7	4.00×10^9 3.94×10^9 3.92×10^9 3.95×10^9	4.17×10^9	.948
57a	1.97	39.0	1.446×10^6 1.43×10^6	1.26×10^7 1.27×10^7	2.19×10^9 2.14×10^9 2.17×10^9	2.17×10^9	1.00
57	4.45	39.4	3.27×10^6 3.27×10^6		4.94×10^9 5.08×10^9 4.84×10^9 4.83×10^9 4.85×10^9 4.96×10^9	4.94×10^9	.996
57b	2.48	39.7	1.803×10^6 1.805×10^6 1.807×10^6 1.806×10^6	1.59×10^7 1.60×10^7 1.59×10^7	2.61×10^9 2.66×10^9 2.66×10^9 2.73×10^9 2.71×10^9 2.67×10^9 2.67×10^9 2.65×10^9	2.72×10^9	.981

TABLE I (Continued)

Cap. No.	Length cm.	Diam. (calc.) micra	Observed resistance with 1.0 N KCl ohms	Observed resistance with 0.1 N KCl ohms	Observed resistance with 0.0005 N KCl ohms	Calculated resistance with 0.0005 N KCl ohms	$\frac{\text{Observed}}{\text{Calculated}}$ with 0.0005 N KCl
59	4.66	40.5	3.26×10^6	2.87×10^7	4.71×10^9	4.90×10^9	.967
			3.29×10^6	2.85×10^7	4.77×10^9		
			3.26×10^6	2.87×10^7	4.76×10^9		
			3.23×10^6		4.70×10^9		
			3.23×10^6				
			3.23×10^6				
			3.26×10^6				
58a	1.90	96.0	2.38×10^5		3.54×10^8	3.56×10^8	.992
			2.37×10^5		3.53×10^8		
			2.35×10^5		3.55×10^8		
			2.35×10^5		3.50×10^8		
					3.52×10^8		
					3.55×10^8		
58	4.77	96.4	5.87×10^5		8.76×10^8	8.86×10^8	.986
			5.85×10^5		8.72×10^8		
					8.68×10^8		
					8.81×10^8		
58b	2.85	97.6	3.40×10^5		5.07×10^8	5.13×10^8	.988
			3.39×10^5		5.06×10^8		
			3.41×10^5		5.02×10^8		
			3.41×10^5		5.14×10^8		
					5.07×10^8		
25	6.15	102.8	6.68×10^5		1.014×10^9	1.007×10^9	1.01
			6.65×10^5		1.026×10^9		
					1.020×10^9		
					1.010×10^9		
					1.014×10^9		
					1.015×10^9		
					1.020×10^9		
63a	.25	5.78		7.45×10^7	1.05×10^{10}	1.29×10^{10}	.814
				7.43×10^7	1.06×10^{10}		
					1.04×10^{10}		
64a	.33	5.22		1.20×10^8	1.70×10^{10}	2.085×10^{10}	.818
				1.20×10^8	1.71×10^{10}		
67	1.77	18.6		4.65×10^7	7.28×10^9	8.06×10^9	.908
				4.64×10^7	7.42×10^9		
					7.23×10^9		
					7.34×10^9		
68	.62	1.82		1.865×10^9	2.18×10^{11}	3.24×10^{11}	.686
					2.26×10^{11}		

In the same way the resistance determinations can be carried out, using stream potential of capillary instead of impressed e.m.f. In this case a pressure of 60 cm. Hg is applied, the stream potential determined and the potentiometer then set at zero. The current from the stream potential then charges the condenser through the capillary resistance from time t, the galvanometer deflection being measured as before. The observed capillary resistance is the same whether potentiometer or stream potential is the charging e.m.f. This fact is of great theoretical interest, as it shows, among other things, that the resistances of a column of liquid in motion and at rest are the same, that the relatively rapid passage of liquid does not alter those surface conditions which determine surface conductance and that the stream potential can be made to furnish a reasonable amount of current (a great deal more than is required for its own measurement by the null point potentiometer-condenser method) without being affected. The figures in Table I which were obtained by using stream potential as source of e.m.f. are italicized.

Table I is a summary of all the results obtained on 21 capillaries ranging from 0.00182 to 0.1028 mm. bore. The length is the measured length, the diameter is that calculated from the observed resistance with 0.1 or 1.0 N KCl. This method of calculating diameter is valid only if the observed resistance of capillary plus connections is identical, within the limits of measurements, with the calculated normal resistance of the capillary alone when concentrated solution is used. The practical identity of these two resistances depends upon three conditions, first, that the resistance of connections be negligible, second, that the surface conductance be negligible and, third, that the pinch effect be negligible. The truth of these three conditions has already been established in the preceding paper. Since we are interested in actual conductances we have seen no reason to correct, as McBain has done, for conductance of solvent; in any event the correction is negligible.

Since resistance of connections and pinch effect are always negligible and with a concentrated solution surface conductance is also negligible, the diameter of the capillary is calculated from the equation diameter $= 2\sqrt{\frac{\rho\ l}{\pi R}}$ where ρ is specific volume resistance of solution (8.95 ohms for 1.0 N and 77.8 for 0.1 N KCl), l is length of capillary in cm. and R is observed resistance in ohms. The value so obtained is the mean diameter of the capillary and has been taken as a better measure of diameter than the microscopic measurements. Having established its dimensions one next calculates the normal volume resistance of the capillary filled with 0.0005 N KCl, the 6th column of Table I. The 7th column compares observed and calculated resistances with dilute solution and shows far less surface conductance than found by McBain and coworkers.

A further analysis of our results with 0.0005 N KCl is given in Table II and Fig. 2. The last column in Table II gives the specific surface conductance, κ_s, calculated for each capillary.[7] In Fig. 2 the distance of the line OD above the X axis designates C_v/C_v, representing 100 per cent of the normal conductance. For large tubes there is no other significant conductance but as diameter decreases an increasing amount of surface conductance is added. The distance of the line OE above OD represents the ratio C_s/C_v for the capillary diameter designated on the X axis. The line OE is drawn through the experimental points, the number by each point designates the capillary. The distance of OE above the X axis at any given diameter represents $\frac{C_s + C_v}{C_v}$, the ratio of total or observed conductance to calculated or volume conductance; the reciprocals of these values coincide with the values in the 7th column of Table I.

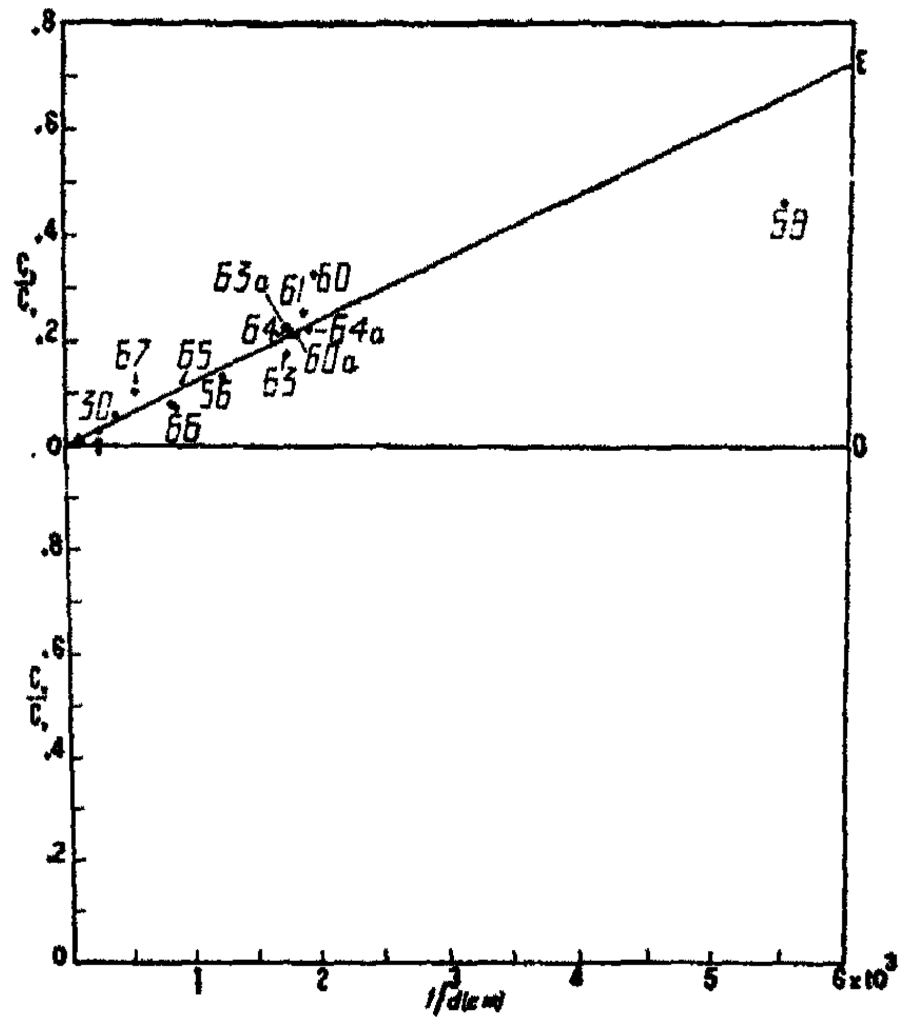


FIG. 2

It will be further noted that the slope of the line OE affords a method of calculating the mean specific surface conductance, κ_s, of all our experiments. $C_s = \kappa_s \frac{\pi d}{l}$ and $C_v = \kappa_v \frac{\pi d^2}{4l}$ where C_s and C_v are the surface and volume conductances, respectively, in mhos, of a capillary of length l and diameter d, and κ_s and κ_v are the specific surface and volume conductances. Then $C_s/C_v = 4\,\kappa_s/d\,\kappa_v$. This is of the form of the straight line equation $y = ax$, where $y = C_s/C_v$, $a = 4\,\kappa_s/\kappa_v$ and $x = 1/d$. Since then we are plotting C_s/C_v against $1/d$, the slope of the line is $4\,\kappa_s/\kappa_v$. The figure shows that the slope is $\frac{.242}{2 \times 10^3}$ or 1.21×10^{-4}. Therefore, $4\,\kappa_s/\kappa_v = 1.21 \times 10^{-4}$. But $\kappa_v = 7.41 \times 10^{-6}$, the normal specific conductance of 0.0005 N KCl. Therefore, $\kappa_s = 2.24 \times 10^{-9}$ mhos.

TABLE II

No.	Length (cm.)	Diam. (calc.) micra	R (observed) ohms	R_v (calc.) ohms	R_s $\left(\frac{R_vR}{R_v-R}\right)$ ohms	R_s/R_v	C_s/C_v	$\frac{1}{d(\text{cm.})}$	κ_s $\left(\frac{C_s l}{\pi d}\right)$ mhos
60	1.8	5.10	8.87×10^{10}	1.18×10^{11}	3.57×10^{11}	3.03	.330	1.96×10^{3}	3.13×10^{-9}
61	.76	5.34	3.66×10^{10}	4.59×10^{10}	1.81×10^{11}	3.94	.254	1.87×10^{3}	2.52×10^{-9}
64	1.25	5.64	5.53×10^{10}	6.75×10^{10}	3.06×10^{11}	4.53	.221	1.77×10^{3}	2.31×10^{-9}
63	.75	5.76	3.34×10^{10}	3.93×10^{10}	2.23×10^{11}	5.67	.176	1.74×10^{3}	1.89×10^{-9}
60a	.94	5.48	4.41×10^{10}	5.36×10^{10}	2.49×10^{11}	4.64	.216	1.82×10^{3}	2.19×10^{-9}
56	1.40	8.0	3.31×10^{10}	3.76×10^{10}	2.76×10^{11}	7.34	.136	1.25×10^{3}	2.02×10^{-9}
66	.54	11.4	6.68×10^{9}	7.16×10^{9}	9.97×10^{10}	13.9	.072	$.877\times10^{3}$	1.52×10^{-9}
65	.89	12.0	9.84×10^{9}	1.06×10^{10}	1.37×10^{11}	12.9	.078	$.833\times10^{3}$	1.72×10^{-9}
30	1.60	25.6	3.95×10^{9}	4.17×10^{9}	7.50×10^{10}	18.0	.056	$.391\times10^{3}$	2.65×10^{-9}
57a	1.97	39.0	2.17×10^{9}	2.17×10^{9}	∞	∞	0	$.256\times10^{3}$	0
57	4.45	39.4	4.92×10^{9}	4.94×10^{9}	1.215×10^{12}	250	.004	$.254\times10^{3}$	indeterminate
57b	2.48	39.7	2.67×10^{9}	2.72×10^{9}	1.36×10^{11}	53	.019	$.252\times10^{3}$	1.39×10^{-9}
59	4.66	40.5	4.74×10^{9}	4.90×10^{9}	1.45×10^{11}	30	.033	$.247\times10^{3}$	2.53×10^{-9}
58a	1.90	96.0	3.53×10^{8}	3.56×10^{8}	4.19×10^{10}	120	.0083	$.104\times10^{3}$	1.52×10^{-9}
58	4.77	96.4	8.74×10^{8}	8.86×10^{8}	6.48×10^{10}	73	.013	$.104\times10^{3}$	2.46×10^{-9}
58b	2.85	97.6	5.07×10^{8}	5.13×10^{8}	4.34×10^{10}	85	.012	$.102\times10^{3}$	2.14×10^{-9}
25	6.15	102.8	1.017×10^{9}	1.007×10^{9}	indeterminate			$.097\times10^{3}$	indeterminate
63a	.25	5.78	1.05×10^{10}	1.29×10^{10}	5.65×10^{10}	4.38	.228	1.73×10^{3}	2.45×10^{-9}
64a	.33	5.22	1.705×10^{10}	2.085×10^{10}	9.36×10^{10}	4.49	.223	1.92×10^{3}	2.16×10^{-9}
67	1.77	18.6	7.32×10^{9}	8.06×10^{9}	7.97×10^{10}	9.90	.101	$.538\times10^{3}$	3.49×10^{-9}
68	.62	1.82	2.22×10^{11}	3.24×10^{11}	7.04×10^{11}	2.17	.462	5.50×10^{3}	1.55×10^{-9}

The arithmetic average of specific surface conductances obtained from all the capillaries of 0.025 mm. or less bore is 2.27×10^{-9} mhos. Obviously the results with the smaller capillaries, where the ratio of surface to volume is great, are the most dependable. The single 1.8μ capillary, no. 68, is probably an exception to this statement; technical difficulties increase rapidly as one gets below 5μ, which is about the optimum diameter for this work. With the 0.04 and 0.10 mm. capillaries the surface conductance is so small a fraction of the whole that its measurement involves a considerable error. Three of our 0.10 and 2 of our 0.04 mm. capillaries gave figures close to the average; the surface conductance with the others of these sizes is indeterminate. It must be remembered that with a 0.10 mm. capillary an error of 0.1 per cent in resistance determination gives an error of 10 per cent in specific surface conductance.

Discussion. McBain and Peaker found 13.0×10^{-8} mhos as the specific surface conductance with 0.001 N KCl and pyrex glass; this would have been not less than 1×10^{-7} for 0.0005 N KCl. As compared with their figure (our extrapolation) of 1×10^{-7} we find 2.24×10^{-9}, i.e., their figure for κ_s is 45 times as large as ours. We believe that the error of our methods of measurement is less than theirs; our ratio of surface to volume is many times as high, our cell resistance can be neglected and we had no "pinch effect." As a possible explanation of this great discrepancy in results we offer the suggestion that a large part of their observed increase in conductance was due to traces of chromic acid. The time effects described by McBain, Peaker and King might be explained on this basis. Our capillaries were cleaned by sucking hot water through them for an hour, followed in some cases by steaming for an hour; we found that the steaming process was probably not essential in conductance determinations. We did not use any cleaning solution and we have seen no change in capillary resistance with time.[8]

The increase of conductance with time in McBain's experiments might also be partly due to a liberation of electrolytes from the glass itself; when the ratio of surface to volume becomes high this factor is exaggerated, particularly with dilute solutions. The possibility of our solutions becoming more concentrated by the leaching of the glass surface was avoided by having a very slow continuous passage of solution through the capillary; in McBain's work the solution was stationary. The point might be raised that complete lack of relative motion between solution and glass surface is essential to the building up of a conducting layer. It seems unreasonable, however, that the forces of adsorption could be negatived by such a feeble agitation as was exhibited in our capillaries where the measurement was made by impressing an external source of e.m.f. In our work the resistance of a capillary was the same whether the solution was passing through it relatively rapidly under a pressure of 600 mm. Hg, the stream potential being used as a source of e.m.f., or whether the solution was moving at the extremely slow rate attained under a pressure of 1 or 2 mm. mercury. It seems only reasonable that if the movement of the solution past the glass surface disturbed the development of the conducting layer, this disturbance would be measurably greater when the rate of movement was increased three hundred to six hundredfold. We are convinced that the state of a very slow exchange of solution is less open to objection than is no movement of solution. The suggestion that McBain's finding of a much higher specific surface conductance than ours may be due to the liberation of electrolytes from adsorbed chromic acid or from the glass itself is, of course, not capable of direct proof. The cause of the discrepancy may be some other source of error yet undetected. A discussion of some of the theoretical implications of these data with an extension of the work to include KCl solutions of other concentrations will appear in a later communication.

Summary

1. An arrangement for determining either stream potential or resistance of pyrex capillaries filled with salt solution is described. Resistances up to 2.22×10^{11} ohms are measured by the rate of condenser charge method. Evidence is presented that polarization is avoided.

2. There is no change of resistance with time.

3. Capillaries of from 0.00182 to 0.10 mm. bore were used, macroscopic surface to volume ratios as high as 22,000 to 1 being obtained as compared with 1600 to 1 by McBain, Peaker and King.

4. A specific surface conductance for pyrex glass and 0.0005 N KCl of 2.24×10^{-9} mhos was found, as compared with an extrapolated value of 1×10^{-7} by McBain, Peaker and King, their figure being 45 times as great as ours.

5. The suggestion is made that the conductance figures of McBain and coworkers may be erroneously high because of contamination of solution by chromic acid or by leaching out of electrolytes from the glass. The possibility of this occurrence has been avoided in our work.

The work reported in this and in the preceding paper has been aided by a grant made by the Rockefeller Foundation to Washington University for research in science.

Bibliography and Footnotes

[1] McBain, Peaker and King: J. Am. Chem. Soc., **51**, 3294 (1929).

[2] McBain and Peaker: J. Phys. Chem., **34**, 1033 (1930).

[3] White, Urban and Krick: J. Phys. Chem., **36**, 120 (1932).

[4] Van Atta: Rev. Sci. Instr., **1**, 687 (1930).

[5] Bishop: Am. J. Physiol., **85**, 417 (1928).

[6] Bishop: Proc. Soc. Exp. Biol. Med., **27**, 260 (1930).

[7] Specific surface conductance is calculated by either of the following expressions. $\kappa_s = C_s l/\pi d$, where κ_s is specific surface conductance, C_s, l and d are the surface conductance in mhos, the length in cm. and the diameter in cm. of a capillary. C_s is the reciprocal of the 6th column in Table II. $\kappa_s = \dfrac{(R_v - R)\,\kappa_v}{R \times \text{ratio}\,\dfrac{\text{surface}}{\text{volume}}}$, where R_v is the calculated or volume resistance in ohms of a capillary, R the observed resistance and κ_v the normal or volume specific conductance. The ratio $\dfrac{\text{surface}}{\text{volume}}$ for a capillary is $\dfrac{40{,}000}{d}$, where d is the diameter in micra.

[8] Since these data were obtained and this paper written, further work on conductance in the smallest capillaries, both with 5×10^{-4} molar and with other concentrations of KCl, has not shown exact reproducibility with the same consistency as obtained in this series. Whether or not this is due to an artefact we are not yet prepared to state.

VISCOSITY OF THE SILICIC ACID GEL-FORMING MIXTURES

BY MATA PRASAD, S. M. MEHTA AND J. B. DESAI

Prasad and Hattiangadi[1] have shown that when solutions of sodium silicate and of acids (or acidic ammonium acetate) are mixed together, crystalloidal silicic acid first formed goes over to the colloidal state and then follows the coagulation of the colloid solution by the electrolytes present in the mixture. Prakash and Dhar[2] have shown that the viscosity measurements of the jelly-forming mixtures reveal (1) the passage of the crystalloidal substance into colloidal state (2) the gradual neutralisation of the charge on the colloidal micelles (3) the formation of the specific structure of jellies. The present investigation was undertaken with a view to distinguish these three stages in the process of formation of the silicic acid gels.

The viscosity of silicic acid sols with and without the addition of electrolytes has been measured by Dhar and Chakravarty[3] who find that with increasing quantities of the electrolytes the viscosity of the sol at first falls, then rises to a maximum and again falls. Dhar[4] concludes that the degree of hydration and the viscosity of the sol increase as the charge on the colloidal particles is decreased. Thus it appears that the viscosity measurements of a colloidal system undergoing coagulation can also be utilised to measure the degree of hydration of the colloidal particles.

Experimental

Scarpa's apparatus[5] modified by Farrow[6] has been adopted with the following changes: (i) the connection of the guard tube opening the viscometer cylinder to the atmosphere has been kept at the top of the ground-glass stopper and not inside the cylinder thus ensuring constancy of the concentration of the solution under investigation (ii) ground-glass stoppers have been substituted for the wooden and rubber corks used by Scarpa and Farrow.

The viscometer with the guard tube is enclosed in an electrically heated air thermostat maintained at 40°C within ± 0.02°C.

The dimensions of the viscometer used are:

(i) Volume of the bulb between the two fixed marks........3.17 c.c.

(ii) Diameter of the capillary.............................8.9 mm.

(iii) Length of the capillary...............................7.5 cms.

---

[1] J. Indian Chem. Soc., 6, 893 (1929).
[2] J. Indian Chem. Soc., 6, 391 (1929).
[3] Kolloid-Z., 44, 225 (1928).
[4] J. Phys. Chem., 29, 1556 (1925).
[5] Gazz., 40, 271 (1910).
[6] J. Chem. Soc., 101, 341 (1912).

The viscometer bulb of a small volume was selected because the rate of increase of viscosity of the gel-forming mixtures with time was found to be very great at a later stage of gel-formation and hence a viscosity reading could be taken in as short a time as possible.

Solutions of sodium silicate and acetic acid were prepared as described in the previous communication.

The gel-forming mixtures were prepared by mixing equal volumes (20 c.c.) of sodium silicate and acetic acid solutions and the viscosity of the mixtures with (i) different silica content and (ii) different amounts of the acid was measured at different intervals of time till the gel set.

The time of rise "t_1" and the time of fall "t_2" were measured by an accurate stop-watch. Another stop-watch started at the time of mixing the gel-forming constituents indicated the time since mixing at which the time of rise and of fall were measured. The mean of the time at which the mixture was made to rise and that at which it reached the lower mark while falling, was taken to indicate the time "T" at which the viscosity reading of the mixture was taken.

TABLE I

A. Alkaline gel-forming mixtures

Silica content—4 per cent

C = 0.35N pH = 9.86		C = 0.36 N (pH = 9.74)		C = 0.37 N (pH = 9.03)	
T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$
3′ 26″	7929	5′ 9″	8991	2′ 42″	8736
9′ 12″	8187	11′ 35″	9274	6′ 16″	9426
12′ 7″	8271	16′ 38″	9788	7′ 44″	9924
25′ 43″	9326	20′ 21″	10360	14′ 40″	13020
31′ 9″	9965	26′ 53″	11500	18′ 52″	15630
50′ 25″	12350	30′ 21″	12150	21′ 33″	18870
52′ 0″	12670	40′ 34″	14500	24′ 25″	23200
56′ 7″	13490	43′ 0″	15090	27′ 44″	32290
59′ 54″	14460	56′ 24″	20480	29′ 53″	∞
70′ 41″	16970	58′ 50″	22000		
75′ 41″	18270	71′ 43″	30490		
78′ 6″	19130	75′ 33″	38420		
97′ 18″	27790	78′ 0″	∞		
100′ 9″	30460				
103′ 55″	34810				
108′ 0″	39680				
114′ 45″	53520				
119′ 40″	∞				

TABLE I

B. Acidic gel-forming mixtures

Silica content—4 per cent

C = 0.50 N (pH = 5.4)		C = 0.55 N (pH = 5.28)		C = 0.60 N (pH = 5.19)		C = 0.65 N (pH = 5.11)	
T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$
4′ 49″	8330	3′ 7″	7702	5′ 14″	7667	6′ 46″	7767
6′ 13″	8529	5′ 40″	7617	14′ 15″	7602	20′ 21″	7789
10′ 8″	10970	18′ 48″	8007	19′ 12″	7617	25′ 49″	7929
11′ 55″	13390	24′ 5″	8636	41′ 2″	9466	32′ 53″	8307
14′ 4″	19570	30′ 56″	10390	50′ 21″	11950	41′ 7″	8945
16′ 0″	∝	32′ 29″	11190	53′ 45″	13840	44′ 36″	9371
		34′ 8″	12200	55′ 41″	15250	49′ 36″	10150
		37′ 45″	15360	60′ 5″	21190	54′ 41″	11160
		40′ 3″	19280	62′ 5″	28270	59′ 8″	12730
		41′ 50″	23390	64′ 0″	∝	61′ 25″	13690
		43′ 11″	∝			70′ 20″	20810
						73′ 2″	26200
						74′ 38″	31810
						76′ 0″	∝

TABLE II

A: Alkaline gel-forming mixtures

Silica content—5 per cent

C = 0.40 N (pH = 9.97)		C = 0.41 N (pH = 9.86)		C = 0.43 N (pH = 9.74)	
T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$
8′ 17″	9303	2′ 29″	9588	3′ 6″	11190
10′ 37″	9561	6′ 1″	10290	4′ 45″	12620
24′ 21″	11050	9′ 6″	11160	6′ 46″	15330
31′ 54″	12070	12′ 59″	12180	9′ 7″	21210
39′ 30″	12970	20′ 50″	14960	10′ 30″	26610
45′ 22″	14100	22′ 59″	15820	12′ 10″	∝
53′ 24″	15960	25′ 16″	17410		
60′ 44″	17970	35′ 22″	30860		
63′ 5″	18750	39′ 50″	44510		
70′ 42″	22500	42′ 40″	∝		
76′ 44″	26980				
80′ 15″	29950				
87′ 40″	39330				
93′ 13″	51390				
97′ 28″	63450				
101′ 0″	∝				

From t_1 and t_2 (expressed in tenth of a second) the viscosity η is calculated from

$$\eta = \kappa \left(\frac{t_1 t_2}{t_1 + t_2} \right)_s \quad \ldots\ldots\ldots\ldots \quad \text{(i)}$$

where $K = \eta_w \left(\frac{t_1 + t_2}{t_1 t_2} \right)_w$ the calibration data of the apparatus, obtained from pure distilled water.[1] Taking the value of η_w to be 0.006535 (c.g.s. units) at 40°C from Thorpe and Rodger's data[2] the value of K was found to be 7118.5×10^{-8}. The coefficient of viscosity of the various gel-forming mixtures was then calculated from (i) and the results are given in the following tables, in which c represents the concentration of acetic acid added. Curves in which viscosity is plotted against time have been drawn and one of the set is shown in Fig. 1.

TABLE II

B. Acidic gel-forming mixtures
Silica content—5 per cent

C = 0.65 N (pH = 5.3)		C = 0.70 N (pH = 5.2)		C = 0.75 N (pH = 5.15)		C = 0.80 N (pH = 5.1)	
T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$
3′ 1″	9665	3′ 6″	8999	2′ 58″	8806	3′ 18″	8869
6′ 10″	10750	8′ 47″	9620	6′ 4″	9126	8′ 48″	8855
8′ 2″	11980	13′ 33″	10600	19′ 38″	10970	13′ 6″	9133
9′ 55″	14160	16′ 53″	12260	23′ 3″	12480	20′ 42″	9965
12′ 13″	19950	18′ 47″	13680	26′ 54″	15430	26′ 38″	11040
13′ 30″	∝	20′ 16″	15980	29′ 2″	18340	29′ 52″	12060
		23′ 5″	20240	31′ 34″	24550	33′ 40″	13690
		24′ 32″	23750	34′ 16″	28720	35′ 34″	15130
		26′ 0″	∝	37′ 5″	∝	37′ 43″	17680
						40′ 15″	22190
						43′ 35″	34420
						45′ 50″	∝

Discussion of Results

It appears from the curves shown in Fig. 1 that the viscosity increases slowly for some time after mixing the gel-forming constituents and afterwards the rate of increase becomes very rapid. The slow increase in viscosity may be due to the formation of the colloidal particles in the gel-forming mixtures and the rapid increase may correspond to the neutralisation of charge and consequent increased hydration of the particles and to the formation of definite structures in gels. Curves plotted with logarithm of viscosity against time are not straight lines as found by Prakash and Dhar[3] but are continuous curves having nearly the same shape as those shown in Fig. 1.

---

[1] Cf. Scarpa: Loc. cit. and Farrow: Loc. cit.

[2] Phil. Trans., 185, A II, 397 (1894).

[3] Loc. cit.

The first portion of the viscosity curves for the acidic mixtures is less steep than that for the alkaline ones and this may indicate that the rate of formation of the colloidal particles in the former mixtures is slower than in the latter ones. Further, the steepness of the curves for the two types of mixtures beyond a certain point shows that the increase in the viscosity of the acidic mixtures is more rapid than that of the alkaline ones. This is probably due to the increased rate of hydration of the particles in the acidic mixtures.

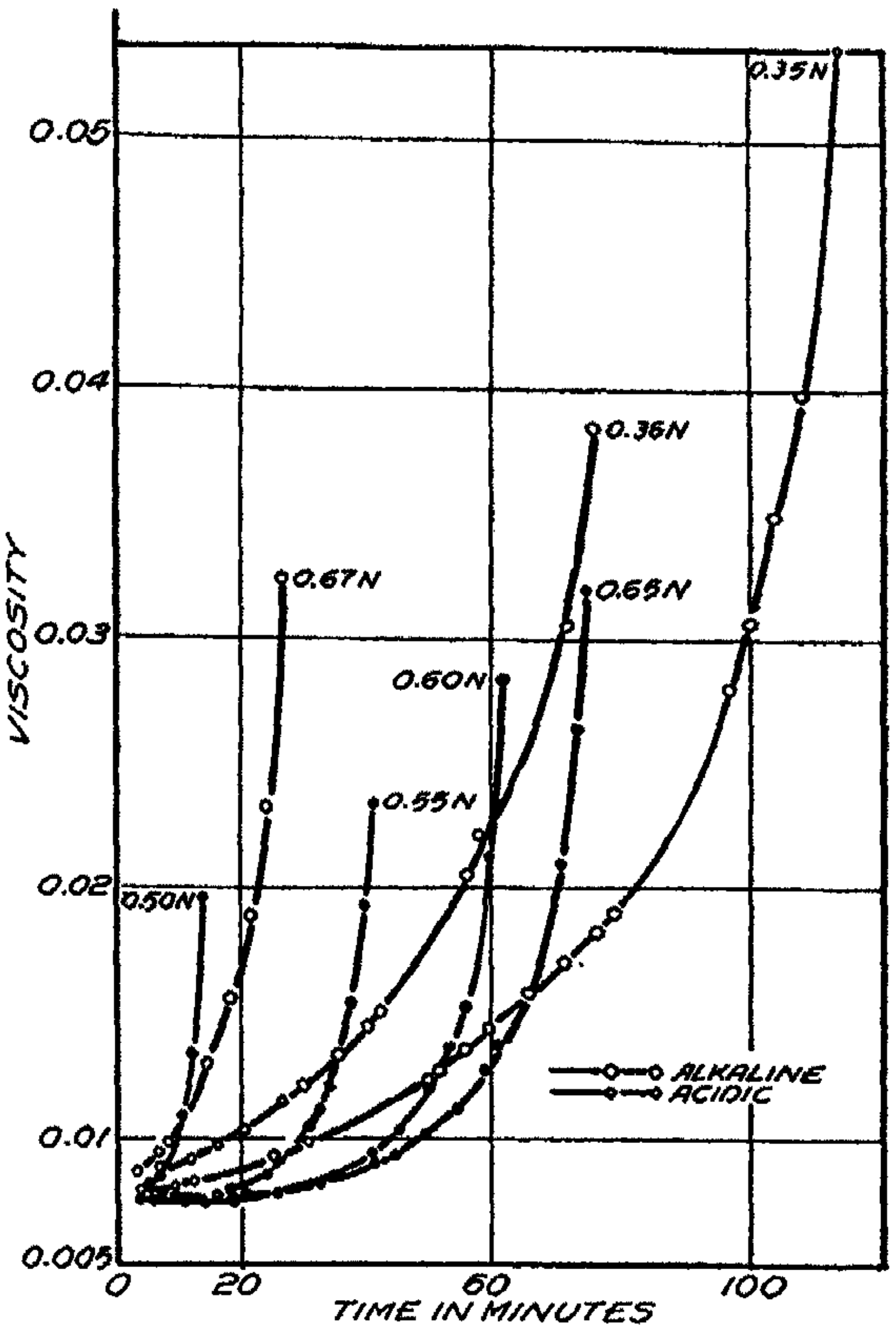


FIG. 1
Sodium silicate: 4%

Hatschek[1] has suggested that the viscosity of a colloidal system depends upon two factors (i) the volume of the disperse phase and (ii) the volume of the dispersion medium round each particle of the disperse phase. Dhar[2] has also pointed out that at constant concentration an increase in the degree of dispersion increases the hydration and the viscosity of the hydrophile colloids. From the extinction coefficient measurements the authors[3] have shown that

---

[1] Kolloidchem. Z., 12, 238-48 (1913).

[2] Loc. cit.

[3] Loc. cit.

the particles in the acidic mixtures are smaller in size than those in the alkaline ones. The increased rate of hydration of the particles in the acidic mixtures may, therefore, be due to the smallness of the particles in these mixtures. The greater hydration and the smaller size of the particles in the acidic mixtures than in the alkaline ones also explains the transparency of the acidic mixtures observed by Prasad and Hattiangadi.[1]

It will be seen that with an increase in the H ion concentration of the mixtures the rate of increase of viscosity at first increases till a mixture setting in minimum time is reached and then slowly begins to decrease. This is due to the decrease in the density of the electric charge and consequent increase in the rate of hydration of the colloidal particles in alkaline mixtures and vice versa for the acidic ones.

The values of viscosity at the time beyond which further measurements are impossible are higher in alkaline mixtures than in acidic ones. This again points to the rapid increase in the hydration of the particles in the acidic mixtures, that is, indicates such a great increase in viscosity after the last point given in the curve that the next reading could not be taken. As the gels set in a much longer time than that for which the viscosity readings could be taken no information regarding the ultimate hydration of the particles can be obtained from these measurements.

Hatschek[2] has shown that the hydration factor of a colloid particle can be obtained from f/c where c is the concentration of the colloidal solution by weight and f, the ratio of the volume of the disperse phase to the total given by

$$f = \left(\frac{\eta' - \eta}{\eta'}\right)^3$$

where η_1 and η are the viscosities of the colloidal solution and the dispersion medium respectively. The values of f have been calculated from the first and the last readings of the viscosities given in the Tables I and II and are denoted by f_1 and f_2 in the following table in which C represents the concentration of acetic acid.

TABLE III

(a) Conc. of SiO_2—4 per cent

C	0.35 N	0.36 N	0.37 N	0.50 N	0.55 N	0.60 N	0.65 N
$f_1 \times 10^3$	5.437	10.22	15.99	10.01	3.479	3.22	3.99
$f_2 \times 10^3$	676.4	571.9	507.5	295.6	374.2	454.6	501.9

(b) Conc. of SiO_2—5 per cent

C	0.4 N	0.41 N	0.43 N	0.65 N	0.70 N	0.75 N	0.80 N
$f_1 \times 10^3$	26.35	32.26	72.04	33.95	20.52	17.15	18.24
$f_2 \times 10^3$	722.3	620.9	429.0	304.0	381.0	460.7	531.5

The above table gives an idea of the enormous change taking place in the hydration of the particles long before the gel has completely set.

---

[1] Loc. cit., p. 653.

[2] Kolloid-Z., 27, 163 (1920).

Hatschek and Jane[1] have shown that the viscosity of the hydrophile sols and emulsions are directly related to their elasticity. It appears, therefore, from the results of viscosity measurements that the elasticity of the silicic acid particles considerably increases during the process of gel formation. The fundamental assumption made by Smoluchowski[2] in deriving a theory of the kinetics of coagulation is the complete inelasticity of the colloidal particles. The slight variations observed in the verification of the theory during a certain interval of gelation of silicic acid and the large variations at a later stage are probably due to the increased elasticity of the particles.

Summary

(1) Viscosity of silicic acid gel-forming mixtures has been measured with the progress of time by Scarpa's method as modified by Farrow and the time viscosity curves have been plotted.

(2) It is suggested that the slow rate of increase of viscosity during the preliminary stages of gelation is due to an increase in the number of colloidal particles. After a certain time the change in viscosity becomes fairly rapid: the rate of increase depends upon the size of the colloidal particles.

(3) The increase or decrease in the rate of change of viscosity on increasing the concentration of acetic acid in the alkaline or acidic mixtures has been explained on the relation between the charge on the colloidal particles and their hydration.

(4) The hydration factor has been calculated according to Hatschek's equation and it is shown that enormous changes in hydration take place during gelation.

Physical and Inorganic Chemistry Laboratories,
Royal Institute of Science,
Bombay.

---

[1] Kolloid-Z., 39, 300 (1926).

[2] Physik. Z., 17, 557 (1916); Z. physik. Chem., 92, 129 (1917).

INFLUENCE OF NON-ELECTROLYTES ON THE VISCOSITY OF SILICIC ACID GEL-FORMING MIXTURES

BY MATA PRASAD, S. M. MEHTA AND J. B. DESAI

The sensitising and peptising influence of non-electrolytes is well known in the case of several colloidal solutions. Billitzer[1] found that a negatively charged platinum sol could be sensitised, discharged and charged positively by the addition of suitable amounts of alcohols. Klein[2] found that negatively charged sols of arsenious sulphide, silica, gold and ferric oxide are coagulated by alcohols, while positively charged sols of ferric oxide and silica are not affected. Prasad and Hattiangadi[3] while studying the effect of non-electrolytes on the setting of silicic acid gels found that the alcohols accelerate the gel-formation in the alkaline mixtures while they retard it in acid ones.

This behaviour of alcohols is explained on (i) the decrease in the dielectric constant of the mixture and (ii) the changes in the adsorbabilities of ions by the colloid particles.[4] Both these factors tend to bring about a change in the density of the charge of the particles. Mukherjee and Ghosh[5] have shown by cataphoretic experiments that the density of charge in the colloidal arsenious sulphide is decreased by the addition of alcohols. A change in the charge of the colloidal particles will cause a change in their degree of hydration as well as in the viscosity of the colloidal system.[6]

The present investigation deals with the influence of alcohols on the viscosity of the two types of gel-forming mixtures and was undertaken with a view to examine the changes in the hydration of the particles in the two types of silicic acid gels.

Experimental

10 cc. of acetic acid of double the concentration required for the experiment were mixed with a known amount of alcohol and the total volume was made to 20 cc. by diluting with distilled water. This solution was then mixed with 20 cc. of sodium silicate solution containing 4% silica prepared as described in the previous paper[7] and the mixture was immediately transferred to the viscometer. Viscosity measurements were then taken as described in the previous paper.[8]

pH value of the mixture in absence of alcohol was determined by mixing solutions of sodium silicate and acetic acid of required concentrations and using colorimetric method for the purpose.

---

[1] Z. physik. Chem., 45, 312 (1903).

[2] Kolloid-Z., 29, 247 (1921).

[3] J. Indian Chem. Soc., 6, 991 (1929).

[4] Cf. Ostwald: "Grundriss der Kolloidchemie," p. 441; Mukherjee and collaborators: J. Indian Chem. Soc., 2, 307 (1925); Weiser: J. Phys. Chem. 28, 1253 (1924).

[5] J. Indian Chem. Soc., 1, 213 (1924).

[6] Cf. Dhar: J. Phys. Chem., 29, 1556 (1925).

[7] J. Phys. Chem., 36, 1384 (1932).

[8] Loc. cit.

In the following tables Q represents the cc. of alcohol in the mixture.

(a) The effect of ethyl alcohol in the alkaline mixtures.

The results obtained are given in Tables I and II and the time viscosity curves corresponding to Table I are shown in Fig. 1.

TABLE I

Acetic acid: 0.35 N
Reaction: Alkaline
pH: 9.86

Q : 0.0 cc.		0.5 cc.		1.0 cc.		2.0 cc.	
T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$
3′ 26″	7929	2′ 34″	9588	3′ 17″	9840	3′ 41″	11330
12′ 7″	8271	7′ 23″	9986	8′ 10″	10760	5′ 29″	11900
25′ 43″	9326	15′ 4″	10810	13′ 15″	12280	7′ 8″	13040
31′ 9″	9965	22′ 3″	11910	17′ 27″	13930	8′ 52″	14400
48′ 30″	11990	27′ 18″	12980	21′ 25″	16350	15′ 11″	22390
57′ 54″	13780	31′ 7″	13770	23′ 36″	18380	19′ 25″	48660
70′ 41″	16970	35′ 7″	14710	26′ 5″	21830	22′ 30″	∝
75′ 41″	18270	40′ 3″	16600	29′ 9″	26540		
83′ 7″	20870	44′ 55″	19110	32′ 35″	35370		
97′ 18″	27790	50′ 8″	22650	34′ 45″	∝		
100′ 9″	30460	53′ 13″	25110				
108′ 0″	39680	56′ 26″	28310				
114′ 45″	53520	60′ 3″	33000				
119′ 40″	∝	64′ 3″	40550				
		70′ 8″	73310				
		73′ 50″	∝				

TABLE II

Acetic acid: 0.36 N
Reaction: Alkaline
pH: 9.74

Q : 0.0 cc.		0. 5 cc.		1.0 cc.		2.0 cc.	
T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$
5′ 9″	8991	2′ 49″	10490	4′ 51″	11010	2′ 51″	11000
11′ 35″	9274	4′ 25″	10650	6′ 32″	11590	4′ 28″	12130
13′ 18″	9448	9′ 19″	11150	8′ 13″	12220	6′ 17″	13590
16′ 38″	9788	11′ 3″	11740	10′ 0″	12900	8′ 24″	16090
20′ 21″	10360	16′ 52″	13730	11′ 51″	14050	12′ 36″	25480
26′ 53″	11500	18′ 49″	14680	13′ 55″	15270	15′ 10″	∝
30′ 21″	12150	23′ 0″	17040	16′ 23″	17550		
43′ 0″	15090	25′ 20″	19130	18′ 52″	20680		
50′ 44″	17180	27′ 55″	21900	21′ 38″	25650		
53′ 0″	19320	30′ 57″	26130	25′ 18″	38830		
56′ 24″	20480	34′ 30″	32600	27′ 35″	∝		
71′ 43″	30490	36′ 41″	40310				
75′ 53″	38420	38′ 50″	∝				
78′ 0″	∝						

Tables I and II and the curves in Fig. 1 show that ethyl alcohol exerts an accelerating influence on the rate of increase of viscosity of the alkaline gel-forming mixtures. This is in agreement with the observations of Prasad and and Hattiangadi.[1] It appears that the increased rate of viscosity is caused by the increased rate of hydration due to the decrease in the density of the charge of the particles brought about by the increasing amounts of alcohol.

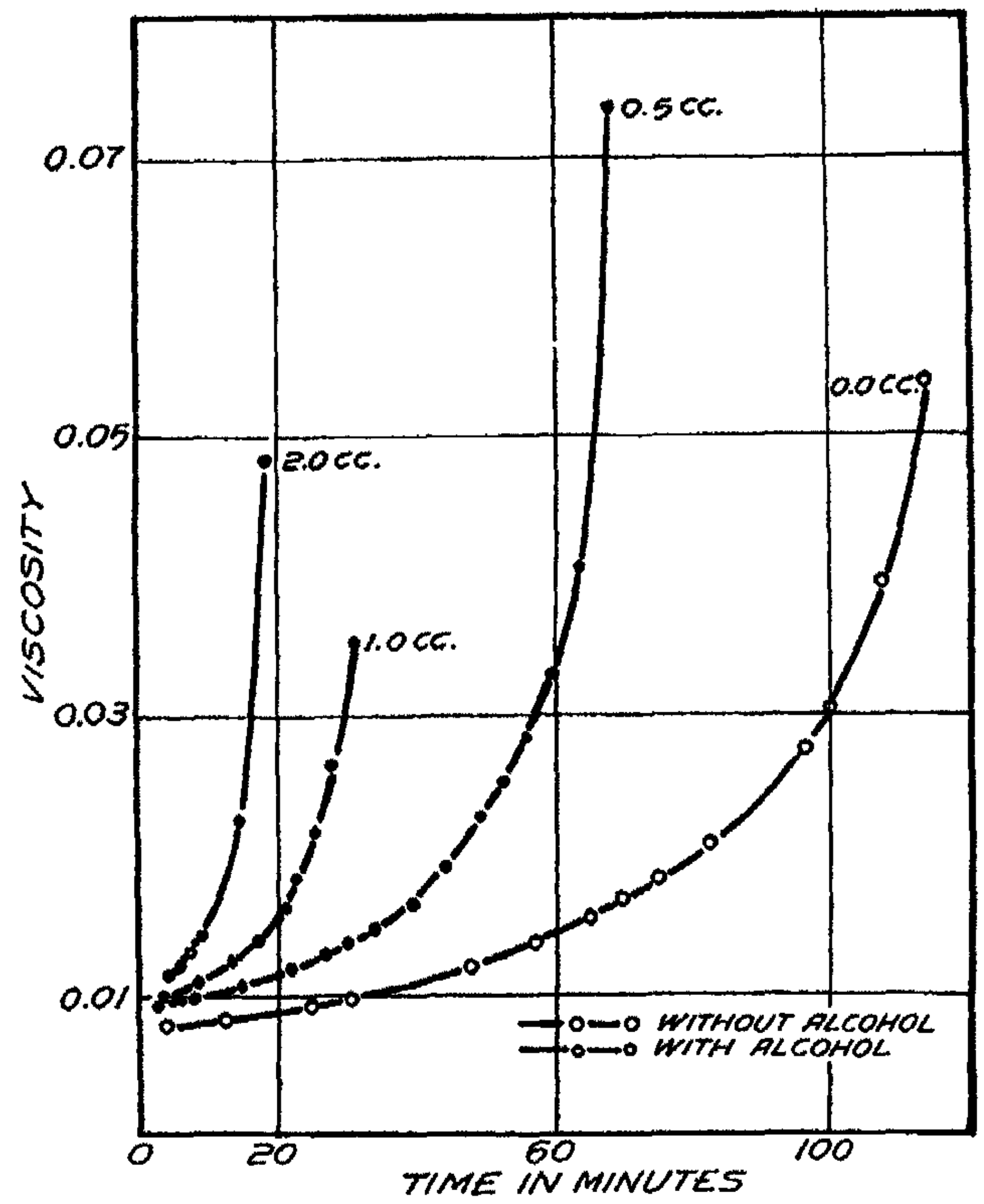


Fig. 1
Effect of alcohol on viscosity
Silica Content: 4%
Acetic acid: 0.35 N

On increasing the amount of ethyl alcohol beyond 2 cc. in the gel-forming mixture it is found that the mixture either sets instantaneously or a flocculent precipitate is obtained due to the low solubility of sodium silicate in alcohols.

(b) The effect of ethyl alcohol in the acidic mixtures.

The results obtained are given in Tables III, IV and V and one set of time-viscosity curves is shown in Fig. 2.

---

[1] Loc. cit.

TABLE III

Acetic acid : 0.55 N
Reaction : Acidic
pH : 5.28

Q : 0.0 cc.		0.25 cc.		0.5 cc.		0.75 cc.		2.0 cc.	
T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$
3′ 7″	7702	3′ 9″	7530	5′ 12″	7916	5′ 3″	7683	3′ 46″	8529
6′ 56″	7580	11′ 24″	7660	10′ 55″	8200	13′ 4″	8024	6′ 37″	8559
9′ 7″	7602	15′ 12″	7902	14′ 5″	8604	18′ 33″	8399	9′ 41″	8578
12′ 48″	7638	17′ 48″	8143	17′ 2″	9177	21′ 12″	8752	16′ 48″	8806
16′ 7″	7702	20′ 18″	8429	18′ 25″	9563	22′ 34″	8913	19′ 35″	8966
18′ 48″	8007	21′ 38″	8636	21′ 15″	10480	24′ 3″	9194	30′ 57″	10960
21′ 26″	8294	22′ 58″	8855	23′ 3″	11340	27′ 5″	9908	34′ 23″	12260
24′ 5″	8636	24′ 25″	9212	24′ 49″	12470	28′ 41″	10410	36′ 4″	13140
27′ 58″	9404	28′ 9″	10470	26′ 55″	14550	33′ 29″	12720	38′ 0″	14530
30′ 56″	10390	29′ 45″	11140	29′ 7″	18000	35′ 20″	14380	42′ 21″	20550
32′ 29″	11190	33′ 14″	13750	30′ 21″	21040	37′ 28″	17210	45′ 29″	32710
34′ 8″	12200	35′ 14″	16040	31′ 40″	∝	40′ 2″	23290	47′ 30″	∝
35′ 51″	13420	37′ 36″	21460			41′ 30″	∝		
37′ 45″	15360	38′ 23″	29770						
40′ 3″	19280	39′ 30″	∝						
41′ 50″	23390								
43′ 10″	∝								

TABLE IV

Acetic acid : 0.60 N
Reaction : Acidic
pH : 5.19

Q : 0.0 cc.		1.0 cc.		2.0 cc.		4.0 cc.		6.0 cc.	
T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$
5′ 14″	7667	3′ 0″	9183	3′ 49″	9419	5′ 0″	8200	3′ 21″	9665
6′ 36″	7602	10′ 24″	9333	12′ 44″	9526	12′ 13″	8565	9′ 51″	9620
11′ 51″	7580	13′ 18″	9296	17′ 17″	9759	16′ 51″	8728	14′ 36″	9752
14′ 15″	7602	16′ 5″	9376	26′ 45″	10270	22′ 51″	9397	17′ 52″	9824
19′ 12″	7617	20′ 19″	9588	30′ 0″	10400	27′ 3″	9620	25′ 37″	10100
41′ 2″	9466	24′ 50″	9888	33′ 6″	10870	36′ 2″	10210	30′ 2″	10420
47′ 18″	10850	28′ 48″	10100	38 6″	11800	39′ 15″	10760	34′ 6″	10640
50′ 21″	11950	30′ 48″	10350	43′ 21″	13150	40′ 44″	11090	38′ 44″	11080
52′ 0″	12730	37′ 48″	11980	47′ 48″	14950	42′ 15″	11280	50′ 3″	12520
53′ 45″	13840	43′ 15″	13770	51′ 28″	16960	45′ 44″	12000	53′ 50″	13520
55′ 41″	15250	45′ 10″	14560	54′ 31″	18910	49′ 38″	12980	55′ 51″	14080
60′ 5″	21190	47′ 9″	15690	57′ 12″	21990	51′ 52″	13730	58′ 0″	14700
62′ 5″	28270	49′ 16″	17210	62′ 1″	32700	53′ 56″	14620	60′ 0″	15310
64′ 0″	∝	51′ 34″	19220	64′ 0″	∝	56′ 2″	15520	61′ 59″	16060
		54′ 6″	22580			58′ 27″	16880	64′ 10″	17080
		57′ 9″	29920			60′ 51″	18880	69′ 0″	20410
		59′ 0″	∝			63′ 37″	21490	71′ 49″	22980
						66′ 30″	25630	74′ 43″	26510
						69′ 7″	35060	78′ 0″	33060
						71′ 20″	∝	79′ 58″	38700
								81′ 0″	∝

TABLE V

Acetic acid : 0.65 N
Reaction : Acidic
pH : 5.11

Q : 0.0 cc.		0.25 cc.		1.0 cc.		2.0 cc.		6.0 cc.	
T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$
3′ 58″	7739	4′ 58″	7502	4′ 33″	7560	3′ 27″	8570	4′ 48″	9448
14′ 39″	7702	10′ 4″	7580	13′ 11″	7721	12′ 28″	8742	14′ 31″	9590
23′ 37″	7881	18′ 54″	7602	19′ 57″	7794	16′ 12″	8756	19′ 14″	9736
29′ 33″	8132	31′ 44″	7894	27′ 26″	7923	20′ 18″	8826	27′ 52″	9895
34′ 22″	8337	39′ 18″	8429	32′ 56″	8095	24′ 48″	8849	32′ 47″	9908
42′ 57″	9124	53′ 41″	10410	43′ 37″	8642	27′ 38″	9040	37′ 31″	10140
51′ 5″	10420	60′ 41″	12160	51′ 0″	9397	33′ 25″	9177	42′ 25″	10440
61′ 25″	13690	64′ 13″	13540	54′ 32″	9951	39′ 17″	9342	47′ 5″	10530
70′ 20″	20810	70′ 45″	18280	59′ 4″	10760	49′ 32″	10040	53′ 48″	10950
73′ 2″	26200	73′ 27″	21690	65′ 33″	12460	52′ 53″	10440	61′ 15″	11770
74′ 38″	31810	76′ 45″	29890	69′ 35″	14030	69′ 1″	12730	68′ 58″	12800
76′ 0″	∝	78′ 40″	∝	71′ 36″	15080	74′ 43″	14040	73′ 35″	13580
				73′ 47″	16580	79′ 6″	15470	81′ 30″	15360
				76′ 1″	18430	81′ 47″	16810	86′ 15″	16960
				78′ 31″	21400	86′ 34″	19730	88′ 31″	17760
				81′ 17″	26310	91′ 57″	24920	91′ 3″	18810
				82′ 54″	31060	95′ 19″	29780	93′ 32″	20260
				84′ 30″	∝	102′ 45″	63400	96′ 10″	22250
						109′ 5″	∝	102′ 2″	27770
								105′ 30″	33230
								110′ 3″	47850
								115′ 17″	91700
								120′ 0″	∝

It appears that in moderately acidic mixtures (0.55 N and 0.60 N, Tables III and IV) quantities of alcohol less than 0.75 cc. accelerate the rate of increase of viscosity and quantities greater than this retard it; but in higher acidic mixtures (Table V) alcohols exert only a retarding influence. The latter observation is due to a decrease in the rate of hydration caused by an increase in the density of the charge of the colloidal particles. This is in agreement with the observations of Prasad and Hattiangadi[1] who found that in acidic mixtures alcohols act as protective agents.

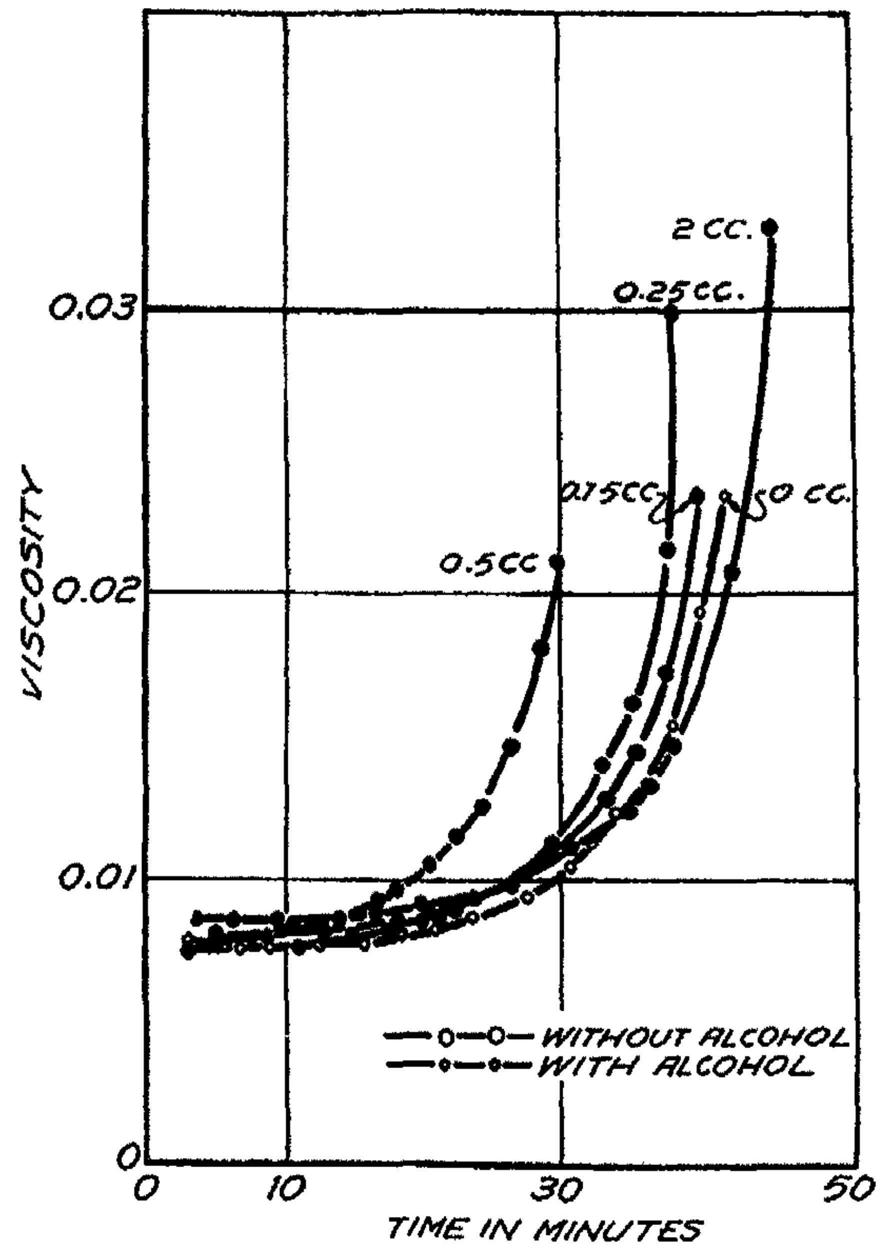


FIG. 2

Effect of alcohol on viscosity
Silica Content: 4%
Acetic acid: 0.55 N

The increase in the rate of viscosity in the presence of small amounts of alcohols in feebly acidic mixtures may be due to the decrease in the density of charge of the colloidal particles. This coagulating effect of alcohols even in acidic mixtures was not noticed by Prasad and Hattiangadi because they did not use such small amounts of alcohol as used in this investigation.

---

[1] Loc. cit.

It is evident that in moderately acidic mixtures (0.55 N and 0.60 N Tables III and IV) the rate of increase of viscosity is accelerated by small quantities of ethyl alcohol and retarded by larger amounts. But in higher acidic mixtures (Table V) ethyl alcohol exerts only a retarding influence.

(c) The comparative effect of alcohols in the alkaline and acidic mixtures. The effect of methyl, ethyl and propyl alcohols has been studied and the results obtained are given in Table VI and VII.

TABLE VI

Acetic acid: 0.36 N
Reaction: Alkaline
pH: 9.74

Methyl alcohol 1.0 cc.		Propyl alcohol 1.0 cc.	
T	$\eta \times 10^6$	T	$\eta \times 10^6$
3′ 50″	8450	4′ 15″	9164
7′ 46″	9319	5′ 40″	9482
15′ 7″	12000	7′ 15″	10040
16′ 48″	12980	10′ 19″	11290
20′ 25″	15680	11′ 53″	12130
24′ 50″	21950	13′ 34″	13220
27′ 44″	30920	17′ 36″	17850
30′ 21″	48400	20′ 6″	23100
33′ 15″	∝	22′ 40″	29020
		25′ 5″	∝

TABLE VII

Acetic acid: 0.60 N
Reaction: Acidic
pH: 5.2

Methyl alcohol 1.0 cc.		Propyl alcohol 1.0 cc.		Methyl alcohol 4.0 cc.		Propyl alcohol 4.0 cc.	
T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$	T	$\eta \times 10^6$
4′ 10″	7647	6′ 51″	7865	4′ 45″	8450	7′ 12″	9596
5′ 42″	7650	12′ 26″	7830	15′ 37″	8468	16′ 40″	9610
9′ 26″	7617	17′ 58″	7916	18′ 57″	8549	21′ 38″	9716
30′ 29″	8770	23′ 23″	8112	25′ 13″	8910	38′ 19″	11040
34′ 44″	9354	31′ 42″	8892	31′ 11″	9333	40′ 20″	11420
42′ 16″	11240	35′ 55″	9419	45′ 43″	11920	44′ 8″	12000
43′ 53″	12010	38′ 56″	10040	53′ 29″	15440	49′ 49″	13500
45′ 31″	12770	41′ 56″	10790	55′ 34″	17120	53′ 48″	15010
47′ 17″	13710	45′ 8″	11940	57′ 50″	19500	55′ 48″	16040
49′ 6″	15240	52′ 25″	17150	60′ 32″	23240	59′ 23″	17690
51′ 9″	17470	57′ 56″	28680	63′ 48″	32450	60′ 46″	19320
53′ 29″	21230	59′ 44″	∝	66′ 55″	∝	63′ ′15″	22040
56′ 52″	35670					66′ 7″	26360
60′ 0″	∝					69′ 45″	37590
						72′ 24″	∝

The time-viscosity curves are shown in Fig. 3 and for the sake of comparison the curves for the same mixture without the addition of alcohol and with 1.0 cc. of ethyl alcohol are also drawn in the same figure.

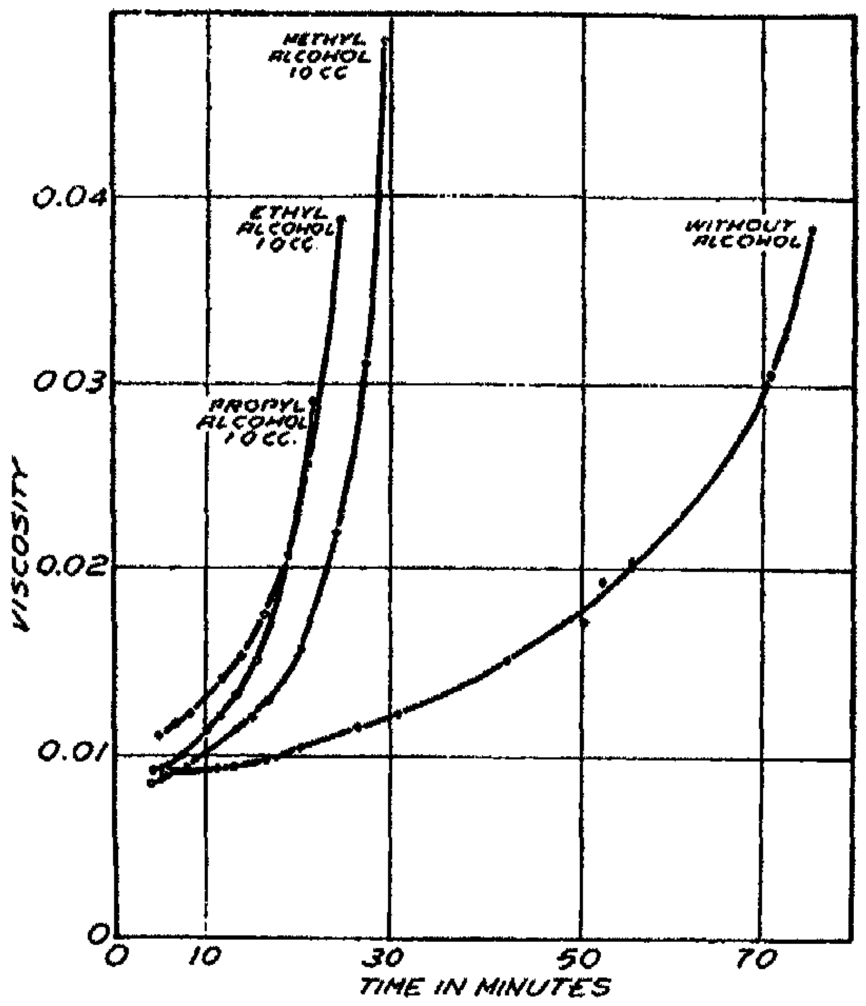


Fig. 3
Effect of alcohols on viscosity
Silica Content: 4%
Acetic acid: 0.36 N

The time-viscosity curves are shown in Fig. 4 and the two corresponding curves with ethyl alcohol and one without alcohol (Table IV) are also drawn in the same figure for the sake of comparison.

It will be seen that in the presence of alcohols the rate of increase of viscosity and hence the hydration is

(i) increased in alkaline medium and the order of the effect of alcohols is

$$C_3H_7OH > C_2H_5OH > CH_3OH$$

(ii) increased in moderately acidic medium when small quantities of alcohols are added. The order of this influence is the reverse of the previous one, that is

$$CH_3OH > C_2H_5OH > C_3H_7OH$$

(iii) decreased (a) in highly acidic medium (b) in moderately acidic medium when the amount of alcohols added is great. The order of the alcohols is the same as in the alkaline medium, that is,

$$C_3H_7OH > C_2H_5OH > CH_3OH$$

The order of the influence of alcohols in the alkaline medium is the same as that found by Prasad and Hattiangadi[1] on the time of setting of these gels.

---

[1] Loc. cit.

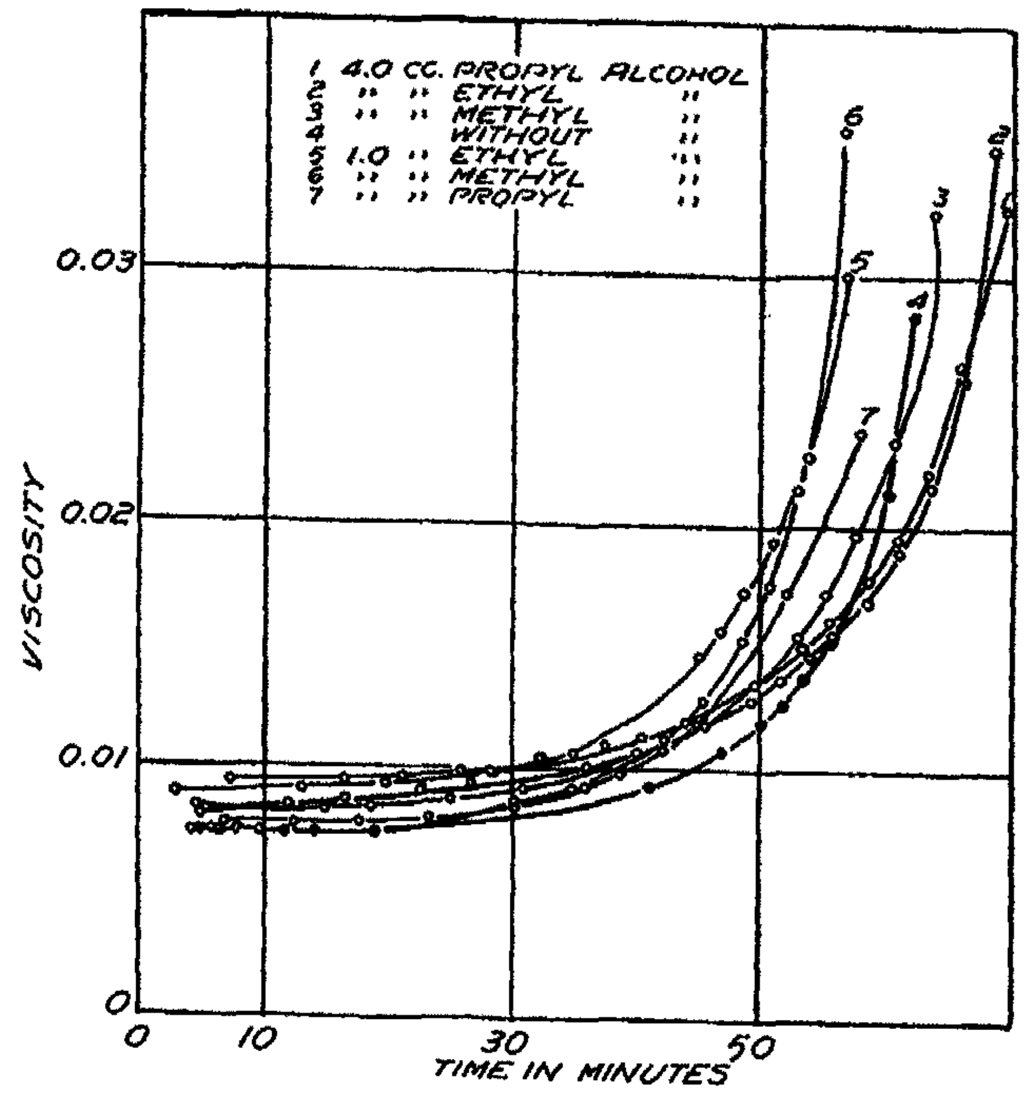


FIG. 4
Effect of alcohols on viscosity
Silica Content: 4%
Acetic acid: 0.60 N

The peculiar behaviour of non-electrolytes in sensitising the colloidal silicic acid particles in alkaline mixtures and protecting those in acidic ones cannot be explained on one single theory. Chaudhary[1] has pointed out that besides diminishing the dielectric constant of the system and changing the adsorbabilities of ions by the colloid particles, the non-electrolytes may also change the cohesive forces operative in a colloidal system. It will be interesting to carry out the charge measurements in the presence of alcohols under the various circumstances mentioned above and to see that the changes in the density of charge take place in the manner assumed above.

Summary

The influence of alcohols on the viscosity of the silicic acid gel-forming mixtures has been studied by Scarpa's method as modified by Farrow and the accelerating influence of alcohols on the rate of increase of viscosity in alkaline mixtures as well as in moderately acidic ones (within a very small range of the alcohol added) has been explained on the assumption of the diminution in the dielectric constant of the mixture. The retarding influence of the alcohols in acidic mixtures, however, still remains unexplained.

Physical and Inorganic Chemistry Laboratories,
Royal Institute of Science,
Bombay.

---

[1] J. Phys. Chem., 32, 480 (1928).

SOME SOLVENT PROPERTIES OF SOAP SOLUTIONS. I

BY E. LESTER SMITH

It is well known that phenol and cresol are more soluble in soap solutions than in water; advantage is taken of this phenomenon in the preparation of disinfecting solutions (e.g. Liquor Cresol Saponatus B.P., Liquor Cresol Glycerinatus B.P.C.) and it has formed the subject of several researches. Cyclohexanol and certain hydrocarbons have been incorporated with soaps to enhance their detergent action. It does not seem to be realised, however, that the solvent power of soap solutions is by no means restricted to these substances but is perfectly general. Every organic liquid that has been investigated is many times more soluble in soap solution (e.g. 10% sodium oleate), than in water; these solvated soap solutions differ greatly among themselves in their viscosity, foaming power, and the stability of their emulsions with excess of the organic liquid. The mixture of sterols, alcohols, hydrocarbons, etc., constituting the unsaponifiable fraction of most natural oils, though quite insoluble in water must obviously be soluble in soap solution, since soaps prepared from such oils yield clear aqueous solutions unless the unsaponifiable content is excessive. Moreover this unsaponifiable matter is retained by the soap with considerable tenacity against the competing solvent effect of extracting solvents, which also vary considerably among themselves in their effectiveness for extracting the unsaponifiable matter.

Although some of these facts are mentioned without comment in papers dealing with the estimation of unsaponifiable matter, they have hitherto excited curiously little interest, despite their evident bearing on a number of problems in theoretical and practical chemistry.

The present series of communications may be regarded as an attempt to map out this field, to link up and extend the few investigations on record and to relate the whole to our knowledge of the nature of aqueous soap solutions.

Review of Previous Publications

Pickering[1] observed the highly interesting fact that soap solutions can not only *emulsify* oils, but can actually *dissolve* considerable proportions of oil under suitable conditions. It appears that a certain soap manufacturer noticed that oils (presumably glyceridic) were soluble in soap solutions, and communicated the observations to Pickering, who extended it to mineral oils. Benzene and various paraffin oils were mixed intimately with potassium stearate or palmitate (in the form of 50% paste with water), the mixture was then diluted considerably with water, and the amounts of oil dissolved and emulsified, were determined after the emulsions had creamed. The soap would dissolve its own weight or more of oil, and retain it on dilution with water, but less oil was dissolved if the soap was diluted before mixing with the oil.

---

[1] J. Chem. Soc., 1917 III, 86.

Fischer[1] measured the "gelatin capacity" of a series of pure soaps for water, alcohol, and various organic liquids, i.e. the amount of liquid which could be held by 1 mol of the soap as a gel showing no syneresis. The entirely different physical states of gel and curd were however not clearly distinguished in this work.[2]

Bailey[3] describes the following system: water, phenol, sodium oleate at 20°, 40° and 60°; water, cresol, sodium oleate at 20°. The data are plotted in the manner usual for ternary systems, i.e. in equilateral triangles. The curves are of the binodal type which Bancroft has shown to be typical of systems of two partially miscible liquids and a third consolute liquid.[4]

The phenolic substance is completely miscible with soap solutions above a certain concentration.

Jenčič[5] has studied the solubility of cresols in soap solutions of the acetic series, in order to determine the minimum of soap necessary to give a homogeneous solution with a mixture of equal parts of water and cresol at ordinary temperatures, and also (*ibid.* 168) the minimum soap concentrations at which soap cresol mixtures yield gels.

Weichherz[6] in a study of xylol-water emulsions stabilised by soap (sodium oleate) found that concentrated soap solutions yield water-in-oil emulsions provided the phase-volume ratio is within a certain range, whereas dilute soap solutions yield in general oil-in-water emulsions: in the former case soap is dissolved in the xylol. Thus on adding water to a solution of soap in xylol a water-in-oil emulsion is first produced, which on addition of water beyond a critical phase volume ratio inverts to an oil in water emulsion. On account of the low solubility of sodium oleate in xylol, the work was extended by the addition of phenol to the system. The investigation of the quaternary system was limited to a study of the phase volume ratios and emulsion types produced by addition of water to an arbitrarily chosen mixture of xylol 79.94%, phenol 12.91%, and sodium oleate 7.15%. The mixture remained homogeneous up to a certain small water concentration, then further addition caused separation into two phases, the aqueous phase being small in volume, and forming unstable water-in-oil emulsions with the hydrocarbon phase; the aqueous phase decreased in volume as water was added, then disappeared, so that a second narrow homogeneous region appears on the diagram; still further additions of water again caused separation into two phases which formed relatively stable oil in water emulsions.

Three of the four ternary systems possible with the four components xylol, phenol, sodium oleate, water, were investigated, and also the variation of the viscosity of the quaternary system with increase of water concentra-

---

[1] "Soaps and Proteins" (1921).

[2] See Laing and McBain: Kolloid-Z., **35**, 18 (1924).

[3] J. Chem. Soc., **123**, 2579 (1923).

[4] Bancroft: Phys. Rev., **3**, 21 (1895); J. Phys. Chem., **1**, 34 (1896); **1**, 760 (1897); **3**, 217 (1899); Proc. Am. Acad., **30**, 324 (1894); Taylor: J. Phys. Chem., **1**, 461, 542 (1897).

[5] Kolloid-Z., **42**, 69 (1927).

[6] Kolloid-Z., **47**, 133; **49**, 158 (1929).

tion, and its behaviour at different temperatures. The findings could all be explained satisfactorily on the basis of the micelle theory of the structure of soap solutions developed by McBain. The author points out that it is not certain whether the solvents are adsorbed on the surfaces of the micelles, or whether any significant penetration or permeation occurs, but observes that the latter possibility is not unlikely.

More recently, Angelescu and Popescu[1] have studied in considerable detail the systems ortho-cresol, water, and the sodium potassium, ammonium, and lithium soaps of stearic, palmitic, and oleic acids, paying particular attention to the surface tension and viscosity of the solutions. Addition of o-cresol to sodium or potassium oleate solutions stronger than 0.1 N, causes at 20° first an increase in the viscosity to a maximum at about 2% cresol, then a decrease to a minimum at about 4% cresol, followed by a slow increase. With the palmitates, in general only a slow increase in viscosity occurs, similar to that which occurs with sodium hydroxide solution. The stearates are solid at 20° but at 40° to 50° behave similarly to the palmitates. The surface tension in most cases falls to a minimum for a small phenol concentration, then rises slowly. The solubility of o.-cresol in solutions of the three sodium soaps and in sodium hydroxide solutions was also measured. In the latter case a chemical reaction occurs, whereas in the case of the soap this possibility is excluded. Nevertheless, the solubility in the soap solutions is much greater than in the sodium hydroxide, particularly with the oleate and palmitate.

These results are explained on the micellar theory of the constitution of soap solutions. The maximum in the viscosity curve can probably be explained by Ostwald's hypothesis that, as the dispersion of a colloidal solution is increased, the viscosity passes through a maximum. Addition of cresol increases the dispersion of the colloidal particles until they almost reach the molecular state, corresponding to the minimum of the viscosity curve, whereupon further addition causes a slow increase as with sodium hydroxide or dilute soap solutions. This conclusion is substantiated by measurement of the specific conductivity of 0.2 N sodium oleate-cresol solutions, which passes through a maximum corresponding to the minimum viscosity, indicating that the soap is most fully dispersed at this stage. The authors conclude that the whole of the observations can be explained in a highly remarkable and satisfactory manner if it is assumed that the o.-cresol effects a reduction in the size of the colloidal soap particles, and that according to the theory of W. Ostwald a viscosity maximum occurs at a certain degree of dispersion.

It will be shown later that the results obtained in the present research (much of which was completed before the papers of Weichherz and of Angelescu and Popescu became available to the author) may be explained on very similar lines.

The author's interest in this subject was aroused by a technical research on which he was engaged, concerning the extraction of the unsaponifiable fraction from saponified fish liver oils, as a stage in the preparation of a con-

---

[1] Kolloid-Z., 51, 247, 536 (1930).

centrate of vitamins A and D. Besides the tendency of the soap solutions to emulsify almost all the solvents with which extraction was attempted, some quite unexpected problems arose. Among these were the high solubility of the solvents in soap solutions, the occurrence in some cases of systems of three liquid phases, and principally the surprisingly low partition coefficients for the unsaponifiable matter, between some solvents and soap solutions (saturated with the solvent.) The observation that the presence of alcohol in the system, besides rendering emulsions less stable, often increased the partition coefficient, did not render the problem less perplexing.

The small value of the partition coefficient with even the best solvents, such as ether, renders difficult the complete extraction of the unsaponifiable fraction. Tests of the published methods for estimating the total unsaponifiable matter of oils and fats showed that scarcely any of them give accurate results for this reason. In some cases, however, it was found that this source of error is partially compensated by failure to remove or estimate soap and fatty acid present in the extract. The details of this work have been published elsewhere.[1]

A few measurements of partition coefficients for vitamin A have also been published in a paper relating to a technique for the colorimetric estimation of this vitamin.[2]

Apart from the purely technical side, the present research has followed three main lines, which will form the subjects of this and subsequent papers.

1. Measurement of the solubility of a range of organic liquids in sodium oleate solutions, and observations on the salting-out of soap in the presence of organic liquids.

2. Measurements of partition coefficients for unsaponifiable matter, an azo dye and aniline between certain solvents and soap solutions saturated with the solvent.

3. Study of the phase equilibria in the quaternary system, sodium oleate, water, ethyl acetate, and sodium chloride.

Solubility of Organic Liquids in Sodium Oleate Solution

Experimental. Oleic acid was prepared from olive oil by the method described by Lawrence.[3] Sodium oleate was prepared in solution only, by heating the oleic acid with the calculated volume of standard sodium hydroxide (prepared from washed sticks and containing not more than 0.2% carbonate). Slight measured additions of oleic acid or soda were then made until a sample of the solution was just neutral to phenolphthalein on mixing with an equal volume of neutral ethyl alcohol. Laing and McBain[4] have shown that certain sodium oleate solutions can be obtained at room temperatures as sol, transparent jelly or opaque white curd. The preliminary experiments were

---

[1] Analyst, 53, 632 (1928).

[2] Biochem. J., 24, 1942 (1930).

[3] "Soap Films."

[4] J. Chem. Soc., 117, 1507 (1920).

made on a 0.4 N_w[1] solution, in the sol form. To a weighed quantity in a narrow-necked flask the organic liquid was added in small portions until a slight excess was present. Small additions of the soap solution were then made until the solution was just saturated with the organic liquid at 20°, becoming cloudy from separation of the latter at lower temperatures. No attempt was made to purify the solvents rigorously; in most cases they were taken from laboratory stock and redistilled, the fraction of correct boiling point being used. Accuracy was limited by the high viscosity of some of the solutions, the slowness with which some of the liquids dissolve, and the difficulty of detecting visually an excess of such liquids as ethyl ether, hexane, ethyl and methyl acetates, which yield almost transparent emulsions with the soap solution. The solubility of the liquids in water was also determined when no value could be found in the literature. In addition an emulsion of equal parts of the organic solvent and the saturated soap solution was prepared as follows, and its stability noted: to 5 ml of the soap solution in a test-tube was added 5 ml of the solvent in 1 ml portions, giving 20 vigorous shakes by hand after each addition, and an extra 20 shakes after the last. Some of the emulsions "broke" or "separated" in a short time, i.e. separated completely into two clear layers; others were "permanent" or "stable," i.e. the oil phase remained dispersed in globules for months, although in most cases "creaming" occurred, i.e. partial separation into aqueous phase and emulsion richer in the disperse phase. The mechanism of these phenomena is discussed in previous papers.[2]

Most of the organic liquids investigated show a perfectly definite solubility in the soap solution. At the saturation point the solution becomes cloudy on cooling and clears at the same temperature on warming slowly. This is not the case, however, with some solvents practically insoluble in water, such as anisol and the hydrocarbons. A certain proportion of such liquids can be dissolved by shaking and warming the 0.4 N_w soap solution with the liquid. A larger amount can however be "coaxed" into solution by other methods, for example by mixing the solvent into a stronger soap solution, which may be a curd initially, and then gradually adding water, or by mixing the solvent with oleic acid, stirring with the requisite amount of strong alkali (e.g. 2 N) and then diluting. The apparent solubility of these organic liquids in the soap solution varies with the manner in which the solution is prepared. For example if a mixture of equal weights of oleic acid and benzene is stirred with sufficient 2 N sodium hydroxide to neutralise the oleic acid, and the resulting gel of middle soap then diluted with water, a clear solution will result; neutralisation with N/2 alkali will on the other hand yield a cloudy solution. This is in line with the findings of Pickering.[3]

A value for the solubility in 0.4 N_w sodium oleate of a substance which behaved in this way was obtained as follows: oleic acid and the organic

---

[1] 0.4 weight normal, i.e. 0.4 mols per kilo of water; 100 gm. contains 10.8 gm. sodium oleate.

[2] Quart. J. Pharm., 3, 354, 362 (1930).

[3] Loc. cit.

liquid were weighed into a tube and the amount of 2 N sodium hydroxide necessary to neutralise the oleic acid stirred thoroughly into the mixture by means of a perforated plunger.

The resulting gel was then diluted gradually with sufficient water to make the soap 0.4 N_w. If the solution was clear, the experiment was repeated with increasing proportions of the organic liquid, until the solubility limit was reached, and the final solution appeared cloudy with excess of the liquid. The value obtained by this trial and error method does not necessarily represent the maximum solubility of the organic liquid in 0.4 N_w sodium oleate. In the case of benzene, however, which was studied in some detail, no greater amount could be got into solution, whether by the use of stronger or weaker sodium hydroxide solution to neutralise the mixture of benzene and oleic acid, by mixing the benzene with strong sodium oleate solution, or by using an excess of benzene and estimating the amount dissolved by methods similar to those used by Pickering.

Where two figures for solubility are recorded in the tables, the lower refers to the amount which can be dissolved directly by the 0.4 N_w solution, the higher to the value obtained by the above procedure.

TABLE I

Solubility of Aliphatic Compounds in 0.4 N_w Sodium Oleate Solution at 20°

Substance	Formula	100 gm. 0.4 N_w sodium oleate dissolves:	100 gm. water dissolves:	Stability of Emulsion
Hexane	C_6H_{14}	2.4 — 7.3 gm	Trace	Permanent
Chloroform	$CHCl_3$	20.6 gm	0.8[b] gm	"
Carbon tetrachloride	CCl_4	6.65 gm	0.08[b] gm	"
N butyl alcohol	C_4H_9OH	*Miscible* 0.2 N_w NaOH dissolves 59 gm	8.48[b] gm	Separated[c] in 4 mins.
Amyl alcohol[a]	$C_5H_{11}OH$	*Miscible* 0.2 N_w NaOH dissolves 58 gm	5.2 gm	Separated[c] in 4 mins.
Methyl acetate	CH_2COOCH_3	71 gm	32.0[b] gm	Separated in 1½ mins.
Ethyl acetate	$CH_3COOC_2H_5$	18.7 gm	8.6[b] gm	Separated in 10 mins.
Ethyl ether	$C_2H_5OC_2H_5$	20.6 gm	7.3[b] gm	Separated in 3½ hrs.
Paraldehyde	$(CH_3CHO)_3$	Not determined	11.6[b] gm	Separated in 10 mins.
Furfuraldehyde	C_4H_3OCHO	14.75 gm.	9.05[b] gm	Separated in 30 mins.

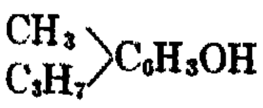
[a] Sharples Corporation's "Pentasol."
[b] Inter. Crit. Tables.
[c] Using 0.2 N_w sodium oleate.

Discussion of Results

The results obtained for aliphatic compounds or various types are shown in Table I, and for a series of mono-substitution products of benzene (including a few hydrogenated and di- and tri-substitution products) in Table II. At first sight there appears to be no rhyme or reason in the widely different solubilities and emulsifiabilities of these substances. For example, the extremes of complete miscibility and low solubility are exhibited by such closely related compounds as phenol and its methylation product, anisol. Substances of the same class behave quite differently. Among the esters for example, ethyl benzoate and amyl acetate yield permanent emulsions, while methyl and ethyl acetates yield emulsions which break in a few minutes.

Table II

Solubility of Aromatic Compounds in 0.4 N_w Sodium Oleate at 20°

Substance	Formula	100 gm. 0.4 N_w sodium oleate dissolves:	100 gm. water dissolves:	Stability of Emulsion
Benzene	C_6H_6	4.0 — 11.9 gm	0.15 gm[b]	Permanent
Toluene	$C_6H_5CH_3$	3.5 — 11.4 gm	Trace	Permanent
Nitrobenzene	$C_6H_5NO_2$	4.32 gm	0.19 gm[f]	Permanent
Aniline	$C_6H_5NH_2$	11.5 gm	3.62 gm[f]	Separated in 2 hrs.
p-Toluidine	$CH_3C_6H_4NH_2$	13.5 gm[a]	1.80 gm[af]	Permanent[a]
Phenol	C_6H_5OH	[c]*Miscible* 0.2 N_w NaOH dissolves 108 gm	8.93 gm[f]	Separated in 10 mins.[c]
o-Cresol	$CH_3C_6H_4OH$	37.6 gm[d]	2.87 gm[e]	Separated in 15 mins.
Thymol	 $\left.\begin{matrix}CH_3\\C_3H_7\end{matrix}\right\rangle C_6H_3OH$	2.0 — 6.3 gm[a]	0.08 gm[g]	Permanents[a]
Benzyl alcohol	$C_6H_5CH_2OH$	19.0 gm	3.8 gm	Separated in 15 mins.
Cyclohexanol	$C_6H_{11}OH$	59 gm	6 gm	Separated in 30 mins.
Ethyl benzoate	$C_6H_5COOC_2H_5$	5.4 gm	0.08 gm	Permanent
Anisol	$C_6H_5OCH_3$	2.1 — 7.2 gm	Trace	Permanent
Acetophenone	$C_6H_5COCH_3$	7.7	Trace[e]	Stable. Separated in 14 days
Methyl cyclohexanone	$C_7H_{12}O$	22.5 gm	2.2 gm	Separated in 20 mins.
Benzaldehyde	C_6H_5CHO	5.8 gm	0.3 gm[f]	Permanent

[a] At 45°.

[b] Hill: J. Am. Chem. Soc., 45, 1143 (1923).

[c] Using 0.2 N_w sodium oleate.

[d] Angelescu & Popescu: Loc. cit.

[e] Bailey: Loc. cit.

[f] Inter. Crit. Tables.

[g] Fehling's, "Neues Handwörterbuch der Chemie."

Nevertheless, some striking relationships are revealed if the organic liquids are divided into two groups according to their solubility in water, taking as an arbitrary dividing line a solubility of about 2%. It then becomes evident that with few exceptions the liquids only slightly soluble in water have a solubility in the soap solution of under 10%; moreover they usually increase the viscosity of the solution and yield stable emulsions with the soap solution. On the contrary, liquids more soluble in water have a solubility in the soap solution of 10% or above, frequently decrease its viscosity, and yield unstable emulsions.

No other scheme of classification shows any such correlation; for example in Table III the organic substances are arranged in a manner calculated to

TABLE III

Stability of Emulsions of Organic Liquids in 0.4 N_w Sodium Oleate

Class of Compound	Emulsion unstable	Emulsion stable
Hydrocarbons		Hexane Benzene Toluene Xylene
Chlorinated hydrocarbons		Chloroform Carbon tetrachloride Ethylene dichloride Ethylene trichloride Ethyl bromide
Nitro compounds		Nitrobenzene
Amines	Aniline	[a]p-Toluidine
Phenols	[b]Phenol o-Cresol	[a]Thymol
Alcohols	[b]N butyl alcohol [b]Isobutyl alcohol [b]Amyl alcohol Benzyl alcohol Cyclohexanol	Caprylic alcohol
Esters	Methyl acetate Ethyl acetate	Amyl acetate Ethyl benzoate
Ethers	[a]Ethyl ether	Anisol
Ketones	Methyl cyclohexanone	[b]Acetophenone
Aldehydes	Furfuraldehyde Paraldehyde	Benzaldehyde

[a] At 45°.
[b] Using 0.2 N_w sodium oleate.
[c] Required 3½ hours to separate.
[d] Separated in 14 days.

reveal any possible relation between type of compound and emulsifiability. A glance at the table shows that every substance which cannot be emulsified permanently by the soap solution is paralleled by another of the same class, often a homologue, which can be emulsified. The converse is however not true: no hydrocarbon or halogenated hydrocarbon has been found which cannot be emulsified.

It should perhaps be mentioned that previous studies of emulsification have not usually dealt with "oils" appreciably soluble in water, nor with such concentrated soap solutions. Solubility in water does not necessarily predispose to non-emulsifiability however; in the course of alkaloid assays on crude drugs, ether is often emulsified by the gums and saponins present; ethyl acetate can be permanently emulsified by gum acacia. With regard to the effect of soap concentration, Pickering[1] speaks of an *optimum* soap concentration for the emulsification of paraffin hydrocarbons; moreover, some of the liquids not emulsified by 0.4 N_w sodium oleate form more stable emulsions with dilute soap solutions.

Interpretation of Results

Previous workers have made some attempts to explain the high solubility of phenolic substances in soap solutions, but it appears to the author that two quite separate effects have hitherto been confused in such interpretations; namely, the effect of the colloidal soap in dissolving or adsorbing the organic liquid, and the effect of the latter on the degree of dispersion of the soap. McBain and his colleagues have given us an admirably clear picture of the nature of aqueous soap solutions, which is too familiar to need much elaboration here.[2] Neglecting the slight hydrolysis, a soap solution contains molecularly dispersed soap, sodium ions, simple fatty acid ions, colloidal aggregations of the latter (ionic micelles) and neutral soap micelles. More recent work[3] indicates that the two species of colloidal particle do in fact remain distinct from one another. The reversibility of equilibria in soap systems requires that every molecule comprising the colloid particles should be exposed to the liquid: the ionic micelle is pictured as "ten eels tied together by their tails" and the neutral colloid as a double layer of oriented molecules.[4] McBain has postulated that such a solution behaves towards external equilibria as a single phase. Nevertheless, for the present purpose it is essential to regard it as a two-phase system of hydrated colloidal soap particles (the two species not being differentiated) and a dispersion medium which is a dilute molecular solution of soap. Let us consider the behaviour of this system on addition of a substance such as cresol or ethyl acetate. The dispersion medium must dissolve the organic liquid to about the same extent as water, so that at the saturation point the dispersion medium becomes a saturated aqueous solution of the solvent; this

---

[1] J. Chem. Soc., 91, 2001 (1907).

[2] See for example McBain and Salmon: J. Am. Chem. Soc., 42, 426 (1920); McBain, Taylor and Laing: J. Chem. Soc., 121, 621 (1922).

[3] Quick: J. Chem. Soc., 127, 1401 (1925).

[4] McBain: J. Am. Chem. Soc., 50, 1636 (1928).

alteration, like the addition of alcohol, is almost certain to affect the degree of dispersion of the soap—to render it "less colloidal" in fact. This term may cover a number of changes: more soap may pass into molecular solution: the average number of molecules per micelle may decrease: the hydration of the micelles may decrease: ionisation and hydrolysis, i.e. the ratio of ionic micelle to neutral colloid and acid soap, may be affected. Such changes are responsible for the variations in viscosity, surface tension, and conductivity, noted by Angelescu and Popescu[1] on the addition of o-cresol to soap. The rest of the organic liquid dissolved by the soap solution must, of necessity, be held in some fashion by the remaining colloidal soap particles. Whether it is adsorbed on their surface: whether (as Weichherz speculates) the solvent penetrates into the particles: or whether water of hydration is partially replaced by solvent molecules, must remain at present matters for speculation. Indeed, it may be doubted whether there is any essential difference between these possibilities, for if we accept McBain's conceptions of the micellar structures, then the particles become as it were "all outside," and there is no question of penetration into their interiors. Again, how definitely can one mark off a certain proportion of the water in the system as "bound" to the colloid as water of hydration?

An attempt to distinguish quantitatively between the molecularly dissolved and adsorbed solvent will form part of a later communication, but at this point one may draw attention to the very large amount of solvent adsorbed in proportion to the soap, in many cases. To take as an example the solubility of methyl acetate in 0.4 N_w sodium oleate solution; deducting the proportion dissolved by the water, it can be calculated that each gram of sodium oleate is responsible for the adsorption of about 3.6 gm of methyl acetate, or nearly 14 molecules of ester per molecule of soap. Allowing that part of the soap must be in molecular solution and thus ineffective, the true adsorption must be higher. This enormous adsorptive power may be compared with that of carbon, the most active preparations of which can adsorb rather less than their own weight of the most readily adsorbed solvents. The adsorptive power of sodium oleate for o-cresol and amyl alcohol is even greater, but it is less for other substances. These adsorption studies are also unique inasmuch as the adsorbent is a pure chemical substance in the form of a reversible colloid, the nature of which is fairly well understood; results are thus perfectly reproducible and independent of the mode of preparation of the adsorbent, but of course the latter cannot be separated from the aqueous menstrum (except by ultrafiltration).[2]

These considerations apply so far only to liquids which are appreciably soluble in water. But some liquids which are virtually insoluble in water are highly soluble in soap solution; such liquids must be held entirely by the colloidal soap particles. We might expect that equilibrium would not be attained so readily in these cases on shaking the soap solution with the organic

---

[1] Loc. cit.

[2] See McBain and Jenkins: J. Chem. Soc., 121, 2325 (1922); McBain and Kistler: J. Phys. Chem., 35, 130 (1931).

liquid. In actual fact dissolution of such liquids in sodium oleate solution is often slow; the low rate of solution does not, however, appear adequate to explain the fact that in some cases the maximum solubility cannot be attained by shaking the soap solution directly with the organic liquid, but only by indirect means. Pickering[1] noticed this effect and suggested that once the liquid is emulsified, it is prevented from dissolving by protective films of soap surrounding the globules. Such an explanation does not accord well with modern theories of emulsification by soaps. One may perhaps suggest more reasonably that soap micelles which are already fully hydrated will not adsorb many molecules of a hydrocarbon (for example); in a strong soap solution, on the other hand, the micelles cannot be fully hydrated, but may if given the opportunity, adsorb hydrocarbon molecules to their maximum capacity, and on subsequent dilution retain the latter instead of taking up more water of hydration. In other words, we may suppose that a liquid such as phenol or ethyl acetate may easily displace water of hydration from a soap micelle, or itself be displaced thereby; whereas prior hydration of the micelle may prevent solvation with a non-polar liquid which has no affinity for water, and conversely prior solvation may prevent hydration on subsequent dilution with water; thus water and hydrocarbon, perhaps because they are attached to different parts of the soap molecule, are not mutually displaceable. Such a hypothesis is put forward only as a tentative suggestion at present especially since a curious phenomenon which was repeatedly observed with benzene throws some doubt on its validity. A soap solution containing nearly the saturation concentration of benzene (prepared by diluting a stronger solution to which the benzene had been added) remained perfectly clear on warming to 50° or 60°, and on *slowly* cooling again; but on cooling *rapidly* it became white and cloudy from separation of benzene. The solution cleared again almost immediately on warming, or on allowing to stand at room temperature it cleared in the course of an hour or so. The cycle of changes could be carried out repeatedly with the same solutions. The same phenomenon was observed with hexane.

We have seen that an organic liquid, which is appreciably soluble in water, is not only adsorbed by the colloidal particles of a soap solution, but by virtue of its solubility in the dispersion medium, it is likely to affect also the dispersion of the colloid. A liquid insoluble in water cannot have much effect on the degree of dispersion and nature of the colloid, since the dispersion medium remains unchanged, although the size of the particles must of course be increased by adsorption of large molecules of an organic liquid. It is evident from the data presented that it is this same factor, namely the presence or absence of the organic liquid dissolved in the dispersion medium, which controls the stability of emulsions of the liquid in question.

Bearing of Solvent Power of Soaps on Other Problems

The solvent action of soap solutions on oils has been almost entirely overlooked in connection with two problems on which it has an important bearing.

---

[1] J. Chem. Soc., 111, 86 (1917).

One of these is the mechanism of the saponification of oils by aqueous alkali. This is usually assumed to be purely an interface reaction, and the only function assigned to the soap formed is that of increasing the interface by its emulsifying action. It is now evident that the soap may play a more intimate part in the process by acting as a solvent for the oil; an investigation of the problem, which it is hoped to publish shortly, shows that this is indeed the case.

The other problem is the detergent action of soaps. Investigators have usually experimented either with solid dirt—carbon black, manganese dioxide, etc.,[1] or with oils or grease,[2] and seldom with both. Consequently different theories have been advanced, and while it is generally agreed that the solid dirt is peptised by the colloidal soap, grease is supposed only to be emulsified. Pickering[3] was the first to point out that soap solutions, particularly when concentrated, may actually dissolve oils, and he emphasised the consequent advantage of washing with concentrated soap solutions. Actually there is no real necessity to distinguish between the two types of dirt. The peptisation of solid dirt and the dissolution of oil are one and the same phenomenon, namely adsorption of the foreign matter by the colloidal soap particles in such fashion that in either case they pass through a filter. Similarly the suspension of excess of the solid dirt and the emulsification of excess oil are phenomena of the same nature. In each case particles of the foreign matter are temporarily suspended in the liquid in such fashion that they are retained by a filter, and, in course of time, settle or rise in the solution under the action of gravity.

Practical Applications of Solvent Power of Soaps

The most important application of soaps is of course their use as detergents, a function which is due in part to their solvent action on grease. Attempts have been made to increase their detergent value by incorporating cyclohexanol, benzene and other grease solvents into the soap, an operation which again owes its possibility to the solvent power of the soap for these substances. Another well-known example is the use of soap solutions to dissolve cresols to form concentrated disinfecting solutions which yield emulsions on dilution with water.

An ingenious application of this property of soaps to analytical chemistry has been described by Wilkie.[4] In determinations of the unsaponifiable fraction of waxes by extraction with ether from an aqueous solution of the saponified wax, the small solubility of the soap of the wax fatty acids is a source of trouble. Wilkie proposes to dissolve the wax in 9 times its weight of castor oil before proceeding with the analysis, applying finally a correction for the relatively small weight of unsaponifiable matter contributed by the castor oil. This method gives no trouble, because the castor oil soaps function as a solvent for the wax soaps.

---

[1] See for example McBain, Harborne and King: J. Phys. Chem., 28, 1 (1924); also Fall: J. Phys. Chem., 31, 801 (1927).

[2] See for example Hillyer: J. Am. Chem. Soc., 25, 511 (1903).

[3] J. Chem. Soc., 111, 86 (1917).

[4] Analyst, 42, 200 (1917).

Soaps containing a small proportion of unsaponified oil dissolve to a clear solution in water. If alcohol is added the solvent power of the soap is reduced because it passes more completely into molecular solution, and the oil is thrown out of solution, rendering the liquid cloudy. This observation forms the basis of a delicate quantitative test for unsaponified oil in soaps or fatty acids, devised by the author.[1]

Salting-out in Soap-Solvent Systems

When salt is added to a soap solution containing an organic solvent, or when the soap concentration exceeds a limiting value, the soap is generally salted out, either as a solid curd or as a liquid layer; excess of the solvent may then constitute a third phase. A preliminary note on this subject has already been published[2] but further work has shown the existence of more types of equilibria than are there enumerated.

It is simplest to study these from the point of view of the addition of the solvent to a soap-water-salt system. The study of a number of such systems by McBain and his colleagues[3] has revealed the following types of salting-out:

1. Isotropic solution (nigre).
   Isotropic solution (lye).
2. Middle soap.
   Isotropic solution.
3. Neat soap.
   Isotropic solution (nigre or lye).
4. Neat soap.
   Middle soap.
5. Curd soap.
   Isotropic solution (nigre or lye).
6. Neat soap.
   Middle soap.
   Isotropic solution (nigre).
7. Neat soap.
   Isotropic solution (nigre).
   Isotropic solution (lye).
8. Neat soap.
   Isotropic solution (sat. lye).
   Salt.
9. Curd soap.
   Neat soap.
   Isotropic solution (lye).
10. Curd soap.
    Isotropic solution (sat. lye).
    Salt.
11. Curd soap.
    Neat soap.
    Middle soap.
    Isotropic solution
12. Curd soap.
    Neat soap.
    Isotropic solution (sat. lye).
    Salt.

---

[1] Analyst, 56, 9 (1931).

[2] Nature, 127, 91 (1931).

[3] McBain and Burnett: J. Chem. Soc., 121, 1320 (1922); McBain and Langdon: 127, 852 (1925); McBain and Elford: 1926, 421; McBain and Pitter: 1926, 893; McBain and Field: J. Phys. Chem., 30, 1545 (1926); McBain, Lazarus and Pitter: Z. physik. Chem., 147, 87 (1930).

All these "condensed systems" are also in equilibrium with the vapour phase which, however, will not be considered or counted as one of the phases. The three-phase systems are invariant in composition at an arbitrarily chosen temperature, while the four-phase systems can only exist at one definite temperature. We may expect any of these systems to persist on adding a small proportion of a solvent such as ethyl acetate. Larger additions may then destroy one of the phases, or if they all persist on saturation with the solvent, excess of the latter will constitute a new third, fourth, or fifth phase. The presence of vapour as an additional phase in equilibrium with the others is to be understood throughout. In addition, new equilibria may be introduced with the extra component. The following notes refer to a few of these possible systems which have already been realised.

In general, solvents seem to have a "liquefying" effect on the soap systems; this has been noted particularly with ethyl acetate and ethyl alcohol, but is probably fairly general. Thus a curd-lye system is often liquefied to isotropic solution, and so on. Acetone, on the contrary, has a dehydrating effect; it tends to precipitate curd from an isotropic solution.

A system which appears to correspond with the nigre-lye equilibrium is commonly observed in the extraction of unsaponifiable matter from soap solutions with ether, although only one reference to the phenomenon could be found in the literature.[1] When a considerable excess of alkali has been used for saponification, and when alcohol is also present, separation into three liquid layers often occurs. The lowest is alkaline lye, containing only a trace of soap: the middle is an isotropic soap solution, containing alcohol and much ether: the upper is ether, containing traces of water, alcohol and soap. The same phenomenon can be observed in many similar systems. A pair of solvents such as aniline and hexane, which themselves form a three-layer system with water, can be made to yield a four-layer system with soap solution and lye, as previously described.[2] In some cases in which the solvent is miscible with soap solutions above a certain concentration, salting-out yields a nigre-lye system in which the upper layer is completely miscible with the solvent, so that no third layer appears. This occurs for instance with sodium oleate and isobutyl alcohol, or sodium oleate and ethyl acetate above about 50°. Such systems may persist when the lye is saturated with salt so that solid salt may constitute a third phase. On the other hand, the three- and four-layer systems described above have not been observed in equilibrium with solid salt; similarly in the absence of organic solvent, the lye-nigre system only persists over a limited range of salt concentration in the lye.

Neat soap can exist in the presence of an excess of many organic liquids. This phenomenon permits the preparation of another series of three-layer systems—solvent, neat soap, isotropic solution (nigre or lye). Such systems must often have been produced unwittingly by the addition of salts to emulsions stabilised by soap, but appear to have been first observed by Wellman

---

[1] Archbutt and Deeley: "Lubrication and Lubricants," 320 (1927).

[2] Nature, 127, 91 (1931).

and Tartar.[1] They found that on allowing a sodium stearate or palmitate solution to stand in contact with benzene at 25°, some of the soap was "transferred to the benzene phase in the form of a gel." A similar phenomenon occurred with sodium oleate and benzene on addition of salt. The effect was observed with 13 organic liquids. Systems in which such transference of soap occurred generally yielded water in oil emulsions on shaking. Wellman and Tartar did not clearly recognise the nature of this transferred soap, but some of the gels which they describe are in fact strongly anisotropic and may probably be classified as neat soap. This is particularly the case with sodium oleate salted out by sodium chloride in presence of such liquids as ether, chloroform and ethyl acetate. The "gels" obtained by spontaneous transfer of sodium stearate or palmitate to benzene or chloroform are, however, quite different in character, consisting apparently of masses of curd fibres enmeshing the organic liquid instead of water; they are formed presumably by virtue of the superior wetting power of the organic liquid for soap curd, and owe their translucency to a similarity in the refractive indices of the solid soap fibres and the liquid.

In the absence of solvents, neat soap does not exist in equilibrium with saturated lye and solid salt, except at high temperatures. In the presence of some solvents, however, such an equilibrium is possible at ordinary temperatures, giving the four-phase system solvent, neat soap, saturated lye, salt.

Salting-out to curd is also possible in the presence of excess of many solvents, giving rise to the system solvent, curd, isotropic solution (nigre or lye), which may also of course exist in the presence of solid salt as a fourth phase. There is obviously the theoretical possibility of a five-phase system—solvent, curd, neat soap, saturated lye, solid salt. In the four-component system constituted by a pure soap, an organic liquid, water and salt, five phases cannot coexist at an arbitrarily chosen pressure and temperature. By good fortune, however, such an equilibrium was actually observed in studying the system sodium oleate, sodium chloride, water and ethyl acetate. The quintuple point occurs in the neighbourhood of 25°, but is difficult to fix accurately, since it is not easy to establish equilibrium between five phases, one of which is a plastic gel.

In the absence of solvent, the system neat soap, nigre, lye, exists over a very narrow range of salt concentration. It should be possible to find an organic liquid which would coexist in equilibrium with these three phases, yielding another system of four liquid layers, but this phenomenon has not yet been observed.

There remain to discuss, the systems containing middle soap. It appears that this phase is less resistant to organic solvents than the other liquid crystal phase, neat soap. Sodium or potassium oleate in this condition will absorb a little ethyl acetate for example, but before the saturation point is reached, the middle soap breaks down to an emulsion, probably of neat soap and isotropic solution. Nevertheless middle soap appears to exist in equilibrium with solvents which are only slightly absorbed by the soap. These phenomena are

---

[1] J. Phys. Chem., 34, 379 (1930).

difficult to investigate, since middle soap forms a stiff plastic mass even in the presence of solvent, forming an ointment-like emulsion with excess of the latter. Moreover, although neat and middle soap can be readily distinguished from ordinary soap solutions, even when the latter are in the gel state, by examination under the polarising microscope, it is less easy to distinguish them from one another. One must be guided by the concentration ranges in which the two phases normally occur, by their different consistencies, and the fact that middle soap never exists in equilibrium with lye; but these properties are liable to be modified by the solvent.

Emulsions stabilised by Soap

The present studies have been concerned primarily with soap, and only incidentally with emulsions. Nevertheless, or perhaps for that very reason, they seem to throw a little light on the perplexing subject of the type and stability of emulsions, so that one may perhaps be pardoned for adding to the mass of literature on that subject. In most previous studies (of inversion by electrolytes for example), the soap has been, as it were, lost in an inseparable mixture of oil and water. Thus it has been almost impossible to discover anything about the condition of the soap—whether it is dissolved in the oil or water phase, or "adsorbed" at the interface: its hydration, solvation, and colloidal nature. Yet these things are obviously and admittedly the key to an understanding of the emulsion problem. Despite the large amount of work done in this field, the fact that sodium soaps are slightly soluble in hydrocarbons has only recently received mention in connection with emulsions[1] although several papers on the estimation of unsaponifiable matter refer to the fact. Similarly Wellman and Tartar even more recently have found that soap solutions may salt out in the presence of an organic liquid, transferring part of the soap to the latter phase, and that this condition can be correlated with the formation of water in oil emulsions on shaking. The work of Pickering seems to have received scant attention and no other investigator has mentioned the possibility of a transfer of organic liquid to the soap solution. The suggestion by Wellman and Tartar that the distribution of soap between the phases is the main type-determining factor marks an important advance, but in the light of the present work it seems possible to generalise still further. The following rules correlate emulsion type with the condition of the soap without reference to any theory of emulsification, and violence to any known experimental data.

1. When the soap is in colloidal solution in the aqueous phase, it tends to stabilise oil in water emulsions.

2. When the soap is salted out from the aqueous phase, it tends to stabilise water in oil emulsions.

3. When the soap is partially salted out, it may stabilise either type of emulsion, depending on other conditions.

---

[1] Weichherz: Kolloid-Z., **47**, 133; **49**, 158 (1929).

The term "salted-out" is here used in the widest possible sense, to cover removal of soap from solution in the aqueous phase, whether by increase in its own concentration, decrease of temperature, or addition of salts of the same or a different base, and irrespective of whether the salted out soap passes into solution in the oil phase, forms a third layer of isotropic or anisotropic solution, or appears as a solid curd insoluble in either phase; the emulsifying power of the soap in some of these conditions may be feeble.

The expression "tends to stabilise" has been used deliberately. It is not true for example that any relative volumes of oil and aqueous soap solution will yield a stable oil-in-water emulsion when shaken together. We have shown that some "oils" yield emulsions which exist for a few minutes or hours only. If the volume of oil greatly exceeds that of the soap solution, shaking may fail to subdivide the oil within the aqueous phase, although addition of the oil in small portions each followed by shaking may serve completely to emulsify the same volume of oil. It should be remembered that no pharmacist would ever prepare an emulsion (except a dilute emulsion of an essential oil) by simply shaking together all the ingredients. There is also a limit to the proportion of oil which a dilute soap solution can emulsify, though whether this is due to an approach to the limit of the specific emulsifying power of the soap, or to withdrawal of the soap into the oil layer (probably as acid soap) is not clear.

The emulsifying power of salted-out soap would appear to be feebler than that of soap in aqueous solution, since the water in oil emulsions are usually coarse. A finely dispersed and stable emulsion of this type can, however, be produced by stirring a natural glyceridic oil with strong aqueous alkali, as in the cold saponification process. A very low percentage of fatty acid in the oil will suffice (0.05%) and the emulsion must presumably be stabilised by minute particles of solid soap.

The most interesting emulsions are the third class, in which the soap is *partially* salted out. By focussing attention on the condition and phase distribution of the soap, rather than on its chemical nature, or on phase volume ratios, the phenomena of inversion receive a simple interpretation. The soap in the two conditions—aqueous solution and salted-out—must be regarded as having opposing or antagonistic emulsifying properties; it is as if there were two emulsifying agents present, stabilising, respectively, oil in water and water in oil emulsions, although in this case they may have the same chemical composition (or they may be soaps of different bases, e.g. Na and Ca). Evidently, when the soap is just beginning to salt out, the emulsion will probably be of the oil in water type; when it is almost completely salted out, it will probably be of the water-in-oil type. Between these two conditions it is not surprising that emulsions of either type can be prepared from the same mixture by different methods of shaking or mixing. The phenomenon is analogous to that observed by the author[1] when emulsifying cod-liver oil with the minimum of gum acacia. Exposure of this oil to the air causes slight oxida-

---

[1] Quart. J. Pharm., 3, 373 (1930).

tion resulting in the formation of a trace of resin which stabilises water in oil emulsions. With care, an oil-in-water emulsion could be prepared, but too rapid addition of the oil caused inversion; this also occurred frequently on passing the emulsion through a homogenising machine. The phase-volume ratio, as emphasised by Weichherz[1] is not a primary type-determining factor, but sometimes appears to be so, because it determines the distribution of soap between the phases.

Summary

Organic liquids in general are much more soluble in soap solutions than in water.

Most liquids more soluble in water than about 2% have a definite solubility of 10% or over in $0.4\ N_w$ aqueous sodium oleate at 20°, lower the viscosity of the solution and yield unstable emulsions with the soap solution.

Most liquids less soluble in water than about 2% have a solubility of less than 10% in 0.4 N sodium oleate at 20°, increase the viscosity of the solution, and yield stable emulsions with the soap solution.

This behaviour is general and independent of the chemical nature of the organic liquid.

Some liquids practically insoluble in water have a range of solubilities in this soap solution, depending on the method of preparation of the solution.

The phase equilibria possible in the four-component systems soap, water, salt, and an organic liquid are reviewed.

An attempt is made to correlate these phenomena with the detergent and emulsifying actions of soaps, and with present knowledge of the constitution of soap solutions.

Glaxo Research Laboratory, London, N. W. 1.
Research Laboratory, Chelsea Polytechnic, London, S. W. 3.
January 13, 1932.

---

[1] Loc. cit.

THE COLLOIDAL SYSTEM, AGED HYDROUS ALUMINA-BASIC ALUMINUM CHLORIDE

BY H. V. TARTAR AND V. R. DAMERELL

Introduction

The preparation and study of colloidal hydrous alumina and ferric oxide have been the subject of many previous investigations. Two methods[1] of preparation have been used mostly, with some modifications. Solutions of salts have been boiled in which the acid produced by hydrolysis was volatile, and dialysis has been employed on salt solutions to which varying amounts of ammonia have been added, or none at all. The removal of the anion of the original salt, and of ammonia has been the difficulty in all of this work. Thus in the method of Neidle and Barab,[2] working with colloidal hydrous ferric oxide, the sols obtained had a ratio of equivalents of chlorine to aluminum of about 1 to 40. Bradfield,[3] by using a high-speed centrifuge, reduced this ratio to about 1 to 400.

The work presented herein received its impetus when it was found that hydrous alumina could be freed from anion by washing with dilute ammonia solution, after which practically all of the ammonia could be removed by further washing with distilled water. Using this method, sufficiently pure aged hydrous alumina could be obtained to warrant making *comparisons between the system disperse phase-peptizing solution and the peptizing solution alone.* This type of comparison was considered valuable as it enabled significant conclusions to be drawn regarding the behaviour of the disperse phase.

Aged hydrous alumina prepared in this way, even in its purest form, was in a colloidally dispersed state. It was found to be further stabilized, however, by the addition of various acids and salts. Basic aluminum chloride was found to act in this way, and for several reasons was chosen as the peptizing agent to be employed in this work. Thus equilibrium was reached much more rapidly than with hydrochloric acid, and an increase in acidity always resulted which served as a valuable indication of adsorptive power under various conditions.

Another phase of the work studied was the problem of reproducibility. The question of whether identical sols could be prepared starting from different materials, such as preparing the aged hydrous alumina from different aluminum salts, was considered important, and various attempts were made to settle this.

---

[1] For a good bibliography of these methods see Weiser: "The Hydrous Oxides" (1926).

[2] J. Am. Chem. Soc., 39, 80 (1917).

[3] J. Am. Chem. Soc., 44, 965 (1929).

Experimental

Preparation of Aged Hydrous Alumina.

Hydrous alumina was prepared from the recrystallized chloride, nitrate and sulfate by precipitation with an excess of ammonia from cold solution. Varying amounts up to a pound of the salt in question were used, and the operation was carried out in a twelve-liter pyrex flask. The precipitate was washed by decantation, using a siphon, with distilled water for several weeks, a slight excess of ammonia being always kept present until a test portion showed that all of the anion of the original salt had been removed. Then it was washed without the addition of ammonia until it began to peptize, at which point it was centrifuged once for a short length of time in an International centrifuge No. 1 at 2500 r.p.m. and the hydroxide resuspended in distilled water by use of a shaking machine. This method yielded a colloid of great purity. None of the original anion could be detected by the usual tests on samples dissolved in acids. The ammonia content was found to be so low as to be essentially negligible. The determination was made by treating a known volume of the colloid with a large excess of solid sodium hydroxide, distilling into cold water, diluting the distillate to a known volume, and estimating the ammonia content by comparison with a known ammonia solution, using Nessler's reagent. Thus a sol prepared as above from the chloride gave a ratio of one equivalent of ammonia to 6000 equivalents of alumina. A sol prepared from the sulfate, washed and centrifuged a greater number of times, gave a ratio of one equivalent ammonia to 25000 equivalents of alumina.

Recent work by the junior author[1] has indicated that the aged hydrous alumina prepared in this manner is the hydrate $Al_2O_3.3\ H_2O$. X-ray work has indicated that it is definitely crystalline, being probably the hydrate bayerite. However, in view of the method of preparation the name aged hydrous alumina will be retained.

Preparation of Basic Aluminum Chloride Solutions.

Aluminum chloride, designated as chemically pure, was dissolved in distilled water (specific conductance 5×10^{-6} mhos), filtered and recrystallized without the addition of hydrochloric acid. Two stock solutions were made at different stages of the work from different amounts of recrystallized salt. Hereafter they will be referred to as solution A and B.

	Equivalents Aluminum per liter	Equivalents Chlorine per liter
Solution A	1.338	1.256
Solution B	0.2277	0.2166

These basic solutions, when treated with pure aged hydrous alumina showed the peculiar phenomenon of increasing in acidity. (See Tables I, II, III). This change is attributed largely to the adsorption of such ions as $Al(OH)^{++}$ or AlO^{+}, which would be expected to be present in greater amounts

---

[1] Damerell: J. Phys. Chem., 35, 1061-7 (1931).

in the basic solutions than in solutions of the normal salt. Thus solution B, not so basic as solution A, did not show such a great increase in acidity when aged hydrous alumina was added. According to Heyrovsky,[1] the normal chloride gives no increase in acidity when treated with hydrous alumina.

Preparation of the Sols.

Sols were made by adding the pure aged hydrous alumina in distilled water to the basic aluminum chloride solutions. Sols prepared in this way were found to reach equilibrium in several days, as shown by tests with the hydrogen electrode. *Basic aluminum chloride solutions were used instead of hydrochloric acid because previous experiments showed that many months were necessary for sols peptized with the latter to come to equilibrium.*

Change of acidity of sols peptized with hydrochloric acid

Equivalents alumina/liter	Equivalents HCl/liter	pH after standing seven weeks	pH after standing one year
0.045	0.006	2.93	4.03
0.045	0.013	2.30	3.89

This fact makes it doubtful, in the systems of many other investigators who peptized their disperse phase with hydrochloric acid or other acids, *whether equilibrium was established at the time that their measurements were made.*

Hydrogen Ion Activity Measurements.

Hydrogen ion activity was determined with the hydrogen electrode, used in conjunction with a normal calomel half-cell. The hydrogen electrodes were prepared by a modified method of Clark described earlier.[2] At least two electrodes were used on each solution tested, and the potentials were required to check within a few tenths of a millivolt. Twentieth molar potassium acid phthalate solution was used as a buffer in testing the worthiness of the electrodes. It was consistently found that electrodes began to give low voltage readings after they had been used for some time in contact with the colloid. A type K Leeds and Northrup potentiometer and a wall galvanometer were used, and all voltage readings were taken with the cells in a thermostat kept at 25° ± 0.03°. Sörensen values were calculated from the formula:

$$\text{pH} = \frac{\text{Observed E.M.F.} - 0.2848}{0.05911}$$

(a) *Change in hydrogen ion activity of basic aluminum chloride solution with the addition of increasing amounts of aged hydrous alumina.* Aged hydrous alumina prepared from the sulfate was used. A stock sol, 2.025 normal, with respect to aluminum content, was prepared and diluted with varying amounts of water and basic aluminum chloride solution A to give a series

---

[1] J. Chem. Soc., **117**, 21 (1920).

[2] Damerell: J. Chem. Education, **7**, 1664 (1930).

of six 250 cc. samples. They were allowed to stand for over a month, with occasional shaking, although experience showed that equilibrium was established in two or three days. The results are shown in Table I.

TABLE I

Change of acidity upon adding aged hydrous alumina to basic aluminum chloride solutions

Equivalents of chlorine/liter from basic aluminum chloride	Equivalents of aged hydrous alumina/liter	pH
0.005	0.00	4.13
0.005	0.05	3.80
0.005	0.10	3.79
0.005	0.30	3.78
0.005	0.70	3.775
0.005	1.45	3.765

(b) *Change of acidity upon adding increasing amounts of basic aluminum chloride to aged hydrous alumina.* The aged hydrous alumina was prepared from the sulfate. Ten 250 cc. samples were made from the stock alumina sol and basic aluminum chloride solution A. These sols were allowed to stand a month with occasional shaking. A trace of potassium chloride was added to the first members of the series to increase conductivity since otherwise the galvanometer did not give satisfactory deflections. In Table II are shown these hydrogen ion activities, together with the activities of the same strength basic aluminum chloride solutions not containing the colloid.

TABLE II

Acidity of various basic aluminum chloride solutions with and without 0.05 equivalents of aged hydrous alumina per liter

Equivalents of chlorine/liter from basic aluminum chloride	pH of soln. alone	pH of soln. plus aged hydrous alumina
0.00	7.00	7.07
0.0005	—	4.26
0.001	4.455	4.06
0.005	4.15	3.78
0.01	4.03	3.685
0.02	3.93	3.655
0.05	3.76	3.605
0.07	3.705	3.605
0.10	3.62	3.575
0.20	—	3.48

(c) *Variation of acidity of basic aluminum chloride solution upon addition of equal amounts of aged hydrous alumina of different average particle size.* Alumina prepared from the nitrate was used here. A flask of the purified colloid dispersed in water was allowed to partially settle. Then portions were taken from the top, middle and bottom, and each analyzed for alumina in the usual way. From the analyses, a sol was made up from each containing just 0.05 equivalents of alumina per liter of the sol. Enough basic aluminum chloride had also been added to make the final concentration of each sol 0.01 equivalents per liter. They were allowed to stand a week, and the hydrogen ion activity measured on each. As the results show in Table III, the smaller size particle caused the greater acidity.

TABLE III

Acidities of basic aluminum chloride solutions containing equal amounts of aged hydrous alumina of different average particle size

Equivalents of chlorine per liter from basic aluminum chloride	Equivalents of added alumina/liter	Average size of particle	pH
0.01	0.00	—	4.03
0.01	0.05	large	3.94
0.01	0.05	medium	3.87
0.01	0.05	small	3.825

(d) *Change of acidity upon settling.* Several sols containing varying amounts of alumina and basic aluminum chloride were allowed to settle, the pH of the top portion of the sol then being determined. As seen in Table IV, these activities are slightly different than those of the shaken up sol.

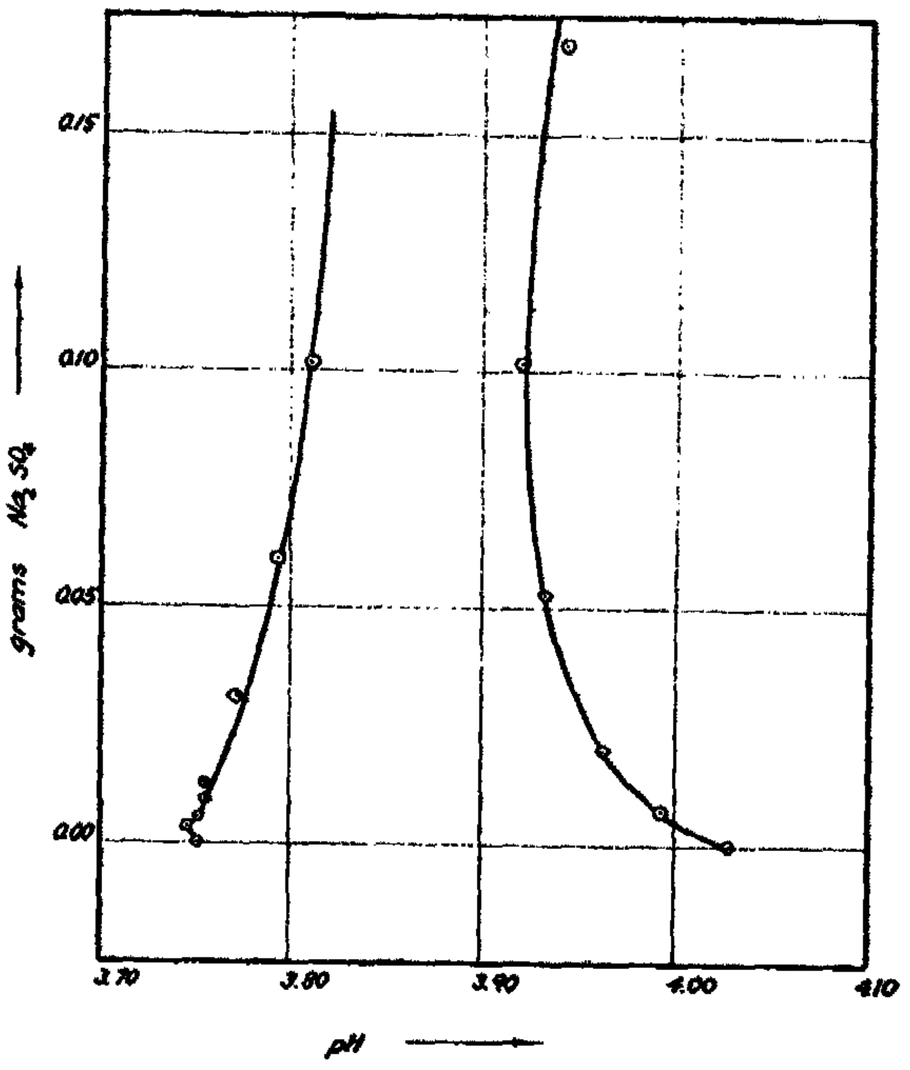
TABLE IV

Decrease of acidity upon settling

	pH of settled sol	pH of shaken up sol
Sol I	3.675	3.66
Sol II	3.735	3.72
Sol III	3.725	3.71

An explanation of this peculiar effect will be offered later.

(e) *Change of acidity upon precipitation with sodium sulfate.* The sodium sulfate was prepared by recrystallization and ignition, and the anhydrous salt used in all cases. To avoid any changes in equilibrium that might result from dilution, weighed amounts of the solid salt were used instead of solutions. For comparison, a duplicate series containing only basic aluminum chloride and sodium sulfate was prepared in one experiment, and the acidities determined. The difference obtained in the two cases could thus be attributed to the effect of the disperse phase. The results are given in Tables V and VI. The slight break in the pH curve, which can be observed much better in Graph I, seems to occur in all such precipitation curves. In some cases it was so small as to be within the limits of experimental error, while in other cases it was more noticeable, although never of great magnitude. (See Tables V, VI, VII, VIII, and IX.)



Graph I
Change of acidity with addition of sodium sulphate

Table V

Change of acidity upon adding increasing amounts of sodium sulfate to colloidal aged hydrous alumina peptized with basic aluminum chloride solution A. (250 cc. samples were used)

Equivalents chlorine per liter from basic aluminum chloride	Equivalents aged hydrous alumina per liter	Grams sodium sulfate added	pH of mixture
0.012	0.0454	0.0000	3.78
0.012	0.0454	0.0010	3.76
0.012	0.0454	0.0034	3.755
0.012	0.0454	0.0058	3.75
0.012	0.0454	0 0088	3.73
0.012	0.0454	0.0106	3.75
0.012	0.0454	0 0138	3.765

(f) *Change of acidity upon precipitation with potassium chloride.* This was conducted in a similar manner to (e). Potassium chloride was prepared by recrystallization and ignition, and in all cases the solid salt was used, to avoid errors that might result from dilution. Three series were run, one with just basic aluminum chloride solution and two with basic aluminum chloride

TABLE VI

Change of acidity upon adding increasing amounts of sodium sulfate to 0.01 normal basic aluminum chloride solution (normality based on chloride content) from stock solution A, with and without 0.05 equivalents/liter of aged hydrous alumina prepared from the chloride. 250 cc. samples taken

Grams of sodium sulfate	pH of solution plus alumina	pH of solution alone
0.0000	3.755	4.03
0.0035	3.750	
0.0052	3.755	
0.0075		3.995
0.0092	3.76	
0.0135	3.76	
0.0200		3.965
0.0312	3.775	
0.0535		3.935
0.0608	3.795	
0.102	3.81	3.92
0.17		3.94
0.24	3.835	3.95

solution plus aged hydrous alumina, prepared from the nitrate and chloride. The time required for the precipitation mixture to come to equilibrium was found by testing the first series at intervals to be in the neighborhood of three weeks. The last series was therefore allowed to stand a month before obtaining the hydrogen ion activities. The series containing just basic aluminum chloride and potassium chloride came to equilibrium much faster. The results are shown in Tables VIII and IX. A series of precipitations was also run using a mastic sol prepared by Tartar and Draves[1] in their work, to determine whether the small break in the hydrogen ion activity curve was able to be detected in this case at the precipitation point. Such an effect was noticed, but it is seen to be very small. The results are given in Table VII.

TABLE VII

Change of acidity upon adding increasing amounts of potassium chloride to mastic sol, containing 10 grams of mastic per liter of sol.
250 cc. samples were used

Grams of potassium chloride	pH
0.1	3.825
0.25	3.815
0.4	3.825
0.6	3.83
1.2	3.825
3.6	3.80

---

[1] J. Phys. Chem., 30, 763 (1926).

TABLE VIII

Change of acidity upon adding increasing amounts of potassium chloride to 0.01 normal basic aluminum chloride solution (normality based on chloride content) from stock solution A, and containing 0.045 equivalents of aged hydrous alumina from the nitrate. 200 cc. samples taken

Grams potassium chloride added	pH after 2 days	pH after 7 days	pH after 27 days
0.0	3.79	3.79	3.79
0.5	3.90	3.87	3.84
1.0	3.94	3.91	3.885
1.5	3.97	3.915	3.895
2.0	3.975	3.946	3.925
2.5	3.995	3.96	3.945
3.0	4.01	3.965	3.955

TABLE IX

Change of acidity after a month upon adding increasing amounts of potassium chloride to 0.01 normal basic aluminum chloride solution (normality based on chloride content) from stock solution A, and containing 0.050 equivalents of aged hydrous alumina per liter prepared from the chloride, or containing no alumina. 250 cc. samples taken

Weight of potassium chloride in grams	pH of solution alone	pH of solution plus alumina
0.0	4.03	3.75
0.5	—	3.825
1.0	4.15	3.85
1.5	—	3.885
2.0	—	3.91
2.5	—	3.92
3.0	—	3.93
3.5	—	3.94
4.0	4.21	—
10.0	4.215	3.945
25.0	4.245	3.96

Chloride Ion Activity Measurements.

Chloride ion activities were measured in the usual way. A platinum wire sealed into a piece of glass tubing was immersed in mercury which in turn was covered with calomel, and the solution to be investigated was introduced over this after having been saturated with calomel. The half cell so prepared was allowed to stand for several hours, and then its potential was measured against a normal potassium chloride calomel half-cell, using a saturated potassium chloride bridge. With this method, essentially the same chloride ion activity was observed in basic aluminum chloride solutions with and without the colloid, when hydrous alumina that had aged for many months was employed. With hydrous alumina prepared for only a few weeks, however, a slight adsorption of chlorine apparently took place. The results are given in Tables X and XI.

TABLE X

Voltage obtained when basic aluminum chloride solutions with and without aged hydrous alumina were saturated with calomel, put over mercury, and referred to a one normal potassium chloride calomel mercury half-cell at 25°. Alumina was prepared fourteen months previously from the sulfate

Stock solution of basic aluminum chloride	Equivalents/liter of chlorine from basic aluminum chloride	Equivalents/liter of aged hydrous alumina	Voltage
A	0.012	0.00	0.1075
	0.012	0.05	0.1080
B	0.010	0.00	0.1094
			0.1094
B	0.010	0.0102	0.1093
			0.1097
B	0.010	0.0297	0.1095
			0.1095
B	0.010	0.0481	0.1095
			0.1097

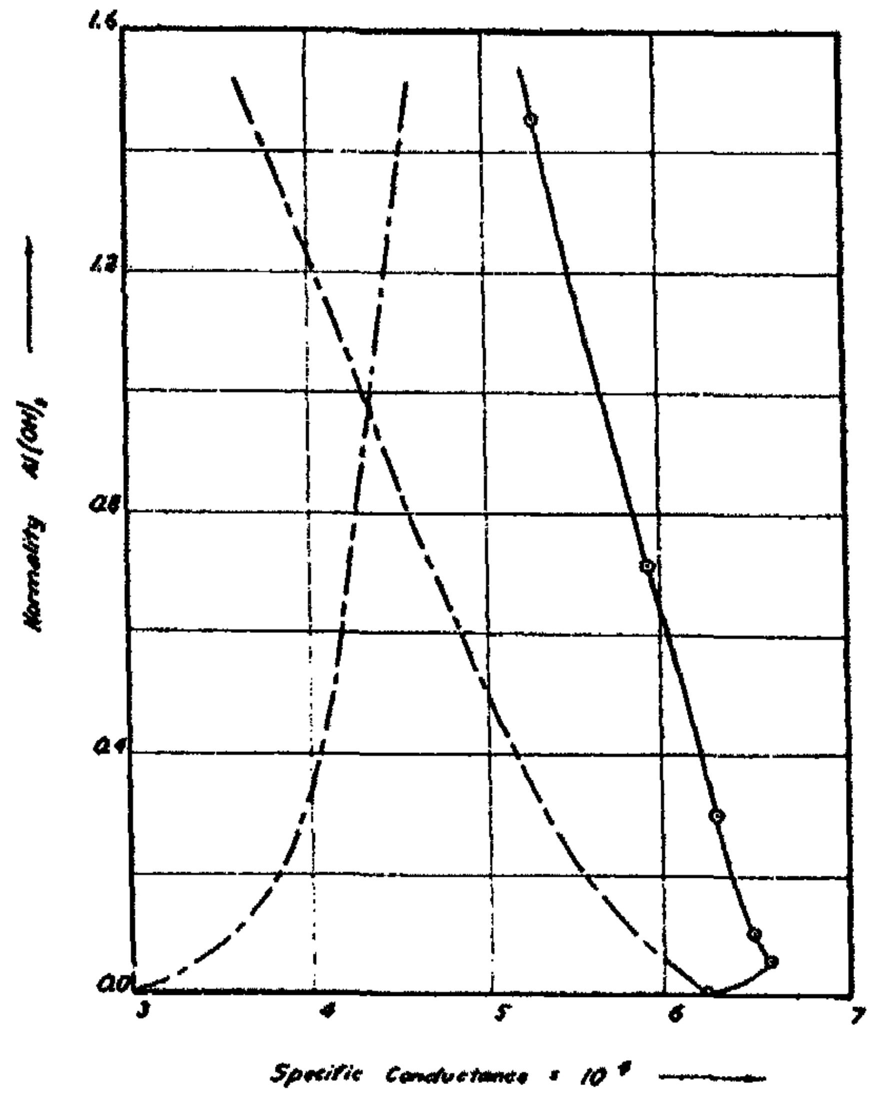
TABLE XI

Similar to Table X, except aged hydrous alumina had been prepared seven weeks previously from the chloride

Stock chloride solution	Equiv./liter Cl	Equiv./liter alumina	Voltage
B	0.010	0.00	0.1094
			0.1094
B	0.010	0.0112	0.1126
			0.1127
B	0.010	0.0300	0.1128
			0.1127

Conductance Measurements.

The specific conductance of the series containing increasing amounts of aged hydrous alumina was determined at 25°C. and the results are given in Table XII. The changes taking place here are brought out better in Graph II. The specific conductance of the series containing a constant amount of aged hydrous alumina and increasing amounts of basic aluminum chloride is also given in Table XIII.



Graph II

Change of specific conductance with increasing amounts of aged hydrous alumina

Table XII

Conductance of basic aluminum chloride solution containing increasing amounts of aged hydrous alumina

Equivalents chlorine per liter from basic aluminum chloride	Equivalents per liter of aged hydrous alumina	Specific Conductance in mhos
0.005	0.00	0.0006215
0.005	0.05	0.0006578
0.005	0.10	0.0006501
0.005	0.30	0.0006274
0.005	0.70	0.0005943
0.005	1.45	0.0005315

Determination of Aluminum in True Solution by Difference.

It was desired to know, if possible, the composition of the intermicellular liquid, since a knowledge of this was necessary in order to compare it to the original basic aluminum chloride solution. Ultra-filtration could have been used, but it was decided that the chance of error was no greater in the following procedure, which was chosen because of greater simplicity.

TABLE XIII

Conductance of series containing a constant amount of aged hydrous alumina and increasing amounts of basic aluminum chloride from stock solution A at 25°C.

Equivalents chlorine per liter from basic aluminum chloride	Equivalents per liter of aged hydrous alumina	Specific Conductance in mhos
0.00	0.05	6.6×10^{-6}
0.0005	0.05	8.57×10^{-5}
0.001	0.05	1.6×10^{-4}
0.005	0.05	6.43×10^{-4}
0.01	0.05	1.19×10^{-3}
0.02	0.05	2.22×10^{-3}
0.05	0.05	4.98×10^{-3}
0.07	0.05	6.28×10^{-3}
0.10	0.05	8.98×10^{-3}
0.20	0.05	1.675×10^{-2}

Samples of the colloid were analyzed for total chlorine and total aluminum in the usual gravimetric manner. Further samples of the same colloid were treated with ammonium oxalate, and the colloid, which precipitated very quickly, was filtered and washed repeatedly with distilled water. It was then dried and ignited to constant weight in the usual way. Any adsorbed ammonium oxalate would be expected to volatize with this treatment. By subtracting the weight of aluminum oxide representing only the colloid from the weight of aluminum oxide representing the total aluminum present, the aluminum in solution was computed. This was compared to the total chlorine, since electrometric measurements had indicated that there was essentially no chloride ion adsorption, except by the hydrous alumina prepared only a few weeks. It seems probable, from the results which are given in Table XIV, that the electrolyte present in the intermicellular liquid corresponded closely to normal aluminum chloride.

TABLE XIV

Analysis for aluminum in true solution

Grams colloidal aged hydrous alumina as Al_2O_3	Grams total aluminum as Al_2O_3	Grams Difference	Equivalents aluminum in true solution	Equivalents chlorine in true solution
(1) 0.0643	0.0761			0.0072
(2) 0.0648	0.0766			0.0073
Ave. 0.0645	0.0763	0.01180	0.00695	0.00725

Attempt to reproduce Aged Hydrous Alumina Colloids starting with Different Aluminum Salts.

An extensive series of experiments was conducted in an attempt to prepare a reproducible aged hydrous alumina colloid. The hydrous alumina could not be peptized with hydrochloric acid because of the length of time required to reach equilibrium. Using basic aluminum chloride as the peptizing agent many experiments were tried with sols of just the same composition in which the aged hydrous alumina was prepared from different salts. In all cases the results indicated that similar colloids did not result when the aged hydrous alumina was prepared from different sources. Thus in Table XV is given the hydrogen ion activities of two series of colloids, one series containing aged hydrous alumina prepared from the sulfate, the other containing aged hydrous alumina prepared from the chloride. They are seen to be dissimilar.

TABLE XV

Hydrogen ion activities of two series containing aged hydrous alumina from different sources

Equivalents/liter of chlorine from basic aluminum chloride	Equivalents/liter of aged hydrous alumina	Source of aged hydrous alumina	pH
0.01	0.00	sulfate	3.82
0.01	0.0102	"	3.75
0.01	0.0297	"	3.685
0.01	0.0481	"	3.67
0.01	0.00	chloride	3.82
0.01	0.0112	"	3.77
0.01	0.0300	"	3.75

It was thought that the two members of Table XV having a pH of 3.75 might have the same total surface, and to test this further, the minimal precipitation value was determined using potassium chloride. The break was difficult to determine, due to the very gradual variation in each precipitation series. The approximate amounts of potassium chloride necessary to precipitate 10 cc. of each was found to be

Sol (3) of chloride series	0.15 grams
Sol (2) of sulfate series	0.10 grams

Discussion of Results

The increase of acidity in (a), (b) and (c) can be explained as the result of equilibrium changes due to adsorption of ions such as $Al(OH)^{++}$ or AlO^{+}. Thus in a reaction of the following type:

$$Al^{+++} + H_2O \rightarrow Al(OH)^{++} + H^{+}$$

acidity would be expected to increase due to the removal of $Al(OH)^{++}$ or similar ions by adsorption. This view is strengthened by the results of the analysis of intermicellular liquid for aluminum, which together with the knowledge that essentially no chloride ion adsorption has taken place (except for freshly prepared hydrous alumina), establishes a ratio of equivalents of chlorine to aluminum of 1.04 to 1.00. Since the starting ratio of equivalents chlorine to alumina was 1.0 to 1.1 (for stock solution A) it appears probable that aluminum was adsorbed as a basic ion.

Furthermore, the adsorption of $Al(OH)^{++}$ and related ions, rather than Al^{+++} ions only, is in harmony with the principle of Gouy.[1] He believed that in the neighborhood of a charged plate the concentration of ions of like charge diminished exponentially as the valence increased. If this were true, ions having a positive valence of less than three would be expected to be present in the neighborhood of the positively charged particle in greater amount in proportion to the tervalent aluminum ion than in the bulk of the solution, and this would favor the adsorption of hydrogen ions and hydroxylated aluminum ions. But this adsorption may also be preferential in character, since if it depended only on charge, adsorption of such ions as $AlCl^{++}$ and $AlCl_2^+$ might be expected.

This adsorption does not explain the decrease of acidity upon settling, however, as shown in Table IV. It seems improbable also, in the case of coagulation (especially with sodium sulfate) that the observed results are due entirely to the displacement of adsorbed ions by the oppositely charged precipitating ion, so that they are again brought out into the solution, with corresponding effect on hydrogen ion concentration. A better explanation offers itself regarding these effects, which may well be a factor in all of the acidity changes observed. Gouy[1] has concluded that in the neighborhood of a charged plate there will be an excess of ions of opposite charge to the plate and a corresponding scarcity of ions of the same charge. Applying this to a colloidal solution containing many positively charged particles, one would expect the hydrogen ions not adsorbed by the particles to be present in lower concentration in the immediate vicinity of the particles than in the bulk of the solution.

Thus if the hydrogen electrode be considered to be positively charged, the hydrogen ion activity which it measured would consist of the activity in that part of the solution farthest removed from the particles, on account of the likeness of charge on the electrode and particles. Due to the repulsive effect of the particles on all positive ions, this activity would be expected to be slightly higher than if the particles were not present, since in the latter case, the space in the immediate neighborhood of the particles, which was sparsely occupied with hydrogen ions, would now become available to the crowded ions in the bulk of the solution. Any factor causing removal of particles, then, would be expected to cause a decrease of acidity in the bulk of the solution.

Two such factors are present, in precipitation and settling. In the former, the particles are removed from the system, and their charge is greatly diminished or even changed. In the latter, part of the particles are taken away from the system by gravity, and while their charge is probably not changed, its repulsive force is probably in part lost against the sides and bottom of the container. This inhibition of repulsive effect is thought to be one of the factors influential in causing the decrease of hydrogen ion activity observed during precipitation and settling.

---

[1] Gouy: J. Phys., (4) 9, 457 (1910).

A third source of increased activity of hydrogen ions is that due to the volume occupied by the colloidal particles. The aluminum chloride solutions were diluted in the one case by water, and in the other case by water plus colloid, so that the volume of the water actually added was slightly less. This factor must be very small, however, except in the case of the more concentrated sols.

The chloride ion activity measurements seem to have established the fact that essentially no chloride ion adsorption took place on the particles, except in the case of the two sols made from the hydrous alumina prepared only a few weeks.

The change in conductivity can be explained on the basis of adsorption. Thus the curve obtained in the conductance of basic aluminum chloride solution containing increasing amounts of colloidal alumina, as shown in Graph II, may be considered as the resultant of two curves, one sloping upward, corresponding to the increasing conductance of the colloid, as more and more of it was added; the other sloping down, corresponding to the decreasing conductance of the electrolyte as more and more of it was adsorbed on the particles. The decreasing volume of intermicellular solution between electrodes, due to the increasing volume of the colloid, would also be expected to cause a decreasing conductance.

In the method described here for the preparation of colloidal aged hydrous alumina, two factors enter into the treatment which evidently influence the purity of the resulting sols, and which have not usually been considered in previous methods of preparation of hydrous oxide sols. One is the allowance of plenty of time for aging (several weeks or months), and the other is the precaution of keeping excess ammonia present until all of the anion of the original salt has been removed. The aging is thought not to be necessary in the anion removal, since with a sample of hydrous oxide freshly precipitated from an aluminum chloride solution it was found possible to remove all of the chloride ion by repeated centrifuging in a few hours when a slight excess of ammonia was kept present. In the experiment just described, after all of the original anion had been removed, the sample was further centrifuged without addition of ammonia until the tendency to peptize began to overcome the centrifugal force. At this point considerable ammonia could still be detected with Nessler's reagent. At a corresponding point with the aged sols, on the other hand, the ammonia content was very much lower. Keeping the solution alkaline with ammonia is thought to be the condition necessary for complete removal of the anion of the original salt.

Summary

(1). A simple method has been described for the preparation of colloidal aged hydrous alumina.

(2) Using this method, colloidal aged hydrous alumina has been prepared from the nitrate, chloride and sulfate of alumina in which all of the anion of the original salt has been removed.

(3) The conclusion of Bradfield[1] that sulfate precipitation is reversible has been confirmed.

(4) The alumina prepared in this way contained ammonia in amounts as low as 1 equivalent to 25,000 equivalents of alumina, and a sol containing 0.05 equivalents of (colloidal) aged hydrous alumina per liter had a specific conductance as low as 6.6×10^{-6} mhos.

(5) The colloid was further stabilized by addition of basic aluminum chloride or hydrochloric acid.

(6) Equilibrium was established in a few days, using basic aluminum chloride. Many months were necessary for equilibrium to be established using hydrochloric acid.

(7) A study of ion distribution on sols stabilized with basic aluminum chloride has been made by means of hydrogen ion activity measurements, chloride ion activity measurements and conductance measurements. The results may be explained as being due to (a) adsorption of hydroxylated aluminum ions by the colloidal particles; (b) ion distribution in accordance with Gouy's conception of a diffuse outer double layer; (c) effect of the colloid on decreasing the volume of solution in a given amount of sol.

(8) The effect of the conditions of aging and alkalinity in the preparation of sols has been discussed.

(9) An unsuccessful attempt has been made to prepare two sols having just the same properties starting with aged hydrous alumina from two different aluminum salts.

---

[1] J. Am. Chem. Soc., **44**, 965 (1922).

INVESTIGATION OF THE DIFFERENTLY COLORED FORMS OF CERTAIN DERIVATIVES OF DIPHENYLAMINE

BY NICHOLAS MICHAEL CULLINANE, OLGA EDWINA EMBREY,
AND DANIEL RICHARD DAVIES

A considerable number of substances are described in the chemical literature as existing in modifications of different color. In many cases the only differences in properties noted were the colors, in which the variations were usually not very pronounced. Such color differences can frequently be accounted for by the presence of traces of impurity, differences in the degree of fineness of the particles, differences in texture, and pleochroism, the forms being otherwise identical. Thus red phosphorus when fine-grained is scarlet in color, and when coarse-grained is violet. Further, the red and yellow forms of mercuric oxide are identical except in color. Mercuric iodide exists in two dimorphic forms, the red being stable below, and the yellow above, 128°. Yet in liquid air the red form becomes yellow, and in liquid hydrogen, white.

The existence of a body in varieties of different color may also be due to polymorphism, and here differences in other physical properties besides color are observed, such as crystalline structure, melting point, solubility, density, these differences being found only in the solid state. On transformation of the solids into the liquid or the vapor state, or by solution, all differences between the forms disappear.

Further, the alteration in color of a substance may be caused by change in chemical structure, for instance polymerisation, tautomerism, or stereoisomerism, and in cases of this type differences in properties will persist in the liquid state, or in solution, at least for some time.

Many organic compounds exist in forms of different color, but only in comparatively few cases have the crystallographical structures of physico-chemical properties been compared. In the present research a number of compounds were prepared in forms of varying color, and their crystalline structures, densities, solubilities, colors in different solvents and refractive indices of their solutions compared. In some cases the forms were found to be identical in all respects except color, some were shown to be dimorphic, and some were observed to exhibit chemical isomerism.

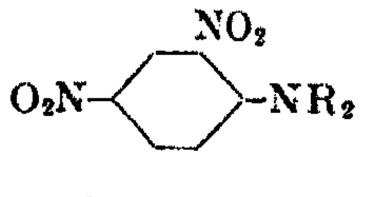
A. Hantzsch[1] has prepared several compounds which exist in modifications of different color, termed 'chromoisomerides,' and he attributes the change in color to change of structure. Among them are a number of nitroanilines, including some diphenylamines. The forms appear to differ only in the solid state, yielding with the same solvents optically identical solutions, possessing the same colors, refractive indices, and absorption spectra. He states that polymorphism is out of the question since solutions of certain 'chromoisomer-

---

[1] A. Hantzsch: Ber., 43, 1662 (1910).

ides' in different media are different in color, and as the solute is found to be unimolecular it is assumed that the variation in color of the solutions is due to the presence of different 'chromoisomerides.' However, it is shown in the present communication that similar variations in color in different solvents exist where there is no indication of chemical isomerism or even polymorphism. Such color differences may be due, at any rate in some cases, to the presence of solvates, for many such additive compounds, derived from diphenylamines, are known. In fact Hantzsch,[1] in a later paper on acridine derivatives, postulates the formation of solvates to account for similar color variations.

Since 'chromoisomerism' as observed by Hantzsch appears to be evident only in the solid condition, in order to prove the existence of chemical isomerism he has recourse to a comparison of the physical properties of certain homologous series; for example, the members of the homologous series.



where R is methyl, ethyl or propyl, all give yellow solutions in chloroform, and the increments in molecular refraction on replacing methyl by ethyl, or ethyl by propyl, are respectively 9.5 and 9.4, these values being in close agreement with the theoretical value 9.2 (Brühl). On the other hand, in the case of the corresponding 3:4-dinitroanilines, the solutions in pyridine of the dimethyl and diethyl derivatives are respectively yellow and orange, and the observed increment is 7.8 as compared with the theoretical value 9.2. From this result Hantzsch concludes that the two substances cannot belong to an homologous series, but to two different isomeric series, and hence the difference in color is due to isomerism. It seems quite likely, however, that this anomalous result is due to the formation in solution of different amounts of the additive compound of solvent and solute, for pyridine is basic and the nitroanilines slightly acidic.

Although in some cases the 'chromoisomeric' modifications of Hantzsch may be chemical isomerides, yet the existence of isomerism among the nitroanilines does not seem to have been satisfactorily proved by him. His conclusions appear to be rather too far-reaching, for polymorphism is in most cases sufficient to account for his experimental results, and it is usual to assume the existence of polymorphism until there is satisfactory evidence of chemical isomerism. It is also possible that in some instances the forms are actually identical save in color, for although sometimes the melting points differed, in many cases the only distinction observed was in color.

In the present research a number of nitrodiphenylamines of similar constitutions to those prepared by Hantzsch were examined.

2:4:6-Trinitro-4'-methyldiphenylamine (picryl-p-toluidine) exists in two forms, and a crystallographical investigation of them by Lenk[2] showed that

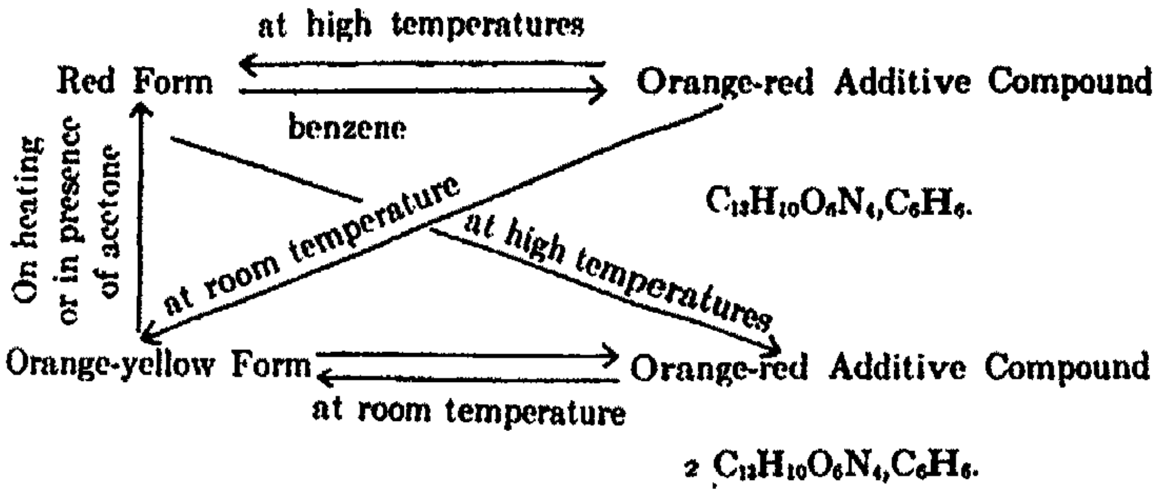
---

[1] Hantzsch: Ber., **44**, 1783 (1911).

[2] J. prakt. Chem., (2) **79**, 548 (1909).

the one modification was composed of yellow or orange-yellow monoclinic needles, and the other of dark red needles belonging to the rhombic system. The results obtained in the present research for the densities of the two forms confirmed this distinction but did not indicate whether the case was one of dimorphism or of chemical isomerism. However, it was further observed, contrary to the statement of Hantzsch[1] that solutions of picryl-p-toluidine in all media were orange in color, that the colors in solution varied considerably with the solvent, and furthermore that the colors of the two modifications in the same solvent differed considerably in some cases. Thus solutions of equal concentration in acetone were orange-red (yellow form) and orange with a yellow tint (red form); in pyridine very deep orange-red (yellow form) and reddish-orange (red form). In other media differences in color, though not so pronounced as in these two solvents, were also noticed. The yellow variety always gave the deeper color in solution. Molecular weight determinations in benzene proved here (as in the case of all the compounds examined) that both modifications were unimolecular. The refractive indices of solutions of equal concentration of the two forms in pyridine were different.

It was observed that the red form of picryl-p-toluidine yielded with benzene an orange-red solvate of different composition from that furnished by the orange-yellow variety. On heating, both additive compounds were converted into the red solvate-free form, while at the ordinary temperature both solvates were slowly transformed into the orange-yellow modification of the amine. Further, the latter form was changed into the red variety on heating alone or on standing in contact with acetone.



From the above results the two modifications of picryl-p-toluidine must be chemical isomerides.

It is interesting to compare the foregoing phenomena with those observed by P. Pfeiffer[2] and his coworkers in the case of certain nitro derivatives of stilbene. They found, for example, that 2-nitro-4′-methoxystilbene-4-carboxylic acid existed in a yellow and an orange form of identical melting point; these would normally be considered dimorphic modifications except that the following reversible phenomena occurred: the yellow acid gave an

---

[1] Hantzsch: Ber., **43**, 1679 (1910).

[2] Ber., **48**, 1777 (1915); **49**, 2426 (1916); **51**, 554 (1918).

orange pyridine salt, whilst the orange acid gave a yellow pyridine salt of the same composition as the other, the acids being regenerated by treatment with hydrochloric acid. It was found possible to carry out the following reactions:

$$\begin{tikzcd}
\text{Orange Pyridine Salt} \arrow[r, "\text{pyridine}"] \arrow[d, shift right=2, "\text{HCl}"'] & \text{Yellow Pyridine salt} \arrow[d, shift right=2, "\text{HCl}"'] \\
\text{Yellow Acid} \arrow[u, shift right=2, "\text{pyridine}"'] & \text{Orange Acid} \arrow[l, "\text{heat}"'] \arrow[u, shift right=2, "\text{pyridine}"']
\end{tikzcd}$$

The different varieties of the one substance isolated by Pfeiffer yielded identical colors in a given solvent, but the colors varied considerably with the medium employed, this result being attributed by him to the formation in solution of different solvates, some of which were isolated.

The melting points of the two modifications of picryl-p-toluidine were observed to be the same, viz., 165.5°; this was evidently due to the conversion of one form into the other by heat, since the orange-yellow crystals on being heated gradually turned red at 150-155°. A mixture of the two varieties also gave the same melting point.

2:4-Dinitro-5-methyl-2′-methoxydiphenylamine was found by the present authors to occur in two forms of different color. These were then subjected to an optical and crystallographical examination. Owing to the specialised methods of preparation of the forms of this and the other substances herein described it was difficult in some cases to isolate suitable crystals, but in general the results confirmed those obtained by the physico-chemical methods. All the crystallo-optical examinations were carried out by Mr. A. Stuart. In the case of 2:4-dinitro-5-methyl-2′-methoxydiphenylamine he reports as follows:[1] "These two substances are crystallographically and optically distinct, the one being composed of brownish-yellow transparent monoclinic plates (which become yellow on being powdered) with a maximum extinction angle of 27°, and pronounced pleochroism, and the other of scarlet monoclinic needles with a maximum extinction angle of 5°, and pleochroism hardly noticeable. Different crystallographical forms occur in each and no angular measurements correspond."

The densities of the two substances were found to be different, and also the solubilities in chloroform. In contact with acetone the metastable form was transformed into the stable one (this occurred in the case of all the compounds investigated) and hence the solubilities in this solvent were observed to be identical within the limits of experimental error. No change of either modification took place in presence of chloroform. The stable variety was found to be less soluble than the metastable form.

The colors of solutions of 2:4-dinitro-5-methyl-2′-methoxydiphenylamine varied with the solvent employed; thus in benzene the color was orange, in acetic acid deeper orange, in alcohol and acetone a little deeper than in acetic acid, in chloroform reddish-orange, and in pyridine reddish-orange (slightly

---

[1] A more detailed and complete report will appear in a future communication.

deeper than in chloroform). The brownish-yellow modification gave a slightly deeper color in the last two media (in all experiments 0.1 g. of solute was dissolved in 30 g. of solvent). Also the refractive indices of solutions of equal concentration of the two forms in pyridine were quite different. Hence, the two modifications of 2:4-dinitro-5-methyl-2'-methoxydiphenylamine must be chemical isomerides.

The red form turned yellowish on heating, and accordingly the melting points of both varieties were the same.

2:4-Dinitro-5-methyl-4'-ethoxydiphenylamine also crystallised in two forms. Stuart reports: "The two substances are different in respect of color, crystal habit, transparency, and internal structure, one occurring in perfectly translucent bright-yellow monoclinic needles having an extinction angle of 31°; the other in rather opaque orange-red rhomb-like crystals giving no definite extinction between crossed nicols. The nature of these crystals precluded further investigation." The orange-red solid was produced by the action of heat on the yellow crystals. The latter when rapidly heated shrank considerably at about 125°, turning reddish, and then melted at the same temperature as the other modification. The transition point of the yellow variety is therefore in the neighbourhood of 125°.

The densities and solubilities in chloroform of the two forms were different. The bright-yellow modification is the stable one, and it was found to be less soluble than the orange-red solid. Solutions of equal concentration in the one solvent were identical in color, although the colors varied with the medium. The refractive indices of solutions of equal concentration in pyridine were identical within the limits of experimental error. As no differences in properties were observed except in the solid state the two forms of 2:4-dinitro-5-methyl-4'-ethoxydiphenylamine must be considered dimorphic.

2:4-Dinitro-2'-methoxydiphenylamine occurs in two forms of distinctive color, long thin orange-yellow needles and bright red needles. Stuart reports: "The two modifications are very much alike optically despite the startling difference in color. Both show that the length of the needles is the direction of fast vibration; pleochroism in each case is very slight, and extinction straight." The identity of the two modifications was proved by determinations of their densities and solubilities.

The orange-yellow variety on being heated became reddish at about 145° and melted at 165.5°, which was also the melting point of the red form. In a recent paper by Gallas and Alonso[1] a red modification of this compound is described, melting at 165°, and a yellow form which changed to red at 125-145° and melted at 153-159°. The two forms obtained by the present authors, however, tho prepared by the same methods as those employed by Gallas and Alonso, both melted at 165.5°.

The refractive indices of solutions of equal concentration of the forms were also approximately the same and both were observed to be unimolecular in benzene.

---

[1] Gallas and Alonso: Anales Soc. Españ. Fís. Quím., 28, 645 (1930).

TABLE I

	Benzene	Acetic acid	Acetone	Alcohol	Chloroform	Pyridine
2:4-Dinitro-5-methyl-4'-ethoxydiphenylamine. (both forms)	Orange.	Orange (slightly deeper than in benzene).	Orange (slightly deeper than in acetic acid).	Slightly deeper than in acetone.	Reddish-orange (slightly deeper than in pyridine).	Reddish-orange.
2:4-Dinitro -2'-methoxydiphenylamine. (both forms)	Orange.	Orange with red tint.	Orange with red tint.	Reddish-orange.	Reddish-orange (slightly deeper than in alcohol).	Deep reddish-orange.
Picryl Aniline. (both forms)	Orange-yellow.	Orange-yellow (slightly deeper than in benzene).	Deep orange-red.	Orange.	Orange with red tint.	Deep wine-red.
2:4-Dinitro -3'-methoxydiphenylamine.	Yellow.	Orange-yellow (very slightly deeper than in alcohol).	Slightly deeper than in benzene.	Slightly deeper than in acetone.	Orange (very slightly deeper than in pyridine).	Orange.
2:4-Dinitro-5-methyl-3'-methoxydiphenylamine.	Yellow.	Orange-yellow (very slightly deeper than in alcohol).	Slightly deeper than in benzene.	Very slightly deeper than in acetone.	Orange.	Orange (slightly deeper than in chloroform).
2:4-Dinitro-2'-ethoxydiphenylamine.	Yellowish-orange.	Orange (very slightly deeper than in alcohol).	Slightly deeper than in benzene.	Orange (slightly deeper than in acetone).	Reddish-orange (slightly deeper than in pyridine).	Reddish-orange.
2:4-Dinitro-3'-ethoxydiphenylamine.	Yellow.	Slightly deeper than in alcohol.	Yellow with orange tint.	Orange-yellow (slightly deeper than in acetone).	Very slightly deeper than in pyridine.	Orange.
2:4-Dinitro -5-methyl-2'-ethoxydiphenylamine.	Orange-yellow.	Orange (very slightly deeper than in alcohol).	Slightly deeper than in benzene.	Very slightly deeper than in acetone.	Reddish-orange.	Reddish-orange (slightly deeper than in chloroform)
2:4-Dinitro-5-methyl-3'-ethoxydiphenylamine.	Yellow.	Orange-yellow (very slightly deeper than in acetone).	Very slightly deeper than in alcohol.	Slightly deeper than in benzene.	Orange.	Orange (slightly deeper than in chloroform).

In the case of this substance the physical properties (except the colors) of the two modifications were the same and the colors of solutions of equal strengths in the one solvent were identical, yet the color varied considerably with the medium employed altho there was no indication of isomerism or even polymorphism.

2:4:6-Trinitrodiphenylamine (picryl aniline) was isolated as large reddish-orange monoclinic prisms with a mauve colored reflex and also as very small bright-yellow prisms which were similar in appearance, but a complete examination was not possible owing to their minute size. Both varieties melted at 180.5°. It was noticed that the larger crystals varied from red to orange in color, the exact hue appearing to depend upon their size (in all cases yellowish crystals were formed on powdering). This possibly accounts for the various descriptions of the amine in the literature, deep red prisms,[1] scarlet prisms,[2] orange needles,[3] yellow needles.[4] Bamberger and Müller[5] considered that there were two forms, orange-red needles and scarlet-red prisms, while Hantzsch[6] stated that there was only one, a reddish-orange, modification.

The two varieties prepared by us gave the same density, and the solubilities in acetic acid and in chloroform were likewise identical. The colors of the two modifications in the same solvent were alike, but they varied considerably in different media. The forms were both found to be unimolecular in benzene, and the refractive indices of solutions of equal concentration in pyridine were in close agreement.

The only difference then noted between the two varieties of picryl aniline was the color; they were identical in all other properties examined.

Table I gives a comparison of the colors of solutions of the compounds in various solvents, and also of some other substances (obtained in one form only) of analogous constitutions. The colors were compared by means of a Klett Top Reader Colorimeter (in all cases 0.1 g. of solute in 30 g. of solvent was taken).

Experimental Part

Before carrying out the experiments described below each compound was first of all completely purified by repeated recrystallisation. Then the two forms were prepared and examined.

The density determinations were carried out by means of a 25 cc. Regnault density bottle, the specific gravities of both solids being determined simultaneously under identical conditions. Water was found to be an unsuitable liquid to use for in most cases the solids floated (partly at least) on the surface, and also it was not easy to remove air bubbles completely. Light petroleum ether (b.p. 40°-50°), the density of which is considerably lower than that of

---

[1] Ullmann and Nadai: Ber., **41**, 1876 (1908).

[2] Sudborough and Picton: J. Chem. Soc., **89**, 583 (1906).

[3] Leemann and Grandmougin: Ber., **41**, 130 (1908).

[4] Giua and Cherchi: Gazz., **49** II, 152 (1919).

[5] Ber., **33**, 108 (1900).

[6] Hantzsch: Ber., **43**, 1678 (1910).

water, was found to be quite satisfactory. Only a minute trace of either modification dissolved in this liquid, nevertheless a solution of the light petroleum ether saturated at the temperature of the experiment with the substance was employed. Any slight differences in solubility between the forms was negligible. Air bubbles were removed by connecting the pyknometer to the pump. The bottle was placed in a vessel of water at the required temperature for a half hour before each weighing was taken.

For the determination of the solubilities excess of each solid together with the purified solvent was placed in a flask, fitted with a ground-glass stopper, and immersed in a thermostat at the required temperature, which did not vary by more than 0.1°. The mixture was frequently shaken until equilibrium was attained. A portion of the solution was then transferred to a weighing bottle by means of a pipette (also at the thermostat temperature). The latter consisted of a glass tube closed at one end and containing near the closed end a small hole corresponding to which was a similar hole in the ground-glass neck of the bottle. By rotation of the stopper in the neck the two holes could be brought into coincidence, and by this means the pressure inside the vessel was made equal to the atmospheric pressure, and then by further rotation of the stopper the bottle was made airtight. The weighing-bottle and contents were then weighed and the solvent evaporated off to constant weight.

The refractive indices of solutions of each form were determined for sodium light in pyridine by means of a Pulfrich refractometer; and the molecular weights were determined cryoscopically.

The solvents used were purified as follows. Benzene was obtained pure by removal of thiophene by means of concentrated sulphuric acid, drying over calcium chloride, and distilling. Then it was thrice frozen, dried again, distilled from sodium and fractionated. The acetone after standing over potassium permanganate was distilled, converted into the sodium iodide derivative, and again distilled. After standing over calcium chloride it was once more distilled, treated with potassium carbonate and fractionated. The chloroform was successively washed with sodium hydroxide, hydrochloric acid, and water, dried by means of calcium chloride, and distilled from phosphoric oxide. The pyridine was refluxed with quicklime and fractionally distilled. The acetic acid was partially frozen thrice, fractionally distilled, dried, and again fractionated.

2:4:6-Trinitro-4'Methyldiphenylamine (*Picryl-p-Toluidine*). The orange-yellow form of this compound, according to Busch and Pungs,[1] was got by addition of hydrogen chloride to a solution of the amine in alcohol containing some alkali, and according to Hantzsch[2] by recrystallization from chloroform, carbon tetrachloride, benzene or acetone. It was found by the present authors that by evaporation at the ordinary temperature of a solution of moderate concentration in acetone the orange-yellow crystals were usually produced. It was, however, difficult in most cases to prepare the orange-yellow variety uncontaminated by the red. From a solution in alcohol containing a little

---

[1] Busch and Pungs: J. prakt. Chem., (2) 79, 547 (1909).

[2] Hantzsch: Ber., 43, 1679 (1910).

hydrochloric acid the orange-yellow solid first separated, but this partly changed on standing to the red form. From benzene an orange-red solvate resulted. The orange-yellow modification was best obtained by recrystallization of the mixed forms or even of the red form from hot carbon tetrachloride. The statement of Busch and Pungs that the red variety can only be converted into the orange-yellow form thro the alkali salt is therefore incorrect.

The red form is the stable one and separates from hot concentrated solution in acetone. It is readily obtained pure for the orange-yellow modification on standing in presence of acetone is transformed in a short time into the red compound. According to Busch and Pungs it can also be obtained from benzene containing some alcohol and also from alcohol to which ammonium hydroxide has been added. This form is also said to be deposited from dilute solution in alcohol, and from pyridine.

The melting point of the red modification is given by Busch and Pungs as 165°, two degrees higher than that of the orange-yellow form. Hantzsch states that both substances melt at 164°, while Ullmann and Nadai[1] describe picryl-p-toluidine as red needles melting at 169°. It was observed in the present work that the melting points of both forms were the same, viz. 165.5°, the orange-yellow crystals on being heated turning red gradually. It was remarked that after heating the orange-yellow variety above its melting point yellow and red crystals separated out side by side on cooling. Prolonged heating of the orange-yellow solid to a temperature just below its melting point caused it to be completely converted into the red.

Two additive compounds with benzene were isolated. The orange-yellow crystals were dissolved in boiling benzene and on allowing the solution to cool orange-red needles separated out. These were dried rapidly and a weighed portion heated to 100° for several hours until the weight was constant.

Wt. of sample G.	Benzene found %	Benzene calcd. for $2C_{13}H_{10}O_6N_4, C_6H_6$
1.5939	11.0	10.9

On heating this solvate it shrank slightly at about 100-110° and reddened somewhat, becoming quite red at 155-160° and melting at 165.5°. After several weeks at the ordinary temperature it changed into the orange-yellow form of picryl-p-toluidine.

Similar experiments were carried out with the red modification of the amine. The solvate, obtained in the same way as that from the orange-yellow variety, gave the following results on analysis:

Wt. of sample G.	Benzene found %	Benzene calcd. for $C_{13}H_{10}O_6N_4, C_6H_6$
0.6605	20.4	19.7

This solvate also shrank on heating at about 100° and deepened in color. At about 150° it became quite red and melted at 165.5° to a deep-red liquid.

---

[1] Ullmann and Nadai: Ber., 41, 1876 (1908).

The densities of the two forms of picryl-p-toluidine were determined by the method above described and gave the following results:

	Temp. °	Density g./ml.
Orange-yellow form	14.2	1.467
Deep-red form	14.2	1.626

The molecular weights of the two forms were determined cryoscopically in benzene, the freezing constant for the solvent being found by a separate experiment.

	Mol. wt. found	Mol. wt. calcd. for $C_{13}H_{10}O_6N_4$
Orange-yellow form	314; 323	318
Deep-red form	318; 315	318

The refractive indices of solutions of the two forms gave the following results:

	Solvent	Strength of soln. %	Angle of deflection Mean	Refractive index $n_D^{20°}$
Orange-yellow form	Pyridine	5	Absorption too great; no reading	——
Deep-red form	Pyridine	5	34°38.5′	1.51785
Orange-yellow form	Pyridine	2.5	35°33.5′	1.51289
Deep-red form	Pyridine	2.5	35°44.5′	1.51189

2:4-Dinitro-5-Methyl-2′-Methoxydiphenylamine. This compound was obtained in two modifications. As a rule slow crystallization at the ordinary temperature from acetone yielded large brownish-yellow transparent crystals melting at 146° to a deep-red liquid. Slow evaporation of the solvent from a solution in light petroleum ether at the ordinary temperature, or separation from hot alcohol gave in most cases this form also, which was the stable one, for on allowing the other variety to stand in presence of acetone in the cold it reverted in a short time to the yellow modification.

By crystallization from a hot solution in acetone the brownish-yellow crystals were found to be mixed with red needles, which could be obtained in small quantity free from the other form by mechanical separation. On adding cold light petroleum ether to a warm moderately concentrated solution in benzene red mixed with yellow crystals were deposited. The red solid became yellowish on heating; its melting point was also 146° and was undepressed by admixture with the other modification. The preparation of the red variety in quantity uncontaminated by the yellow was difficult. The most satisfactory method consisted in refluxing the amine for 30 mins. with a large volume of light petroleum ether (60-80°) containing a little benzene, then decanting rapidly thro a hot filter into an ice-cooled flask. The latter was continuously shaken and the red solid filtered off and dried.

2:4-Dinitro-5-methyl-2'-methoxydiphenylamine was found to be readily soluble in benzene, acetone, chloroform, or pyridine, moderately soluble in alcohol, and sparingly soluble in light petroleum ether.

Anal. Calcd. for $C_{14}H_{13}O_5N_3$: C 55.4, H 4.7, N, 13.9. Found (brownish-yellow form) C 55.1, H 4.5, N, 13.9; (red form) C 55.2, H 4.4, N 13.9.

The following results were obtained for the densities of the two forms:

	Temp. o	Density g./ml.
Red form	15.2	1.485
Brownish-yellow form	15.2	1.414

Red form after standing in contact with acetone for three days, the color having changed to yellow:

	15.2	1.411

The last result shows that the red modification was converted into the yellow in presence of acetone. Hence, the solubilities of both varieties were found to be the same in this solvent. In chloroform no change in color occurred and the solubilities of the two forms in this medium were quite different.

	Temp. o	Solvent	Solubility G. solute in 100 g. soln.
Brownish-yellow form	24.5	Acetone	4.685
Red form	24.5	Acetone	4.691
Brownish-yellow form	31.93	Acetone	5.853
Red form	31.93	Acetone	5.853
Brownish-yellow form	31.95	Chloroform	15.861
Red form	31.95	Chloroform	16.998

The molecular weights determined cryoscopically in benzene were as follows:

	Mol. wt. found	Mol. wt. calcd. for $C_{14}H_{13}O_5N_3$
Brownish-yellow form	305	303
Red form	307	303

The refractive indices of solutions of both forms at 20° were as follows:

	Solvent	Strength of soln. %	Angle of deflection Mean	Refractive index $n_D^{20°}$
Brownish-yellow form	Pyridine	5	34°49′	1.51691
Red form	Pyridine	5	35°3′	1.51565

2:4-Dinitro-5-Methyl-4'-Ethoxydiphenylamine. The original product was dark in color, but a more light-colored compound was obtained by dissolving the substance in acetic acid and pouring the solution into much water with vigorous shaking. It was then washed with water and recrystallized several times.

From hot acetone-alcohol by rapid cooling bright-yellow crystals were obtained melting at 148.5°. Similarly rapid recrystallization from warm solutions in either of these solvents or precipitation from cold moderately concentrated solution in benzene by means of light petroleum ether yielded the yellow form, which was the stable one.

A second modification was formed by heating the yellow solid to 130° for several hours, the product consisting of orange-red crystals.

Both varieties were readily soluble in hot acetone, benzene, acetic acid, pyridine, or chloroform, slightly soluble in alcohol, and sparingly soluble in light petroleum ether.

As the yellow form was converted into the orange-red on heating without loss in weight the former only was analysed.

Anal. Calcd. for $C_{15}N_{16}O_5N_3$: N, 13.25. Found: N, 13.4.

The densities of the two modifications were different, but after standing in presence of acetone the density of the orange-red crystals was observed to be approximately the same as that of the yellow, the specific gravity of which was unaffected by similar treatment.

	Temp. °	Density g./ml.
Bright-yellow form	14.2	1.444
Orange-red form	14.2	1.371

Orange-red form after standing in presence of acetone for 3 days, the color having changed to yellow:

	14.2	1.445

As the orange-red form was transformed into the yellow in acetone the solubilities of both were in close agreement in this solvent. In chloroform no color change of either form was noted and their solubilities were different in this medium.

	Temp. °	Solvent	Solubility G. solute in 100 g. soln.
Bright-yellow form	31.8	Acetone	7.756
Orange-red form	31.8	Acetone	7.757
Bright-yellow form	37.1	Acetone	9.789
Orange-red form	37.1	Acetone	9.792
Bright-yellow form	31.95	Chloroform	19.104
Orange-red form	31.95	Chloroform	19.343

The following results were obtained for the molecular weights, determined cryoscopically in benzene:

	Mol. wt. found	Mol. wt. calcd. for $C_{15}H_{15}O_5N_3$
Bright-yellow form	313	317
Orange-red form	315	317

The refractive indices of solutions of the two modifications were as follows:

	Solvent	Strength of soln. %	Angle of deflection Mean	Refractive index $n_D^{20°}$
Bright-yellow form	Pyridine	5	35°27′	1.51358
Orange-red form	Pyridine	5	35°25′	1.51366

2:4-Dinitro-2′-Methoxydiphenylamine. The condensation product was purified by repeated recrystallization from acetone. The two forms were prepared by the following methods, which, however, could not always be repeated:

By allowing a hot concentrated solution in alcohol to cool slowly the scarlet variety separated out.

On rapid cooling of a warm solution of moderate concentration in acetone orange-yellow flocculent crystals were deposited. This modification was also formed by slow evaporation from a solution in alcohol-acetone. Recrystallization from hot alcohol yielded at a high temperature the red solid; when the solution had cooled to just above the room temperature the orange-yellow crystals were produced.

2:4-Dinitro-2′-methoxydiphenylamine was found to be soluble in hot acetone, chloroform, pyridine, or glacial acetic acid, moderately soluble in alcohol, and sparingly soluble in light petroleum ether.

As the orange-yellow modification became red on heating without loss in weight the former only was analysed.

Anal. Calcd. for $C_{13}H_{11}O_5N_3$: N, 14.5. Found: N, 14.45.

The densities of the forms were as follows:

	Temp. °	Density g./ml.
Orange-yellow form	14.4	1.468
Scarlet form	14.4	1.464

The solubilities of both forms were in very close agreement.

	Temp. °	Solvent	Solubility G. solute in 100 g. soln.
Orange-yellow form	31.5	Acetone	4.467
Scarlet form	31.5	Acetone	4.461
Orange-yellow form	37.1	Acetone	5.461
Scarlet form	37.1	Acetone	5.467
Orange-yellow form	29.8	Chloroform	7.979
Scarlet form	29.8	Chloroform	7.960

The molecular weights, determined cryoscopically in benzene were as follows:

	Mol. wt. found	Mol. wt. calcd. for $C_{13}H_{11}O_5N_3$
Orange-yellow form	271; 282	289
Scarlet form	281; 285	289

The refractive indices of solutions of the two forms were as follows:

	Solvent	Strength of soln. %	Angle of deflection Mean	Refractive index $n_D^{20°}$
Orange-yellow form	Pyridine	5	34°45′	1.51727
Scarlet form	Pyridine	5	34°44′	1.51736

2:4:6-Trinitrodiphenylamine (*Picryl Aniline*). By slow crystallization of the above compound from acetone at the ordinary temperature reddish-orange crystals separated. Crystals of the same color were also obtained from alcohol, even when some hydrochloric acid was present.

On pouring a fairly dilute solution of the diphenylamine in boiling acetic acid into a large volume of water with vigorous agitation small bright yellow crystals were precipitated. These were immediately filtered, washed with water, and dried.

The densities of the two varieties were as follows:

	Temp. °	Density g./ml.
Bright-yellow form	14.1	1.571
Red-orange form	14.1	1.570

The following results were obtained for the solubilities of the two forms:

	Temp. °	Solvent	Solubility G. solute in 100 g. soln.
Bright-yellow form	24.3	Acetone	7.665
Red-orange form	24.3	Acetone	7.658
Bright-yellow form	29.3	Acetone	8.551
Red-orange form	29.3	Acetone	8.567
Bright-yellow form	14.5	Acetic acid	0.7580
Red-orange form	14.5	Acetic acid	0.7555
Bright-yellow form	24.3	Acetic acid	0.9065
Red-orange form	24.3	Acetic acid	0.9036
Bright-yellow form	29.8	Chloroform	1.483
Red-orange form	29.8	Chloroform	1.489

The molecular weights determined cryoscopically in benzene were as follows:

	Mol. wt. found	Mol. wt. calcd. for $C_{12}H_8O_6N_4$
Bright-yellow form	306	304
Red-orange form	311	304

The refractive indices of solutions of the forms were in close agreement.

	Solvent	Strength of soln. %	Angle of deflection Mean	Refractive index $n_D^{20°}$
Bright-yellow form	Pyridine	5	34°38′	1.51790
Red-orange form	Pyridine	5	34°39′	1.51781

In conclusion we wish to express our thanks to Prof. W. J. Jones for his valuable suggestions, and also for his help in the determination of the refractive indices.

Summary

1. 2:4:6-Trinitro-4′-methyldiphenylamine exists in two modifications of different color, crystalline structure, and density. Moreover each form yields a different additive compound with benzene, and solutions of equal concentration in pyridine possess different colors and refractive indices. The two forms are therefore chemical isomerides.

2. The two forms of 2:4-dinitro-5-methyl-2′-methoxydiphenylamine are different in color, crystallographical properties, density, and solubility. Solutions of equal strength in pyridine are different in color and refractive index. Hence, the two modifications are also isomeric forms.

3. The two modifications of 2:4-dinitro-5-methyl-4′-ethoxydiphenylamine are dissimilar in crystallo-optical properties, density, and solubility. As no distinctions were observed except in the solid state they are considered to be dimorphic forms.

4. The two forms of 2:4-dinitro-2′-methoxydiphenylamine and of 2:4:6-trinitrodiphenylamine are of distinctive color. The modifications appear to be similar in crystallographical properties, and their densities, solubilities, colors and refractive indices of solutions of equal concentration are in very close agreement. The two forms are therefore identical save in color.

University College,
Cardiff, Wales.
February 5, 1932.

THE DETERMINATION OF ALUMINUM AND OF EXCESS ACID IN ALUMINUM SALTS*

BY HERBERT L. DAVIS

Certain salts of aluminum, notably the sulphate and the chloride, have important industrial uses in water purification, textile mordants, paper sizing, etc. These salts, however, in common with certain other similar salts, do not crystallize ordinarily in the pure state, but, unless special precautions are taken, will be found to contain more or less than the theoretical amount of acid. The determination of the deviation of a given salt from the composition of the neutral salt has been made the object of numerous investigations and each author of a text or handbook on industrial analysis gives his favorite method. The present paper will describe a method which for speed and simplicity appears to be definitely superior to the methods in common use. This method is an extension of a previous paper[1] in which it was demonstrated that the amount of aluminum present in a salt known to be a normal salt free from excess (or deficiency) of acid could be determined by a simple titration with standard alkali in the presence of phenolphthalein if the system be boiled sufficiently to displace the acid adsorbed on the alumina. This titration is equally valid if thymol blue be the indicator used and this indicator permits the determination of the free acid since aluminum chloride and aluminum sulphate give solutions which lie within the intermediate yellow color range and a slight excess of acid depresses the pH value so as to show the red color.

In the paper referred to above a study was made of the titration curves of aluminum chloride and of aluminum sulphate with alkali, and a comparison was made with similar curves obtained by Hildebrand[2] and by Blum.[3] The curves of these authors showed initial portions in which on addition of alkali the pH of the solutions changed in about the manner shown by the last addition of alkali to a solution of hydrochloric acid. The fact that these initial portions were absent from our determinations and from other experiments in the literature on salts known to contain no excess acid pointed to their explanation as being due to excess acid. The present paper confirms this explanation and utilizes it for the measurement of the amount of free acid present.

The curves of Hildebrand and of Blum are neither self-consistent nor in accord with the facts but we may take as our starting point the data gathered recently by Miss Farnham. She reported that salts of aluminum known to be neutral showed the following pH values.

---

* This work is part of the programme now being carried out at Cornell University under a grant to Professor Bancroft from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

[1] Davis and Farnham: J. Phys. Chem., 36, 1057 (1932).

[2] Hildebrand: J. Am. Chem. Soc., 35, 863 (1913).

[3] Blum: J. Am. Chem. Soc., 35, 1499 (1913).

TABLE I

The pH of Solutions of Aluminum Salts

	N	0.3 N	0.1 N
Aluminum chloride	2.3	2.9	3.0
Aluminum sulphate	2.8	3.0	3.4

These figures are in agreement with the well-known greater acidity of solutions of aluminum chloride than of solutions of the sulphate and the change with dilution is the expected one. On adding alkali to these solutions the pH changes rather slightly until about two thirds of the theoretical amount of alkali has been added. This buffer action is quite marked and has recently been used satisfactorily to buffer an oxidation-reduction reaction. In the case of the chloride such a system will be quite clear, the alumina being peptized by the aluminum and hydrogen ions remaining.

The curves of Hildebrand and of Blum indicate and our own experiments confirm that the addition of a small amount of excess acid depresses the pH value sharply. The excess acid could of course be determined from the pH titration curve electrometrically but this method is somewhat cumbersome and such a titration cold cannot be used to determine the amount of aluminum present. Both parts of the problem could be solved by the use of indicators changing color at the appropriate values which should be a little less than pH 3 for the excess acid and about pH 8 for the aluminum. Thymol Blue is almost ideal for such a titration since its colors and ranges are:

Red 1.2 – 2.8 Yellow 8.0 – 9.6 Blue

Tests show that it is entirely suitable if certain precautions be observed.

In the first place it was established that thymol blue gives results which are perfectly reliable in the titration of normal solutions of aluminum chloride or aluminum sulphate with 1.19 N NaOH. This titration is essentially the titration of the strong acids freed by hydrolysis and these acids are adsorbed strongly by the alumina unless the systems be boiled while slightly alkaline until no more alkali is neutralized and then the slight excess of alkali is titrated with standard acid. The change from the yellow to blue of thymol blue is not quite so easily perceived as is the change from colorless to red of phenolphthalein, but is perfectly satisfactory and accurate.

Then came the more important problem of the free acid. Consideration of an ordinary titration curve of a strong acid with alkali will show that an indicator changing over the range from 1.2 to 2.8 should not give a sharp color change but will require several drops of alkali to change from the full red to the full yellow and that it will require two or three drops more of alkali to produce a pH of 8 corresponding to the first appearance of the blue of thymol blue. This was all confirmed for thymol blue and in addition it was found that if one dissolved five grams of sodium chloride in fifteen cc of water, one drop of normal hydrochloric acid produces a very deep red color of the indicator. Without the salt the effect of the acid is plainly perceptible but blank solutions are a necessity for comparison while with the salt the color change produced is much more marked. This increase in the chemical potential of the hydrogen ion by adding salt is found to be a very useful property in the present method, for it was found that accurate analysis of the aluminum sulphate required the addition of salt.

One of the first questions to be answered was one having to do with the effect of concentration of the aluminum salts. A sample of aluminum chloride was dissolved cold in a small amount of water and diluted in steps, four drops of thymol blue being added to each of four eight cc samples. It was then found that a solution 1.7 N with $AlCl_3$ was very faintly acid (showed a slight reddish tinge) while the solutions 0.85 N was fully yellow and was given a distinct red tinge by the addition of one drop of normal hydrochloric acid. This confirmed previous experience that normal $AlCl_3$ solutions were quite satisfactory in that the excess of acid added to them could be titrated sharply by adding alkali to the pH 2.8 point.

With aluminum sulphate, a solution 4.2 N gave a faint reddish tinge, while solutions 2.1 N or less were fully yellow. These more dilute solutions did not develop the red color even with two drops of normal acid until one gram of sodium chloride was added to each eight cc solution when all became distinctly reddish. In the absence of sodium chloride some buffer action still persists, probably an adsorption of acid on alumina produced by hydrolysis which is well known to be greater in the sulphate than in the chloride solutions. Two grams of sodium chloride added to ten cc of normal aluminum sulphate solution gives only a very faint reddish tinge since it activates the sulphuric acid produced by the hydrolysis, but the salt makes the indicator change much sharper when excess acid is added. The combined effect of high salt concentrations, excess acid, and heating results in the coagulation of some of the thymol blue and for this reason heating of such systems is not recommended, especially in the case of the sulphate solutions.

These preliminary experiments establish the method as reliable and this was borne out by numerous titrations. For the most part these started with normal solutions of aluminum chloride or sulphate and it is suggested that an unknown salt to be examined be dissolved in sufficient water to give about a normal solution. The acid and alkali used were 0.97 N and 1.24 N, respectively. The simplest method is to add a known excess of acid to a known solution of aluminum salt and then add alkali until the final disappearance of the red tinge of the indicator. In practice it was found that a better method is to add sufficient alkali to produce a definite yellow color, permit the alumina precipitated by the local high concentration of the alkali drops to redisperse and then to add acid to the clear yellow solution to the first appearance of the reddish tinge corresponding to pH 2.8. This will give a rapid measure of the free acid present which will ordinarily be accurate to less than two percent. It is then a simple matter to continue adding alkali and, with heating, titrate to find the alkali needed to precipitate the alumina or rather to neutralize the acid resulting from the hydrolysis of the normal aluminum salt. Two samples of our aluminum sulphate (from Baker) were neutral in being without excess acid and showed 15.6 and 15.7% alumina while gravimetric determinations showed 15.7 and 15.8% alumina. With aluminum sulphate it is necessary to add about two grams of pure sodium chloride for each ten cc of titrating solution. This sharpens the color change at the neutralization of the excess acid and does not affect the final determination of the amount of aluminum present.

As has been pointed out, it is more difficult to see the last disappearance of the red tinge at pH 2.8 than its first appearance on adding acid and, furthermore, the precipitation of alumina obscures this end point when it is being reached by adding alkali to the system. In certain respects, therefore, it is desirable to follow another procedure. To the system containing aluminum salt and excess acid, a known amount of standard alkali is added until the alumina is redissolved and repeptized to a practically clear system colored deep blue by the thymol blue indicator. Then standard acid is added cold until the last blue tinge of the indicator changes to the full yellow at pH 8. This amount of acid is an accurate measure of the excess of alkali added. Then the addition of acid is continued until a drop gives the first appearance of the red tinge. This acid is an accurate measure of the aluminum present. Heating is permissible in the chloride solutions but not in the sulphate solutions and salt addition should be made to the latter. The difference between the equivalents of alkali originally added and the total amounts of acid used to titrate back to pH 2.8 is a measure of the excess acid present. If we represent the acid and alkali used in terms of cc of normal reagent, we have;

A = Total normal cc of alkali added to produce clear system.
B = Excess alkali added above that required to reach pH 8.
C = Alkali equivalent to the aluminum present.
D = Alkali equivalent to the excess acid present.

$$A = B + C + D \qquad \text{and} \quad A - (B + C) = D$$

In that thymol blue gives the dividing lines between B and C and between C and D, it is most admirably suited for the rapid and accurate solving of this problem.

This second procedure points at once to the solution of another problem in permitting the equally rapid analysis of so-called sodium aluminate solutions. Lunge and Keane[1] say of this compound: "Sodium aluminate is used in dyeing, printing, in preparing lakes, and sometimes in sizing paper: also in the manufacture of milk glass, for hardening bricks and in soap making. The analysis is generally limited to the estimation of sodium oxide and of alumina; impurities such as insoluble matter, silica, and iron are sometimes determined." They determine alumina by precipitating it with carbon dioxide until the color of phenolphthalein is discharged and in the filtrate from the alumina the sodium carbonate is titrated with standard acid and methyl orange. It is obviously much more simple and rapid to titrate the sodium aluminate with standard acid and thymol blue first to the discharge of the blue color to determine the ~~alumina~~ present and then to titrate to the appearance of the red tinge to determine the alumina present. Hydrochloric acid is greatly to be preferred over sulphuric for this titration.

---

[1] Lunge and Keane: "Technical Methods of Chemical Analysis," 2, 375 (1928).

The general scheme of these titrations is to be found in the work of Bayer[1] who used the titrations with tropaeolin oo [red (1.4 – 2.6) yellow] and with litmus. The difference between these titrations represented aluminum. It is not clear that Bayer used the method directly for excess acid but that may be read into his paper which is quite complete. Schmatolla[2] titrated neutral aluminum sulphates with phenolphthalein and Kolthoff[3] and Tingle[4] have used the same procedure.

Other methods for the determination of excess acid include an extraction of the salt with alcohol to take out the acid.[5] Another general device is to remove the aluminum ion so that it cannot take part in the acid-base reaction. One method is to convert it into the insoluble $AlF_3.3KF$ by adding an excess of potassium fluoride[6] or to put the aluminum ion into the complex ion[7] of the salt $K_3Al(C_2O_4)_3$ and the excess acid can then be titrated. Feigl and Kraus determine the free acid after their treatment as did Stock[8] directly without such treatment.

Methyl orange has been used and its lower limit (2.9 to 3.1, depending on the product) would probably be suitable. The color change with thymol blue is easier to see and only the one indicator is needed. The use of methyl orange and phenolphthalein[9] for the zinc salts is relevant. The modern theory of pH and indicators is a helpful generalization for application in such titrations as these.

Summary

1. The earlier work on the volumetric determination of aluminum in solutions of its salts has been extended to include a similar method for the excess acid sometimes found in such solutions.

2. Using thymol blue as the indicator it has been shown to be possible to titrate first the excess acid and then the aluminum present in a sample of salt. If the salt is a basic salt then a portion of a known excess of standard acid will be used in correcting this and the remainder will be titrated by the method.

3. The determination of sodium oxide and of alumina present in a sodium aluminate solution can be made similarly by the use of the same indicator.

Cornell University.

---

[1] Bayer: Z. anal. Chem., **24**, 542 (1885).

[2] Schmatolla: Ber., **38**, 985 (1905).

[3] Kolthoff: Z. anorg. Chem., **112**, 185 (1920).

[4] Tingle: J. Ind. Eng. Chem., **13**, 420 (1921).

[5] Williams: Chem. News, **56**, 194 (1887); Beilstein and Grosset: Z. anal. Chem., **29**, 73 (1890); J. Soc. Chem. Ind., **9**, 416 (1890).

[6] Craig: J. Soc. Chem. Ind., **30**, 184 (1911).

[7] Feigl and Kraus: Ber., **58B**, 398 (1925).

[8] Stock: Compt. rend., **130**, 175 (1900); J. Soc. Chem. Ind., **19**, 276 (1900); J. Chem. Soc., **78**, 247, 315 (1900).

[9] Lescoeur: Bull., (3) **13**, 280 (1895).

THE MICROSCOPIC METHOD OF ELECTROPHORESIS

BY HAROLD A. ABRAMSON

In a recent discussion of the microscopic method of determining the mobilities of microscopically visible particles Mukherjee[1] has pointed out certain difficulties which, he believes, lessen the precision at present attainable in measurements of this sort. These criticisms certainly do apply in poorly conducted experiments, not only for the microscopic method but for all measurements of electric mobility including ionic mobilities. It may be of interest to investigators to know that with the technic devised by Northrop and Kunitz[2] and as employed by the writer[3] the experimental difficulties (quoted and italicized below) mentioned by Mukherjee are eliminated.

1. *"Firstly, there is an error in calculating the potential gradient."*

It has been shown that the electric field is uniform and that the field strength, X, can be accurately calculated within the limits of error by means of Ohm's law

$$X = IR/q$$

(I = current; R = specific resistance of the suspension; q = cross-section of the electrophoresis cell).[2,3]

2. *"Secondly, disturbances arising out of 'polarization' and electrolysis are greater in these small vessels."*

Non-polarizable electrodes are employed in a fashion which excludes contamination due to electrolysis.[2,3,4]

3. *"The third and most important consideration is that particles stick to the walls forming patches of surface of different properties."*

The cell can easily be cleaned with cleaning mixture or any solvent between measurements for it is made of one piece of glass, having no rubber connections. Further, since measurements of any one system need not take more than three minutes, asymmetry of the cell due to differences of the walls need under most circumstances not be greater than the limits of experimental error. The cell can also be used vertically with large oil droplets.

College of Physicians and Surgeons,
Department of Biological Chemistry,
630 West 168th Street,
New York City.

---

[1] J. N. Mukherjee: J. Phys. Chem., **36**, 595 (1932).

[2] J. H. Northrop and M. Kunitz: J. Gen. Physiol., **7**, 729 (1925).

[3] H. A. Abramson: J. Gen. Physiol., **12**, 469 (1929); H. A. Abramson and E. B. Grossman: **14**, 563 (1931).

[4] K. Ellis: Z. physik. Chem., **78**, 321 (1911).

THE PEPTIZATION OF CUPROUS OXIDE AND THE ELECTRODEPOSITION FROM AND DECOLORIZATION OF AMMONIACAL COPPER SOLUTIONS

BY E. A. VUILLEUMIER

When copper is plated from an ammoniacal cupric solution the deposit obtained is relatively dense, smooth and adherent. The author observed, however, some years ago, that when the electrolyte had been in contact with metallic copper for a few hours prior to the electrolysis there was a striking change in the nature of the deposit to be obtained. It then consisted of a dull red, thick, moss-like, coarse, non-adherent mass, which under a low power microscope was seen to consist of relatively large, bright copper crystals. It was also observed that upon the addition of concentrated ammonia or ammonium sulphate (but not sodium sulphate), or by thorough oxidation by aeration of the partially reduced electrolyte good results, i.e., dense, smooth, adherent deposits were again obtainable.

The present investigation indicates that a cuprous oxide cathode film is responsible for the unsatisfactory deposit; that an electrolyte from which an unsatisfactory deposit is obtained is one which does not peptize cuprous oxide.

It was found that cuprous oxide is readily peptized by concentrated ammonia water, or by ammonium sulphate in the presence of diluted ammonia water.

Furthermore it was found that an ammoniacal cupric solution could be decolorized by metallic copper only upon adding concentrated ammonia or ammonium sulphate.

Concentrated ammonia water or ammonium sulphate in the presence of diluted ammonia water evidently prevents the coating of metallic copper by a film of cuprous oxide, or peptizes the film if formed. Such a film would explain the incomplete reduction of the cupric solution, and, forming on the cathode, would, where broken through, give rise to a mass of relatively large, non-adherent crystals.

Procedure

A stock solution was prepared by dissolving 25 grams of the pentahydrate of cupric sulphate and 60 c.c. of concentrated ammonia water in sufficient water to make a liter of solution. A 100 c.c. portion of this solution was electrolyzed for 20 minutes at a current density of 6 milliamperes per square centimeter, using copper electrodes. A dense, bright, adherent, relatively smooth, and therefore good, deposit was obtained. The electrolysis was discontinued, but the electrodes were allowed to remain in the bath over night. The electrodes were then replaced by fresh ones. The solution was again electrolyzed, and after 20 minutes a coarse, non-adherent mass was observed. A good, fresh electrolyte was also converted into a bad one by allowing a strip of copper to stand in it for three hours, or by adding a centigram of cuprous oxide. The addition of two grams of ammonium sulphate, or of an excess of concentrated ammonia, to the unsatisfactory bath resulted in a good deposit.

Several attempts were made to decolorize the slightly ammoniacal stock electrolyte by means of copper in the absence of air. The solution, however, remained dark blue indefinitely. But upon adding concentrated ammonia or ammonium sulphate to the solution it was promptly decolorized by the metallic copper.

If a film of cuprous oxide is responsible for the bad deposits, and for making it impossible to decolorize the stock solution by means of copper, it was to be expected that cuprous oxide would be peptized by concentrated ammonia water, or by ammonium sulphate, but not by diluted ammonia. It was found that the oxide was readily dissolved in concentrated ammonia water. Diluted ammonia water, or ammonium sulphate separately, were found to be without effect. But when ammonium sulphate was added to a slightly ammoniacal suspension of cuprous oxide the liquid rapidly became clear and colorless.

Summary

1. By electrolyzing a cupric ammonia complex a relatively dense, smooth, adherent, i.e., good deposit is obtained.

2. If metallic copper or cuprous oxide is dissolved in the ammoniacal cupric solution the deposit obtained consists of a thick, coarse, non-adherent mass of relatively large copper crystals.

3. The addition of concentrated ammonia water, or of ammonium sulphate to this now unsatisfactory electrolyte results in a good deposit upon further electrolysis.

4. A cuprous oxide film on the cathode is apparently responsible for the unsatisfactory deposit. Where this film is broken there grow loose crystals of copper.

5. An electrolyte from which an unsatisfactory deposit is obtained is one which does not peptize cuprous oxide.

6. Cuprous oxide is peptized by concentrated ammonia, or by ammonium sulphate in the presence of a small amount of ammonia.

7. The cuprous oxide film formed on copper added to a slightly ammoniacal cupric solution prevents the decolorization of the solution. The addition of concentrated ammonia or of ammonium sulphate peptizes the oxide, and the solution is decolorized.

Acknowledgment

The author desires to express his sincere thanks to Professor Bancroft for his interest in this problem, and to Professor Dennis for making available the facilities of the Cornell laboratory.

The preliminary observations described in the paper were verified by Mr. C. C. Bowman.

Dickinson College,
Carlisle, Pa.

POLYMERIZATION AND DECOMPOSITION OF ACETYLENE HYDROCARBONS*

BY GUSTAV EGLOFF, C. D. LOWRY, JR., AND RAYMOND E. SCHAAD

Few fields in hydrocarbon chemistry offer the variety and the interest presented by the reactions of polymerization and decomposition of the acetylene hydrocarbons. The many products include gases, aliphatic and aromatic liquids, tars, and solids of unusual properties. There is variety too, in the means used to cause reaction, which include heat, chemical reagents, detonants, electric discharge, alpha particles, cathode rays, light, and electro-magnetic fields.

The interest in these reactions lies in part in their variability under changing experimental conditions. A single method of excitation, depending upon the conditions under which it is employed, may give rise to a gas, a low-boiling liquid, or an infusible solid. The elucidation of the mechanisms by which products so varied come from a single substance is a study of compelling interest. Attention is drawn to these reactions, moreover, by their commercial significance. Acetylenes have been proposed—and to some extent used—as a source of carbon, aromatic hydrocarbons, drying oils, synthetic rubber, and porous adsorbents.

Reactions of polymerization and decomposition are considered together for two reasons. As in the case of hydrocarbons of other series, changes of both types may be produced by the same agencies, and they often occur simultaneously.

Almost exclusively the investigations recorded concern acetylene itself. Only a few of the higher members of the series have been studied. This is understandable, as acetylene is readily obtained and there is hope of obtaining useful substances from it, while its homologs, even in the laboratory, are rarities.

I. Acetylene

A. *Introduction.*

The outstanding properties of acetylene are its unsaturation and its endothermic character. To its unsaturation, enabling it to add to itself, or to other substances, may be attributed its ability to form simple and complex polymers. Its endothermic character tenders it unstable, so that violent excitation, particularly at somewhat elevated pressure, will cause it to revert to its elements, sometimes with explosive violence.

Acetylene may be converted into polymers of comparatively simple structure by combination of two, three or four molecules, under the action of chemical reagents or the silent discharge, but only if reaction is carried out

---

* Presented before the Organic Division of the American Chemical Society, Indianapolis, Indiana, Mar. 31-Apr. 3, 1931.

under careful control. Uncontrolled polymerization goes much farther, heat producing aromatic liquids, and high-boiling tars, while the electric discharge, cathode rays, alpha particles, and light give rise to solid substances.

When fairly high temperature—1000° or above—is used, polymerization is negligible and acetylene breaks down to give carbon, hydrogen and methane. At still higher temperatures, for example in the electric arc, acetylene is more stable, and is formed in considerable proportion from methane or from carbon and hydrogen. The calculations of Francis and Kleinschmidt[69] indicate, however, that "it never becomes stable with respect to its elements." Before a temperature is reached at which no decomposition to carbon and hydrogen would occur, the hydrogen becomes monatomic and the equilibrium changes.

Catalysts reduce the temperature at which acetylene undergoes reaction. Some catalysts favor polymerization, while others change the predominant reaction at moderate temperatures from polymerization to decomposition. Metals are the substances which have been most used as contact agents.

B. *Action of Heat.*

The action of heat on acetylene at moderate temperatures—from approximately 300° to 800°—causes primarily polymerization to complex mixtures made up largely of aromatic hydrocarbons. Hydrogen, olefins and paraffins form to some extent, particularly in the upper portion of this temperature range. Below 800° decomposition is insignificant, but above this temperature it is the main reaction, and above 1000° almost the exclusive one. Carbon and hydrogen and some methane are produced. At 1200°-1300° acetylene decomposes completely;[20] at 1700° a trace of acetylene exists in equilibrium with carbon and hydrogen; at 2700° 3 percent, and at arc temperatures 7-8 percent of acetylene is present with hydrogen, methane and ethane.[167,32,166]

Notable are the yields of liquid products that can be obtained by pyrolysis of acetylene, which reach 70 to 99 percent of the hydrocarbon converted. Often 1/3 to 1/2 of the liquid is benzene. The list of substances which have been identified in these liquid tars is surprisingly long. R. Meyer[139-143] and his co-workers have reported the following:—hexene, benzene, toluene, ortho-, meta- and para-xylene, styrene, pseudocumene, mesitylene, indene, hydrindene, naphthalene, tetrahydronaphthalene, α- and β-methylnaphthalene, 1,4-dimethyl-naphthalene, diphenyl, acenaphthene, fluorene, anthracene, phenanthrene, purene, chrysene and fluoranthene.

Other workers have found dihydroanthracene in the products of noncatalytic pyrolysis, while the tar obtained in the presence of copper includes octylene, ethylbenzene, trimethylbenzene, ethyltoluene, propylbenzene, ethylnaphthalene, diethylnaphthalene, and methylstyrene.

In the gaseous products of acetylene decomposition, it has been mentioned that hydrogen and usually methane are present. Carbon almost invariably deposits in the apparatus. Ethane has in some cases been identified, and there have been frequent indefinite reports of "unsaturated and paraffin hydrocarbons."

In much of the work on the pyrolysis of acetylene the hydrocarbon has been passed through empty tubes. Sometimes the tubes were packed with activated carbon, which appears to promote smoother reaction and avoids sudden decomposition, though making no significant change in the character or yield of products. Refractory materials, such as firebrick or pieces of porous earthenware, are of some value as tube packing, particularly after becoming coated with carbon from acetylene decomposition, as this carbon appears to assist smooth reaction to liquid products.

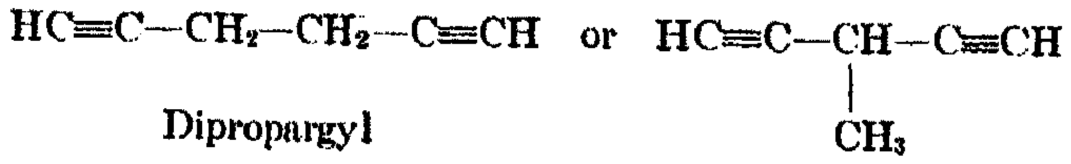
Of pronounced catalytic activity are a number of metals. Copper is the most interesting, as it both reduces the temperature at which polymerization begins and changes its course, so that in place of low-boiling aromatic hydrocarbons there is produced mainly a high-molecular weight, fluffy brown solid, cuprene. Nickel and platinum are predominantly decomposition and hydrogenation catalysts, causing change at temperatures much below those necessary for reaction in their absence, and producing large formation of carbon and hydrogen and small amounts of polymerized products. Cobalt and iron have similar, though less pronounced action. They tend to cause breakdown to carbon and hydrogen, but do not prevent polymerization to liquid products. Manganese also furthers decomposition of acetylene. Finely divided iron, nickel, cobalt, and platinum are sufficiently reactive to initiate reaction at ordinary temperatures, and by passage of acetylene over them they soon become incandescent.

Many other metals, when in contact with acetylene at elevated temperatures, produce some carbonization, but they have not been studied to a sufficient extent to allow definite conclusions regarding their action to be drawn. Acetylide formation occurs with many metals as an accompaniment of decomposition reactions, and one cannot always distinguish between decomposition of acetylene by catalytic action of the metal and decomposition of an acetylide following reaction of the hydrocarbon with the metal.

Since both the polymerization and decomposition of acetylene are exothermic, care must be taken that the heat produced in its pyrolysis is dissipated, lest explosions occur, or the reaction get out of control. In the experimental work, rates of flow are adjusted to avoid decomposition, and often the hydrocarbon is diluted with non-reactive gases for smooth operation. Studies have also been made using a catalyst suspended in oil, for better temperature control.

Reaction Mechanism.—The simplest acetylene polymerization is the combination of two molecules to form vinylacetylene. This reaction was first reported by Mignonac and Saint Aunay[144] in work using the silent discharge at low temperature, and the product isolated and characterized by Nieuwland, Calcott, Downing and Carter.[158] Both groups assume, as first step, an activation of acetylene, Mignonac and St. Aunay supposing this to cause a loosening of the bond holding one hydrogen atom, so that the active molecule adds as H and $-C{\equiv}CH$ to the triple bond of a second acetylene. The later workers represent the activated molecule as $H_2C{=}C{=}$, and suppose a second molecule to add to it as H and $-C{\equiv}CH$ to form vinylacetylene.

By Nieuwland and coworkers further reaction is represented as addition of active acetylene to vinylacetylene to give divinyl acetylene, or activation of vinylacetylene itself and its doubling to a tetramer of acetylene. Mignonac and St. Aunay postulate addition of activated acetylene to the double bond of vinyl acetylene to give either:



$$HC\equiv C-CH_2-CH_2-C\equiv CH \quad \text{or} \quad HC\equiv C-\underset{\substack{|\\ CH_3}}{CH}-C\equiv CH$$

Dipropargyl

Methylpentadiine

The formation of divinylacetylene, they state, is by way of addition of active divinylacetylene to acetylene.

In the silent discharge this addition process apparently continues until solid products are produced, as these solids are unsaturated, are able to absorb oxygen, and appear to be aliphatic in nature. In the action of alpha particles and light on acetylene, solids also form, but there appear to be no intermediate products. Lind and Schultze[128] believe that with alpha radiation a cluster of molecules around an ion is neutralized and at once goes to the final product.

These mechanisms do not cast much light upon the formation of aromatic hydrocarbons when acetylene is subjected to heat. No one has as yet formed aromatics by continuation of the low temperature polymerizations whose first steps are known; nor have any substances intermediate in aromatic formation been identified.

Berthelot[11,12,14] postulated that three molecules of acetylene combine in some way to form benzene, (he gave no intermediate steps) and that the higher aromatics form by successive additions of acetylene molecules to benzene accompanied in some cases by dehydrogenation. Thus, benzene and acetylene would form styrene, and addition of another acetylene molecule and loss of hydrogen form naphthalene. Benzene and styrene would unite and lose hydrogen to form anthracene. Continuation of such a process perhaps gives the solid product of aromatic nature, cuprene, that forms when polymerization occurs in the presence of copper. Activation of acetylene molecules very likely precedes these additions, and Berl and Hofman[8] suppose the formation of radicals during aromatic formation.

To account for the formation of methane, Bone and Coward[31] postulate that the first change is fission of acetylene to $\equiv CH$ radicals, which then add hydrogen to form methane. An alternative mode of formation would be recombination of carbon and hydrogen from acetylene decomposition. The amounts of methane found by Bone and Coward are far higher, however, than can exist in equilibrium with hydrogen and carbon at the temperatures employed. This rules out a direct synthesis and appears to support the radical hypothesis. Further evidence against formation from carbon and hydrogen is the fact that in the work of Bone and Jerdan[32] the yield of methane dropped with time of exposure. Hurd[93] however, criticizes the assumption of radicals as follows:

"The main objection to Bone's mechanism postulating HC≡ is that a split of C≡C requires so much more energy than a C—H split. For a scission of C—C it is estimated at 71 kg. cal; C—H is 90; C=C is 124 and C≡ is much greater. But for C=C to split *one* of the two bonds, giving C—C, would seemingly require no more energy than for C—C to split into C— and C—. Similarly, one of the three bonds of acetylene could split and give rise to polymerization. In the polymer, assuming it is vinylacetylene, there is a double bond. If one of the bonds of the double bond is opened for another polymerization, it could be assumed that ethylidene-diacetylene, CH_3—CH (C≡CH)$_2$, might arise. Now there is a single bonded methyl group which could reasonably be detached as methane. If this occurred, everything else is a C—H scission which would give rise to carbon and hydrogen. This is something akin to Berthelot's interpretation."

Ethylene and ethane no doubt form by direct hydrogenation of acetylene. The cokey deposits sometimes formed are perhaps the result of successive polymerizations and dehydrogenations as postulated by Berthelot, but that this sort of change is the sole means by which carbon forms is not likely to be the case, as an equilibrium condition exists between carbon, hydrogen and acetylene.

1. Without Catalysts

The first experiments on the action of heat on acetylene were carried out by Berthelot. His work on acetylene is a particularly important part of his hydrocarbon investigations, as he assumed acetylene as an intermediate product in the pyrolysis of practically all the hydrocarbons which he studied. In his early experiments,[11,12,14] he heated acetylene to the softening point of glass in a bent tube, one end of which was closed by immersion in mercury. He reported slow decrease in volume and formation of tarry products. At the end of half an hour 97 percent of the original acetylene had disappeared, being converted almost entirely into a liquid, which was mainly benzene, but contained some styrene, naphthalene, anthracene, and unidentified fluorescent hydrocarbons. A little free carbon and a corresponding amount of hydrogen were also produced.

He also found that when passed through a porcelain tube at bright red heat, the change in acetylene was almost entirely decomposition. At this temperature, acetylene decomposed more readily in the presence of carbon than in its absence, and in either case gave largely carbon and hydrogen. Minor products were ethylene, methane, naphthalene, and tar. To explain the separation of carbon, Berthelot assumed that the decomposition of acetylene at red heat consisted of a progressive polymerization, hydrogen splitting off in the process until only carbon remained. When he further increased the temperature,[18,19] and decomposed acetylene by exposure in a quartz tube for one hour at 1307° to 1325°, followed by sudden cooling of the tube to ordinary temperature by immersion in water, the tube was found to contain a brilliant form of carbon, and the gas consisted mainly of hydrogen, mixed with small amounts of methane and carbon monoxide. (Apparently the acetylene was slightly impure).

By carrying out his experiments on a larger scale, Berthelot[13] obtained a greater quantity of the yellow liquid product. It contained 50 percent benzene and 20 percent styrene. Above styrene, a 210°-250° fraction came over in which naphthalene was present. The distillate obtained between 250° and 340°, which was highly fluorescent, was thought to contain hydrogenated anthracene or ditolyl. From this liquid a few crystals of anthracene separated.

The work of Berthelot indicated definitely the predominant trend in the action of heat on acetylene to be toward the production of aromatic hydrocarbons by polymerization at moderate temperatures, and toward carbon and hydrogen at more elevated temperatures.

Subsequent researches will not be taken up in strictly chronological order, but a number of the more recent investigations are placed first to give at the onset a survey of present knowledge in this field.

Pease[102] found that the lowest temperature at which acetylene conversion occurred at a significant rate was about 400°, and produced evidence that polymerization of this hydrocarbon is a bimolecular and homogeneous reaction.

On seven minutes' exposure at 400° reaction was detected by a white mist appearing in the effluent gas, accompanied by an "odor similar to that of carburetted water gas." The reaction accelerated notably as the temperature was raised, so that the mist gave place to a mobile brown liquid. The product was a complex mixture with a wide range of volatility. "It contained benzene along with other volatile hydrocarbons subject to attack by concentrated sulfuric acid. . . . Very little permanent gas was formed until the temperature approached 550°, even though more than half of the acetylene might react." The gas produced was hydrogen with small quantities of methane and ethane. "At 600° regular flashing (a sudden luminous decomposition throughout the mass of the gas) began at higher flow rates, though it was possible to carry the reaction to 650° with low flow rates. In this high temperature range, finely divided carbon carried out of the tube."

Pease reported the polymerization bimolecular, because of retardation of the reaction when nitrogen was mixed with the acetylene before entrance into the heated tube. The fact that the rate of change was decreased by filling the reaction tube with glass packing was taken as evidence that the reaction was homogeneous rather than a wall reaction.

Bone and Coward[31] reported that,

1. At moderate temperatures acetylene shows a strong tendency to polymerize, maximum reaction occurring at 600°-700°, and decreasing above this temperature, so that little polymerization is found at 1000°.

2. At low temperatures acetylene tends to combine with hydrogen, but this is insignificant above 1000°.

3. At 800° and higher, the primary change is dissolution, and considerable amounts of methane form, which is attributed to hydrogenation of $\equiv$CH residues initially formed.

Bone and Coward either circulated the gas through a porcelain tube surrounded by an annular space containing hydrogen to promote even heating, or passed it into or through a glass tube packed with porcelain fragments. At 480°-500° with an exposure of 20 hours about 82 percent of the acetylene reacted. Of this 48 percent polymerized, 39 percent decomposed into carbon and hydrogen, and the remainder was converted into methane, ethane, and ethylene. In an experiment of eight and one-half hours' duration at 650°, 60 percent by weight of the acetylene changed was polymerized, 30 percent resolved into carbon and hydrogen, and the remaining 10 percent appeared as methane, ethane, and ethylene.

At 800°, because of the rapidity of decomposition, the circulation method was abandoned, and the hydrocarbon simply passed into the heated tube, in which it was allowed to remain from 1 to 60 minutes. "Except when the gas was largely diluted with nitrogen or hydrogen, it always 'flashed' as soon as it entered the hot vacuous tube, so that its temperature momentarily must have been considerably higher than was recorded by the pyrometer." Although the greater part of the acetylene was thought to be decomposed during the flashing, the appearance of a mist in the condenser showed that polymerization still occurred. Much methane was formed. Methane was also produced in high yield when acetylene was heated with hydrogen at 800°. This was taken as proof of the suggested mechanism involving hydrogenation of $\equiv$CH radicals to form methane.

At temperatures of 1100° to 1150° polymerization diminished, while formation of carbon and hydrogen increased. Methane was also found at these temperatures. A summary of the results at the higher temperatures is given in Table I.

TABLE I

Decomposition of Acetylene

(Bone and Coward)

Temperature	600°	1000°	1150°
Polymerization, % of acetylene used	19	7.5	5
Analysis of gaseous products, %			
by volume acetylene	1.35	1.55	0
Ethylene	0.45	2.60	0
Ethane	0.50	0	0
Methane	32.40	36.00	23.45
Hydrogen	63.50	59.85	76.55

When Bone and Jerdan[34] admitted acetylene to an exhausted porcelain tube maintained at 1150°, the gas decomposed so rapidly that after an exposure of one minute not more than ten percent remained, and only a mere trace was present after five minutes. During the early stages of reaction considerable quantities of methane formed, which, as the decomposition progressed, was slowly but never completely resolved into its elements. Neither benzene nor ethylene formed at any stage of the decomposition; nor were there any gaseous products besides hydrogen and methane. Carbon was liberated, at first in a form resembling lampblack, but later depositing on the inner surface of the tube in a form resembling gas carbon.

The highest yield of liquid products that has been reported is that of Berl and Hofmann,[8] who obtained a 98.8% conversion. The acetylene was saturated with water at 60-65° (the partial pressure of water was 150 mm.) and passed at 740° with a time of 4 seconds through a glass tube mounted in a copper block and filled with porcelain beads. The contact mass became coated with carbon, and held its effectiveness so that the yield did not drop during the run. The liquid was made up principally of aromatic hydrocarbons and higher acetylenes. The effect of the water was believed due to its reaction to form carbon dioxide, this reaction taking up part of the energy liberated by the decomposing acetylene.

The most extensive work on acetylene pyrolysis has been done by Meyer and his co-workers. To them we owe the identification of the many substances produced by polymerization. They worked on a sufficiently large scale to make extensive separation of products. In their first studies, intended primarily to determine whether the compounds in the pyrolytic tar from acetylene were those of coal tar, Meyer[139] repeated Berthelot's experiments with increased amounts of material, circulating acetylene at the rate of 40 liters per hour through two vertical, electrically heated, porcelain tubes, the first kept at 640° to 650° and the second at 800°. The hydrocarbon was about 1.1 minute in each heating tube. Before pyrolysis the acetylene was diluted with an equal volume of hydrogen, as otherwise it flashed and deposited carbon. After flowing through the heated tubes, the gaseous product, which contained a considerable proportion of methane, was used to dilute further quantities of acetylene.

The tar yield was about 63 percent of the acetylene converted, the remainder forming carbon, hydrogen and methane. The tar from the first tube was rich in light oils and that from the second in high-boiling hydrocarbons. The tars were submitted to repeated fractionation and crystallization and unsaturated hydrocarbons removed by bromine water. In the final product, benzene formed about 20%, toluene, which Berthelot did not find, was definitely identified, but xylenes were not proven. The fraction boiling from 150° to 200° contained indene. Steam distillation of the portion boiling between 200° and 300° yielded naphthalene, diphenyl and fluorene. From the 300° to 450° fraction small amounts of anthracene together with pyrene and chrysene were obtained.

To increase the amounts of tar, Meyer and Tanzen[143] used a more elaborate apparatus consisting of three vertical tubes of "Marquardt Mass" connected in series as to gas flow and heated electrically to 600°, 650°, and 800°, respectively. The yields of tar with this equipment varied from 27 to 57 percent of the acetylene treated. In the tar, in addition to the substances which Meyer had previously isolated, styrene, acenaphthene, and phenanthrene were identified, the first by conversion into its dibromide, and the others by their picrates. From the first runnings of the tar a hydrocarbon was isolated which boiled at 70° and whose analysis, density, vapor density and index of refraction were identical with the constants of "hexene" obtained from mannite, which was probably a mixture of 1-hexene and 2-hexene.

Hoping to find other benzene homologs besides toluene in the lower boiling products from acetylene, Meyer and Fricke[140] systematically distilled the part of the tar from the previous investigation boiling between 50° and 150°. A fraction, which after removal of styrene boiled at 138°-139.5°, was proved to contain m- and p-xylene. The presence of o-xylene and ethylbenzene was suspected, but they could not be identified. From the fractions of the tar boiling between 150° to 250° and 250° to 350°, α- and β-methylnaphthalene, and diphenyl were isolated, together with small quantities of 1,4-dimethylnaphthalene. All of these were identified by their picrates. A fraction boiling between 193° and 206° from which a picrate could not be prepared, gave analytical values corresponding approximately to tetrahydronaphthalene and on oxidation with potassium permanganate and sulfuric acid yielded phthalic acid.

R. Meyer and W. Meyer,[141] in extending the work of Meyer and Tanzen, increased the dilution of the acetylene with hydrogen and held the temperature of the first heating tube to 550°, that of the second about 630°, and of the third at 850° to 900°. As in the earlier work, benzene, toluene and m- and p-xylene were identified, while in addition the presence of o-xylene was proved, and in higher boiling fractions pseudocumene, mesitylene, hydrindene and fluoranthene.

Meyer and Taeger[142] investigated a mixture of picrates obtained from the constituents of acetylene tar boiling above 300°. When decomposed with aqueous ammonia on the water bath this mixture gave a hydrocarbon tar boiling between 100° and 345°. From the fraction boiling up to 260°, fluorene, acenaphthene, anthracene, phenanthrene, pyrene, and fluoranthene were isolated. From the fraction 260° to 345° a small amount of picrate, melting at 231°, gave a hydrocarbon of empirical formula $C_{17}H_{10}$.

In the Presence of Added Carbonaceous Materials.

Many investigators who have carried out the heat treatment of acetylene in the presence of carbon, especially activated charcoal, claim advantages from the addition of carbonaceous material. When acetylene is pyrolyzed, however, carbon is almost always present as a reaction product, so that it is difficult to distinguish the exact effect of the added carbon. While some state that activated charcoal has a distinct action, others believe it to be effective only after becoming coated with carbon from acetylene decomposition, and find packing of other materials to be equally valuable.

Zelinsky and Kasansky[212,213] claimed that packing tubes in which acetylene was pyrolyzed with activated charcoal made possible the use of higher temperatures than could otherwise be employed without risk of flashing or explosion. It was thus possible to operate at the optimum temperature for polymerization, 600°-650°, which was difficult in the absence of the charcoal. The reaction was made smoother and less carbon deposited; no solid polymers formed and although there was some hydrogen in the final gases, no hydrogenation of acetylene occurred; the products were more largely benzene.

In the experiments of Zelinsky and Kasansky the gas was passed through a Jena glass tube containing the charcoal at temperatures up to 650°. The time allowed for reactions was 27 to 40 seconds. When the temperature of the heating tube reached 450°, white vapors appeared in the condenser, and became yellow and more dense as the temperature was increased. At 550° oil formed in the end of the tube and a dense fog filled the receiver. At 580°-600° the tar yield was 15 percent of the acetylene passed through the tube. At 620° to 630° with the same initial gas velocity the tar fog disappeared completely, liquid condensate flowed slowly into the receiver, and the yield was approximately 45 percent. The volume of exit gas was only 25 percent of that of the acetylene entering the apparatus, and about 60 percent of the gas was hydrocarbons heavier than acetylene. At 650° to 655° the yield of liquid condensate was 70 to 74 percent of the acetylene, and practically no gaseous products formed.

The condensate was a reddish brown tar of aromatic odor, and density varying from 0.911 (tar produced at 600°) to 0.995 (at 655°). A composite sample of density near the upper limit yielded 49 percent of light oil boiling below 170° (45 percent below 150°), 11.7 percent of middle oil boiling between 170° and 230°, 9.54 percent of heavy oil boiling from 230° to 270°, 21.2 percent of anthracene oil boiling above 270°, and 6.8 percent pitch. The light oil consisted mainly of benzene (35 percent of the tar), toluene (41 percent), para xylene (0.42 percent), and traces of styrene and indene. From the middle oil 6.7 percent of naphthalene and about 1 percent of fluorene were isolated. Anthracene was separated from the anthracene oil.

When these workers used an unfilled porcelain tube at 600° about 12.5 percent of the acetylene was converted into liquid condensation products during a run of 20 hours, and 2 percent of carbon deposited. Most of the hydrocarbon passed through unchanged. Over asbestos at 650° acetylene formed a thick, black, aromatic tar in yield of about 40 percent.

Kovache and Tricot[115] obtained yields of tar comparable to those of Zelinsky by passing acetylene downward through a vertical porcelain tube packed with activated charcoal, heated electrically at temperatures varied from 450° to 970°. The optimum temperature was about 650°. They reported, however, that charcoal did not aid the condensation until after it had been heated for some time. The condensation of acetylene to tar was effected just as well by a number of the other substances, including wood charcoal, coke, coke impregnated with aluminum oxide, porcelain, quartz, pumice or crushed brick, particularly if their surfaces were covered with a thin layer of carbon formed by decomposition of acetylene. The authors concluded therefore that activated charcoal does not have the specific catalytic action which Zelinsky attributed to it.

In their experiments, depending upon the conditions, 30 to 60 percent of the acetylene passed, or 33 to 76 percent of that which disappeared was converted into tar. A composite of these tars contained 28 percent of benzene, 1.5 percent of toluene, and 7.5 percent of anthracene.

Deposition of carbon, which eventually choked the reaction tube, could not be avoided by lowering the temperature, because when it was lowered enough to stop carbon deposition, polymerization also ceased.

When Kovache and Tricot passed acetylene through a horizontal silica tube packed with fragments of silica or porcelain and heated to 700°, 10 to 40 percent of the gas was converted into a tar of specific gravity 0.95 to 0.98 containing approximately 58 percent of benzene, 13 percent of naphthalene, and small quantities of toluene, dihydroanthracene, and pyrene. Part of the acetylene decomposed and produced carbon, which rapidly clogged the tube.

These workers then improved their apparatus by placing the tube vertically and introducing a water-cooled copper tube inside it, with an annular space of 2.5 to 3 mm. between the two, in order to condense the benzene and remove it as formed from the reaction zone. The yield of liquid tar was increased by this arrangement and the operation was made easier to control. From 70 to 90 percent of the acetylene passed, or about 90 percent of that consumed, was converted into a tar containing about 28 percent of benzene, 0.5 percent of toluene, and 4.3 percent of naphthalene. Rise in operating temperatures increased the velocity of the reaction and also the proportion of heavy hydrocarbons. Under the conditions used, the optimum temperature was 950°. At 1000° the liquid was black and viscous. The disadvantages of the hot-cold tube apparatus were the high heat losses due to the cold tube, and the gradual decrease in efficiency due to fouling of the hot tube by the formation of graphite. The results obtained were considered to preclude the possibility of a commercial synthesis of benzene by pyrolysis of acetylene.

Fischer, Bangert and Pichler[64] found that passage of acetylene over activated charcoal or over silica gel in a porcelain tube at 650° at first produced carbon, hydrogen, and methane. The carbon depositing on the charcoal or silica appeared, however, to be an effective catalyst for polymerization, and the production of liquid hydrocarbons soon began. After five hours of operation 70 percent of the acetylene was converted into tar which contained about equal amounts of light and heavy oils. At 600° the reaction products were the same as at 650°, but the yields were smaller.

The light oil, which boiled up to 150° (75% distilled below 110°), contained 70 percent of aromatic and 30 percent of unsaturated hydrocarbons, had an odor of benzene and was of a clear yellow color. The heavy oil was dark and opaque with a distinct odor of naphthalene. Ten percent of it distilled up to 150°, 50 percent came over to 230°, and solidified on cooling. The remainder was thin tar oil.

Work was done at 750° and 200 mm. mercury pressure, but the use of diminished pressure was said to have no significant advantage.

Dilution of acetylene with hydrogen and carbon dioxide favored light-oil formation and increased the life of the catalyst. Carbon dioxide also revivified the catalyst after use at 700°-720°. When an equi-volume mixture of acetylene and carbon dioxide passed through an empty tube at 600°, 70 percent of the acetylene was converted into liquids, of which about one-half was light oil.

Ika and Ogura[101] studied the polymerization of acetylene passing through a glass U-tube containing several active carbons at 600° and upwards. There was little difference in catalytic activity between activated charcoal, coke and coalite. No special relationship was found between the decolorizing ability and the catalytic action of the carbon, Coarse granular catalysts were most suitable as with fine carbon there was danger of local overheating in the reaction tube.

The optimum reaction temperature, as in the work of others, was 650° to 660°. Under these conditions 60 to 70 percent of the acetylene was converted into oily products containing 50 to 60 percent of light oil, which distilled below 150° and was composed mainly of benzene.

Other Researches.

Rousseau[179] reported the production of black diamond and graphite by decomposition of acetylene at temperatures approaching 3000°.

Haber and Oechelhäuser[82] found that when acetylene was passed into a porcelain tube at 620° the temperature rose immediately and remained at 638° to 645°. The products were largely liquid, consisting of about 40 percent of benzene; naphthalene was not observed; gaseous products equaled 4.2 percent of the acetylene, 3.2 percent being converted into ethylene.

On passing acetylene through a Jena glass tube which was heated gradually, Tiede and Jenisch[199] observed at about 440° the formation of a gray fog, which they took as an indication of the beginning of polymerization, together with a small separation of carbon on the walls of the tube. Raising the temperature increased the fog, and at about 540° the first oil drop appeared. At 600° about 31 percent by weight of the acetylene was converted into oil. Small amounts of paraffins, olefins, and hydrogen were present in the effluent gas which was largely unchanged acetylene.

Hilpert,[83] to form benzene, passed acetylene through a heated Jena glass tube filled with glass fragments. A tar fog appeared at 400°. At 500° a layer of carbon formed slowly on the glass and a tar was obtained containing small amounts of benzene and unidentified unsaturated hydrocarbons.

Sinkinson[196] found that the carbon deposited from decomposing acetylene upon two overlapped wires in a layer .0025 cm. thick was so cohesive that a considerable force was necessary to part the wires.

Walker[202] found that while acetylene was stable at 400°, at 450°, with a low gas velocity, it polymerized to a brown fluorescent liquid which appeared as minute drops in the cooler end of the heating tube. There was also a slight amount of decomposition. No polymerization was observed at this temperature when the gas flow was increased. Somewhat greater polymerization and some decomposition occurred at 550°, at the latter temperature 11 percent of the acetylene being decomposed. The residual gas contained 87.6 percent acetylene, 1.9 percent hydrogen, 7.8 percent ethylene, and traces of methane and ethane.

Fujio[73] passed purified acetylene into a glass or porcelain tube filled with pumice, clay, Japanese acid clay, or brick at 400° to 700°. The yield and chemical nature of the tar produced varied with changes in temperature, rate of passage of acetylene, and the nature of the contact material. The maximum yield of tar, about 82 percent, was obtained by passing the gas over clay at 650°. It was made up almost entirely of aromatic hydrocarbons, including benzene and naphthalene.

When tubes of aluminum, copper, nickel, or iron, or iron coated internally with enamel, tin or iron sulfide were used instead of the glass tube the decomposition into carbon, hydrogen, and other gases was accelerated and was greater than the polymerization. In addition the tar thus produced differed from that obtained with glass, the fraction boiling between 100° and 250° being larger.

Constable[49] decomposed acetylene at a graphite surface supported on china clay rods, heated electrically to temperatures varying from 800° to 1200°, in order to study the catalytic properties of the carbon film.

Hague and Wheeler[83] produced oil and considerable quantities of soft carbon by passing acetylene downwardly through a vertical quartz tube at 600° to 750°. As shown by Table II, the maximum yield of liquid, 61.1 percent of the acetylene treated, was produced in the range 650° to 700°.

TABLE II

The Polymerization and Decomposition of Acetylene

(Hague and Wheeler)

Temp.	Yields in percent by weight of acetylene treated			Gas analyses, percent by volume				
	Total liquids	Benzene fraction	Carbon	Higher olefins	C_2H_2	C_2H_4	H_2	CH_4
600	30.8	—	—	0.8	53.2	4.2	27.9	8.3
650	61.1	26.4	9.7	1.2	29.5	6.9	34.0	23.0
700	61.1	24.8	16.7	1.2	2.4	10.4	43.8	37.1
750	46.7	18.3	22.1	0.2	0.7	8.8	50.1	37.5

Ipatiev[102] suggested the possibility of producing aromatic hydrocarbons commercially from acetylene from waste calcium carbide, which has no market value and must be destroyed. He stated that in a semi-manufacturing scale plant the Bayerische Stickstoffwerke obtained up to 65 percent of aromatics by passing acetylene through an electrically heated furnace containing carbon plates separated by clay plates impregnated with a catalyst, at a temperature of 600-650°.

Polymerization of acetylene by action of heat on the gas in the burner before it reached the orifice, followed by decomposition of the polymers in the flame was the cause assigned by Bullier[39] and Gaud[74] for carbon formation on acetylene burners.

Bradley and Parr[38] reported that acetylene was completely decomposed into its elements by contact with carbon at 725°.

Kennaway[112] found that by passing acetylene through a silica tube filled with pieces of porous plate at 700° to 920° a tar was produced, which could produce cancer in mice on application over a long period.

Acetylene has been proposed as a source of carbon by Salvadori.[189]

Patents.

Gros[79] claimed to produce a mixture of aromatic hydrocarbons from acetylene or gaseous mixtures containing acetylene by passing the gas through a reaction vessel filled with pieces of retort carbon heated electrically to 500° to 700°. The carbon filling was said to have no catalytic action, but to prevent local increase of temperature, which might cause spontaneous decomposition of the acetylene. He stated that a temperature of about 500° was best suited to the production of benzene and toluene. In another patent[80] covering a similar process, he gives as an example heating a mixture of 50 percent acetylene and 50 percent hydrogen to 580° to produce a mixture of liquid hydrocarbons containing 38.1 percent benzene, 2.6 percent toluene, and 7.5 percent naphthalene.

Ylla-Conte,[206,207,208,209] patented an apparatus for producing benzene and other liquid hydrocarbons from acetylene by subjecting the gas to a temperature of 450° to 600° in large iron or steel vessels and circulating the gas through a refrigerating apparatus outside the reaction vessel to remove the benzene and liquid products formed. The uncondensed gas was injected into the reaction vessel to mix with the gas undergoing treatment and to prevent undue rise of temperature.

It was stated that once the process was started it was unnecessary to heat the acetylene, and the operation was continuous and automatic. By regulating the speed of circulation through the refrigerant it was possible to vary the quality of the products.

A number of patents have been taken out on the preparation of high-grade carbon black by decomposition of acetylene.[190] Hubau[92] explodes acetylene in steel vessels under a pressure of 2 to 5 atmospheres. Hostmann Steinbergsche Farbenfabriken Ges.[90] also ignite the gas under pressure. Frank[70] dilutes with carbon monoxide or carbon dioxide before decomposition. Berger and Wirth[7] also dilute the hydrocarbons.

Wheeler, McAulay and Francis[210] pyrolyze a variety of hydrocarbons and hydrocarbon mixtures, including acetylene, by passage in two or more stages, through a space heated to 1000°-1200°. The liquid products, which include benzene and its homologs and olefinic substances, are separated from the gases between treatments.

2. With Catalysts

A. *Metals.*

i. Cobalt, Copper, Iron, Nickel, Platinum

The course of acetylene pyrolysis is greatly changed by the presence of metals. Of particular importance is copper, which has strong polymerizing action and produces a characteristic solid, cuprene. Polymerizing action, it will be recalled, is possessed by a salt of copper, cuprous chloride, even at room temperatures. Iron lowers the initial temperature of acetylene decomposition, and favors decomposition to carbon and hydrogen, though not excluding production of oils. Nickel aids decomposition to carbon and hydrogen and causes partial hydrogenation of the acetylene, as well as some polymerization, which may go as far as the production of a solid cuprene-like substance. Platinum is also a decomposition and hydrogenation catalyst, but loses its efficiency at high temperatures through becoming coated with carbon.

The effectiveness of cobalt is said to lie between that of nickel and of iron. The metal lowers the initial decomposition temperature of the hydrocarbon, giving rise both to carbon and hydrogen and to polymerized products. Pyrophoric iron, nickel or cobalt will become incandescent in a stream of acetylene, as will also finely divided platinum.

The metals are arranged alphabetically in two groups, first those of pronounced reactivity with which important results have been obtained—cobalt, copper, iron, nickel and platinum—and, second, those which have been subject to but little investigation, or have been found to have no pronounced effect on the course of the pyrolysis. Little effort is made to analyze the action of the metal, whether it should be classed as a catalytic agent, or be considered rather as a participant in a chemical reaction. With the five metals discussed in detail, there is, probably, true catalytic action. With some other metals, the change occurring is largely acetylide formation, and not catalysis. Acetylide formation is almost always accompanied by deposition of carbon, which is taken to indicate decomposition of the acetylene and to constitute justification for the inclusion of the results in this paper.

Cobalt.—Moissan and Moureu,[149,151] found that passage of a rapid current of acetylene over pyrophoric cobalt (prepared by reduction of the oxide at the lowest possible temperature) caused the metal to become incandescent. Carbon, hydrogen and a liquid hydrocarbon product rich in benzene were formed.

These investigators believed that the generation of heat was initiated by the energetic absorption of the acetylene by the porous reduced metal, and that the heat then acted on the acetylene to cause part of it to polymerize and part to decompose. When the acetylene was diluted with nitrogen, there was no incandescence, although the hydrocarbon was absorbed and slightly decomposed.

Sabatier and Senderens,[186,188] observed that finely divided cobalt had no action on acetylene or acetylene mixed with hydrogen at room temperature, but when exposed to the hydrocarbon at temperatures above 200° the metal became incandescent and the gas was almost completely decomposed. They considered the effectiveness of cobalt to be less than that of nickel and greater than that of iron. Greenish yellow liquids formed, resembling those obtained with nickel. These resembled natural petroleums, and their formation was used as the basis for an acetylene theory of petroleum formation. The gaseous products were largely hydrogen and ethane, with a trace of benzene, while the heating tube filled with a black material, consisting of carbon mixed with cobalt, containing a small amount of a fibrous hydrocarbon similar to cuprene.

Hodgkinson[89] also reported cobalt to induce reaction when heated in acetylene to about 200°. The metal became corroded and pitted, and quite brittle. Carburisation was greater and soot formation less when the gas was diluted with ammonia.

In the work of Tiede and Jenisch[199] cobalt caused separation of carbon from 380°, and oil formation at 480°.

Fischer, Peters, and Koch[66] produced complete decomposition of acetylene by passing it over cobalt at 300°. There was no liquid product and methane was the only substance identified.

Cobalt is used by the I. G. Farbenindustrie, A. G.[99] in the treatment of acetylene to produce lamp black.

Copper.—The main product of the action of heat on acetylene in the presence of copper (or its oxides) is a voluminous brown solid "cuprene." Oily products and gases are produced in smaller amount at the same time. The formation of cuprene has been frequently and extensively investigated. It is a polymer of indefinite composition, aromatic in nature, though of undetermined structure. A trace of oxygen seems to be required to initiate its formation.

Cuprene was first reported by Erdmann and Köthner[59] who found that a light brown, highly voluminous solid was formed by the action of acetylene at 230° upon cuprous oxide, or more slowly by action on finely divided copper. The passage of acetylene during 18 hours over one gram of cuprous oxide yielded 7 grams of this product, which occupied a space of nearly 300 cc. In addition, a black carbonaceous mass formed, and at "red heat (400°–500°C.)" carbon was deposited in graphitic form. Below 180° only liquid polymers formed.

Erdmann and Köthner considered the brown fluffy product to be a complex, non-explosive, copper acetylide of the formula $C_{44}H_{64}Cu_3$. When heated with an excess of zinc dust it yielded 20 percent by weight of an oil boiling between 190° and 250°, having an odor similar to that of Caucasian naphtha. If the mixture with zinc dust was heated to a higher temperature, aromatic hydrocarbons, including naphthalene, appeared in the distillate, while a portion which dissolved in caustic soda appeared to be cresol.

From experiments made by passing acetylene over heated copper oxide, Gooch and Baldwin[76] came to the conclusion that the "Kupferacetylen" obtained by Erdmann and Köthner[59] was not a copper acetylide but a hydrocarbon or hydrocarbons mixed with copper or an oxide of copper. The copper content of this product, they found, varied between 1.5 and 24.2 percent, and depended upon the conditions of the experiment. While they readily obtained it by the action of acetylene on either cuprous or cupric oxide, when a roll of copper gauze was carefully reduced in hydrogen, oxidized at one end in the outer portion of the flame of a Bunsen burner, and then exposed to a current of acetylene at 225° to 250°, it yielded the spongy product upon the oxidized end only. "These results go to show that, while metallic copper may, at comparatively high temperatures, induce the polymerization of acetylene, it is an oxidizing action which, at moderately low temperatures, starts the formation of the peculiar derivatives under consideration."

When Alexander[1] passed dry acetylene over spongy copper contained in a tube which was heated slowly, the action started at about 225°. The copper began to swell, the effluent gas stream became slower, and drops of a heavy distillate with a petroleum-like odor separated in the cooler parts of the tube. The reaction proceeded smoothly between 240° and 250° but above 260° carbon deposited on the walls of the tube in a lustrous black layer. No gaseous products were formed at 240°–250°. A light brown cork-like mass eventually filled the entire tube. This mass contained two percent of copper, which was thought to be held mechanically, as treatment with hydrochloric acid containing ferric chloride lowered the copper content to 0.2 percent.

The most extensive investigations of the decomposition of acetylene in the presence of copper were made by Sabatier and Senderens.[180,181,182,188] They found that the admission of acetylene to copper, reduced from the oxide by hydrogen at low temperature, immediately caused a reaction even in the cold, manifested by a slight rise in the temperature of the metal and by a petroleum-like odor of the effluent gases. This reaction, which lasted for only an instant, was thought due to hydrogenation of acetylene by hydrogen adsorbed by the copper. When this brief reaction ceased the metal became cold. It did not occur with copper which had been reduced by carbon monoxide or by hydrogen at red heat.

If the temperature was raised above 180°, the copper turned brown, and the pressure decreased rapidly because of rapid polymerization of the acetylene. In the cooler part of the tube a colorless liquid deposited, consisting mainly of olefin hydrocarbons. Microscopic examinations of the copper showed no appreciable change in its structure. Prolonged action of acetylene at 180° to 250° caused the copper to swell, and form a yellowish brown mass composed of microscopic filaments, which filled the heating tube. This material, when compressed, resembled tinder, and was reported to consist of a non-volatile hydrocarbon mixed with about 1.5 percent of copper. The composition of this substance corresponded to the empirical formula $(C_7H_6)_n$. Sabatier and Senderens suggested the name "cuprene" for this hydrocarbon on account of its method of formation.

Besides the formation of cuprene, there was condensation of greenish liquids which consisted of a mixture of unsaturated and aromatic hydrocarbons (benzene, styrene, etc.). The small amount of gas which left the heating tube had the following composition (percent by volume):

H_2	C_2H_6	C_2H_4	C_3H_6 and C_4H_8	C_2H_2
20.2	12.1	45.2	16.5	6.0

In the presence of copper sheet or wire the reaction was identical with that obtained over reduced copper. Well-cleaned copper when heated at 200° to 250° in a current of acetylene was covered by the same sort of brown layer, which became yellowish as its thickness increased. Some of the deposit placed in a clean tube and heated at 180° to 250° in a current of acetylene, again swelled and filled the tube. After three or four such successive swellings in acetylene at 200°, a material was obtained which was no longer modified by further heating.

By suddenly conducting a current of acetylene over a column of reduced copper heated only in the middle portion, to about 250°, Sabatier and Senderens obtained a lively reaction which sometimes attained incandescence, producing cuprene mixed with carbon.

The formation of cuprene was regarded as "doubtless due to the formation of an unstable acetylide capable of reacting with acetylene to form a new condensed molecule, thus:

$$n\ C_2H_2 + n\ Cu = n\ C_2Cu + n\ H_2$$

$$\text{and}\quad n\ C_2Cu + 6n\ C_2H_2 = \underset{\text{cuprene}}{(C_7H_6)_{2n}} + \underset{\text{regenerated}}{n\ Cu.}$$

"The regenerated metal is capable of repeating the reaction indefinitely. The hydrogen set free combines with a portion of the acetylene over the copper to give chiefly ethylene hydrocarbons."

Hilpert[88] reported that passage of acetylene over heated copper immediately produced a brown deposit on the metal which in a short time obstructed the tube entirely, while a tar with unpleasant odor was formed in small quantities.

Comparative experiments in which Kaufmann and Schneider[110] conducted acetylene over reduced copper, cuprous oxide, cupric oxides, and a residue produced by heating anhydrous copper ferrocyanide in a current of air at 250° for 15 minutes, showed that the last gave the best yields of cuprene. Traces of a green oily liquid also deposited in the cooler parts of the heating tube.

The condensation product varied in color with the catalyst and the length of the heating. That obtained in the presence of the decomposed copper ferrocyanide was yellow to light brown, while that resulting with the other contact agents was dark brown to black. By further treatment with acetylene the dark material was converted into a lighter colored product containing less copper. If the time of heating was short, the product was loose and voluminous; but, if heating was continued six to eight hours, it was a cork-like solid. The empirical composition of the products obtained with different temperatures and catalysts varied between $(C_{11}H_{10})_x$ and $(C_{15}H_{10})_x$.

By working with very pure acetylene produced by the action of alcoholic potassium hydroxide on ethylene dibromide Kaufmann and Mohnhaupt[109] found that the conversion of acetylene into cuprene in the presence of reduced copper at 230° to 300° did not take place in the complete absence of oxygen. These investigators believed that cuprene formation was due to production of an intermediate additive compound of acetylene with cuprous or cupric oxide which immediately underwent pyrolysis. The acetylene released by the decomposition of the addition compound was considered to be particularly reactive, and consequently, to undergo reactions more profound than those involved in the pyrogenic changes of acetylene when heated alone. These reactions were thought to lead through a series of intermediates to the inactive cuprene. The regenerated copper oxide was considered capable of adding acetylene as before.

A study of the cuprene showed that it did not absorb oxygen in the cold, halogenated with difficulty, and on oxidation with nitric acid formed mellitic acid. This indicated an aromatic nucleus. As to the remainder of its structure, its hydrogen content was too low for it to have saturated side chains, while the difficulty of bromination ruled out unsaturated side chains. A polycyclic aromatic structure was, therefore, most probable.

The solid product from action of the silent discharge on acetylene, somewhat similar to cuprene, in appearance, eagerly absorbed oxygen, and was thought from this and other properties to be essentially aliphatic in composition.

Schläpfer and Stadler[192] reported that the Elektrizitätswerk Lonza A.-G. prepared cuprene on a large scale by passing technical acetylene over copper at about 300°. The reaction was carried out in reaction vessels of several cubic meters capacity containing the finely divided metal. After air was expelled by acetylene, the apparatus was heated until the reaction began, which required a temperature of about 200°. The heat of reaction then caused the temperature to rise quickly to 250°–300°. At this temperature the operation was conducted for several days by continuously introducing acetylene, to which an inert gas had been added in order to prevent too energetic reaction. The acetylene produced 75 to 80 percent by weight of cuprene, 5.5 to 7 percent of tar, and 13 to 17 percent of gases.

The cuprene-tar was a greenish-blue liquid of specific gravity 0.878 to 0.910. Fractional distillation at atmospheric pressure up to 112°, then at 12 mm. to 170°, and finally at 0.3 to 0.5 mm. to 220°, followed by treatment of the fractions with sulfuric acid and bromine showed that the tar consisted mainly of aromatic hydrocarbons, with smaller quantities of olefins, and a small proportion of paraffin hydrocarbons boiling between 28° and 64° at 720 mm. The substances which Schläpfer and Stadler isolated from the tar were: hexylene, octylene, benzene, toluene, xylene, ethylbenzene, styrene, methylstyrene, trimethylbenzene, ethylmethylbenzene, propylbenzene, naphthalene, methylnaphthalene, ethylnaphthalene, diethylnaphthalene, anthracene, and an unidentified aromatic hydrocarbon $C_{10}H_{14}$.

Fischer and Peters[65] studied hydrogenation and polymerization of acetylene in mixture with hydrogen in the presence of a catalyst of copper precipitated on Kieselguhr suspended in paraffin oil.

Herzog[87] discussed the technical application and uses of cuprene. While full details of its manufacture have not been published, it is known that acetylene is passed over copper or bronze powder at 200-260° under pressure somewhat above atmospheric during action of the silent electric discharge. The temperature and pressure employed affect the properties of the product. Choking of the reaction tube is avoided in a patent of the Elektrizitätswerke Lonza[56] by a stirring mechanism. This company eliminates coking and obtains a purer product by dilution of the hydrocarbon with 5 to 15% nitrogen.

To reduce the space needed for reaction pure or dilute acetylene is introduced into a high-boiling liquid, such as stearic acid or paraffin oil, containing copper bronze at 250°-300°. The product is purified by washing with alkali or a solvent. The favorable action of a small amount of oxygen on cuprene formation, which has already been mentioned, is covered in a patent of Horwitz,[91] who increases yields by mixing acetylene with air, oxygen, or an oxygen supplying agent.

Many industrial uses of cuprene have been covered by patent and some of them no doubt put into practice. The utility of cuprene is based on its chemical indifference and physical structure. Herzog[87] gives a patent bibliography of this field. Among the uses he mentions are the replacement of cork in the linoleum industry, as a porous mass in acetylene cylinders, use as an absorbent for liquids, including fuels, disinfectants, and liquid oxygen explosives, as a rubber filler, as a constituent of dynamite, and of black powder.

Acetylene and benzol in the presence of aluminum chloride give a product much like cuprene, that has been patented by Consortium-Elektrochemische Industrie.[48]

In preparing solid high molecular polymerization products from acetylene for use as constituents of explosives Wohl[204] brought acetylene into contact with cupric oxide at about 230°.

The N. V. Electro-Zuurstof-en-Waterstoffabriek[157] states that high molecular weight products similar to cuprene are obtained by passing acetylene at 200° to 400° over copper, nickel, iron, or their oxides to which a small quantity of magnesium has been added. It is claimed that the cuprene may be used as a catalyst for the production of more cuprene by adding a small proportion of magnesium. "The product may be used to decolorize blue methylated spirit or to clean dirty water."

Tiede and Jenisch[199] observed that separation of carbon and formation of oil began at 310° when acetylene was passed over massive copper. At 600° the oil formed was equivalent to 14.5 percent by weight of the acetylene treated.

Erdmann[57] obtained graphite by slow decomposition of acetylene over copper at 400°-500°C.

Berl and Hofmann[8] found that at 580° copper caused carbon deposition and did not favor polymerization.

Deposition of a small amount of carbon was the only reaction which Hodgkinson[89] observed when acetylene was passed over copper heated at its melting point (1038°).

Iron.—Iron reduces the temperature at which acetylene decomposes. In its presence, acetylene is converted largely to carbon and hydrogen, although olefins and paraffins, particularly ethane, form simultaneously. Oily liquid products containing benzene, appear also, but only to a slight extent. Reaction may be so vigorous that the metal, originally at a low temperature, becomes incandescent. This is notably true if pyrophoric iron is used.

Berthelot[11,12,14] noted a reduction in initial temperature of acetylene decomposition when iron was present, and as products reported carbon, hydrogen (about 50 percent of the volume of the acetylene decomposed), and "empyreumatic hydrocarbons," which were said to differ from the products of the action of heat alone on acetylene. Acetylene mixed with an equal volume of nitrogen, carbon monoxide, methane, or ethane decomposed a little more slowly than did the undiluted gas.

Ramsay[169] passed a mixture of acetylene and hydrogen cyanide through a "bright-red-hot" iron tube and obtained a small quantity of distillate which, judged by its odor, contained benzene.

Moissan and Moureu[149,151] found that pyrophoric iron, prepared by reduction of the oxide with hydrogen at the lowest possible temperature, caused rapid reaction when brought in contact with acetylene at ordinary temperatures, so that the metal became incandescent. While part of the acetylene was converted into a liquid product rich in benzene, the greater part was split into carbon and hydrogen.

Sabatier and Senderens[186,188] found that the passage of acetylene, or mixtures of acetylene and small proportions of hydrogen, over iron obtained by reduction of ferric oxide, raised the metal from room temperature to incandescence and produced a black voluminous carbon in which iron was disseminated. A small amount of brownish liquid condensed, which was made up almost exclusively of aromatic hydrocarbons. The gaseous product contained hydrogen. If the entire tube containing the reduced iron was kept above 180°, considerable hydrogenation of acetylene took place, this occurring beyond the point in the tube at which the metal was incandescent. The exit gas contained 64 percent of hydrogen with smaller amounts of benzene, olefins and ethane.

Hilpert[88] reported that decomposition of acetylene began at 300° in the presence of finely powdered iron, and at 400° reaction was so rapid that separation of carbon soon obstructed the heating tube.

Hodgkinson[89] reported that when iron was heated in acetylene, either pure or diluted, the metal, if in moderately small pieces as wire, frequently glowed, the glow passing along the whole mass of metal employed. Carbon deposited on the iron and carburisation occurred. Some of the carbon formed from the acetylene entered the metal, and some of the iron entered the soot-like deposit formed upon it, so that this deposit was found to contain as much as three percent of iron. The carburising of iron by heating in acetylene was very rapid, especially above 800°, and appeared to reach a maximum just below 1000°. Photomicrographs of iron carburised by heating in acetylene for periods of one to three hours at 1050° showed distinct diffusion of carbon into metal. In acetylene diluted with ammonia, iron was carburised more rapidly than by acetylene alone, and the amount of extraneous carbon deposited was reduced.

Tiede and Jenisch[199] observed that carbon separation began at 400° and oil formation at 540° when acetylene was passed over iron. At 600° the yield of oil was only 0.6 percent by weight of the acetylene treated. Hydrogen and paraffins made up 99 percent of the effluent gas, which was free from olefins and contained only traces of undecomposed acetylene. Comparative experiments without the catalyst gave an oil yield of 16.8 percent, an effluent gas containing 2.3 percent of hydrogen and paraffins, and 97.5 percent unchanged acetylene.

Bradley and Parr[38] found that acetylene was completely decomposed into its elements by contact with iron surfaces at 725°.

Rimarski and Konschak[170] produced almost complete decomposition of acetylene by slow passage at atmospheric pressure through an iron tube at 600° to 900°. No explosions occurred at 900° with pressures up to two atmospheres absolute.

Fischer, Peters, and Koch[66] found that when a mixture of 9 percent acetylene and 91 percent hydrogen was passed over iron a temperature of 300° to 340° was necessary to cause reaction. Both oil production and carbon deposition occurred.

Berl and Hofmann[8] reported that at about 580° iron was distinctly unfavorable to oil formation and caused heavy deposition of carbon.

Erdmann and Köthner[59] stated that when heated in acetylene iron acted somewhat like copper, aiding the conversion to oily hydrocarbons. As has been shown, most workers report that iron favors the formation of carbon and hydrogen.

The I. G. Farbenindustrie A. G.[99] claims the use of activated iron to treat acetylene for the preparation of lamp-black.

Nickel.—The effects of nickel on acetylene are summarized by Sabatier and Senderens[185,188] (referring largely to its action at 180°) as follows:—

1st. Rapid decomposition into carbon and hydrogen with polymerization to aromatic hydrocarbons.

2nd. Slow condensation into a solid hydrocarbon doubtless identical with cuprene.

3rd. Hydrogenation of the acetylene and of the aromatic hydrocarbons with product of unsaturated, and cyclo-aliphatic hydrocarbons.

"With a tube that is not externally heated, where the incandescence is intense and localized at a single point, the first effect is the greatest, the velocity of the gas rendering the subsequent hydrogenation unimportant."

Sabatier and Senderens[183] in their first work, found that finely divided reduced nickel increased in temperature when acetylene mixed with hydrogen was passed over it at ordinary temperature. Hydrogenation to ethane and ethylene was the predominant reaction, but a liquid product also formed consisting chiefly of paraffin hydrocarbons, with small amounts of higher olefins and benzene. The yield of liquid was greater the higher the temperature and the lower the proportion of hydrogen in the gas mixture. Low hydrogen percentage also increased the proportion of aromatic hydrocarbons in the product. With high acetylene concentrations the metal swelled up and became incandescent.

Moissan and Moureu[149,151] had earlier observed that the passage of acetylene at ordinary temperature over pyrophoric nickel (prepared by reduction of the oxide at the lowest possible temperature) caused the metal to become incandescent. The products were carbon, hydrogen and a liquid mixture rich in benzene.

In later publication Sabatier and Senderens[185,187,188] suggested that the incandescence might be due to an initial heating produced by combination of acetylene with hydrogen adsorbed by the metal, because there was no appreciable reaction below 180° when nickel was used from which hydrogen had been displaced by cooling the metal in nitrogen. About 180° a slow reaction began, but with slow gas flow there was no incandescence. At 250° reaction was more rapid, with both decomposition and hydrogenation of acetylene occurring. The largest constituent of the exit gas was ethylene, with smaller proportions of higher olefins, ethane, and aromatic vapors, but almost no hydrogen. The liquid products were reported to contain olefin, naphthene and aromatic hydrocarbons.

When a rapid current of acetylene was passed through a column of nickel of the same length at 200° to 250° the reaction was accompanied by incandescence, more free hydrogen and ethane, and less ethylene were formed. A small amount (15 cc.) of a deep-green fluorescent liquid was collected which contained hydroaromatic hydrocarbons. At the end of the experiments the heating tubes contained, besides carbon, a solid hydrocarbon resembling cuprene.

When nickel was kept between 180° and 300° for a long time in a slow current of acetylene, the metal swelled and became covered with a solid brown fibrous hydrocarbon similar in appearance to cuprene.

Charitschkow[43] conducted a mixture of acetylene and hydrogen over nickel shavings at 300°, and obtained a product that resembled naphtha. Five percent distilled to 150°, 14.5 percent between 150° and 200°, 29.25 percent between 200° and 270° and there remained a residue of 50.75 percent. All the fractions contained unsaturated hydrocarbons.

Tiede and Jenisch[199] found that carbon separation began at 360° and oil formation at 520° when acetylene was passed over nickel. At 600°, only 6.4 percent by weight of the acetylene was converted into oil. The rate of decomposition was made greater by increasing the fineness of division of the metal.

Hilpert[88] found decomposition of acetylene in the presence of finely divided nickel, to be increased when iron was also present. Above 300° carbon separation was so rapid as to fill the heating tube within a minute—a fact which made this catalyst useless for the preparation of benzene.

Hodgkinson[89] reported that when heated in acetylene, nickel became quite brittle and evidenced corrosion and pitting. Reaction was noted at about 200° and was rapid at 600°. The metal became covered with a soot-like deposit which contained 5 to 15 percent nickel. The metal was carburised more rapidly in a mixture of acetylene and ammonia than in acetylene alone, and the formation of soot was reduced.

Fischer and Peters[65] found hydrogenation from room temperature upwards when acetylene and hydrogen were passed over a catalyst of nickel precipitated on kieselguhr suspended in paraffin oil. At 250° a considerable amount of oily polymerization products was obtained.

The dehydrogenation of acetylene to lampblack by means of activated nickel has been claimed by the I. G. Farbenindustrie A.-G.[99]

Further experimentation with nickel is discussed in the section "Combinations of Metals."

Platinum.—Platinum, when finely divided, promotes the decomposition of acetylene to carbon and hydrogen. It is active even at room temperature, and when acetylene is passed over it becomes incandescent. The coating of the metal with carbon causes its influence to become less as the temperature rises, so that at 600° the reactions found are almost identical with those obtained with heat alone, except that there is a somewhat lower yield of oily products and a pronounced hydrogenation of acetylene through catalysis by the metal.

Moissan and Moureau[149,151] reported that a rapid passage of acetylene over platinum black, spongy platinum, or platinized asbestos at ordinary temperature caused incandescence. The products of the reaction consisted of carbon, hydrogen, and a liquid rich in benzene. If the acetylene was diluted, no incandescence occurred, but slow carbonization and liberation of hydrogen occurred.

Sabatier and Senderens[181,186,188] found that finely divided platinum-black had no action on pure acetylene at ordinary temperature, but that at 150° it caused rapid decomposition to carbon and hydrogen. The heat evolved brought the metal to incandescence, accelerating the decomposition, and caused the polymerization of much of the remaining acetylene into benzene, styrene, and reduction products of naphthalene and anthracene. The hydrogen formed reduced part of the acetylene to ethane and ethylene.

When a mixture of hydrogen and acetylene was passed over the platinum at room temperature, reduction to ethane and ethylene occurred; at 180° higher hydrocarbons, liquid and gaseous, were produced.[184]

Schützenberger[194] also reported that when platinum sponge is heated in a current of acetylene it becomes incandescent, the hydrocarbon is decomposed, and the metal swells and changes into a very finely divided and voluminous black powder containing considerable carbon.

Lewes[117] found that upon being passed through a platinum tube heated to 1000° acetylene yielded a mixture of gases of the following composition: acetylene 25.95%, other unsaturated hydrocarbons (chiefly ethylene, with some benzene vapor) 61.97%, saturated hydrocarbons 3.21%, carbon monoxide 1.01%, oxygen 0.38%, hydrogen 1.50%, nitrogen 5.98%. Each 100 cc. of gas treated yielded 0.095 gram of oil and 0.018 gram of carbon.

When Grehant[77] exposed acetylene in a firedamp eudiometer to a platinum spiral heated electrically to bright redness, it inflamed and deposited carbon.

Zelinsky and Kasansky[213] observed that no reaction occurred when acetylene was passed over platinized asbestos at ordinary temperature, but marked formation of liquid product began at 300°, and vigorous action occurred at 650°, forming a transparent bright yellow aromatic tar in yield of 45 to 50 percent. Forty-five percent of the tar distilled below 150°.

ii. Other Metals

Below are summarized the investigations which have been made on the decomposition of acetylene in the presence of other metals. The metals are taken up in alphabetical order.

Aluminum.—Kusnetsov[116] showed that when acetylene was passed over finely divided aluminum, heated nearly to its melting point (m.p. 659°) it decomposed almost completely into carbon and hydrogen, with formation of a small quantity of aluminum carbide. In similar experiments Durand[55] formed a carbonaceous mass which obstructed the reaction tube.

When Hilpert[88] passed acetylene over aluminum at 400° in a Jena glass tube, pine-tree shaped deposits of carbon formed at first but did not increase in size as reaction went on. As the temperature was increased the aluminum became black. A small quantity of tar formed which was like that obtained in the same tube when packed with glass fragments.

Hodgkinson[89] stated that the separation of a small amount of carbon was the only evidence of reaction when acetylene was passed over aluminum heated to its melting point.

Beryllium.—Durand[55] passed pure dry acetylene over powdered crystalline beryllium contained in a heated glass tube, and found that at about 450° the metal became black, due to a deposit of carbon, some polymerization occurred, and beryllium acetylide was formed.

Cadmium.—Cadmium acetylide mixed with carbon formed when Durand[55] passed acetylene over cadmium filings heated at about 500°.

Hodgkinson[89] reported that when heated to its melting point (321°) in a current of acetylene, cadmium did not change in physical state. A small amount of carbon deposited on the metal, and a greater amount combined with it.

Gold.—Durand[55] found that passage of acetylene over finely divided gold heated to 500° caused deposition of carbon on the metal. There was no evidence of acetylide formation.

Lead.—Carbon deposited when Hilpert[88] passed a slow stream of acetylene into molten lead (m. p. 327°). No benzene was formed even at 500°. Hodgkinson[89] confirmed this result.

Lithium.—Tiede and Jenisch[199] found that acetylene reacted rapidly with heated lithium forming acetylide and hydrogen. Marked separation of carbon also occurred.

Magnesium.—Berthelot[10] reported that an acetylide of magnesium formed when acetylene was passed over heated magnesium.

By cautiously heating powdered magnesium in a current of acetylene Moissan[150] obtained a mixture of carbon and an impure magnesium carbide. Keiser and McMaster[111] reported that when acetylene was passed over heated magnesium a black residue was produced which, with water, gave off acetylene and methyl acetylene and was, therefore, a mixture of magnesium allylide and carbide.

Novak[159,160,161] slowly passed acetylene over magnesium heated to temperatures between 400° and 700°. The products obtained, when decomposed by water, yielded acetylene and methylacetylene, showing that two carbides MgC_2, and MgC_3 had been formed. The reaction began at about 400° with the formation of the carbide MgC_2, the yield of which reached a maximum (40 percent of the reaction products) at 490° and then decreased. The formation of Mg_2C_3 began at 460° and increased regularly with the temperature up to 545°. The amount of carbon formed above 500° was always large. The products obtained between 465° and 515° were hard, compact masses, steel-gray in color, and were decomposed by water only slowly; those obtained above 550° were gray, brittle, and with water decomposed rapidly.

N. V. Electrozuurstof-en-Waterstoffabriek[157] add magnesium to metal or oxide catalysts to improve them for use in cuprene manufacture.

Manganese.—Manganese favors acetylene decomposition. In the work of Tiede and Jenisch[199] in which acetylene was passed over massive manganese in a heated tube, carbon separation began at 450° and oil formation at 480°, against 480° and 540°, respectively, without the catalyst. Under their conditions, when passed over manganese at 600° four percent of the hydrocarbon converted was changed into oil, as compared with 17 percent in the blank run. After contact with manganese but 8.7 percent of the hydrocarbon passed was recovered unchanged against 97.5 percent in a run with no catalyst.

Mercury.—On conducting acetylene through boiling mercury, Hilpert[84] observed small quantities of carbon, but no tar. The formation of traces of mercury alkyls was suspected. Deposition of carbon occurred when Durand[55] exposed acetylene to a temperature of about 500° in the presence of mercury vapor.

Erdmann and Köthner[59] reported that mercury was scarcely acted upon when heated to its boiling point in acetylene.

Palladium.—While no changes took place when Zelinsky and Kasansky[213] conducted acetylene over palladinized asbestos at ordinary temperatures, at 330° the heating tube filled rapidly with carbon. A small quantity of condensate formed, which contained unsaturated hydrocarbons, and blackened and resinified in air.

When Durand[55] conducted acetylene over finely divided palladium heated to about 500°, his only observation was the deposition of carbon on the metal.

When Campbell[41] passed the pure dry acetylene over palladinized copper oxide (one percent palladium), moisture was noticed at 225°-230° and at 300° the tube was choked by a heavy black deposit. No carbon dioxide was formed.

Potassium.—Berthelot[10] observed that when heated gently in acetylene, potassium caught fire and burned, sometimes explosively. An acetylide of potassium was formed, hydrogen was evolved and carbon deposited. Moissan[150] found that at ordinary temperature and pressure potassium had no action on acetylene beyond the formation of potassium acetylide.

Rubidium.—Erdmann and Köthner[59] found that at low temperature, in the presence of acetylene, rubidium became yellow, turning to brown, then took on a dark red glow, and finally became black and brittle. There was copious separation of carbon but no other product was identified.

Sodium.—At low temperatures the only action of sodium on acetylene is the formation of sodium acetylide or sodium carbide.[186] At higher temperatures carbon deposits. When de Forcrand[52] passed a slow current of dry acetylene over sodium in a small iron boat in a glass tube heated to dull redness, the product was 62.13 percent sodium carbide and 37.87 percent carbon. Perhaps the carbon found was formed by decomposition of sodium acetylide, as Moissan[160] found that when sodium acetylide was slowly heated in a tube of Bohemian glass, acetylene was evolved, a small quantity of liquid hydrocarbons formed, and sodium carbide deposited in the tube. When the heating was carried nearly to the melting point of the glass, the sodium carbide decomposed into carbon and sodium.

Sodium acetylide, hydrogen, and carbon were formed rapidly when Tiede and Jenisch[199] conducted acetylene over heated sodium.

Tin.—While no investigators have reported the use of tin alone, Bahr[3] found that tinned iron markedly repressed carbon formation and aided the conversion of acetylene to liquid products, until at about 475° the heat removed the tin coating. He employed tin-nickel alloys as well. Fischer, Schrader and Ehrhardt[67] also used a tinned iron tube. Fujio[73] passed acetylene through a tinned tube and reported that the tinning aided decomposition.

Uranium.—Durand[55] reported that when acetylene was heated to about 500° in the presence of finely divided uranium, carbon deposited on the metal, but there was no evidence of acetylide formation.

Zinc.—Erdmann and Köthner[59] found that a zinc surface was merely blackened when heated in acetylene to the decomposition temperature of the hydrocarbon. There was no evidence of the formation of an acetylide.

Carbon and a little tar (apparently containing no benzene) formed when Hilpert[88] passed acetylene into molten zinc. Hodgkinson[89] found zinc to have no significant action when it was heated to its melting point (419°) in a stream of acetylene.

Tiede and Jenisch[199] made comparisons between results of passing acetylene for a period of three hours through an empty tube at 600°, and results when gas was passed at the same rate and temperature through the tube containing a porcelain boat filled with a metal.

Of the many metals tried the following changed the course of the reaction:

Lithium
Sodium
Iron
Potassium
Nickel
Copper
Manganese
Finely divided palladium and platinum

With the following metals the results of parallel runs with and without the contact agent were alike within experimental error.

- Aluminum
- Antimony
- Bismuth
- Boron
- Cadmium
- Calcium
- Chromium
- Gold
- Lead
- Magnesium
- Molybdenum
- Mercury
- Platinum and palladium in massive form
- Silver
- Silicon
- Tantalum
- Thallium
- Tin
- Titanium
- Tungsten
- Uranium
- Zinc
- Zirconium

iii. Combinations of Metals

When a mixture of acetylene (9 percent) and hydrogen was passed over an iron-copper-alkali-catalyst in a hard-glass tube at 250°, Fischer, Peters, and Koch[66] found that 40 to 70 percent of the acetylene was converted into oil. As the catalyst was not readily poisoned, a high degree of purity in the gas mixture was unnecessary. When the ratio of copper to iron in the catalyst exceeded 1:10, the tube quickly became stopped by a deposit of cuprene, but with a 10 Fe:1 Cu catalyst the tube was operable for 10 days. The addition of nickel to produce a catalyst 10 Fe:1 Cu:1 Ni diminished the formation of cuprene still more and gave a yield of 50 to 55 percent of liquid product, containing 75 percent benzene and 25 percent of heavier oil.

At the same temperature an iron-nickel catalyst (10 Fe:1 Ni) caused a 60 percent conversion into liquid, two-thirds of which was benzene.

With the catalyst 2 Fe:1 Ni at 250°, 30 to 35 percent of the acetylene passed was converted into liquid containing from 85 to 90 percent benzene. Hydrogenation taking place at the same time produced considerable ethane (9 percent of the gaseous products) and smaller amounts of ethylene and higher unsaturated hydrocarbons.

In the presence of the catalyst 10 Cr:1 Ni about 30 percent of liquid products were obtained at 250°. In these experiments variation of the temperature over a range of 100° and fluctuation in the rate of passage of the gas from 2 to 12 liters per hour did not affect the yield or quality of the oils. The products consisted of a heavy oil, free from paraffin wax, which collected in the receiver, and a light oil, 90 percent boiling between 50° and 150°, which was absorbed by activated charcoal. The light oil contained 60 percent of unsaturated hydrocarbons. One cubic meter of coke-oven gas (which contained acetylene) yielded 85 grams of liquid, of which 75 percent was light oil.

Fischer and Peters[65] studied the hydrogenation and polymerization of acetylene in the presence of catalysts suspended in a heavy oil to compare the results given by catalysts used alone and catalysts suspended in liquid. Use of the catalyst in oil suspension had the advantage, particularly in an exothermic reaction, of allowing accurate temperature control and ready dispersal of heat produced. In this work the catalyst was mixed with paraffin oil or methyl naphthalene, and fine bubbles of a mixture of acetylene and hydrogen passed upward through the mixture. The oil was treated with hydrogen in the presence of nickel before use in the acetylene runs.

The progress of the reaction was determined by noting the decrease in the volume of the gas. With a nickel or copper catalyst precipitated on kieselguhr, reaction was evident at 60°, and contraction a maximum at 170°-230°. At temperatures from 100° to 300°, the highest used, all the acetylene was converted. Comparison of results with a nickel-iron-thorium catalyst "dry," and suspended in oil, indicated a greater dependence of reaction rate upon temperature in the liquid studies. With pure nickel, hydrogenation was noticeable even at room temperature. At first only ethane and ethylene were produced, but at 250° the products were ethylene 24.5%, ethane 46.8%, oil, composed of about one-third unsaturates, 22%, "benzine" 6%. When this catalyst was used alone at the same temperature, more polymerization occurred than when the liquid was present. A copper catalyst produced some cuprene as well as the products mentioned.

For large yields of higher hydrocarbons, a mixed catalyst was used. A nickel-iron preparation with the metals in the proportion 1:9 gave at 200°, in a 1:2 mixture of acetylene and hydrogen, 17.4% conversion of the acetylene to ethylene, 5.1% to ethane, 74.3% to liquid hydrocarbons. This is a higher yield, and the product was lighter than that produced by the same catalyst used "dry."

With a copper catalyst, reaction began at 100° and maximum contraction occurred at 230°. Much of the acetylene went to ethylene, some to ethylene and "cuprene tar." No propane, propylene, or higher hydrocarbons were formed over copper alone, although some of these products were always produced when using a mixed catalyst containing copper, iron, and nickel.

By passing acetylene over an alloy containing equal percentages of nickel and tin in the form of fine shavings, Bahr[3] obtained at 280° a condensate with the distinct odor of benzene, at first transparent but soon colored a greenish brown. At about 430° separation of carbon began, and quickly stopped the tube for a distance of 3 to 4 cm. from the entrance of the gas. On lowering the temperature to 380° the carbon separation stopped. With an alloy of 75 percent tin and 25 percent nickel, carbon separation was not quite as profuse, but the reaction was otherwise little different.

When tinned iron turnings were used as contact material a clear condensate appeared in small quantities from 250° and did not take on a brown color even with considerable increase in temperature. As long as the turnings retained the tinned surface there was little evidence of carbon separation. At high temperatures the tin flowed from the turnings leaving the iron surfaces free. At 475° to 480° separation of carbon was observed at a number of points on the catalyst.

Fischer, Schrader and Ehrhardt[67] reported that on passing a mixture of acetylene and hydrogen (in the volume ratio 1:3) through a tinned iron tube at 675° to 700° about 8 percent of the acetylene was converted into benzene. Considerable carbon separated in the heating tube. Decomposition was also studied in the presence of a tin-iron alloy.

Tiede and Jenisch[199] found that alloys of copper with gold, copper with zinc, and copper with aluminum were inactive, while an alloy of copper with nickel aided the decomposition of acetylene. Hilpert[88] passed acetylene over brass turnings without noting any catalytic effect.

Pictet[163,164,165] claimed carbon and hydrogen formation from acetylene or a mixture of acetylene with other hydrocarbons, by their passage through a steel, iron, or porcelain tube, the front part of which was heated to about 500° and the remainder cooled to absorb the heat produced by the dissociation.

Prudhomme[168] outlined a process for manufacturing liquid fuel having the general properties of petrols and benzols, which consisted in adding gases rich in acetylenic hydrocarbons to water gas or producer gas and passing the mixture over a hydrogenation catalyst, then over a dehydrogenation catalyst, and finally over pumice impregnated with nickel and cobalt to effect polymerization of the acetylene hydrocarbons.

Cyclic hydrocarbons, particularly those of a hydroaromatic nature, are prepared by I. G. Farbenindustrie[96] by passing acetylene alone, or in mixtures, over heated condensation catalysts, such as compounds of arsenic or of metals, except arsenic, having a specific gravity of 4.4 and belonging to the second to seventh groups. The products of this step are passed with hydrogen over metallic hydrogenating catalysts. The condensation is effected at 250°-300° and the subsequent hydrogenation at 150°-250°.

I. G. Farbenindustrie[97] thermally decomposes acetylene or other unsaturated hydrocarbons at temperatures below 500°, the upper temperature limit being selected so that 90 percent of less conversion to carbon black occurs. The remainder of the acetylene is converted into saturated hydrocarbons. Cobalt, iron or nickel may be used as catalysts, with such activators as compounds of chromium or of the alkali metals.

iv. Other Substances

Ferric Oxide.—Gooch and Baldwin[76] found that ferric oxide heated in acetylene at temperatures varying from 150° to 360° glowed and became covered with a dark carbonaceous deposit. The iron content of this deposit varied from 2.80 to 5.86 percent.

Silver Oxide.—Gooch and Baldwin[76] found that acetylene acts upon silver oxide at ordinary temperature, giving silver, perhaps resulting from decomposition of an acetylide first formed. The reaction is usually explosive.

Other Oxides.—Berl and Hofmann[8] reported that the oxides which they studied—stannic oxide, calcium oxide, and silicon dioxide—were unfavorable to acetylene polymerization, and turned the reaction toward formation of methane, hydrogen, and carbon.

Ceric Sulphate.—The Compagnie Générale de Produits de Synthèse[47] claimed that hydrocarbon gases containing acetylene and methane coming from a gas producer were polymerized by heating to about 80° in the presence of a catalyst containing ceric sulphate.

Ferric Nitride.—Hodgkinson[89] reported that ferrous nitride when heated in acetylene became highly carburized. Ammonia was also formed.

Ferrous Sulphide.—To avoid carbon deposition during polymerization Bahr[3] heated acetylene in the presence of ferrous sulphide. He used this substance because sulphur compounds had been found effective in checking the decomposition of carbon monoxide to carbon and carbon dioxide. When the acetylene was passed over the ferrous sulphide in a glass tube, the first drop of condensate, of pale yellow color, appeared at 300°. Soon a mobile dark brown tar flowed along the tube. No carbon separation was noticeable and the catalyst retained its metallic luster. Visible separation of carbon occurred above 430°, accompanied by rapid formation of tar fog. Reduction of the temperature to 350° did not stop the separation of carbon on the contact material. Dilution of the acetylene with 50 percent of methane made no noticeable change in the reaction.

It was suggested that failure of the ferrous sulphide to stop carbon formation entirely was due to slow conversion of the contact layers into metallic iron. Iron decomposes acetylene from 300° upwards with separation of carbon. Fujio[73] also used a metal tube coated with iron sulphide and claimed that it aided decomposition and increased the proportion of low-boiling constituents in the tar.

Nickel Carbonyl.—Binnie[29] found that nickel carbonyl, added either as such or made during the process by contact of added carbon monoxide with the nickeled tube, gave yields of oil up to 65 percent when a mixture of acetylene, hydrogen and nitrogen was heated with it at 190°. The oil was low boiling and appeared to contain a large proportion of olefins.

Phosphoric Acid.—Bahr[3] passed acetylene through pumice impregnated with concentrated phosphoric acid. The first separation of carbon was detected at 470° to 480°.

Sodium and Potassium Hydroxides.—Some decomposition of acetylene to carbon and hydrogen took place when Fry, Schulze and Weitkamp[72] passed the gas through a fused mixture of equimolar weights of sodium and potassium hydroxides maintained at 300° to 325°. Methane, and sodium and potassium orthocarbonates were also produced.

Stannous Chloride.—Acetylene passed over pumice which had been impregnated with stannous chloride and heated in hydrogen at 500° showed little change beyond slight separation of carbon.[3] When acetylene with ammonia was passed into the tube filled with stannous chloride-pumice at 400°, as soon as the mixture reached the contact material, flame struck backward in the gas stream and then went out, with dense separation of carbon. The pumice became covered with ammonium chloride and there was a slight formation of tar with a pyridine-like odor.

3. In Admixture with Other Gases

The dilution of acetylene has been found to affect both the speed of reaction and the nature of the products obtained. Some pyrolyses of diluted acetylene have already been taken up. Others are discussed below, particularly those in which a high proportion of diluent is used.

Berthelot[11] found that acetylene mixed with an equal volume of nitrogen, carbon dioxide, methane, or ethane decomposed a little more slowly than the undiluted gas.

Catalysis of acetylene mixed with methane or hydrogen (10 percent acetylene to 90 percent of diluent) was studied by Fischer, Bangert, and Pichler.[64] They found that in this mixture active carbon, silica gel, and to some extent pumice catalyzed the acetylene polymerization, but mica, graphite rods, and barium chloride, or active carbon or silica gel treated with alkali or metallized, produced practically no change at 600° and caused heavy carbon deposition above this temperature. In order to obtain oil from the dilute acetylene in an unpacked tube, a temperature between 680° and 730° was necessary, which was higher than that required with acetylene alone. In a long run, at 660° to 680°, the oil formation reached 40 percent of the acetylene treated. When after 30 days the oil yield began to drop, it was restored by increasing the temperature to 700°-720°. It was then possible to continue the run for 55 days.

Fujio[73] noted that hydrogen, methane, carbon monoxide and carbon dioxide had a marked effect upon the chemical nature of the tar produced by acetylene pyrolysis. Their presence caused reaction to go on more smoothly. Carbon dioxide caused the appearance of a greater percentage of light oils in the product. Fujio also noted, as had others, that the carbon deposited on the catalyst by decomposition of acetylene seemed to play an important rôle.

Binnie[29] pyrolyzed mixtures containing small percentages of acetylene with hydrogen and nitrogen. A mixture of 4 percent acetylene and 96 percent hydrogen passed through a silica tube at 600° produced ethylene and methane. Charcoal or silica gel were not effective catalysts, while copper, iron-nickel, or cobalt precipitated on silica gel were very reactive, and transformed acetylene at little above room temperatures. Reduction of the hydrogen content of the mixture to 20 percent by addition of nitrogen decreased hydrogenation and increased the formation of oil, which reached a maximum of 40 percent of the acetylene used. A nickel catalyst produced ethane but no oil.

Addition of nickel carbonyl in carbon monoxide, or passage of the mixture of acetylene, nitrogen, hydrogen and carbon monoxide through a metal tube coated with nickel, gave increased yields of oil, reaching 65 percent of the acetylene at 190°. The oil boiled to 85° and was apparently olefinic, as it reacted violently with sulfuric acid and bromine. Oil formed in the presence of iron or sulfur was higher boiling.

Patents.—The I. G. Farbenindustrie A. G.[95] reports that an oil was obtained by passing a mixture of acetylene and ethylene at 525°-550° through an externally heated aluminum tube within which silicon was deposited on a plate. An oil of lower boiling point was produced by passing a mixture of acetylene, ethylene, and nitrogen through a vessel coated internally with tin and then with powdered silicon. A condensate containing 13 percent of butadiene was obtained by passing a mixture of acetylene and ethylene through a manganese-copper tube coated internally with tin, while benzene was said to be formed when using a manganese, copper or brass tube coated internally with zinc.

In further patents, the I. G. Farbenindustrie A.-G.[98,100] claims that valuable hydrocarbons such as benzene and butadiene may be obtained from reaction of olefins such as ethylene with acetylene at a high temperature, under such conditions that the hydrocarbons come in contact with elements of the fourth group of the periodic system such as tin, silicon, lead, carbon in the form of graphite, or with zinc or aluminum or alloys having a high content of these elements.

According to Lichtenhahn[119] addition of 5-15 percent of nitrogen to acetylene prior to treatment by the action of heat and catalysts restricted or prevented the coking or discoloration of the condensation products. It was claimed that coke losses were reduced to less than 6 per cent.

N. V. de Bataafsche Petroleum Maatschappij[156] forms oily liquids, boiling from 60°-320°, by heating acetylene to about 440° in the presence of a catalyst such as finely divided iron or magnesium bromide, in an inert liquid medium such as liquid paraffin, transformer oil, or a hydronaphthalene. Ethylene may be added to the acetylene before subjection to this process.

C. *Action of Chemical Reagents.*

Cuprous Chloride.—Nieuwland, Calcott, Downing, and Carter[158] have accomplished the controlled polymerization of acetylene at ordinary temperature by passing it into a cuprous chloride solution containing ammonium chloride to increase the solubility of the copper salt. They isolated vinylacetylene, divinylacetylene and a tetramer of acetylene believed to be 1, 5, 7-octatriene-3-ine.

The first step in this reaction, these workers believe, is formation of a complex cuprous salt which is in equilibrium with normal acetylene and activated acetylene. An activated acetylene molecule then reacts with a molecule of normal acetylene to produce vinylacetylene:

$$HC{\equiv}CH + {=}C{=}CH_2 \longrightarrow HC{\equiv}C{-}CH_2{=}CH_2$$

By reaction with an activated acetylene, vinyl acetylene may then produce divinylacetylene, or a vinylacetylene molecule may become activated and by reaction with a like molecule produce the tetramer. The relatively low yield of tetramer shows this second reaction to be much slower than the vinylacetylene-acetylene reaction. There is also the possibility of an active vinylacetylene molecule reacting with acetylene to form the compound: $H_2C{=}CH{-}CH{=}CH{-}C{\equiv}CH$ which might itself double to a compound $C_{12}H_{12}$. The existence of these last two substances is indicated but has not been proved.

Vinylacetylene is a colorless liquid boiling at 5°. On heating under pressure, it readily polymerizes, with or without polymerizing agents, to form viscous drying oils and finally hard resinous solids. These polymers contain acetylenic hydrogen.

Divinylacetylene is also a colorless liquid, of alliaceous odor, boiling at 83.5°. It readily absorbs oxygen to form an explosive peroxide, and is itself extremely dangerous to handle, as on standing it turns into explosive gels and resin. It decomposes thermally at 105°-110°, but when heated at lower temperatures in an inert atmosphere forms by polymerization a viscous liquid and hard brittle resin. Intermediate in this polymerization are liquids which are drying oils, and are converted by oxidation and polymerization into films which are softened by no solvent and resist all but the most vigorous oxidizing agents. The development of explosive products in the liquid may be prevented by antioxidants.

The C_8H_8 "tetramer" is a colorless liquid chemically similar to divinylacetylene, which polymerizes on gentle heating, and has an apparent boiling point of 156°, with violent decomposition.

A patent of Collins[46] covers the polymerization of divinylacetylene and this tetramer to drying oils. Temperatures of 80° to 100° are used, the degree of polymerization attained depending upon the time and temperature of treatment. In examples, it is stated that four hours refluxing of divinylacetylene in the presence of air (85°-90°) produces a 12-18 percent yield of a viscous polymer having the general properties of a bodied drying oil. The acetylene tetramer is quantitatively converted into a drying oil by heating for three hours at 100°. These substances can also be polymerized in mixture, and in the presence of cobalt driers and of solvents.

Aluminum Chloride.—Baud[5] reported that dry acetylene was rapidly absorbed by anhydrous aluminum chloride in the cold, and at an increased rate of 70°. When it was passed over the salt at 70° to 130°, in part it formed a black sublimate with the empirical composition $7\ (C_{10}H_{15.6}),\ 2Al_2Cl_6$. When this was distilled with quick-lime, three hydrocarbon fractions were obtained with the following boiling ranges and empirical formulas: 150°-190°, between $C_{10}H_{18}$ and $C_{10}H_{16}$; 190°-260°, $C_{10}H_{16}$; 260°-300°, $C_{10}H_{14}$. The greater portion of the acetylene and aluminum chloride formed a non-volatile, black substance easily taking up oxygen, with empirical formula $7\ (C_{20}H_{15}),\ Al_2Cl_6$. On distillation with quicklime this substance yielded a small hydrocarbon fraction corresponding in composition to the formula $C_{15}H_{20}$, boiling from 150°-350°. The higher boiling portions of the distillate were nearly solid and contained anthracene.

D. *The Explosive Decomposition of Acetylene including Detonation and Action of Electric Sparks.*

Acetylene is decomposed to its elements by proper excitation. If a wire is heated in an atmosphere of acetylene, for example, a charge of some detonator, as mercury fulminate, exploded in it, or a spark passed, decomposition will ensue, which may be local, confined to the immediate vicinity of the exciting agency, or may produce a flame wave which will spread with greater or less rapidity throughout the mass of the hydrocarbon. Conditions of temperature and pressure and the rapidity with which heat is dissipated determine whether the breakdown of acetylene is restricted to a small zone, whether it becomes a flame, or a decomposition of explosive violence. At atmospheric pressure, for example, explosion of acetylene is not produced by sparks, but when the gas is under slightly increased pressure, sparking may bring about violent detonation. It is obvious that exact knowledge of acetylene decomposition, and of the conditions under which explosion is possible, are essential to its safe handling and utilization. Because of the widespread commercial use of acetylene, its explosive properties have been extensively investigated.

Berthelot[9] was the first to report that acetylene was decomposed by electric sparks with deposition of carbon.

de Wilde[53] also decomposed acetylene by passage of induction sparks between platinum points.

Maquenne[134] found that acetylene decomposed only partially when 0.1 to 0.2 gram of mercuric fulminate was exploded at the center of a liter flask filled with the gas. The residual gas contained more than 90 percent of acetylene. Decomposition was accompanied by formation of a small cloud of lampblack, and was limited to the gas in the sphere of action of the fulminate. With one gram of the fulminate exploded at the end of long lead tubes filled with acetylene the explosive wave traveled through a distance of 5 to 8 meters, depending upon the diameter of the tubes, decomposing the gas to carbon and hydrogen.

Further work by Berthelot and Vieille[25] confirmed the finding that when acetylene under ordinary pressure was subjected to the action of an electric spark, a red-hot platinum or iron wire, or a charge of fulminate, decomposition did not extend far. When the gas was under a total pressure exceeding two atmospheres, however, the gas acted much as does an explosive mixture. If decomposition was produced at any point it spread rapidly through the entire volume of the gas, which decomposed into hydrogen and bulky pulverulent carbon. Under an initial pressure of 21 kg. per sq. cm., the pressure developed by the decomposition was 210 kg. per sq. cm., and the change was complete in 0.018 second.

Liquefied acetylene was also readily decomposed, though relatively slowly when the change was initiated by simple ignition. When a bomb containing both liquid and gas was set off there was a change in the curve of pressure which indicated two distinct phases of the explosion, one probably corresponding to the decomposition of the gaseous part, and the other, which lasted longer and raised the pressure much higher, to the decomposition of the liquid. With 18 grams of the liquid in a steel bomb of 48.96 cc. capacity, the final pressure was 5,564 kg. per sq. cm.

Shock caused by fall of the steel bomb from a height of 6 meters did not cause the explosion of either compressed or liquefied acetylene. If the bomb broke there was no explosion of the gas compressed to 10 atmospheres, but if the vessel contained liquid acetylene, the fracture was followed after a short time by an explosion. When liquid acetylene was decomposed by a small quantity of fulminate, violent detonation took place and the fragments of the bomb were covered with carbon liberated from the gas.

The publication of this work attracted much notice and was widely quoted.[44,100]

Berthelot and Vieille[27] showed that an intermediate pressure zone, between normal pressure, when explosion does not occur, and a total pressure of two atmospheres where explosion is almost certain, the production of an explosion depended on the means of excitation used and the amount of cooling of the system. They brought about decomposition in this intermediate zone in vessels and tubes of various sizes, thus varying the amount of cooling, and using for initiating reaction an incandescent metal filament or a charge of fulminate. Explosion was produced in glass vessels by ignition at an excess pressure of 52 cm. of mercury, and at 17 cm. of mercury by detonation. In a long metal tube, there was no propagation of the decomposition even when an excess pressure of one atmosphere was used, regardless of whether the excitation was produced by a charge of fulminate or a hot wire.

Bone and Cain[30] and Bone and Jerdan[33] reported that rapid decomposition of acetylene and deposition of carbon occurred when an arc between carbon electrodes acted upon the gas. The gaseous product was hydrogen with a few percent of methane, and the presence of a minute quantity of naphthalene was said to be apparent from the odor.

Gerdes[75] early discussed the decomposition of acetylene with reference to the hazard involved in using this gas to light railroad coaches. He reported that sufficient local overheating might occur when a small amount of water was added to a large amount of carbide—bringing the entire mass to glowing—to exceed the temperature of acetylene decomposition. It was found at the Pintsch works that heating a cylinder containing acetylene compressed to 6 atmospheres, or heating a tube leading to such a cylinder caused violent explosion. Mixtures of acetylene and oil gas decomposed less readily than the pure hydrocarbon, and such a mixture containing 30 percent acetylene was considered safe to use. Addition of 50 percent hydrogen to acetylene made it much less dangerous.

Körting[114] also found that mixtures of oil gas and acetylene were less subject to explosive decomposition than acetylene alone.

Berthelot and Vieille[28] studied mixtures of acetylene with hydrogen and city gas, and found that a decomposition initiated by a hot wire in a 50:50 mixture of acetylene and hydrogen proceeded only a limited distance even at a pressure of 4 atmospheres, while in a 1:3 mixture a pressure of 10 atmospheres was safe. The limits were somewhat lower in small vessels. Higher limits were found in city gas and acetylene mixtures, on account of the absorption of heat by carbon monoxide at high temperature.

Lewes[118] found that contact of water with a large amount of carbide in an acetylene generator could produce a temperature of 804°. A temperature of 780°, he stated, was sufficient to cause complete decomposition of acetylene, while below this polymerization began, producing benzene, styrene, anthracene, naphthalene, as well as ethylene and methane.

Berthelot and Vieille[26] also investigated the explosive properties of acetone solutions of acetylene. Explosion of a fulminate charge in the gas space of a cylinder containing a 41.25 percent solution of acetylene in acetone under pressure of 13 kg/cm² caused no change in the solution. This may be contrasted with the behavior of liquid acetylene, which shattered the steel flask on similar treatment. However a 64 percent acetylene solution under 20 kg/cm² pressure exploded.

The decomposition of the solution, they noted, was slow, requiring 0.4 second, as compared with .00004 second for the explosion of a mixture of hydrogen and oxygen. It was also much slower than the combustion of acetylene. The acetone of the solution was decomposed during the explosion.

Vogel[200] summarized the available information on acetylene decomposition. Liquid acetylene is exploded by a glowing platinum wire or silver fulminate. It explodes even at ordinary pressure, and the explosive force approaches that developed by gun cotton. A sharp shock causes acetylene breakdown only when accompanied by warming or incandescence of a solid substance. This warming may occur during acetylene compression or its passage through a narrow opening. Sharp pressure changes may explode compressed or liquid acetylene.

Janet[104] found that a solution of acetylene even at a pressure above 10 atmospheres—considered by Berthelot and Vieille the safety limit—is safe when it is impregnated in infusorial earth or other porous material.

Claude[45] found that at −80° acetone dissolved 2000 volumes of acetylene at atmospheric pressure, and increased 4 to 5 times in volume. A platinum wire heated electrically to redness could be kept indefinitely in this solution or in liquid acetylene without explosion occurring.

At a conference on the dangers involved in handling acetylene[14] it was reported that acetylene might be passed through a tube at 600°-1,000° without explosion. It was advised that all copper be kept out of contact with compressed acetylene. Pictet was reported to have liquefied acetylene at −80° and to have failed to explode it even by dropping it off cliffs.

Berthelot and Le Chatelier[24] made photographic studies of the velocity of explosion of acetylene detonated by fulminate or chlorate. The acetylene was under pressures of from 6 to 36 kg/cm². The flame was observed in a glass tube, and was found to increase continuously in speed, usually rupturing the tube before a uniform velocity was obtained. Velocities of 1,000 meters per second at 6 kg. and 1,600 meters per second at 30 kg. were observed.

Mixter[145] exploded pure dry acetylene confined in glass tubes under a pressure of 3 atmospheres and heated to temperatures of 325° to 450°, by electric sparks passed between platinum electrodes projecting into the gas. Decomposition was incomplete, as it was also in experiments carried out in a bomb at room temperature. Twenty to 50 percent of acetylene remained in the residual gas. Mixter believed that decomposition was more complete in the experiments of Berthelot and Vieille[25] under pressure varying from 5 to 30 atmospheres.

In further detonation experiments,[146] in which the acetylene was mixed with nitrogen, hydrogen cyanide was produced. As a rule, the amounts of hydrogen cyanide tended to increase as the proportion of nitrogen in the mixture was made larger, but the results were not regular. Ammonia was also detected in some cases, but no cyanogen was found. The relationship between the initial pressure and the amount of acetylene found after explosion was not precisely determined, but the quantity of acetylene increased with pressure up to 4 percent at 3 atmospheres and diminished again at 5 atmospheres.

Using higher pressures of acetylene in a steel bomb immersed in a calorimeter, initiating explosion of the gas by means of electric sparks, Mixter measured the heat of dissociation of acetylene.[147] He found 53,300 calories per gram mole or 2,050 calories per gram. In these experiments at high pressures no measurable quantity of acetylene was found in the gas remaining after an explosion.

A number of cylinders containing liquid acetylene were destroyed in work described by Rasch[170] in a way to afford as much information and satisfy as much curiosity as possible. Against the gas space of one cylinder a large charge of picric acid was exploded, which failed to detonate the liquid below, although the cylinder was ruptured. A smaller charge of picric acid exploded against the lower portion of the cylinder caused violent explosion of the liquid hydrocarbon, which produced a dense cloud of smoke and pulverized the cylinder. A rifle bullet through the gas space caused no explosion, and unfortunately the supply of acetylene ran out before the effect of a bullet through the liquid could be tried.

Frank[71] found that when pure acetylene was exploded under a pressure of five or six atmospheres, the lampblack obtained was contaminated with oily products. The carbon formed was free from oil, however, if the acetylene was mixed before explosion with carbon monoxide or carbon dioxide in the proportions of the equations:

$$C_2H_2 + CO = H_2O\text{, and}$$

$$2C_2H_2 + CO_2 = 5C + 2H_2O$$

The initial pressure of the acetylene-carbon monoxide mixture was at least six atmospheres. Under these conditions the maximum pressure developed during the explosion was 40 to 50 atmospheres. Because of the high temperature of the explosion (it was stated) the reaction was incomplete and only 85 percent of the theoretical quantity of carbon was obtained. The lampblack formed in this way had a high specific gravity (1.93 to 2.0) and an electrical conductivity much greater than that of any other form of carbon.

Caro[42] contributed a lengthy discussion of the causes of acetylene explosions, in which he summarized prior work in detail and reported a considerable amount of experimentation.

Burrell and Oberfell[40] observed that a "mild" explosion accompanied by the formation of much carbon resulted when acetylene under 5 atmospheres pressure was exposed to a white hot platinum coil. The gas exploded "with great violence" at a pressure of 3 atmospheres when a small electric spark from an induction coil was used as the source of ignition.

When Fowler and Mardles[68] subjected acetylene to induction sparks between copper electrodes a bright flash occurred in the bulb containing the acetylene and threads of carbon bridged the spark gap.

Alexejew[2] found that when acetylene decomposition was started by a hot wire, the tendency to form a flame wave at constant temperature was favored by increase in pressure, and at constant pressure by increase in temperature. He proposed a relationship $N p^2 + M p\sqrt{T} = 1$ for conditions of propagation of the decomposition, where M and N are constants. This is only approximate, as the amount of cooling which occurs during the decomposition, a vital factor in its spreading, is largely determined by the vessel in which reaction takes place. Thus, in a tube of 3 cm. diameter at 280°-440° Alexejew found that no flame was produced, while in an 8.5 cm. tube violent explosion occurred at 260°. At any given temperature, a small addition of hydrogen, nitrogen, ammonia, or ethylene, raised the pressure necessary for inflammation; a somewhat greater addition reduced the necessary pressure, and large addition caused a new increase in the pressure needed. Slight addition of mercury vapor somewhat lowered the "inflaming pressure," while with more mercury an increase was observed. These results he explained from a kinetic standpoint, the explanation involving the formation of cyanogen when nitrogen was added.

Rimarski and Konschak[177] found that in contact with heated iron surfaces acetylene decomposed explosively at temperatures above 510°, while below this temperature no explosion occurred. Some contact agents greatly lowered the temperature of decomposition. Copper at 300°-250°, finely divided iron under 180°, finely divided silver gently heated caused acetylene breakdown, and reduced the flashing temperature to 460°-500°. Iron, copper and manganese oxides were able to cause explosive decomposition between 240° and 310°, while active carbon, aluminum oxide, and silicon dioxide had a midposition, producing explosive decomposition at 400°-500°. By adiabatic compression in the presence of iron, acetylene was broken down by a pressure of 27 kg./cm^2.

Following a disastrous fire in an acetylene manufacturing plant, Rimarski[175] reviewed the literature on the explosive decomposition of acetylene, summarized his own work on this reaction, and outlined the safeguards necessary in handling this hydrocarbon. Some of this work had been previously published from the Physikal-Technischen Reichsanstalt.[173]

He reported that "glowing" carbide—carbide made incandescent by adding a small amount of water to a large amount of carbide—caused explosion of acetylene at 1.6 atmospheres total pressure. A glowing platinum wire caused decomposition of pure, dry acetylene as under the following conditions:

At 10° under a pressure 0.6 atmosphere above atmospheric
100° " " " 0.33 " " "
140° " " " 0.10 " " "

If the wire was fused in the gas, decomposition was produced still more readily. Water vapor raised the explosive limits.

The Reichsanstalt work showed that when passing acetylene through a heated tube:

1. At 500° at pressures to 3 kg./cm² no explosive decomposition occurred.
2. At 510°, under 2.05 kg./cm² pressure, and a flow rate of 0.4 liters per minute, explosion first occurred. With increasing temperature and flow rate the pressure necessary for explosion dropped.
3. Extrapolation to zero (quiet gas) gave 1.37 atmospheres at 540°-590° as an explosive limit.
4. A pressure of 170 kg./cm² had to be attained to explode acetylene by adiabatic compression.

When working at initial pressures up to 9 kg./cm², the final explosion pressures were about eleven times the initial. Presence of water or acetone vapor reduced the pressure attained. If a detonation wave occurred, however, the pressure increase might be much greater, even reaching 80 times the initial pressure. Rimarski[174] had reviewed this work briefly in earlier papers.

At about the same time Schläpfer and Brunner[191] investigated the relation of polymerization and thermal decomposition of acetylene to its explosion. They introduced acetylene into small evacuated quartz or Pyrex flasks, at definite temperatures. Decomposition occurred only at temperatures above 500°; polymerization was already apparent at 300° and went on rapidly above 450°. Polymerization released heat and this heat, if not dissipated, could bring the acetylene into the explosive zone. By choice of decomposition conditions, however, polymerization could be practically eliminated. In the technical preparation of carbon by spark decomposition of acetylene, for instance, the gas is heated with extreme rapidity, producing a carbon uncontaminated with tar.

The reaction at 420° was studied kinetically and appeared to be bimolecular. As glass powder produced no change in reaction rate the changes occurring were believed to be homogeneous. Pease,[162] it will be remembered, came to the same conclusions. Fine iron powder catalyzed decomposition of carbon to its elements, an effect intensified by deposition of carbon upon it. If the iron was present in but small amount, decomposition and polymerization went on simultaneously.

Explosive decomposition of acetylene, they stated, might occur by local overheating and spreading of the decomposition to all parts of the gaseous mass, usually as a "puff," but in some cases as a real explosion, or by heating of the entire mass to explosion temperature. In the work of Berthelot and Vieille, and of Rimarski, no regular relationship had been found between temperature of streaming gas and pressure necessary to make explosion possible, so that this spontaneous decomposition of acetylene appeared to be different from the combustion of hydrocarbon mixtures with oxygen. Schläpfer and Brunner found a direct relationship, the pressure needed for explosion dropping as temperature increased. Pressure variation was of greatest moment at high temperatures. They attributed the discrepancy between their work and Rimarski's to the presence of finely divided carbon in the latter's experiments. Carbon accelerates the decomposition, but does not reduce the pressure necessary to explosion and may increase it. At the surface of the carbon, and of finely divided iron also, rapid decomposition goes on, but the decomposition does not spread into the body of the gas. Finely divided materials have in some other cases been found to check explosions.

Small reaction tubes carry away the heat produced by polymerization more effectively than do large tubes, so that there is less danger of explosion in small tubes. Slow heating produces more polymerization and less decomposition than rapid heating. Under 0.6 atmosphere pressure above normal they found explosion at 700°, a lower pressure than reported by Rimarski, who apparently heated his gases more slowly. Below 500° these workers concluded that there was no danger of explosion under the pressures technically used in acetylene preparation.

The action of iron oxides on these reactions is complex. Magnetic oxide appears first to catalyze a polymerization at 530°, a temperature at which the oxygen of ferric oxide apparently forms carbon dioxide. The oxides appeared in some cases to check decomposition, and in no case to lower the explosive limit, although Rimarski and Konschak claimed that metal oxides such as those of iron and copper might lower the flashing temperature several hundred degrees. This lowering, in the earlier work, Schläpfer and Brunner attributed to local overheating, as Rimarski and Konschak had found that there was active reaction at the oxide surface.

Impurities which might be present in commercial acetylene, such as water vapor, phosphines, silicanes, or ammonia, appeared not to influence the decomposition. Oxygen alone reduced the explosive temperature, probably through increased temperature and pressure caused by combustion. The minimum pressures found for spontaneous decomposition of acetylene were as follows:

550° — 2.5 atmospheres
600° — 1.5 "
700° — 0.6 "

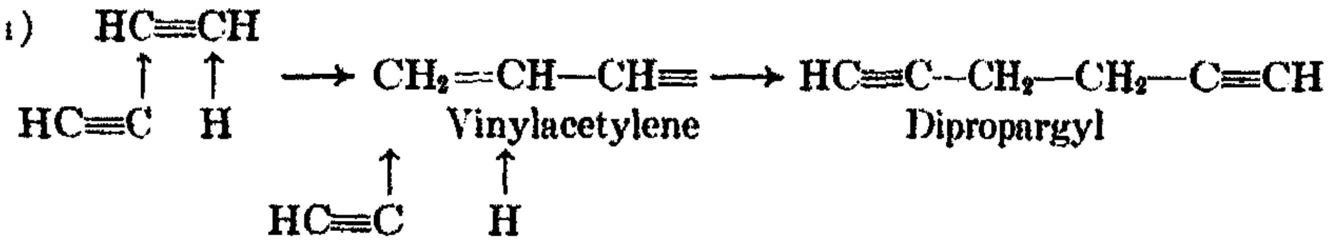
Morani[152] produced pigment carbon by explosion under pressure of a mixture of acetylene and air, mixed with an exothermic gas as methane, ethane, or illuminating gas.

E. *Action of Electric Discharge.*

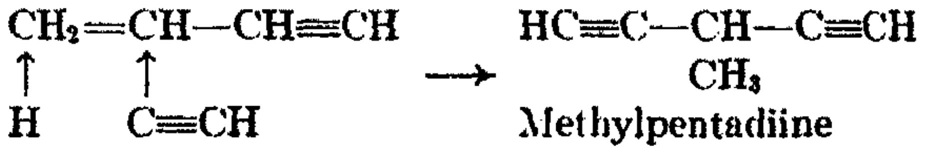
In contrast with the disruptive effects of the electric spark, the silent electric discharge converts acetylene into polymers. Low-boiling polymers may be obtained by careful control of conditions, but if reaction proceeds without regulation, the product is usually a brown resin, somewhat explosive, and avidly absorbing oxygen if brought in contact with air.

By means of high-frequency discharge, with the electrodes kept at −60°, Mignonac and de Saint-Aunay[144] obtained from acetylene a 70 percent yield of a colorless liquid whose molecular weight indicated it to be a trimer of acetylene. It slowly underwent further polymerization. It was not, however, a pure compound. Formation of metal derivatives showed it to contain 40% of diacetylenes, and no monoacetylenes. Oxidation with potassium permanganate or ozone converted it into formic, oxalic, propionic, and succinic acids; hydrolysis of the ozonide gave formaldehyde and reduction of the trimer in the presence of platinum produced hexane. These reactions were taken to indicate that the trimer was a mixture of dipropargyl, $HC{\vdots}C\cdot CH_2\cdot CH_2\cdot C{\vdots}CH$; methylpentadiine, $HC{\vdots}C\cdot CHMeC{\vdots}CH$; and divinyl acetylene $H_2C{:}CH\cdot C{\vdots}C\cdot CH{:}CH_2$.

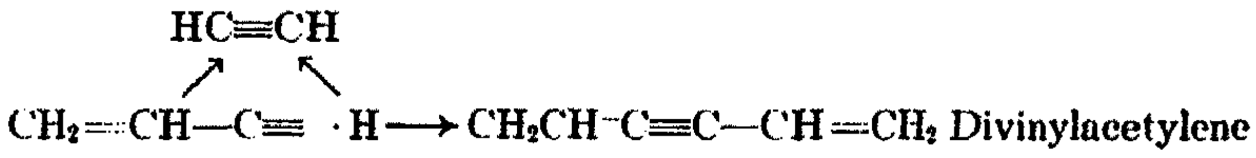
The reaction was thought to take place through activation of acetylene molecules, each of which then added as H— and —C≡CH to the triple bond of an ordinary acetylene molecule to form vinylacetylene, or to vinylacetylene to form dispropargyl or methylpentadiine. It was further suggested that vinylacetylene might become activated and add as $CH_2{:}CH\cdot C{\vdots}C\cdot$ and $\cdot H$ to a neutral acetylene molecule to produce divinyl acetylene. This mechanism of polymerization is outlined by the following equations:

(1)


$$\underset{\overset{\uparrow}{HC\equiv C}}{HC}{\equiv}\underset{\overset{\uparrow}{H}}{CH} \longrightarrow \underset{\text{Vinylacetylene}}{CH_2{=}CH{-}CH{\equiv}} \longrightarrow \underset{\text{Dipropargyl}}{HC{\equiv}C{-}CH_2{-}CH_2{-}C{\equiv}CH}$$

(2)


$$\underset{\overset{\uparrow}{H}}{CH_2}{=}\underset{\overset{\uparrow}{C\equiv CH}}{CH}{-}CH{\equiv}CH \longrightarrow \underset{\text{Methylpentadiine}}{HC{\equiv}C{-}\underset{CH_3}{CH}{-}C{\equiv}CH}$$

(3)


$$\overset{HC\equiv CH}{\nearrow\ \nwarrow}$$
$$CH_2{=}CH{-}C{\equiv}\ \cdot H \longrightarrow CH_2CH{-}C{\equiv}C{-}CH{=}CH_2 \text{ Divinylacetylene}$$

In the work of other investigators, which will be taken up in approximately chronological order, no such temperature control was used and polymerization went much farther, yielding heavy liquids or solids.

de Wilde[54] reported that the silent electric discharge acting on acetylene produced a yellow oily liquid which solidified after a few hours to a brown amorphous substance.

A. Thénard[197] observed that acetylene exposed to the action of the silent electrical discharge was condensed to liquid and solid products having the same empirical formula as acetylene.

Berthelot[15,16,17] found that the silent discharge converted acetylene into a thick, brown liquid, a brown solid polymer, and a small amount of gas. The gases consisted of 92 percent hydrogen, 4 percent ethane, and 4 percent ethylene. Heated in an atmosphere of nitrogen, the solid polymer decomposed with evolution of heat, and produced a small quantity of styrene, slightly volatile tarry hydrocarbon material, a carbonaceous residue and a small amount of gas.

Schützenberger[105] found that acetylene, sealed in glass bulbs and subjected to the silent electrical discharge, condensed to a resinous solid. Evidently air was present, as the product contained oxygen.

By subjecting acetylene to high-frequency discharge, Jackson and Northall-Laurie[103] also obtained a semi-solid brown substance which set to a hard insoluble solid on exposure to air. If care was taken to avoid secondary reactions caused by too prolonged action of the discharge the solid was, by analysis, a polymer of acetylene. It absorbed oxygen readily up to about 8%. When heated out of contact with air, an oil distilled off and small amounts of methane and hydrogen were evolved.

Losanitsch[130] found that the silent electrical discharge converted acetylene into a thick brown liquid which later changed into a solid mass. This mass consisted of two parts—one which was soluble in an alcohol-ether mixture and after evaporation of the solvents remained as a viscous, fragrant mass; the other, present in larger quantity, a tarry-odored solid insoluble in all solvents tried. Under similar conditions Jovitschitsch[105] obtained an extremely insoluble condensation product which he reported possessed strong "radio-active" properties. Because of inconsistencies in his analysis—carbon plus hydrogen not totalling 100 percent—he claimed the transformation of elements by the electrical discharge.

Losanitsch[131] found, as had others, that the condensation product obtained from acetylene by action of the electrical discharge absorbed oxygen rapidly on exposure to air. During the oxygen absorption, iodine was liberated from potassium iodide and a photographic plate was acted upon, but these changes stopped as soon as the oxygen absorption ended. Losanitsch stated, therefore, that the "radio-activity" of Jovitschitsch was undoubtedly produced by very small quantities of ozone. Later Losanitsch[132] reported that acetylene was not only polymerized, but also decomposed into carbon and hydrogen by the electrical discharge *in vacuo*. The carbon produced remained mixed with the polymerized product, while the hydrogen united with acetylene to form a soft soluble mass.

Jovitschitsch[106] again could not make the carbon and hydrogen figures on the electrical condensation products of acetylene reach 100 percent, and, as before, Losanitsch[133] attributed this result to absorption of oxygen by the polymerized product, which later analysis by Jovitschitsch[107] confirmed.

By subjecting acetylene to the action of the silent discharge while the gas passed through the annular space between two concentric glass tubes, Kaufmann[108] obtained, when the reaction vessel was allowed to become warm, a mixture of solid and liquid. If the vessel was kept cold, a liquid was the only product. This liquid was a brown viscous oil, polymeric with acetylene and unstable, which changed on warming, on being kept in solution, or by the attack of almost any chemical agent, into a solid that appeared to be identical with the product described by de Wilde.[54] The liquid decomposed and carbonized above 100°, but a small quantity distilled at 70° under 10 mm. pressure. The residue in the flask after distillation changed to a plastic mass which eventually became brittle. The solid product which formed in the warm reaction vessel was obtained more conveniently by warming a solution of the liquid product in ether at about 60°. It was a pale yellow, odorless powder which was insoluble in all solvents.

Both the liquid and the solid rapidly absorbed oxygen and during such absorption they produced an action on a photographic plate, this result confirming the earlier work of Losanitsch.[131] Although not acted upon by a dilute solution of bromine the solid was attacked by bromine in concentrated solution, and hydrogen bromide was evolved. The liquid absorbed bromine, producing a pale yellow powder with the empirical composition $(C_2H_2Br)_{x}$. A solution of the liquid in carbon tetrachloride, on treatment with alcoholic silver nitrate, yielded a pale yellow precipitate of a silver derivative, which exploded on heating. This indicated the presence of the acetylenic hydrogen. By oxidation with alkaline potassium permanganate the liquid product yielded benzoic, isophthalic, and terephthalic acids, which were also obtained, although with greater difficulty, by oxidizing the solid product under the same condition. When boiled with 47 percent nitric acid the solid product yielded nitro-compounds of high molecular weight, together with a little benzoic acid. Kaufmann considered this solid essentially aliphatic, as distinguished from the aromatic substance cuprene obtained by heat polymerization of acetylene in the presence of copper.

Epner[58] claimed that liquid motor fuels might be obtained from acetylene by passing the gas through an alternating current field of high tension, with frequency above 500 cycles, and preferably of the order of 10,000 cycles, at a temperature higher than the boiling point of the product.

In studying the hydrogenation of hydrocarbons under influence of the electric discharge, Volmar and Hirtz[201] submitted acetylene in the presence of hydrogen to a discharge at 10,000 volts. The acetylene readily polymerized and the hydrogen acted on both the acetylene and its polymers, giving a complex mixture. Acetylenic substances to C_{10} and saturated hydrocarbons to C_8 were reported. Reduction of pressure decreased the polymerization, while the yield of higher saturated and olefinic hydrocarbons increased with reduction in hydrogen. The polymerization was thought to be preceded by activation of acetylene.

Lind and Schultze[128] made a series of runs at low pressure with varied times of exposure to the discharge for information regarding the mechanism of condensation. Explaining the reaction as preceded by a clustering of molecules they concluded that as soon as an ionized molecule was formed the reaction to a solid took place quickly. (They term the brown, solid product, "cuprene," although it seems not to have been proved identical with the product of heat in the presence of copper, and there is some evidence that the two are not alike). Hydrogen was liberated during the reaction, but its amount did not increase by prolonging exposure to the discharge, nor was any produced by action of the discharge on the precipitated solid in the absence of gas. Traces of either ethylene or ethane were also found.

Lind and Schultze found that contrary to the result with alpha radiation, acetylene is in part hydrogenated when exposed with hydrogen to the electric discharge. A solid product, ethane, propane and liquids form at the same time. In a second publication[129] they compared the results of an ozonizer type of discharge on acetylene and other hydrocarbons. Deposition of solid on the walls of the chamber retarded the reaction.

Harkins and Gans[84] found that when exposed to the electrodeless discharge acetylene formed an insoluble reddish-brown solid. There was no formation of gas. In the spectrum obtained there were bands indicating CH, C, C_2 molecules, C^+ ions, and H, which were the bands also given by benzene.

In the manufacture of cuprene the silent discharge is sometimes used while the acetylene is heated in the presence of copper.

F. *Action of Alpha Particles.*

Mund and Koch[153] introduced 58 millicuries of radon into one bulb of a differential manometer containing acetylene at about atmospheric pressure. They found that in 8 days the pressure decreased 278 mm. and traces of a voluminous brownish-yellow, amorphous powder deposited on the walls of the vessel. Later they[154] determined the rate of polymerization of acetylene containing approximately 5×10^{-6} percent radon, and found that each alpha particle emitted by the emanation caused the disappearance of 4.38×10^6 molecules of acetylene. Since 2.13×10^5 gaseous were ions produced, 20.5 molecules of acetylene disappeared for each ion pair formed. In further work[155] "no variation exceeding experimental error could be detected in the number of molecules of acetylene polymerized per pair of ions produced in the system (1) at different pressures; (2) at temperatures 0°C., 20°C. and 100°C.; and (3) in the presence of small quantities of air. The general mean value of eleven measurements obtained in the absence of oxygen, with two concordant results previously reported, gave 20.2 as ratio of the number of molecules of acetylene polymerized per pair of ions produced."

Lind and Bardwell[121] also found that exposure of acetylene to radium emanation produced a solid yellowish powder similar to "cuprene," and a small amount of hydrogen.

When an equal volume of nitrogen was mixed with the acetylene it accelerated the rate of polymerization, an effect termed "ionic catalysis." The nitrogen ions formed by the action of the α-particles from the radon apparently served as additional clustering and polymerization centers. Lind and Bardwell reported "that the number of acetylene molecules condensing for each N_2^+ ion is approximately 20, the same as for each $C_2H_2^+$ and polymerization by both routes proceeds simultaneously. In other words $\frac{-M(C_2H_2)}{N(C_2H_2+N_2)} = 20$."
(−M is the number of acetylene molecules disappearing, N the number of ions.)

Further experiments of Lind and Bardwell[122] in which "helium, neon, and argon were separately mixed with acetylene and a small quantity of radon was introduced as ionizing source" gave "the same results as for nitrogen; the ratios;

$$\frac{-MC_2H_2}{N(C_2H_2+He)}, \frac{-MC_2H_2}{N(C_2H_2+Ne)} \text{ and } \frac{-MC_2H_2}{N(C_2H_2+A)}$$

were all initially equal to about 20, the value for $\frac{-MC_2H_2}{NC_2H_2}$ in the case of pure acetylene. This value is maintained even when the ionization of the inert is as much as 50 percent of the total."

Extension of the study of inert gases as "ionic" catalysts[123,124] showed that krypton and xenon also catalyzed the polymerization of acetylene. Carbon dioxide had a similar effect, but in this case the ratio

$$\frac{-MC_2H_2}{N(C_2H_2+CO_2)} \text{ was } 17.4$$

As a mechanism for the polymerization of acetylene Lind, Bardwell and Perry[125] stated that "the simplest assumption is that a cluster containing at least 19 neutral molecules of acetylene is formed around each $C_2H_2^+$, and that the free electron (which has no affinity for neutral acetylene) finally neutralizes the cluster, which owing to the number of unsaturated valences then becomes stabilized as a polymer which precipitates as a solid

$$C_2H_2^+ + 19\ C_2H_2 \longrightarrow (C_2H_2)_{20}^+ + (-) \longrightarrow (C_2H_2)_{20}\text{"}$$

Because of failure to find a solvent for the yellowish solid polymer these investigators were unable to determine its molecular weight. The fact that neither oxygen, which would be expected to act as a inhibitor, nor other gases, which would be expected to be positive catalysts, affected the ion yield, supports a clustering rather than a chain mechanism.

G. *Action of Cathode Rays.*

High-voltage electrons from a cathode ray tube provided with an aluminum window acting on acetylene produce a yellow substance similar to the product obtained with the corona discharge or with radium emanation. Coolidge[50] first reported this action.

McLennan, Perrin, and Treton[137] bombarded acetylene with high-speed electrons in a cathode ray tube similar to that described by Coolidge.[51] No change in pressure occurred until the voltage exceeded 85 kilovolts, when a slight mist formed throughout the reaction coil and a pale yellow amorphous solid deposited on the walls. Reaction was accompanied by a decrease in pressure. The yellow solid had no measurable vapor pressure and on bombarding it there was no increase of pressure. The reaction appeared unimolecular, as the rate of change of pressure was proportional to the pressure for any given voltage, and the velocity coefficient increased directly as the voltage.

The number of electrons passing through the window of the cathode ray tube was determined by collecting them in a Faraday cylinder and measuring the current. It was found that the number of molecules of acetylene reacting was of the same order as the number of ions formed by the electrons passing through the window.

A. L. Marshall reported[135] that when acetylene gas was exposed to cathode rays a white cloud rapidly filled the whole chamber, and fluffy white yellow powder deposited on the walls. Apparently the reaction was exclusively polymerization, with no elimination of hydrogen. The rate of disappearance of acetylene was approximately proportional to the acetylene pressure. Dilution of acetylene with nitrogen considerably increased the rate of reaction over that of acetylene alone at a pressure equal to the partial pressure of acetylene in the mixture.

When heating the acetylene during the raying, it was found that the yield was not altered, but as the temperature rose the powder appeared to increase in density, and changed in color from light yellow to chocolate brown at 400°. Marshall decomposed the yellow powder by heating it in an evacuated system, but obtained erratic results, which he attributed to the fact that the polymer had absorbed a considerable proportion of oxygen. He found that it would take up about 30% of its weight of oxygen on standing in air.

H. *Action of Light.*

There has been considerable interest in the action of light on acetylene, from the standpoint of the product obtained, the wave-length of the effective light and the quantum yield. Lind[120] points out the interest in comparing in the case of acetylene, the photochemical reaction and the ionization reactions, such as produced by alpha particles. In both cases the primary step is activation, involving a single electron in a single molecule. Formation of a gas ion involves complete removal of an electron from the molecule, while photochemical activation is attributed to the shift of an electron from its normal orbit to one of higher energy.

In both ionic and photo-reactions, changes normally requiring high temperature are brought about at room temperature. In ionization changes, clustering appears to be the first step. This prevents a chain reaction, and also enables the molecules to withstand the shattering effect of ionizing forces. In photochemical change clustering about an excited molecule is also assumed.

Lind and Livingston[126,127] investigated the quantum yield in the photochemical polymerization of acetylene. They exposed the hydrocarbon in a glass vessel at constant temperature to radiation from a "hot" mercury vapor arc. The product was a brown, inert solid believed to be cuprene. The reaction appeared to occur in one step, with no side reactions or gaseous products. The reaction velocity was proportional to the pressure as long as this did not exceed 30 cm. of mercury, and approached a constant value at higher pressures. This was interpreted as indicating that the rate of polymerization was proportional to the intensity of the absorbed light. The temperature coefficient of the change was 1.25 per 10°, which may have been simply the coefficient of light adsorption. Experiments with screens of varied ultra-violet transparency showed that light of 2537 Å and longer was not effective in causing polymerization, probably because acetylene does not absorb these wavelengths. The quantum yield found (ratio of molecules polymerized to light quanta absorbed) was 9.2 ± 1.5. The investigators drew attention to the fact that this was about half the yield per ion pair in polymerization by the action of alpha particles, or approximately equal to the average yield per ion.

Bone and Wilson[35] found that pure acetylene exposed to bright sunlight in glass bulbs for two or three days gave a faint brown deposit which increased in thickness and became darker as the exposure was prolonged. No deposit formed in a portion of the tube which was protected from the light. Besides unchanged acetylene the residual gas contained about two percent of a "fairly dense hydrocarbon" (not saturated) possibly mixed with a small quantity of hydrogen.

D. Berthelot and H. Gaudechon[21,22,23] observed that exposure of acetylene to ultra-violet light from a mercury vapor lamp for several seconds caused precipitation of a yellowish-brown, waxy solid. The polymerization of acetylene was not accompanied by decomposition nor by formation of benzene. The reaction was not modified by the presence of hydrogen or nitrogen in the acetylene. It was stated, however, in contradiction to Bone and Wilson, that exposure of acetylene to sunlight for one year in thin quartz tubes produced neither change in volume nor polymerization.

Bates and Taylor[4] reported that acetylene was polymerized to the yellow solid "cuprene" both by ultra-violet light and by excited mercury atoms. The rate of reaction was increased by cooling the vertical Cooper-Hewitt arc used by immersion in running water.

When a hydrogen-acetylene-mercury mixture was illuminated by the cooled arc, "cuprene" was deposited on all portions of the reaction vessel except that adjacent to the arc, which became coated with a colorless oil. The cuprene which condensed in this region was apparently immediately acted upon by hydrogen atoms. The resulting gas was made up of 95.7 percent hydrogen and 4.3 percent unsaturated hydrocarbons.

Reinicke[171] reported that while sunlight, or light from an incandescent lamp or an iron arc did not change acetylene, it was polymerized even in absence of air or moisture when illuminated by a quartz mercury arc at pressures of one to ten atmospheres. The product was a yellow amorphous solid insoluble in most solvents. The polymerization was not a heat effect, as it went on even when the vessel containing the acetylene was cooled to 12°. The rays causing the action were of a shorter wave-length than 3000 Å, as the polymerization was stopped when uviolglass screened the source of light. When the acetylene was confined over a solution of copper salts, radiation gave rise to low-melting colorless crystals, in addition to the amorphous solid. These crystals appeared to be a formaldehyde polymer. They were thought to be the same as the crystalline product of Thiele[198] who reported contraction and an unidentified white precipitate on exposure of acetylene to light from a quartz lamp. Carbon, said by Romer[178] to be formed from acetylene by the action of light, was in no case observed.

I. *Action of Canal Rays.*

Kinoshita[113] subjected acetylene to the action of canal rays, using an exposure of three hours with 2000 volts at 1-3 milliamperes. Carbon was deposited on the walls and the gas pressure dropped, probably as a result of polymerization. The accompanying spectrum plainly showed C and H lines.

J. *Action of Electromagnetic Field.*

Moens and Juliard[148] found that acetylene was rapidly polymerized to a yellowish white powder when exposed to electromagnetic fields of high frequency.

II. Rearrangement of Higher Acetylenes

Under the influence of heat and alkaline reagents a number of acetylenes have been found to rearrange. Acetylenes having the triple bond with the 1-position change to isomers having the triple bond in the 2-position and these, by a change in method, may be reconverted into derivatives of the 1-alkalines. This sort of shift,

$$R{-}CH_2{-}C{\equiv}CH \longrightarrow RC{\equiv}C{-}CH_3$$

resembles the commonly occurring shift in a three-carbon system

$$R{-}CH_2{-}CH{=}CH_2 \longrightarrow RCH{=}C{-}CH_3$$

and both are in a sense analogous to the rearrangement in ketoenol tautomerism.

The most complete work on rearrangement of this type is that of Faworsky.[60] He found that ethylacetylene, on 16 hours heating in a sealed tube with alcoholic potash at 170° was converted into dimethylacetylene. This with slightly diluted sulfuric acid formed hexamethylbenzene. Other monosubstituted acetylenes which he investigated underwent a similar shift. Thus propylacetylene gave methylethylacetylene on treatment with alcoholic potash for 24 hours at 170°. The disubstituted acetylene did not polymerize with sulfuric acid. This isomerization was also brought about by alcoholic soda and by sodium alcoholate. Faworsky proposed a mechanism involving addition of alkali alcoholate followed by loss of alcohol to form an allene and further reaction with alcoholate. He postulated that such acetylenes as isopropylacetylene would go only as far as the allene stage, and confirmed this by experiment (isopropylacetylene gave dimethylallene). The behavior of ter-butylacetylene, also accorded with his mechanism, as even under extreme conditions alcoholic potash produced no change.

In his second paper, Faworsky[61] reversed the shifts previously studied by contact of the 2-acetylene with sodium. Methylethylacetylene gave the sodium derivative of propylacetylene, methylpropylacetylene gave butylacetylene, dimethyl allene gave isopropylacetylene. He[62] also found that methylacetylene on heating with alcoholic potash did not go, as might have been expected, to allene, but was in part converted into an unsaturated ether $CH_3C(OC_2H_5) = CH_2$, which he considered the first step in his rearrangement mechanism. Further change to allene was blocked by the resistance of the methyl hydrogens to removal to form alcohol.

Further work[65] showed that amyl and hexylacetylenes underwent rearrangements of this type.

Behal[6] obtained methylbutylacetylene when heptine-1 was heated at 140° to 150° with alcoholic potash for 24 hours.

Wislicenus and Schmidt[203] found that rearrangement by alcoholic alkali was not always complete, some ethylacetylene remaining even after most of it had been converted into dimethylacetylene.

Bourguel[37] studied the reverse rearrangement by which 2- and even 3-acetylenes were converted into sodium derivatives of the 1-acetylenes by action of sodamide. He found this change to take place with butine, pentine, octine, and nonine.

By passing a mixture containing 80 percent of heptine-1 over soda lime in an iron tube heated to 380°, Guest claimed that rearrangement to heptane-2 proceeded to the extent of 70 percent. At 250° no rearrangement occurred, nor was there any significant change at 350° without the contact agent. The reverse change was brought about by heating with sodamide. The mixture obtained from the rearrangement over soda lime, which was reported to contain upwards of 80 percent heptine-2, was heated for twelve hours at 160° with finely divided sodamide suspended in 35 cc. of mineral oil. After washing and distilling, the final product contained 64 percent of heptine-1.

Hurd[93] believes that many of these rearrangements do not go completely from the 1-acetylene to the 2-acetylene stage, but stop with the allene. Rearrangement to the allene would involve disappearance of the active acetylenic hydrogen, which has been used as a criterion of rearrangement, and the allenes could easily be mistaken for 2-acetylenes.

III. Methylacetylene

The pyrolysis of methylacetylene was investigated by Meinert and Hurd.[135] The dry gas was passed through an electrically heated vertical pyrex tube at from 500° to 650°. Largely liquid products were produced at 575°, 88 percent of the hydrocarbon which was changed being converted into liquids. When the temperature was raised to 575°, ethylene, methane and hydrogen increased, and liquid products dropped to 61 percent. The liquids contained no aromatic hydrocarbons, and were therefore radically different from the polymerized products of acetylene, while they closely resembled the liquid produced by allene pyrolysis. It was therefore supposed that pyrolysis began by a conversion of methylacetylene to allene.

A summary of this work is given in Table III.

The liquids, boiled from 60°-215°, were not aromatic, and decolorized bromine. Apparently they consisted of polymers such as were formed from allene—a dimer, a tetramer and higher substances.

Absorption of methylacetylene in sulfuric acid followed by distillation, was found by Schrohe[193] to convert it into mesitylene.

TABLE III

Pyrolysis of Methylacetylene

(Meinert and Hurd)

Temperature °C.	550	575	650
Contact time, seconds	76	48	30
Volume entering gas, l.	13.05	6.73	2.13
Volume exit gas, l.	7.92	3.77	1.76
Analysis of exit gas, % by volume			
Acetylene	52.0	48.0	14.0
Allene[a]	18.6	16.8	11.8
Ethylene	3.6	3.0	23.1
Hydrogen	6.8	5.9	18.9
Paraffins	11.6		27.6
n in C_nH_{2n+2}	1.34		1.17
Extent of pyrolysis, %	64.5	67.	87.
Gaseous products formed per liter methylacetylene pyrolyzed, cc.			
Allene[a]	192	159	125
Ethylene	37.1	28.5	246
Hydrogen	72.0	57.0	201
Paraffins	123.0		294
Liquid yield, % of methylacetylene pyrolyzed	58.8	88.0	61.0

[a] "allene" may include some propylene.

IV. Dimethylacetylene

The formation of dimethylacetylene from ethylacetylene and its conversion by sulfuric acid and heat into hexamethylbenzene by Fawrosky[60] has already been mentioned.

V. Ethylacetylene

Hurd and Meinert[94] passed ethylacetylene through a vertical pyrex tube, as in the pyrolysis of methylacetylene. The hydrocarbon was quite stable at 500°, only 23 percent decomposing with a contact time of 35 seconds. At 580° with the same contact time, conversion was complete. Less liquid and more gas were produced than was the case with methylacetylene.

Data from their runs are given in Table IV:

Table IV

Pyrolysis of Ethylacetylene

(Hurd and Meinert)

Temperature °C.	500	550	580	600
Contact time, seconds	34.8	34.5	35.0	30.0
Percentage decomposition	22.6	47.0	95–100	95–100
Wt. of liquid formed, g.	1.5	4.0	6.7	6.0
Liquids formed % by wt. of ethylacetylene pyrolyzed	43.0	53.0	36.5	36.6
Analysis of off-gas, % by volume				
Carbon dioxide	83.0	22.4	7.3	5.0
Acetylenes	—	15.6	12.8	9.4
Gas soluble in 82.5% H_2SO_4	—	7.8	8.7	7.6
Ethylene	—	6.6	9.7	10.8
Hydrogen	—	4.6	13.6	17.0
Paraffins	—	37.4	40.1	43.4
n in C_nH_{2n+2}	—	1.49	1.23	1.18
Gaseous products formed per liter of ethylacetylene pyrolyzed, cc.				
Acetylenes		88.4	110	94.2
Gas soluble in 82.5% H_2SO_4		43.9	76.5	76.2
Ethylene		33.8	83.8	108
Hydrogen		26.0	118	170
Paraffins		211.0	346	435

A study of the off-gas indicated that acetylene itself made up at least 80 percent of the "acetylenes" reported, while the gases absorbed in 82.5 percent sulfuric acid were almost entirely propylene, with possibly small amounts of allene, but no methylallene.

About half of the liquid products boiled from 30° to 200°. The liquids were not aromatic, and while they were not identified they resembled those formed by pyrolysis of methylallene, allene, and methylacetylene.

VI. Pentine

Bouchardt[35] reported that "valerylene" (b.45-50°) a mixture of pentine isomers prepared from amyl alcohol (the alcohol a fermentation product) was polymerized by heating at 250°. That portion of the product boiling between 170° and 190° consisted mainly of "divalerylene."

VII. Heptine

Renard[172] pyrolyzed a heptine boiling at 103°-105° by passing the vapors through an iron tube one meter long, heated to "redness visible only in the dark." He obtained per liter of the hydrocarbon, 37 liters of gas, 720 cc. of brownish-yellow liquid, and about two grams of carbon. The gas consisted of hydrogen mixed with small quantities of unidentified hydrocarbons. From the liquid, Renard isolated 20 to 25 cc. of a pentine, 100 to 110 cc. of a hexine (boiling at 70° to 73°), 20 to 25 cc. of benzene, and 180 to 200 cc. of toluene. Of the fraction which distilled above 115°, about half came over below 180°, and left a thick residue, solid at ordinary temperatures, which was said to contain no aromatic hydrocarbons. Renard concluded that under the influence of heat, heptine decomposed primarily into hydrogen and toluene, with a small amount of a pentine and a hexine. The benzene was considered to arise from the hexine.

By exposing heptine-1 to the action of the silent electrical discharge *in vacuo*, Losanitch[132] obtained "diheptine," whose formula was given as

$$(CH_3(CH_2)_4C \vdots CH)_2,$$

a colorless, mobile liquid miscible in alcohol, ether, and benzene; triheptine, a thick, odorous liquid soluble in ether and in benzene; and "undecaheptine," a dark red, thick mass also soluble in ether and benzene.

VIII. Octine

Losanitsch[132] reported that the action of the silent electrical discharge converted octine-1 into "dioctine," $(C_8H_{14})_2$, a colorless liquid soluble in alcohol, ether, and benzene; and "nonaoctine," $(C_8H_{14})_9$, a dark red, soft mass soluble in ether and benzene but insoluble in alcohol.

IX. Hexadiine-2, 4

Vapors of dimethyl diacetylene $CH_3C \vdots C . C \vdots C . CH_3$ subjected suddenly to red heat were found, by Griner[78] to decompose, leaving a residue of carbon. This compound is stable, as it withstands shock and gradual heating to high temperatures without explosion.

X. Vinylacetylene and Divinylacetylene

The polymerization of these substances by heat as reported by Nieuwland, Calcott, Downing, and Carter,[158] and by Collins[46] has been discussed in the section "Acetylene; Action of Chemical Reagents."

Heisig[85] reported that on exposure to the action of alpha particles from radon, vinylacetylene condenses to a white solid, which becomes orange on continued exposure. About eleven molecules of the hydrocarbon polymerize per ion pair formed. Practically no hydrogen or methane is evolved.

XI. Summary Tables

Acetylene

Action of Heat—Non-Catalytic

Temperature	
300-800°	Largely polymerization, optimum 600-700°. Products are aromatic hydrocarbons in great variety, with some olefins and paraffin hydrocarbons. The presence of carbon promotes smooth reaction. In upper portion of this temperature range, some decomposition to carbon, hydrogen, and methane occurs.
800-1000°	Both decomposition and polymerization occurring, the former taking ascendency.
1000° and above	Almost exclusively decomposition to carbon, hydrogen, and methane. Some acetylene in equilibrium with these at above 1700°.

Catalytic

Contact Agent Metals	Reference	Temp.	Type of Reaction and Products reported
Aluminum	Hilpert[88]	400°	Carbon, tar
	Kusnetsov[116]	About 659°	Decomposition—Carbon hydrogen, aluminum carbide
	Hodgkinson[89]	About 659°	Carbon
Beryllium	Durand[55]	450°	Decomposition, some polymerization. Carbon, beryllium acetylide
Cadmium	Hodgkinson[89]	321°	Carbon, acetylide
	Durand[55]	500°	Carbon, acetylide
Cobalt	Moissan and Moureu[149,151]	Room	Metal becomes incandescent Carbon, hydrogen, tar rich in benzene
	Sabatier and Senderens[186,188]	Above 200°	Carbon
	Tiede and Jenisch[199]	380°	Carbon
		480°	Oil
	Fischer, Peters and Koch[66]	300°	Methane
Copper	Erdmann and Köthner[59]	To 180°	Polymerization-liquids,
		230°	Cuprene, carbon
		400-500°	Decomposition—carbon

Catalytic (Continued)

Contact Agent Metals	Reference	Temp.	Type of Reaction and Products reported
Copper (Cont'd)	Gooch and Baldwin[76]	225-250°	Cuprene
	Alexander[1]	225-250°	Cuprene, heavy tar
		Over 260°	Carbon
	Sabatier and Senderens[180,181,182,185]	180°-250°	Olefinic and aromatic liquid, cuprene, hydrogen, ethane, gaseous olefins
	Hilpert[88]	—	Brown deposit
	Kaufmann and Schneider[110]	— —	Cuprene Oily liquid
	Kaufmann and Mohnhaupt[109]	230-300°	Cuprene
	Schläpfer and Stadler[192]	300°	75-80% cuprene 55-57% aromatic tar 13-17% gas
	Tiede and Jenish[199]	310°-600°	Oil
	Erdmann[57]	400°-500°	Graphite
	Berl and Hofmann[8]	580°	Carbon
	Hodgkinson[89]	1038°	Carbon
Gold	Durand[55]	500°	Carbon
Iron	Berthelot[11,12,14]	—	Reaction began at lower temperature than without catalyst Carbon, hydrogen, "empyreumatic hydrocarbons
	Ramsay[169]	Red heat	Oil, apparently benzene
	Moissan and Moureau[149,151]	Room	Pyrophoric metal became incandescent. Carbon, hydrogen, liquid rich in benzene
	Sabatier and Senderens[186,188]	Room	Carbon, hydrogen, ethane, olefins, aromatic liquid
	Hilpert[88]	300°-400°	Carbon
	Hodgkinson[89]	To 1050°	Carbon
	Tiede and Jenisch[199]	400° 540° 600°	Carbon formation began Oil formation began Very little oil—rapid decomposition to carbon and hydrogen
	Bradley and Parr[38]	725°	Complete decomposition
	Rimarski and Konschak[176]	600°-900°	Almost complete decomposition
	Fischer, Peters and Koch[66]	300°-400°	9% acetylene 91% hydrogen, gave both oil and carbon

Catalytic (Continued)

Contact Agent Metals	Reference	Temp.	Type of Reaction and Products reported
Iron (Cont'd)	Berl and Hofmann[8]	580°	Largely formation of carbon
	Erdmann and Köthner[59]	—	Aided oil formation
Lead	Hilpert[88]	327°-500°	Carbon, no benzene formation
	Hodgkinson[89]		Same
Lithium	Tiede and Jenisch[199]	—	Carbon, hydrogen, acetylide
Magnesium	Berthelot[10]	—	Acetylide
	Moissan[150]	—	Carbon, carbide
	Keiser and McMaster[111]	—	Magnesium allylide and carbide
	Novak[159,160,161]	400°-700°	Carbide and allylide, carbon
Manganese	Tiede and Jenisch[199]	440°	Carbon separation
		480°	Oil formation
		600°	Largely decomposition to carbon and hydrogen
Mercury	Hilpert[88]	—	Carbon
	Durand[55]	500°	Carbon
Nickel	Sabatier and Senderens[183,185,187,188]	Room	Liquid containing paraffins, olefins and aromatics from acetylene-hydrogen mixture
			Metal becomes incandescent
		Room	Metal incandescent—carbon, hydrogen, liquid rich in benzene
		180°	Lowest reaction temperature of nickel was free of hydrogen
		250°	Rapid reaction, decomposition, polymerization and hydrogenation. Paraffins, naphthenes, olefins, aromatic hydrocarbons formed
	Moissan and Moureu[149,151]	180°-300°	Slow reaction to cuprene
	Charitschkow[43]	300°	Acetylene + hydrogen gave liquid product
	Tiede and Jenisch[199]	360°	Carbon separated
		520°	Soil formed
	Hilpert[88]	300°	Carbon formed rapidly if iron was also present

Catalytic (Continued)

Contact Agent Metals	Reference	Temp.	Type of Reaction and Products reported
Nickel (Cont'd)	Hodgkinson[89]	200°	Reaction noted—carbon formed
		600°	Rapid reaction
Palladium	Zelinsky and Kasansky[213]	300°	Carbon and a small amount of unsaturated condensate
	Durand[55]	500°	Carbon
Platinum	Moissan and Moureu[149-151]	Room	Metal becomes incandescent Carbon, hydrogen, liquid rich in benzene
	Sabatier and Senderens[181,186,188]	150°	Carbon and hydrogen, ethane, ethylene, benzene, styrene, reduced naphthalene and anthracene
	Schützenberger[194]	—	Carbon
	Lewes[117]	1000°	Ethylene, small amount of hydrogen and paraffins, oil, carbon
	Grehant[77]	—	Carbon
	Zelinsky and Kasansky[213]	300°	Liquid
		650°	Tar
Rubidium	Erdmann and Köthner[59]	—	Carbon
Sodium	de Forcrand[62]	Dull red	Sodium carbide, carbon
	Tiede and Jenisch[199]	—	Sodium acetylide, hydrogen and carbon
Tin	Bahr[3]	Below 475°	Aided polymerization
Uranium	Durand[55]	500°	Carbon
Potassium	Berthelot[10]	—	Gentle heating gave acetyline, carbon, hydrogen
	Moissan[150]	Room	Acetylide
Zinc	Erdmann and Köthner[59]	—	Apparently carbon deposited
	Hodgkinson[89]	To 419°	No significant action
	Hilpert[88]	Over 419°	Carbon, tar

The following additional metals were reported by Tiede and Jenisch[199] to have no effect on acetylene pyrolysis.

- Antimony
- Bismuth
- Boron
- Cadmium
- Calcium
- Chromium
- Molybdenum
- Silver
- Silicon
- Tantalum
- Thallium
- Titanium
- Tungsten
- Zirconium

Oxides

Contact Agent Metals	Reference	Temp.	Type of Reaction and Products reported
Ferric oxide	Gooch and Baldwin[76]	150°-360°	Carbon
Silver oxide	Gooch and Baldwin[76]	Room	Explosive reaction, silver
Calcium oxide	Berl and Hofmann[8]	—	Methane, carbon, hydrogen
Stannic oxide	Berl and Hofmann[8]	—	Methane, carbon, hydrogen
Silicon dioxide	Berl and Hofmann[8]	—	Methane, carbon, hydrogen
Ceric sulfate	Comp. gén. deProduits de Synthèse[47]	80°	Polymerization
Ferric nitride	Hodgkinson[89]	—	Carbon
Ferrous sulfide	Bahr[3]	300°	Oil formed
		430°	Carbon separation as well as oil
	Fujio[73]	—	Increases low-boiling constituents in tar
Nickel carbonyl	Binnie[29]	190°	Low boiling unsaturated oil
Phosphoric acid	Bahr[3]	470°-480°	Carbon
Sodium and potassium hydroxide	Fry, Schultze, Weitcamp[72]	325°	Carbon, hydrogen, methane
Stannous chloride	Bahr[3]	500°	Little change

Action of Chemical Reagents

Reagent	Reference		Conditions and Results
Cuprous chloride	Nieuwland, Calcott, Downing and Carter[158]		Room temp. produced vinyl acetylene, divinyl acetylene, and an acetylene tetramer
Aluminum chloride	Baud[5]	70°-130°	Anthracene and high boiling unidentified hydrocarbons

Action of Electric Discharge

Reference	Conditions and Results
Mignonac and St. Aunay[144]	At 80°, dipropargyl, methylpentadiine, divinyl acetylene
de Wilde[54]	Yellow liquid changing to solid
Thénard[197]	Liquid and solid polymers
Berthelot[15,16,17]	Brown liquid, brown solid, hydrogen, ethane, ethylene
Schützenberger[195]	Resinous solid
Jackson and Northall-Laurie[103]	Brown solid

Action of Electric Discharge (Continued)

Reference	Conditions and Results
Losanitsch[130,131,132,133]	Brown liquid turning to solid. In vacuo some carbon and hydrogen also
Jovitschitsch[105,106]	Insoluble solid
Kaufmann[108]	Viscous liquid and solid, apparently aliphatic
Lind and Schultze[129]	Solid, termed cuprene, hydrogen, ethylene or ethane. With hydrogen, ethane, propane and liquids
Volmer and Hirtz[201]	Acetylene with hydrogen gave higher acetylenes, olefins and paraffins

Action of Alpha Particles

Mund and Koch[153]	Yellow solid—variation in temperature and pressure did not change results
Lind and Bardwell[121,122,123,124]	Yellow solid—like cuprene

Action of Cathode Rays

Coolidge[60]	Yellow solid
McLennan, Perrin, Treton[137]	Yellow amorphous solid
Marshall[135]	Yellow to brown powder, depending on temperature

Action of Light

Bone and Wilson[35]	Sunlight, brown solid, trace of gaseous product
Berthelot and Gaudechon[21,22,23]	Ultra-violet gave yellowish-brown waxy solid. Sunlight had no effect
Bates and Taylor[4]	Ultra-violet or excited mercury atoms gave yellow solid, and liquid oil
Lind and Livingston[126,127]	Ultra-violet gave a brown inert solid. Effective wave-length below 2537 Å
Reinicke[171]	Ultra-violet gave yellow insoluble solid

Action of Canal Rays

Kinoshita[113]	Carbon, signs of polymerization

Action of Electro-Magnetic Field

Moens and Juliard[148]	Yellow-white powder

Methylacetylene

Reference	Conditions	Products
Meinert and Hurd[138]	Heat at 500°-650°	Largely unsaturated liquids. Some hydrogen, gaseous olefins, and paraffins
Schrohe[193]	Sulfuric Acid	Mesitylene

Reference	Conditions	Products
	Dimethylacetylene	
Faworsky[60]	Heat and sulfuric acid	Hexamethylbenzene
	Ethylacetylene	
Hurd and Meinert[94]	Heat at 500°-600°	Unsaturated liquids, gaseous olefins, paraffins, and hydrogen
	Pentine	
Bouchardat[36]	Heat at 250°	Dimer and other polymers
	Heptine	
Renard[172]	Dull red heat	Pentine, hexine, benzene, toluene, hydrogen and unidentified gaseous hydrocarbons
Losanitsch[132]	Silent discharge	Polymers—diheptine and higher
	Octine	
Losanitsch[132]	Silent discharge	Polymers, dioctine and higher
	Hexadiine-2, 4	
Griner[78]	Red heat	Carbon
	Vinylacetylene and Divinylacetylene	
Nieuwland, Calcott Dunning, Carter[158]	Heat and catalysts	Drying oils and resins
Collins[46]	Heat and catalysts	Drying oils and resins
Heisig[85]	Alpha particles	White to orange solid

XII. References

[1] Alexander: Ber., 32, 2381-4 (1899).

[2] Alexejew: Izvestiya. Pedagog. Schelaputin Inst. Moscow, 4, 1267 (1915); Chem. Zentr., 1925 II, 1588.

[3] Bahr: Ges. Abhandl. Kenntnis Kohle, 8, 283 (1924-7), published (1929).

[4] Bates and Taylor: J. Am. Chem. Soc., 49, 2438-56 (1927).

[5] Baud: Compt. rend., 130, 1319-22 (1900).

[6] Behal: Bull., 49, 581-4 (1888).

[7] Berger and Wirth: Ger. 92,801.

[8] Berl and Hofmann: Z. angew. Chem., 44, 259 (1931).

[9] Berthelot: Compt. rend., 54, 1044 (1862); Ann. Chim. Phys., (3) 67, 70 (1863).

[10] Berthelot: Ann. Chim. Phys., (4) 9, 402-7 (1866).

[11] Berthelot: Ann. Chim. Phys., (4) 9, 445-69 (1866); Berthelot: "Les Carbures d'Hydrogène," 1, 83-9 (1901).

[12] Berthelot: Bull., (2) 6, 268-72 (1866).

[13] Berthelot: Compt. rend., 63, 479, 515 (1866); Ann. Chim. Phys., (4) 12, 52-81 (1867).

[14] Berthelot: Compt. rend., 62, 905 (1866).

[15] Berthelot: Ann. Chim. Phys., (5) **10**, 67 (1877); "Les Carbures d'Hydrogène" **1**, 51, 117 (1901).

[16] Berthelot: Compt. rend., **111**, 471-2 (1890); Ann. Chim. Phys., (6) **24**, 135-7 (1891).

[17] Berthelot: Compt. rend., **126**, 570 (1898).

[18] Berthelot: Ann. Chim. Phys., (7) **22**, 445 (1901).

[19] Bertholot: Ann. Chim. Phys., (8) *6*, *184* (*1905*).

[20] Berthelot: Compt. rend, **140**, 910 (1905).

[21] Berthelot and Gaudechon: Compt. rend., **150**, 1169-72 (1910).

[22] Berthelot and Gaudechon: Rev. gén. sci., **22**, 330 (1911).

[23] Berthelot and Gaudechon: Compt. rend., **155**, 207-10 (1912).

[24] Berthelot and Le Chatelier: Compt. rend., **129**, 427 (1899); Ann. Chim. Phys., (7) **20**, 15 (1900).

[25] Berthelot and Vieille: Compt. rend., **123**, 523-30 (1896); Ann. Chim. Phys., (7) **11**, 501 (1897).

[26] Berthelot and Vieille: Compt. rend., **124**, 988 (1897); Ann. Chim. Phys., (7) **13**, 6 (1898); see Claude: Compt. rend., **124**, 626 (1897).

[27] *Berthelot and Vieille: Compt. rend.*, **124**, *1002* (*1897*).

[28] Berthelot and Vieille: Compt. rend., **128**, 777 (1899); Ann. Chim. Phys., (7) **17**, 303 (1899).

[29] Binnie: J. Soc. Chem. Ind., **50**, 297-9 (1931).

[30] Bone and Cain: Chem. News, **74**, 268 (1896); Proc. Chem. Soc., **12**, 177 (1896).

[31] Bone and Coward: J. Chem. Soc., **93**, 1197 (1908); Proc. Chem. Soc., **24**, 167 (1908).

[32] Bone and Jerdan: J. Chem. Soc., **71**, 41 (1897).

[33] Bone and Jerdan: J. Chem. Soc., **71**, 59-60 (1897).

[34] Bone and Jerdan: Proc. Chem. Soc., **17**, 164 (1901).

[35] Bone and Wilson: Proc. Chem. Soc., **14**, 155-6 (1898).

[36] Bouchardat: Compt. rend., **90**, 1560-3 (1880).

[37] *Bourguel: Ann.*, **10**, *3*, *325* (*1925*).

[38] Bradley and Parr: Chem. Met. Eng., **27**, 737-44 (1922).

[39] Bullier: Bull., (3) **17**, 646-54 (1897).

[40] Burrell and Oberfell: Bur. Mines Tech. Paper, **112**, 11-12 (1915).

[41] Campbell: Am. Chem. J., **17**, 690 (1895).

[42] Caro: Verh. Ver. geförderung Gewerbefleisses, **85**, 205-236, 245-292 (1906).

[43] Charitschkow: J. Russ. Phys.-Chem. Soc., **38**, 880-1 (1906); Chem. Zentr., **88**, *I*, 294 (1907).

[44] Chemistry Industry, **20**, 53 (1897).

[45] Claude: Compt. rend., **128**, 303 (1899).

[46] Collins: U. S. 1,812,849, June 30, 1931.

[47] Compagnie Générale des Produits de Synthèse: Fr. 658,643, Aug. 6, 1928. Chem. Abs., **23**, 5305 (1929).

[48] Consortium Electrochemische Industrie: Fr. 59.333, Jan. 22, 1925, Aus. 103.106, Jan. 7, 1925.

[49] Constable: Nature, **122**, 882 (1928).

[50] Coolidge: Science, **62**, 441 (1925).

[51] Coolidge: J. Franklin Inst., **202**, 693 (1926).

[52] de Forcrand: Compt. rend., **120**, 1215-8 (1895).

[53] de Wilde: Bull., (2) **6**, 267 (1866).

[54] de Wilde: Ber., **7**, 357 (1874).

[55] Durand: Bull., **35**, 1141-4 (1924).

[56] Elektrizitätswerke Lonza Swiss, 95,237, May 7, 1921; Ger. 395,549, July 1, 1922; Brit. 200,087, June 22, 1921.

[57] Erdmann: Acetylene in Wiss. und Ind., **1**, 72 (1898).

[58] Epner: Fr. 654,449, May 19, 1928; Chem. Abs., **23**, 3795 (1929).

[59] Erdmann and Köthner: Z. anorg. allgem. Chem., **18**, 48-58 (1898); Köthner: Dissertation, Halle (1896).

[60] Faworsky: J. prakt. chem., (2) **37**, 384-395 (1888).

[61] (2) **37**, 417 (1888).

[62] (2) **37**, 531 (1888).

[63] (2) **44**, 208 (1891).

[64] Fischer, Bangert and Pichler: Brennstoff-Chem., **10**, 279-82 (1929).

[65] Fischer and Peters: Brennstoff-Chem., **12**, 286 (1931).

[66] Fischer, Peters and Koch: Brennstoff-Chem., **10**, 383-5 (1929).

[67] Fischer, Schrader and Ehrhardt: Ges. Abhandl. Kenntnis Kohle, **4**, 389, 393 (1919).

[68] Fowler and Mardles: Trans. Faraday Soc., **23**, 301-6 (1927).

[69] Francis and Kleinschmidt: Proc. Am. Petroleum Inst., **11**, Sect. III, 93-99 (1930); Francis: Ind. Eng. Chem., **20**, 277 (1928).

[70] *Frank: Ger. 112,416.*

[71] Frank: Z. angew. Chem., **18**, 1733-5 (1905).

[72] Fry, Schulze, and Weitkamp: J. Am. Chem. Soc., **46**, 2268-75 (1924).

[73] Fujio: J. Soc. Chem. Ind. Japan, **31**, 77-86 (1928); Chem. Abs., **22**, 2363 (1928).

[74] Gaud: Compt. rend., **134**, 175-7 (1902).

[75] Gerdes: Ann. für Gewerbe und Bauwesen, **40**, 1 (1897) see 4.

[76] Gooch and Baldwin: Am. J. Sci., (4) **8**, 354-8 (1899); Z. anorg. allgem. Chem., **22**, 235-40 (1900).

[77] Grehant: Compt. rend., **146**, 1199-1200 (1908).

[78] Griner: Ann. Chim. Phys., (6) **26**, 357 (1892).

[79] Gros: Brit. 211,461, Feb. 2, 1924.

[80] Gros: Ger. 475,883, Jan. 22, 1924.

[81] Guest: J. Am. Chem. Soc., **50**, 1744-6 (1928).

[82] Haber and Oechelhäuser: J. Gasbel., **39**, 830-34 (1896); Haber: "Experimental Untersuchungen uber Zerzetzung und Verbrennung von Kohlenwasserstoffen," 71-2 (1896).

[83] Hague and Wheeler: J. Chem. Soc., **1929**, 391.

[84] Harkins and Gans: J. Am. Chem. Soc., **52**, 5165 (1930).

[85] Heisig: J. Am. Chem. Soc., **53**, 4460 (1931).

[86] Hermann, Deutsch, and Haehnel: Can. 256,557, Dec. 22, 1925.

[87] Herzog: Chem. Ztg., **55**, 461, 478 (1931); Kunststoffe, **21**, 49 (1931).

[88] Hilpert: Ges. Abhandl. Kenntnis Kohle, **1**, 271-5 (1917).

[89] Hodgkinson: J. Soc. Chem. Ind., **37**, 86-7T (1918).

[90] Hostmann-Steinbergsche Farbenfabriken Ges: Brit. 341,235, Sept. 12 1929.

[91] Horwitz: Ger. 205,705.

[92] Hubau: Ger. 103, 862.

[93] Hurd: Private Communication (1932).

[94] Hurd and Meinert: J. Am. Chem. Soc., **53**, 289 (1931).

[95] I. G. Farbenindustrie A. G.: Brit. 316,422, July 13, 1928.

[96] I. G. Farbenindustrie A. G.: Brit. 334,203, Feb. 23, 1929.

[97] I. G. Farbenindustrie A. G.: Brit. 346,680, Oct. 12, 1929.

[98] I. G. Farbenindustrie A. G.: Fr. 35,190.

[99] I. G. Farbenindustrie A. G.: Fr. 666,586, Dec. 31, 1928; Chem. Abs., **24**, 1476 (1930).

[100] I. G. Farbenindustrie A. G.: Fr. 666,611, Jan. 2, 1929; Chem. Abs., **24**, 1389 (1930).

[101] Ika and Ogura: J. Soc. Chem. Ind. Japan, **30**, 461-9 (1927); Chem. Abs., **21**, 3046-7 (1927).

[102] Ipatiev: Nat'l Petroleum News, **23**, No. 25, 61 (1931).

[103] Jackson and Northall-Laurie: Proc. Chem. Soc., **22**, 155 (1906).

[104] Janet: Z. Calc. Carb. und. Acet., **5**, 237 (1901).

[105] Jovitschitsch: Monatshefte, **29**, 1-14 (1908); Sitz. Akad. Wiss. Wien., **116**, IIb, 1241-54 (1907).

[106] Jovitschitsch: Bull. Sci. Acad. Roy. Belg., (5) **10**, 465 (1924).

[107] Jovitschitsch: Bull. Sci. Acad. Roy. Belg., (5) **13**, 365-70 (1927).

[108] Kaufmann: Ann., **417**, 34-59 (1918).

[109] Kaufmann and Mohnhaupt: Ber., **56**, 2533-6 (1923).

[110] Kaufmann and Schneider: Ber., **55**, 267-82 (1922).

[111] Keiser and McMaster: J. Am. Chem. Soc., **32**, 388-91 (1910).

[112] Kennaway: Brit. Med. J., **1925**, II, 1-4.

[113] Kinoshita: Physik. Z., **8**, 35 (1907).

[114] Körting: J. Gasbel., **42**, 843-8 (1899).

[115] Kovache and Tricot: Chimie et Industrie, **13**, 361-72, 537-47 (1925).

[116] Kusnetzov: Ber., **40**, 2871 (1907).

[117] Lewes: Proc. Roy. Soc., **55**, 100-2 (1894).

[118] Lewes: J. Soc. Chem. Ind., **17**, 532 (1898).

[119] Lichtenhahn: Brit. 200,087, Can. 238,888, Mar. 25, 1924.

[120] Lind: J. Phys. Chem., **32**, 573 (1928).

[121] Lind and Bardwell: Science, **62**, 422-4 (1925).

[122] Lind and Bardwell: Science, **62**, 593-4 (1925).

[123] Lind and Bardwell: Science, **63**, 310-1 (1926).

[124] Lind and Bardwell: J. Am. Chem. Soc., **48**, 1575-1584 (1926).

[125] Lind, Bardwell and Perry: J. Am. Chem. Soc., **48**, 1556-75 (1926).

[126] Lind and Livingston: J. Am. Chem. Soc., **52**, 4613 (1930).

[127] Lind and Livingston: J. Am. Chem. Soc., **54**, 94 (1932).

[128] Lind and Schultze: J. Am. Chem. Soc., **53**, 3355 (1931).

[129] Lind and Schultze: Trans. Am. Electrochem. Soc., **1931**, 165.

[130] Losanitsch: Ber., **40**, 4656-66 (1907).

[131] Losanitsch: Sitz. Akad. Wiss. Wien, **117**, IIb, 467-76 (1908).

[132] Losanitsch: Bull. Soc. stiin. Bucharest, **23**, 3-33 (1914); Chem. Abs., **11**, 254 (1917).

[133] Losanitsch: Bull. Sci. Acad. Roy. Belg., (5) **11**, 325 (1925).

[134] Maquenne: Compt. rend., **121**, 424-7 (1895).

[135] Marshall: Private Communication (1930).

[136] Matignon: Compt. rend., **124**, 775-7 (1897).

[137] McLennan, Perrin and Treton: Proc. Roy. Soc., **125A**, 246-62 (1929).

[138] Meinert and Hurd: J. Am. Chem. Soc., **52**, 4540 (1930).

[139] Meyer: Ber., **45**, 1609-33 (1912).

[140] Meyer and Fricke: Ber., **47**, 2765-74 (1914).

[141] R. Meyer and W. Meyer: Ber., **51**, 1571-87 (1918).

[142] Meyer and Taeger: Ber., **53**, 1261-5 (1920).

[143] Meyer and Tanzen: Ber., **46**, 3183-99 (1913).

[144] Mignonac and de Saint-Aunay: Compt. rend., **188**, 959-61 (1929).

[145] Mixter: Am. J. Sci., (4) **9**, 1-9 (1900).

[146] Mixter: Am. J. Sci., (4) **10**, 299-309 (1900).

[147] Mixter: Am. J. Sci., (4) **12**, 347-57 (1901).

[148] Moens and Juliard: Bull. Sci. Acad. Roy. Belg., **13**, 201-5 (1927).

[149] Moissan: J. Franklin Inst., **143**, 147 (1897).

[150] Moissan: Compt. rend., **126**, 302 (1898).

[151] Moissan and Moureu: Compt. rend., **122**, 1240-3 (1896); Bull., (3) **15**, 1296 (1896).

[152] Morani: Ger. 141, 884.

[153] Mund and Koch: Bull. Soc. Chim. Belg., **34**, 119-26 (1925).

[154] Mund and Koch: Bull. Soc. Chim. Belg., **34**, 241-55 (1925).

[155] Mund and Koch: J. Phys. Chem., **30**, 289-93 (1926).

[156] N. V. de Bataafsche Petroleum Maatschappij, Brit. 344,470, Nov. 13, 1928.

[157] N. V. Electrozuurstof-en-Waterstoffabriek: Brit. 303,797, Jan. 8, 1929; Dutch 20,851, Nov. 15, 1929; Chem. Abs., **24**, 931 (1930).

[158] Nieuwland, Calcott, Downing and Carter: J. Am. Chem. Soc., **53**, 4197 (1931); See also Nieuwland: U. S. 1,811,959 and U. S. 1,812,541, June 30, 1929.

[159] Novak: Ber., **42**, 4209-13 (1909); See Lidov and Kusnetzov, J. Russ. Phys.-Chem. Soc., **37**, 804-3 (1905); Chem Zentr., **1906**, I, 329.

[160] Novak: Ceska adademia Trida II: Matematica-Prirodnicka Rozpravy, **18**, 50 (1909).

[161] Novak: Z. physik. Chem., **73**, 513-46 (1910).

[162] Pease: J. Am. Chem. Soc., **51**, 3470-5 (1929).

[163] Pictet: Ger. 255,733, Oct. 22, 1909; Chem. Abs., **6**, 145 (1912).

[164] Pictet: Brit. 24,256, Oct. 19, 1910.

[165] Pictet: Fr. 421,838, Oct. 26, 1910; J. Soc. Chem. Ind., **30**, 542 (1911).

[166] Pring and Fairlie: J. Chem. Soc., **99**, 1796 (1911).

[167] Pring and Hutton: J. Chem. Soc., **89**, 1591 (1906).

[168] Prudhomme: Brit. 238,931, Aug. 24, 1925.

[169] Ramsay: Phil. Mag., (5) **2**, 269 (1876).

[170] Rasch: Acetylene Wiss. und Ind., **4**, 180 (1900).

[171] Reinicke: Z. angew. Chem., **41**, 1144 (1928).

[172] Renard: Compt. rend., **104**, 574-6 (1887).

[173] Rimarski: Jahresberichte physikal. tech. Reichsanstalt, IV-VII.

[174] Rimarski: Autogene Metallbearbeitung, **22**, No. 10, 134; Acetylene in Wiss. und Ind., **32**. No. 5, 69-73; Chem. Abs., **23**, 4344 (1929).

[175] Rimarski: Z. angew. Chem., **42**, 933 (1929).

[176] Rimarski and Konschak: Acetylene Wiss. und Ind., **31**, 24-9 (1928); Chem. Abs., **22**, 2454 (1928).

[177] Rimarski and Konschak: Acetylene in Wiss. und Ind., **33**, 97 (1930); Acetylene in Sicherheitstechniker Hinsicht, **1925**, 73.

[178] Romer: Ann., **233**, 183 (1886).

[179] Rousseau: Compt. rend., **117**, 164 (1893).

[180] Sabatier: Assn. Française pour l'Avancement des Sciences **28**, I 235-6 (1899); IVe Congrès International de Chimie Appliquee, **1900**, III, 134-42.

[181] Sabatier-Reid: "Catalysis in Organic Chemistry," 329-332 (1923).

[182] Sabatier and Senderens: Bull., (3) **21**, 530 (1899); Compt. rend., **130**, 250-2 (1900).

[183] Sabatier and Senderens: Compt. rend., **128**, 1173-6 (1899); **130**, 1559 (1900).

[184] Sabatier and Senderens: Compt. rend., **131**, 40 (1900).

[185] Sabatier and Senderens: Compt. rend., **131**, 187-190 (1900); see Mailhe: Chem. Ztg., **32**, 244 (1908).

[186] Sabatier and Senderens: Compt. rend., **130**, 1628; **131**, 267-70 (1900); **134**, 1185 (1902).

[187] Sabatier and Senderens: Bull., (3) **25**, 678-84 (1901).

[188] Sabatier and Senderens: Ann. Chim. Phys., (8) **4**, 439-52 (1905).

[189] Salvadori: Gazz., **32**, II, 496 (1902).

[190] Sandman: Z. angew. Chem., **14**, 673 (1901).

[191] Schläpfer and Brunner: Helv. Chim. Acta, **13**, 1125 (1930).

[192] Schläpfer and Stadler: Helv. Chim. Acta, **9**, 185-99 (1926).

[193] Schrohe: Ber., **8**, 17 (1875).

[194] Schützenberger: "Traite de Chimie Generale," I, 723 (1880).

[195] Schützenberger: Compt. rend., **110**, 889-92 (1890).

[196] Sinkinson: Ind. Eng. Chem., **17**, 30 (1925).

[197] Thénard: Compt. rend., **78**, 219 (1874).

[198] Thiele: Z. angew. Chem., **22**, 2472-84 (1909).

[199] Tiede and Jenisch: Brennstoff Chem., **2**, 5-8 (1921).

[200] Vogel: "Handbuch für Acetylene in Technischer und Wissenschaftlichen Hinsicht" (1904).

[201] Volmar and Hirtz: Bull., (4) **49**, 684 (1931).

[202] Walker: J. Phys. Chem., **31**, 970 (1927).

[203] Wislicenus and Schmidt: Ann., **313**, 220 (1900).

[204] Wohl: Z. angew. Chem., **35**, 593 (1922); Brit. 146,258, June 28, 1920; Brit. 145,597, Aug. 4, 1921; Brit. 157,058, Sept. 1, 1921; Ger. 352,838-9, May 5, 1922; Ger. 385,708, Nov. 27, 1923; addition to Ger. 352,838.

[205] Ylla-Conte: Brit. 299,425, Oct. 26, 1927.

[206] Ylla-Conte: Brit. 301,325, Jan. 23, 1929.

[207] Ylla-Conte: Swiss, 143,697, Oct. 23, 1928.

[208] Ylla-Conte: Fr. 662,896, Oct. 25, 1928.

[209] Ylla-Conte: J. Inst. Petroleum Tech., **15**, 744 (1929).

[210] Wheeler, McAulay and Francis: Brit. 342,319, Aug. 21, 1929; Brit. 342,359, Aug. 21, 1929.

[211] Wislicenus and Schmidt: Ann., **313**, 220 (1900).

[212] Zelinsky: Compt. rend., **177**, 882-5 (1923).

[213] Zelinsky (in part with Kasansky): Ber., **57**, 264-76 (1924).

Universal Oil Products Company,
Research Laboratories,
Chicago, Illinois.

THE COLLOID CHEMISTRY OF THE NERVOUS SYSTEMS. IV*

BY WILDER D. BANCROFT, ROBERT S. GUTSELL,** AND JOHN E. RUTZLER, JR.***

More than thirty-two years ago MacLeod found that morphinism could be cured by the use of bromides,[1] still practical advantage has not been taken of this discovery. The fact that MacLeod's work made no useful impression seems to be due to the utter lack of understanding of why sodium bromide should help drug addicts. In the light of the theory of reversible agglomeration intelligent use can be made of MacLeod's facts. The natural attack upon the problem, bearing in mind the work with sodium bromide and the theory of reversible agglomeration, is to attempt to cure drug addiction by the use of sodium rhodanate which is a better peptizing agent than sodium bromide. Since no drug addicts were available who cared to undergo a purely experimental treatment, and since the general medical profession is loath to act upon a theory, it became necessary to perform experiments on addicted dogs.

Tatum, Seevers, and Collins[2] say: "An experimental study of morphine poisoning, both acute and chronic, has for its goal the elucidation of the corresponding conditions in man. A direct study of morphine poisoning in man is complicated by the state of mind of the subject, consequently that aspect of the problem approachable by the methods of the physiological laboratory is more safely based on controlled laboratory experimentation." So, it would seem that in some respects it was well that our first experiments were made on dogs.

Plant and Pierce[3] say that there is quite a bit of variability in the withdrawal symptoms when a group of dogs is withdrawn from morphine abruptly. The withdrawal symptoms of the dogs as a group gave a composite picture which is similar to that obtained in man. These writers conclude that the dog is the best laboratory animal for the study of morphine addiction. Tatum, Seevers, and Collins believe that the monkey is more suitable for such studies than the dog. The dog was used in our work because they are easier to obtain, less expensive, and more hardy.

Since dogs cannot administer morphine to themselves, the only way to test the validity of the theory that reversible agglomeration is responsible for many, if not all, of the symptoms of drug addiction and withdrawal is to withdraw the animals abruptly under the influence of a peptizing agent. Mental rehabilitation can hardly be studied to advantage with dogs.

---

*This work is done under the programme now being carried out at Cornell University and supported in part by a grant from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

**M. D.

***Eli Lilly Fellow.

[1] Bancroft and Rutzler: Proc. Nat. Acad. Sci., 17, 186 (1931).

[2] J. Pharm. Exp. Ther., 36, 447 (1929).

[3] J. Pharm. Exp. Ther., 33, 329 (1928).

With the work of the above five authors as a guide, the experiments reported in this paper were made in order to determine whether or not sodium rhodanate will control the symptoms produced by the abrupt withdrawal of morphine from addicted tissues.

Six dogs were used in this work. Before the experiments were started the animals were allowed to become acclimatized to their new surroundings. This procedure eliminates such things as depression due to homesickness and physiological upsets due to change of food and habits. This collection of dogs included one male collie, designation C1, about two years old, one female collie, designation C2, about two years old; one female mixed hound, designation H1, about one year old; and three female beagles, designations B1, B2, and B3. The beagles were litter-mates, and were about two and one-half months of age. During the period of acclimatization the dogs were studied so that some of their peculiarities could be observed and used for comparison later on. C1 was a wild, brainless dog; he was neither malicious nor interested in human beings. Affection did not seem to appeal to him. When chained up outside, this dog would bark continuously at the sky for long periods at a time. C2 was a thoroughbred; she was very quiet and ladylike, with a tendency to be shy. She was not cowardly, and responded gratefully to human company. H1 was vivacious, and continually sought human affection. B1, B2, and B3 were typical puppies; they were full of life and interested in everything. They banded together when allowed outside. None of these animals showed any tendency whatsoever to be mean; although it was not easy to impress things upon C1.

Others who have experimented on morphine addiction in dogs used large doses of morphine (30 mg. per kg. to more than 100 mg. per kg.). The smallest dosage used by Plant and Pierce was 30 mg. per kilogram; this corresponds to about 32 grains a day for an average-sized man, and is a large dose. They say, p. 342, that "there was no distinct relationship between the size of the dose at withdrawal and the severity of the symptoms although the two animals that showed very marked symptoms were withdrawn at a low dosage level (30 and 40 mgm. per kilogram)." It will be clear, in the light of the theory which will be discussed later, that any continued dosage of morphine sufficient to produce a physiological effect will bring about addiction to the drug. So, in addicting our dogs, small doses of morphine were administered at the start and the dosage level was never increased greatly. The dosage increase per unit of time in the case of C2, B1, B2, and B3 was the same, 0.0032 gram every other day from the 12th to the 41st day. The mode of addiction of these four dogs was therefore identical, disregarding variations in weight. In this manner it was hoped that the dogs could be addicted without profoundly disturbing their physiological processes. Likewise inherent physiological weaknesses should not play such an important rôle in the behavior of the animals on small doses of morphine as on large doses. Therefore the initial amount of morphine used was carefully made small enough so that the dogs were not deeply narcotized by the drug. The dosage was never increased rapidly enough to bring about narcosis.

"Abstinence[1] phenomena are more marked after a progressive rise in dosage than on a constant small or moderate dosage." It is a well-known fact that the morphinist requires more and more of the drug to "keep him comfortable" as the time during which he is addicted becomes longer. This fact is easily explained on the basis of the theory of reversible agglomeration. This corresponds to the well-known cases[2] in which more of a salt is necessary to cause agglomeration if the salt is added slowly to the sol. So, for both practical and theoretical reasons the dogs were given increasing doses of morphine during this study. Fig. 1 shows the amount of morphine injected subcutaneously each day during the course of these experiments. A detailed record of the behavior of the dogs during addiction and withdrawal follows. This is useful because it shows a complete behavior picture which includes many mental reactions not hitherto described.

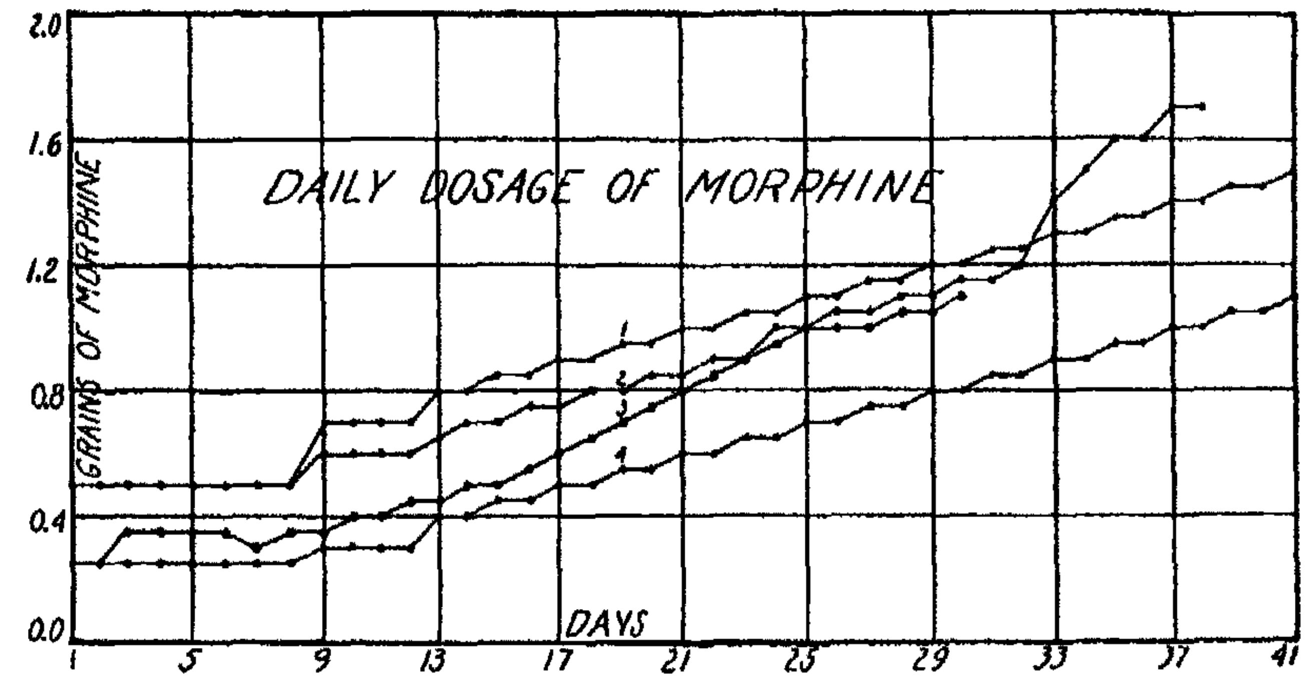


Fig. 1

Curve 1, dog C2 Curve 3, dog H1
Curve 2, dog C1 Curve 4, dogs B1, B2, B3

First Day

The addiction period was initiated on Wednesday, September 16, 1931. B1, B2, and B3 were given one quarter of a grain of morphine sulphate each at 10:15 a. m. The alkaloid was dissolved in sterile distilled water, a procedure which was followed throughout. In less than ten minutes the three dogs quieted down markedly; and each of them vomited. They did not seem to be in great distress; the vomiting was not severe. The two collies, C1 and C2 were given one half grain of morphine apiece. These dogs quieted down and vomited just as the puppies did. All of the dogs were quiet and sleepy during the afternoon; they refused food at night.

Second Day, September 17th

The dogs were injected at 9:30 a. m. They refused food at the morning feeding hour. Each of the dogs appeared to know that something was going

---

[1] Tatum, Seevers, and Collins: J. Pharm. Exp. Ther., 36, 452 (1929).

[2] Bancroft: "Applied Colloid Chemistry," 296 (1926).

to happen to them when the experimenters appeared. The animals became markedly quieted after the injections; all of them vomited. The effects of the morphine seemed to be manifested more quickly than on the first morning. The dogs did not appear to be so lethargic this afternoon as during the first afternoon. Their appetites were better at night.

Third Day, September 18th

The dogs accepted food this morning; they were very lively before the injections which were made at 10 a. m. This provoked vomiting within a very few minutes. All of the dogs except C2 again were depressed by the morphine. Since C2 was naturally quiet and well behaved, the depressing effect of the morphine was not so noticeable. Before noon the dogs were very quiet. C1, the hyperexcitable collie who always before had barked at automobiles, did not even move when an automobile drew up. During the afternoon the dogs slept as much as they did on the afternoon of the second day. Their appetites were somewhat improved.

Fourth Day, September 19th

The injections were made at 10:15 a. m. Vomiting resulted as usual; all of the animals quieted down after the injections. The hind legs of B1, B2, and B3 moved with an ataxic gait. According to Sollmann[1] this ataxia is not an unusual reaction of dogs to morphine. The animals refused their evening meal; in general they acted the same as during the third day.

Fifth Day, September 20th

The dogs were injected at 10:30 a. m. Before the injections were made, a study of the dogs showed them not to be so lively as they have been in the mornings. This may be due to the fact that it was a damp rainy day. It seemed to require a longer time for the morphine to bring about vomiting this morning. The drug quieted the dogs, as usual. The dogs are fed at 6 a. m. and 6 p. m. They have been refusing the evening meal and accepting the morning meal. The animals were more or less somnolent all day. For the last two days C1 has been salivating a great deal. C2 salivated after vomiting today.

Sixth Day, September 21st

Before the injections this morning all of the dogs were more animated than on the fifth day. The dogs were weighed for the first time today. Fig. 2, which will be discussed at different places in this paper, shows how the weights of the dogs varied during the course of the experiment. Morphine was injected at 10:05 a. m. today. The animals did not seem to quiet down so much after the injections today; but they all vomited as usual. C1 salivated profusely when observed during the afternoon. He was very "dopey," and his gait was distinctly ataxic. C2 salivated slightly, and was very quiet. B1, B2, and B3 were salivated, and hardly depressed at all. By and large, the dogs were affected less by the morphine today than on other days. The dogs' appetites continued to be poor.

---

[1] "A Manual of Pharmacology," 219 (1917).

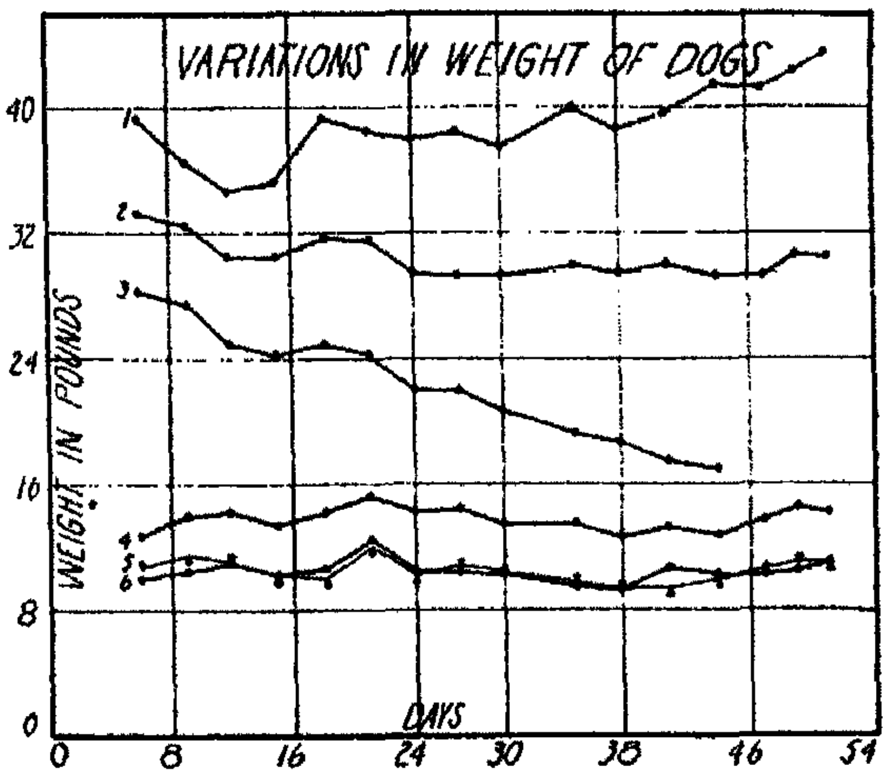


Fig. 2

Curve 1, dog C1
Curve 2, dog C2
Curve 3, dog H1
Curve 4, dog B1
Curve 5, dog B2
Curve 6, dog B3

Seventh Day, September 22nd

B1, B2, and B3 were quite active this morning, as usual. C2 was quiet, but was interested in the events occurring around her. C1 was disinterested this morning. The addiction period of H1 was started this morning. The onset of vomiting after the administration of morphine was somewhat delayed today. C1, C2, and H1 vomited; while B1, B2, and B3 were not observed to vomit at all. H1 was not depressed much by the morphine. The drug definitely did not quiet down B1, B2, and B3 so much as it had heretofore. It can be seen from the behavior of the dogs as a group that they have acquired a tolerance for morphine. During the afternoon C1 was disinterested and exhibited a very ataxic gait. This was a hot day, and C1 may be affected more by the heat than the other dogs. He went out of his way to avoid human beings. C2 was quiet, but acted much brighter than she did yesterday afternoon. B1, B2, and B3 appeared to be unaffected by the morphine that was administered during the morning. H1 was neither vivacious nor badly depressed by the morphine.

Eighth Day, September 23rd

This morning all of the dogs were much livelier than they were on the previous few mornings. C2 seemed very shy and quiet; this is probably the natural temperament of C2 for she is a bright dog, and while shy and quiet she was by no means disinterested. The dogs were unusually friendly toward the experimenters this morning. Morphine was injected at 10:35 a. m. B1, B2, B3, and C1 lost their vivacity after they were injected. No signs of vomiting were noticed. This morning it was possible to inject all of the dogs except H1 without holding them tightly. B1, B2, and B3 no longer appear to be constipated. During the afternoon C1 was more animated than he was yesterday; also, his gait was less ataxic. He appeared to be less afraid of people than he has been. C2 did not exhibit any depression in the afternoon from the injection. The morphine has changed the character of this dog. While she is very friendly when approached, she appears to be seclusive, quieter, and more shy than she was. She does not seem to care for human company any more; but she does not attempt to repel it. B1, B2, and B3 were not excessively quiet this afternoon. Whereas they followed the experimenters around without coaxing this morning before the morphine was administered, they ran away when approached this afternoon. H1 was quieter than during the previous afternoon; but she was not depressed much by the drug.

Ninth Day, September 24th

The dogs were quite lively this morning. C1 appeared to both expect and want the drug. B1, B2, and B3 were very salivated. C2 was brighter today. Since tolerance to the vomiting reaction, and to a lesser degree to the depressing action, has apparently been established, the dosage of morphine was raised this morning. The dogs were weighed before they were injected. All of the dogs vomited following the injections with the exception of H1; they were all quieted by the drug. It is interesting to note that H1 is so constituted that her vomiting center is not stimulated by morphine like the other dogs.

When the experimenters appeared in the afternoon all of the dogs were quiet and very salivated. Upon being released, they were as animated as they were yesterday. Although H1 was more depressed than she was yesterday she was not salivated. All of the animals whined this afternoon. The ataxia exhibited by C1 persisted today.

Tenth Day, September 25th

The dogs acted as usual this morning; they were neither more nor less lively than on the preceding few mornings. However, they are not nearly so lively in the mornings now as they were on the first few mornings of the addiction period. Morphine solution was injected at 10:00 a. m. The dogs became quiet after the injections. H1 vomited for the second time. All of the other dogs vomited. At noon the dogs were still quiet; they were not somnolent or greatly depressed. In general, the morphine has not caused the dogs to be "dopey" and dispirited. Their reactions are better characterized as being less vivacious and somewhat slowed down.

Eleventh Day, September 26th

All of the dogs were quite animated this morning. B1, B2, and B3 began to salivate when the experimenters appeared; they were not salivated beforehand. C2 acted quite differently today. She showed more interest in things, was much less shy, and more interested in human company. The morphine did not cause B2 and H1 to vomit.

Twelfth Day, September 27th

The dogs were fairly lively this morning. B1, B2, and B3, and H1 were especially lively. C2 continues to be less shy and more interested in things. C1 has quieted down in a most striking manner. At the beginning of the experiment he was wild and scatter-brained. Now he is calm and does not evidence his brainless makeup so positively. Morphine was administered at 11:00 a. m. today. H1 did not vomit and was not quieted much by the drug. C2 vomited after the injection and then became rather quiet. C1 vomited also. C1 and C2 commenced to salivate immediately after being injected.

B1, B2, and B3 exhibited some interesting reactions this morning. Upon the appearance of the experimenters they all began to salivate profusely. So profuse was the salivation that the animals soon became wet all over their bodies. While B1 was being injected, B3 looked on and vomited before the injection of B1 was completed. B3 immediately consumed the vomitus showing that she was hungry and probably not nauseated. B2 vomited so quickly after the morphine was injected that the mechanism probably was not a stimulation of the vomiting center; she consumed the vomitus also. Reach[1] considers that salivation before and after the injection of morphine is a withdrawal symptom. Pavlov[2] and Collins and Tatum[3] call it a conditioned reflex. Pavlov also describes reflex vomiting similar to that just pictured. There does not seem to be much question but that Pavlov is right; because, as will be seen later increasing the dosage of morphine failed to stop the salivation. Also, all of the dogs began to salivate when the experimenters appeared, no matter what time of day it was, or whether before or after the injections of morphine were made. It was determined definitely that visitors did not induce this reaction.

Thirteenth Day, September 28th

The dogs were just as lively this morning as they were yesterday morning. They began to salivate shortly after seeing the experimenters, with the single exception of H1. The morphine dosage was increased today for all dogs except H1. The injections were made at 10:00 a.m. B1, B2 and B3 vomited; but the other dogs did not. The larger dosage did not cause the dogs to become more quiet than usual.

During the afternoon the animals acted no differently, so far as general appearance goes, than they did on the smaller dosage. They were not particularly quiet. C2 was shy and self-contained, thus reverting to her earlier condition. B1, B2, B3 and C1 salivated profusely when the experimenters came in sight. The dogs' appetites are better than they have been so far during the experiment.

Fourteenth Day, September 29th

C2 was less shy again today. When one of the experimenters came into the cage she prostrated herself at his feet. C1 is becoming quieter and quieter. H1 still acts very animated in the morning. B1, B2, and B3 have quieted down in the last few days so that they are not nearly so animated in the morning as they were during the first week of addiction. B1, B2, B3 and C1 salivated profusely when the experimenters appeared. Morphine was ad-

---

[1] Z. exp. Path. Therap., 16, 321 (1914).

[2] "Conditioned Reflexes," 35 (1927).

[3] Am. J. Physiol., 74, 14 (1925).

ministered at 10:00 a.m. C1, B2, and B1 vomited within 15 minutes after the injections. To date H1 has been comparatively refractory to the drug; for it has not affected her as much as the other dogs.

Fifteenth Day, September 30th

Profuse salivation commenced today when the experimenters appeared. C2 exhibited a different reaction again today. The cloak of shyness has fallen once more; and she was more investigative. For the past few days this dog has submitted to the injection very undemonstratively. She appears to be ready for it when the experimenters approach her. H1 was vivacious this morning. C1 walked up to the experimenters as though he desired to be injected. When one of the beagles was taken out of the cage and into a room to be weighed and injected, the two other beagles began to howl. All of the dogs submit to the injections quietly so that extremely little restraint is necessary during the manipulation. The injections were made at 10:15 a.m. Each of the dogs was examined for tenderness in the regions where the injections have been given. Since no tenderness was found, the conclusion is drawn that the dogs are not suffering from abscesses.

No vomiting was witnessed after the morphine was administered today. Also, there was little, if any depression produced by the drug. To date the dogs have been on a diet of bread and milk.

Sixteenth Day, October 1st

The dogs presented the same general behavior picture this morning as they have for the last two mornings. The dogs salivated profusely, as usual. Morphine was administered at 10:30 a.m. B2 was taken out of her cage and into a room to be injected. The other two dogs, B1 and B3, howled almost as soon as the room door was closed. The morphine had very little affect on H1; she did not vomit or become depressed. C1 and C2 did not vomit. B1, B2, and B3 did vomit.

C1, C2, and H1 were fed a pound of raw hamburg each; B1, B2, and B3 were each given one-half pound of the raw meat at the evening meal time. C2 refused to eat hers at the time, but ate it during the night.

Seventeenth Day, October 2nd

B1, B2, and B3 were considerably more animated today; C2, H1, and C1 acted as they have for the last few mornings. None of the dogs appears to be constipated. All of the dogs, except H1, salivated when the experimenters appeared. Morphine was administered at 10:30 a.m. The drug did not have any quieting effect on any of the dogs, with the exception of H1. She became only slightly less lively.

About ten minutes after being injected C1 began to whine and bark. He was not barking at anything in particular; he turned his head away from the experimenters when he barked. The bark was a peculiar explosive half-hearted yelp. So far as could be determined there was no external cause for pain. This description of the behavior of C1 illustrates the psychiatric abnormality of the dog which will be considered in detail later.

The dogs were not seen vomiting today. At no time, before or after this day, during the experiment have any of the dogs growled, snapped, or acted mean in any way either during, before, or after the injections.

During the afternoon H1 was quiet and retiring. The other dogs acted the same as they have for the last few mornings before being given morphine. C1, C2, and H1 were each given a pound of raw hamburg. H1 and C2 refused to eat the meat. C2 made vomiting movements when the meat was presented; she consumed the meat during the night. H1 did not eat the meat at all. C1 ate the meat hungrily; he was extraordinarily quiet and gentlemanly in the way he took the meat. B1 and B3 were given three-quarters of a pound of meat. B2 refused the meat.

Eighteenth Day, October 3rd

With the exception of H1, all of the dogs were livelier this morning than they have been during the past week. They all salivated prior to the administration of the drug; this is the first time that H1 has salivated. The injections of morphine were made at 10:00 a.m. B1, B2 and B3 were taken, one at a time, into the weighing room to be given the hypodermic. When B1 was taken into the room, B2 and B3 began to howl. B3 began to howl when B2 was taken into the room. This reaction on the part of the dogs left behind being repeated, as it has, signifies either one of two things; either they wanted the injection of morphine, or they did not want their sister dog taken away from them. In the light of the behavior of the dogs later in the experiment, the former reaction seems to be the more likely.

None of the dogs vomited after their dosage of morphine; likewise they were quieted very little by the drug. Of course, the dogs are not now so animated before the drug is injected as they were during the earlier part of the experiment. C1 was more excitable this morning, and would not stand still while being injected. On the whole, the dogs seem very lively for the amount of morphine that must be in them.

Nineteenth Day, October 4th

Again this morning the dogs seemed a little more lively than they have been for the past week. The experimenters drove up to, and then 30 yards past the door of the experimental barn, and stayed there for about ten minutes. In a few minutes the dogs in the barn began to bark and howl. The loud baying of B1, B2, and B3 could be distinguished clearly. Upon entering the experiment station none of the addicted dogs barked; whereas three other dogs continued to make a disturbance. C1 was profusely salivated at this time. B1, B2, B3, C2, and H1 commenced to salivate upon seeing the experimenters. C1 balked at being injected today, as he did yesterday. The drug did not quiet the dogs, with the exception of H1. She did not show much effect from the injection.

Each of the three beagles was given its morphine just outside of the cage in the sight of the others. While B1 was being injected B2 and B3 bayed loudly. Likewise B3 bayed while B2 was being injected. These dogs now stand still without being restrained at all while being given the hypodermic; they wag their tails during the process. C2 and H1 do not have to be held either. All of the dogs were fed Calo dog food at night. With the exception of H1 they ate well.

Twentieth Day, October 5th

The process of driving past the door of the experiment station was repeated today with the same result as yesterday. The addicted dogs apparently become restless during the middle of the morning before they are given morphine. The restlessness subsides when the drug is given. The hypodermics were given at 11:00 a.m. Prior to this all of the dogs salivated. The morphine did not provoke vomiting.

B1, B2, and B3 repeated their baying performance of yesterday. The drug no longer seems to quiet the dogs after the injections.

Twenty-first Day, October 6th

The dogs did not make a commotion when the experimenters arrived today. Morphine was administered at 11:00 a.m. All of the dogs were salivated this morning. B1, B2, and B3 repeated their act of the last two days. With the exception of C1, all of the animals stand still without being held while the injections are made. There were no evidences of vomiting after the morphine was administered today. C1 is somewhat rebellious while being injected; his high degree of excitability is maintained. C2, C1, and H1 appear to be constipated.

Twenty-second Day, October 7th

Again today the dogs did not make a commotion when the experimenters waited outside of the experiment station. All of the dogs salivated profusely before being injected; B1, B2, and B3 were quite a good deal more salivated than the other dogs. This has been the case ever since these three dogs began to salivate. Morphine was administered at 10:15 a.m. The three puppies did not repeat the baying act.

None of the dogs vomited after being given morphine. C2 was somewhat less shy this morning; she was bothered by diarrhea. C1 had diarrhea also.

Twenty-third Day, October 8th

Another interesting reaction was observed this morning. The day was dark and wet; and all of the experimental dogs were noticeably more quiet than usual. Three other dogs at the experiment station acted no differently than on other days. This same reaction has been observed several times. Quite independently of this the authors have been told by addicts who are not using the drug, but whose nervous systems have not returned to normal, that on dark, damp days they feel depressed. So, there seems to be an analogy here between the behavior of man and dogs.

Morphine was administered at 10:30 a.m. B1 and C1 both vomited after the drug was given. The reaction was not so severe as usual. C1 did not struggle while being injected. His hyperexcitability has disappeared. Neither

C1 nor C2 was bothered by diarrhea today. B1, B2, and B3 are not constipated. Most of the animals now wag their tails while being injected.

Twenty-fourth Day, October 9th

It was cold today, and the addicted dogs were quiet. The other dogs were noisy. All of the experimental dogs began to salivate profusely before being injected. The drug was administered at 10:30 a.m. Only C1 had to be held while this was done. None of the dogs came of their own accord into the room where the injections were made. C1 and B1 vomited after being given the morphine. No signs of diarrhea were seen. C2 was less shy than she has been.

When the experimenters appeared in the afternoon all of the dogs began to salivate. There were other persons observing the animals when the experimenters came; but they did not cause the dogs to salivate. The degree of salivation was not nearly so great as it is in the morning before the dogs are given morphine.

The dogs were fed Ken-L Ration during the afternoon. C1, B1, B2, and B3 consumed it voraciously; the latter three dogs pranced around and fought for it. Yet the dogs refuse bread and milk, which they formerly liked. C2 ate the Ken-L Ration in a very lady-like manner. The experimental dogs have refused all but very appetizing food for the last two weeks.

Twenty-fifth Day, October 10th

All of the dogs salivated profusely this morning, when the experimenters appeared. While the animals were being observed, and before any preparations whatever were made for the injections, C1 and B1 vomited. This was in all probability reflex vomiting. Morphine was administered at 10:00 a.m. None of the dogs vomited after the injections. They were fed Ken-L Ration during the afternoon.

Twenty-sixth Day, October 11th

The experimenters arrived late in the morning. Despite the cold wet day, there was a great deal of barking and excitement. Upon entering the experiment station the addicted dogs became quiet, and showed no signs of excitement. The dogs salivated as usual. H1 was bothered by diarrhea. None of the animals vomited after the morphine was administered at 12:30 p.m.

Twenty-seventh Day, October 12th

The dogs began to salivate soon after the experimenters arrived. Morphine was injected at 10:15 a.m. It has been noticed that a short time after the drug is given the dogs stop salivating. C1 was restless and hyperexcitable while being injected. He protested physically, but did not growl or snap. The other dogs did not have to be held while being injected. None of the animals vomited after being injected; further, they were livelier than usual after the drug was exhibited.

Twenty-eighth Day, October 13th

When the experimenters arrived the dogs salivated, as usual. C1 is almost as scatter-brained and crazy as he was before the experiment was started.

Morphine was administered at 9:15 a.m. C1 again protested against being injected. He vomited shortly after the injection. This was probably reflex vomiting for he consumed the regurgitated material. None of the other dogs vomited.

Twenty-ninth Day, October 14th

In order to observe the reactions of the dogs if the exhibition of morphine were delayed, the animals were not injected until 5:30 p.m. After mid-morning the addicted dogs were markedly uneasy and barked almost continuously until the experimenters came to inject them. The dogs became quiet and began to salivate when we arrived. C2 did not salivate until the injection was started. B1, B2, and B3 were slightly restless and wandered around their cage in an aimless manner. None of the dogs vomited after having morphine. C1 did not protest nearly so much as he did yesterday when given the drug. So it can be assumed that the dogs now have a physical need for morphine.

At times several of the dogs have been bothered by conjunctivitis.

Thirtieth Day, October 15th

All of the dogs were salivated before they were given morphine. The drug was administered at 10:15 a.m. The animals did not vomit after being injected. The morphine quieted the dogs more than usual today; this is probably due to the fact that a shorter time than usual elapsed between the last two injections. The conjunctivitis noticed in H1 and C2 was treated with argyrol.

C1 protested strongly against the injection this morning. For the past week it has been noticed that the dogs attempt to defecate shortly after morphine is administered.

Thirty-first Day, October 16th

Each of the addicted dogs began to salivate when observed by the experimenters. C1 remains scatter-brained and senseless; he protested against being injected. The dogs were quieted by the morphine somewhat more than usual. None of the animals vomited after morphine was exhibited. The conjunctival condition of C2 and H1 is better today; it was treated again with argyrol.

Thirty-second Day, October 17th

Despite the fact that it was a cold and rainy day, the dogs were a little more lively; all salivated prior to receiving the drug. Morphine was injected at 10:00 a.m. B1, B2, and B3 wagged their tails while being injected. This has occurred for several days. It was definitely determined that the animals wag their tails much harder *while the solution is running out of the needle*. The phenomenon commences during the pre-injection handling of the dogs; they do not wag their tails harder when the needle is thrust under the skin.

H1 and C2 are no longer suffering from conjunctivitis.

C1 presents a strange figure; during the injection he acted in a weird, scatter-brained manner. Then he vomited. Following this, for the second time in the last two days, he stood motionless with his head in a corner of the cage for quite a while. Further, during the last few days he has gnawed a two by four inch timber almost half in two. Plant and Pierce[1] consider this to be a withdrawal symptom. Therefore the dosage of morphine was raised more rapidly from this day on.

The dogs were depressed extremely little by the morphine today.

Thirty-third Day, October 18th

The dogs began to salivate as usual this morning upon the appearance of the experimenters. Morphine solution was injected at 11:00 a.m. C1 protested wildly against the injection; in doing so he was not either mean or ugly in any way. He vomited after being given the morphine. B1, B2, and B3 repeated their tail wagging episode. C1 has a maniacal look.

The dogs were fed Ken-L Ration during the afternoon. C1, B1, B2, and B3 took this food voraciously. C2 refused to accept the food while being observed or coaxed. As soon as the experimenters were out of sight, she ate heartily. H1 refused food entirely. A neutral, uninstructed observer remarked casually that C1 looks like a maniac; it should be stressed that this dog has never cared for human society since coming to the experiment station. This afternoon it was again demonstrated that only the experimenters elicit the salivation reaction. A stranger watched the dogs for five minutes, and saw no salivation. Yet, a minute or two after the approach of one of the experimenters the dogs began to salivate. The secretion was not so profuse as it has been on other afternoons.

All of the addicted dogs have undergone a change of character. They slink and act as though they have done something wrong, when they are approached.

Thirty-fourth Day, October 19th

H1 and C2 failed to salivate when the experimenters watched them. C1 was somewhat more quiet this morning. Morphine was administered at 10:30 a.m. C2 vomited severely after the injection. H1, B1, B2, and B3 *began to wag their tails only when the morphine solution began to run through the hypodermic needle.* All of the dogs except H1 seemed hungry when fed Ken-L Ration.

C1 balked at being injected so strongly that it was not advisable to try to administer the morphine while he was being held tightly. The dog quieted down when he was soothed, stroked, and talked to; this was continued, and he submitted to the injection without protesting. It was not necessary to restrain him at all.

Thirty-fifth Day, October 20th

With the exception of H1, the dogs salivated when the experimenters appeared. She did not salivate either before or after the injection. She has conjunctivitis again; it was treated with argyrol. As has been the rule for the past couple of weeks the dogs were quiet before morphine was administered. C2 was difficult to inject again this morning; he stopped making a fuss when he was soothed.

---

[1] J. Pharmacol. Proc., 31, 210 (1927); J. Pharm. Exp. Therap., 33, 343 (1928).

None of the animals vomited after being given morphine. H1 and C2 became much more quiet after the drug was given. H1 and B2 wagged their tails when the liquid ran out of the hypodermic needle.

Thirty-sixth Day, October 21st

There were no unusual occurrences today except the following. C2 vomited after being injected. H1 and C2 were treated with argyrol for conjunctivitis. H1 was not salivated. C1 was difficult to inject. All of the dogs except C1, wag their tails when the morphine solution flows from the needle.

Thirty-seventh Day, October 22nd

Morphine was not administered until 6:00 p.m. The dogs were noisy all afternoon. They were quiet when the experimenters arrived. They became noisy when the experimenters did not enter the barn. It was obvious that the dogs were distinctly more friendly to the experimenters than they usually are. H1 and C2, in particular, came up to us in an extremely friendly manner. C1 began to salivate before he saw the experimenters. H1 did not salivate at all. C1 was not quite so difficult to inject as he has been in the last few days. None of the dogs vomited after morphine was administered.

It was decided that the dogs show sufficiently definite signs of addiction to morphine for them to be prepared for withdrawal. Accordingly C2 and B3 were selected for abrupt withdrawal without sodium rhodanate. The other dogs with the exception of C1 are to receive daily doses of sodium rhodanate for a period of four days prior to abrupt withdrawal. During this time morphine will be continued in increasing doses. C1 will be given sodium rhodanate today and be withdrawn abruptly tomorrow. C1 was given 0.4 grams of sodium rhodanate in a gelatine capsule buried in a small ball of meat. B1 and B2 were given one capsule each containing 0.2 gram of sodium rhodanate in a similar manner. A capsule containing 0.2 gram of sodium rhodanate was forced down the throat of H1. Sodium rhodanate was followed in ten or fifteen minutes by the injection of morphine. The dogs that were given sodium rhodanate seemed to become more quiet than the others after morphine was administered.

Thirty-eighth Day, October 23rd

When observed this morning C2 and B3 did not seem to be quite as bright as the other dogs. All of the dogs except H1 began to salivate when the experimenters appeared. C1 objected strenuously to being injected. Since raising the dosage of morphine more rapidly, this dog has not stopped gnawing the timbers of his cage. It seems therefore that gnawing is not necessarily a withdrawal symptom. In this case it is considered to be a nervousness which parallels his general peculiar character changes. The injections were made at 10:30 a.m., dosage with morphine being continued. B1, B2, and B3 were not given morphine first this morning; they whined while the other dogs were being injected. H1 made vomiting motions after the drug was given.

Sodium rhodanate was given again this morning. The doses administered were: H1, 0.2 gram in a capsule per os, C1, 0.4 gram in a capsule in meat per os, B1, 0.2 gram in a capsule in meat per os, B2, 0.2 gram in water by subcutaneous injection.

Thirty-ninth Day, October 24th

All of the dogs salivated when the experimenters appeared, except H1. The dogs were quiet as has been usual in the morning for the past few weeks. C1 did not look so maniacal today. Morphine was injected at 10:15 a.m., none of the dogs vomited afterward. C1 was withdrawn abruptly today, that is he received no morphine.

Sodium rhodanate was administered again today. C1 was given 0.4 gram in a capsule in meat per os. H1, B1, and B2 were given 0.2 gram each in water solution by subcutaneous injection. The injection was quite painful to B1, it did not pain B2 or H1.

Fortieth Day, October 25th

C2 salivated more profusely than ever today; H1 did not salivate at all, and B2 salivated very little. For the last few days B2 has not salivated much. This dog acts more nearly normal than she has for some time. Morphine was administered at 11:00 a.m. None of the dogs vomited after the injections.

The behavior of C1 deserves special mention. He looks definitely less maniacal than he has lately. This morning he was more friendly than he has been for three or four weeks. He did not act so brainless and crazy as he has during the entire course of the experiment. He was lively in a normal way, which is most unusual. These changes were sharp and well-defined. He still gnaws at the supports of his cage. He passed a soft stool today.

Sodium rhodanate was administered as follows: C1, 0.6 gram in a capsule in meat per os; H1, B1, and B2, 0.2 gram in water solution by subcutaneous injection. These injections did not pain any of the dogs today.

Forty-first Day, October 26th

Morphine was administered at 3:30 p.m. The dosages of sodium rhodanate given were: C1, 0.4 gram in a capsule per os in meat; H1, and B2, 0.2 gram in water solution by subcutaneous injection; B1, 0.3 gram in water solution by subcutaneous injection.

C1 continues to gnaw industriously at the wood supports of his cage. For the first time in many weeks he showed interest in another dog. He does not show signs of diarrhea. The dog salivated less than usual. He showed definite signs of interest in human affection; he sought stroking by the experimenters. When led from place to place he did not balk as he does usually. A rapid, nervous opening and shutting of the jaws was noticed. The action did not last long, and was probably an effort to free his mouth and lips of saliva. This animal is improved much today; remarkable improvement in his general behaviour has been noticed in the last few days.

H1 is in very poor physical condition; she is, and has been, losing weight rapidly. She did not salivate today. Her nose is stopped up by dried mucus; the nasal passages are very dry. The conjunctivitis has disappeared. The injection of sodium rhodanate did not appear to pain her. This dog and B3 have been and are more interested in other dogs than are any of the experimental animals. H1 sprawled out on the floor of her cage and gave the appearance of being drowsy after the injections. She is markedly tender over the hips.

C2 salivated today, as usual. For the last few days she has turned over on her back when the experimenters came to her cage. This may be an indication that she wants the drug. The condition of this dog remains the same as it has been.

B3 now is the liveliest by far of the three litter-mates, B1, B2, and B3. When Ken-L Ration was offered to these three dogs only B3 showed any interest in it; she consumed it all. She wagged her tail when the morphine solution ran out of the needle.

B1 exhibited a reaction of pain to the injection of sodium rhodanate today. After the injections she curled up in her cage and was disinterested.

B2 seems to be disturbed by the treatment. She was disinterested when the experimenters arrived, and remained so after the injections. She has not been so salivated as the other dogs, of late; today she began to salivate quite a little while after B1, and B3 began. The injection of sodium rhodanate did not cause this dog or H1 to be in any pain. B2 vomited often yesterday; she shivered, and was not lively.

When sodium rhodanate is injected the dogs do not wag their tails; whereas they do wag them when morphine is injected.

This is the last day that morphine will be administered to any of the dogs. Abrupt withdrawal will begin, therefore, tomorrow.

Forty-second Day, October 27th

Sodium rhodanate was administered at 12:00 noon as follows: C1, 0.4 gram in a capsule in meat per os; H1, B1, and B2, 0.2 gram in water solution by subcutaneous injection.

H1 did not salivate when the experimenters approached. This dog is a sick dog, and has been that way for a week. The rapid loss of weight has weakened her considerably. She was not well before sodium rhodanate first was administered. During last night she stretched out on her side and was extremely disinterested. She was better this morning; she was more friendly than she has been for a couple of weeks. Her eyes were very pussy today; the condition was treated with argyrol.

C1 was more friendly again today. He is more quiet than he has been for some time; this does not appear to be due to depression. He is merely acting more like a normal dog. His stools are soft; but he does not have diarrhea. His appetite is good. He does not salivate so much as he did; most of the time his ears are pricked up and he is alert.

B2 appeared to be subdued and disinterested; there was no change in her response to human affection, that being strong as usual. This dog did not salivate when the experimenters were around. The injection of sodium rhodanate evidently caused no pain.

B1 was salivated profusely when the experimenters appeared. The injection of sodium rhodanate did not hurt this dog so much today. She did not become disinterested after the injection.

C2 salivated as usual when the experimenters observed her. B3 acted likewise. These two dogs showed no change in condition.

Forty-third Day, October 28th

Sodium rhodanate was administered as follows: C1, 0.4 gram in a capsule in meat per os; B1 and B2, 0.2 gram in water solution by subcutaneous injection. H1 was not given any sodium rhodanate on account of her poor physical condition. This dog has distemper; that is what has been ailing her. Other than to say that H1 did not at any time show withdrawal symptoms, the detailed account of her behavior from this time on will be omitted.

C1 continues to improve; he is a sensible dog now. He has ceased gnawing at the wood in his cage. The dog was only slightly salivated today; and there are indications of diarrhea. Other observers have noticed that this animal is brighter. His appetite is better.

C2 passed soft stools today. Only a very careful study revealed her true condition. The dog appears to be much brighter with not such a far-off look in her eyes. Upon the arrival of the experimenters she entirely forsook her shyness and quiet demeanor and approached them tail wagging, head up, with no hesitation, and without being called. This behavior was so foreign to her general conduct that her actions were like those of a different dog. This performance was repeated; she was then shown the hypodermic syringe which she nosed in a thoughtful manner. When the motions of injecting her were made she wagged her tail much harder. The dog quite definitely wanted the injection. Upon approaching the dog without the syringe in hand, she did not stir out of her corner. This was repeated several times with the same result. This dog either thought that the needle being thrust under the skin was an injection of morphine, or that by being friends she would not be given morphine. If the former situation is the correct one, there is in the actions of this dog a distinct parallel to the behavior of human addicts. On the other hand she may have learned quickly that she was not to have morphine today. The brightness and friendliness exhibited by this dog were probably due to nervousness. A slight horizontal head tremor was noticed.

B3 exhibited the same head tremor as C2; otherwise there was no change in her condition.

B2 was more lively than she was yesterday; she did not salivate when the experimenters appeared. There was no change in the condition of B1.

Forty-fourth Day, October 29th

H1, B1, and B3 were each given 0.2 gram of sodium rhodanate dissolved in water by subcutaneous injection at 12:00 noon. C1 was not given sodium rhodanate.

All of the dogs except H1 and B2 salivated when the experimenters appeared. None of the dogs salivated so profusely as they have been doing.

C2 behaved in the same peculiar manner that she did yesterday. The head tremor persists. The dog passes stools frequently. She refused Ken-L Ration.

B3 defecates often. She is definitely nervous; a slight head tremor is noticed now and then. Today she was not so friendly as B1 and B2 were. The animal would not eat Ken-L Ration. There was a very fine general body tremor that could not be detected with B1 and B2.

B1 and B2 were quite friendly today; but they were not unusually so, as C2 has been. They appear to be very slightly depressed. No special change was noticed today. These dogs are not passing soft stools as B3 and C2 are.

C1 was no different than he was yesterday.

Forty-fifth Day, October 30th

Sodium rhodanate was administered only to C1 today; he was given 0.6 gram in a capsule in meat per os at 5:30 p.m. C1 exhibited some important changes. He has lost all interest in human affection, is scatter-brained again, and has a maniacal look in his eye. Evidences of diarrhea were seen. The dog vomited reflexly upon seeing the experimenters; there was apparently a spastic condition of the stomach. He was hungry for he consumed the vomitus immediately. When being watched he turned his head and body toward the inside corner of the cage. This appeared to be due to negativism rather than to photophobia. The animal salivated when the experimenters appeared. He has resumed gnawing, having gnawed a hole in the wall. Shortly after being given sodium rhodanate the dog vomited again. It is important to note that this dog has not had sodium rhodanate for almost two days, which accounts for his peculiar actions. When one attempted to pat the dog he walked off. Every once in a while he emitted a low moaning whine.

C2 behaved like an entirely different dog today. When observed she was lying stretched out on her side in a disinterested fashion. Although she wagged her tail in a feeble manner, she neither moved the bulk of her body or looked up when the experimenters came. Upon entering the cage she made no movement to arise. After several repetitions of this the dog finally arose slowly. She laid down again almost immediately; and she did not move around during the brief time that she was on her feet. Although the dog was disinterested and was not lively at all, she did not in any way resent affection. The dog salivated when the experimenters came. The head tremor was pronounced today. The dog has diarrhea. She had no appetite, as was evidenced by the fact that fresh meat remained untouched in her pan.

B3 was disinterested today; she did not move when first approached in her cage. She showed little interest in leaving the cage when given an opportunity to do so. When she wandered about the cage a little her movements were slow and aimless. She showed evidences of nervousness. Normally the hungriest of the three young dogs, she refused fresh meat; whereas B1 and B2 ate all that was offered them. B3 salivated when the experimenters appeared. There was a pronounced head tremor today; and the body tremor is stronger than it was yesterday. She is doing considerable gnawing at her cage. B1 and B2 acted about the same as they did yesterday. The dogs seemed to be hungry for meat, particularly B2. No soft stools were noted. The dogs arose when the experimenters entered the cage, and were friendly. They seemed more interested than they did yesterday; they cared for human affection, and did not wander aimlessly about. The general health of B2 seems to be better than it has been since the start of the experiment. B1 salivated when the experimenters appeared, B2 did not.

None of the dogs salivate so profusely as they did when receiving morphine.

Forty-sixth Day, October 31st

Sodium rhodanate was administered at 10:30 a.m. in water solution by subcutaneous injection. H1 was given 0.1 gram, and B1 and B2 0.25 gram each.

C2 was inquisitive about the hypodermic syringe when it was shown to her. She wagged her tail rapidly when motions were made to inject her. She was lying on her side when first observed, and did not get up at all. She wagged her tail feebly when she first saw the experimenters. A very fine body tremor accompanied the head tremor. Her appetite seems somewhat better. The dog continues to pass many stools. She salivated when the experimenters appeared.

B3 acted about the same as she did yesterday. She was perhaps a little more quiet today. She was neither friendly nor unfriendly. The head and body tremor were still present. She salivated when the experimenters appeared. Her appetite seems to be better.

C1 was changed again today. He was more friendly and interested in what was going on. The maniacal look in his eye subsided; he did not face the back of his cage. So, sodium rhodanate again caused a change for the better in this dog. There were signs of diarrhea.

B1 and B2 were more lively today. The general health of B2 in improving rapidly. Both dogs salivated when the experimenters appeared. No soft stools were passed by these dogs. B1 and B2 were extraordinarily demonstrative and friendly today. Since they were not given sodium rhodanate yesterday, this reaction may be interpreted as a desire for morphine such as was shown by C2 on the forty-third day. In complete contrast to B3, B1 and B2 were anxious to leave their cage. A test for the rhodanate ion in the saliva was positive in the case of B1 and B2.

Forty-seventh Day, November 1st

Sodium rhodanate was administered as follows: C1, 0.6 gram in a capsule in meat per os; B1 and B2, 0.2 gram in water solution by subcutaneous injection.

All of the dogs except H1 have had, in general, better appetites since the morphine was withdrawn, despite the fact that at times for periods of about 36 hours some of the animals refused food. Despite the better appetites C2 and B3 have decreased slightly in weight since withdrawal; while B1, B2, and C1 have gained weight steadily. This is shown by the figures in Table I, the values being those on the last part of Fig. 2.

TABLE I

Weights of Dogs in Pounds during Withdrawal

Day	Wght. C1	Wght. C2	Wght. B1	Wght. B2	Wght. B3	Remarks
38	38.75	29.50	12.75	9.25	9.25	C1 withdrawn
41	39.75	30.00	13.25	9.25	10.75	C2, B1, B2, B3 withdrawn
44	41.50	29.25	12.75	9.90	10.25	
47	41.25	29.25	13.75	10.50	10.25	
49	42.25	30.75	14.50	11.0	10.50	
51	43.50	30.50	14.20	11.0	11.00	

The table shows that over the whole post-withdrawal period C1 gained weight steadily. C2, somewhat under her original weight, did not change much. B1 and B2 gained slowly; while B3 stayed about the same. The dogs that were not protected by sodium rhodanate therefore did not pick up so rapidly as those that were protected. Averaging the losses in weight of 18 dogs during the first week of withdrawal in the experiments of Plant and Pierce, we find that it was about one pound. Only one dog in 21 gained weight.

C1 showed continued improvement today. He was friendly, showed an interest in other dogs, wanted to leave his cage, and barked continuously at nothing in particular when chained up outside. Thus, some of his actions were much the same as before he was addicted. He salivated very little when the experimenters appeared. He does not gnaw at his cage any more. There were only a few stools in the cage. The pupils of his eyes were normal.

B3 was somewhat more lively today. The head and body tremors persist. She salivated only slightly when the experimenters appeared. Many soft stools were noted. The dog is still depressed. The pupils of her eyes were widely dilated.

C2 was a little more lively and friendly. She did not arise when the experimenters appeared. When she did arise it was only for short periods of time after which she would resume her reclining position. He head tremor persists. This dog still shows a defect in interest. She exhibits a peculiar blowing movement whereby she blows air out with her mouth closed in such a manner as to make her upper lip move rapidly out and in. C1 exhibited the same picture several days ago. This may be due to nervousness. The pupils of her eyes were about normal.

There was not much change in the condition of B1 and B2 today. They both salivated when the experimenters appeared. B1 salivated more than she has for several days. B2 continues to present a more healthy general appearance; there is a noticeable daily improvement in the condition of this dog. B1 and B2 apparently are passing as many stools as C2 and B3; but the stools of the former are hard while those of the latter are soft. B1 and B2 were not so demonstrative as they were yesterday; but they were neither aloof nor depressed. They were anxious to leave their cage in contrast to B3 and C2. When sodium rhodanate is injected into these dogs they do not wag their tails as they did when morphine was injected. They learned the difference between the two very quickly. The pupils of their eyes were normal.

Forty-eighth Day, November 2nd

All of the dogs except H1, salivated when the experimenters appeared. Likewise, all of them were lively. The head tremor of C2 persists. C1 yelped continuously and senselessly at the sky when put outside. B3 still exhibits the body tremor; she was interested in leaving her cage today. Sodium rhodanate was not given to any of the dogs.

Forty-ninth Day, November 3rd

The pupils of the eyes of the several dogs make an interesting study. According to Lambert[1] dilation of the pupils is a common withdrawal symptom. The pupils of the eyes of B3 were widely dilated and responded only slightly and sluggishly to light. In the case of C2 the pupils were widely dilated; but they were sensitive to light. B1 and B2 presented normal pupils. The pupils of the eyes of C1 were somewhat larger than normal.

B3 has a fine body tremor; she is not disinterested any more. C2 still exhibits a head tremor. All of the dogs began to salivate when the experimenters appeared. B1 and B2 salivated more profusely than the other dogs. They were friendly and interested today.

Sodium rhodanate was not administered.

Fiftieth Day, November 4th

B1 and B2 were quiet today. The pupils of their eyes were somewhat dilated; so they were each given 0.25 gram of sodium rhodanate in water solution by subcutaneous injection. These two dogs eat anything and everything that is given to them.

C2 did not salivate when the experimenters appeared. The other dogs did; it has been noticed that the induction period for salivation is becoming much longer. C2 was not active this morning. She has diarrhea. She is

---

[1] Am. J. Psychiatry, 10, 504 (1930).

not eating food well. B3 has a very poor appetite, also; a pronounced body tremor still persists.

There was no change in the condition of C2 today.

Fifty-first Day, November 5th

The appetites of B3 and C2 continue to be poor. All of the dogs except H1 were active and practically normal today. None of the dogs exhibited dilated pupils. The dogs salivated, as usual, when the experimenters arrived. The pupils of B1 and B2 were normal.

This concludes the post-withdrawal study.

Summary and Discussion

Tables II and III gather together in brief form some of the important data on this experiment.

TABLE II

Dog	Daily Morphine Dosage at Start	Daily Morphine Dosage* at Withdrawal	Weight 6 days after start	Weight at withdrawal	% Increase of Morphine Dosage
C1	1.8 mg/kg.	6.26 mg/kg.	17.8 kg.	17.55 kg.	350
C2	2.1	7.15	15.1	13.6	340
H1	1.3	9.79	12.8	7.9	750
B1	2.8	11.84	5.77	6.0	420
B2	3.3	16.9	4.87	4.2	510
B3	3.6	14.6	4.5	4.87	410

*A 150-pound man addicted to 5 grains of morphine per day would be taking a daily dose of the drug which amounts to 4.76 mg/kg.

TABLE III

Dog	Sex	Number of days on Morphine	Amount NaCNS before Withdrawal	Amount NaCNS after Withdrawal	Days NaCNS Continued after Withdrawal	Total Amount NaCNS
C1	M	38	0.8 gm.	3.4 gm.	10	4.2 gm.
C2	F	41	0.0	0.0	0	0.0
H1	F	35	1.0	0.5	5	1.5
B1	F	41	1.1	1.3	9	2.4
B2	F	41	1.0	1.3	9	2.3
B3	F	41	0.0	0.0	0	0.0

It should be valuable at this point to compare the symptoms and behavior of these dogs during addiction and withdrawal with those found by Plant and Pierce. Symptoms during addiction will be considered first.

Weight. They found a rather rapid loss in weight for the first couple of weeks, while vomiting followed the injections. Three of our dogs gained weight during the first 15 days. The others lost weight, but began to regain it before they stopped vomiting. The weight changes during withdrawal are discussed elsewhere.

Vomiting. The dogs of Plant and Pierce vomited for a period of from five to 15 days at the beginning of the addiction. Our dogs did not vomit regularly after the first sixteen days. Plant and Pierce say: "As a rule when the vomiting had stopped, it did not return again until a very high dosage level was reached. We observed occasional vomiting at various times throughout the addiction period. This was probably reflex vomiting, and should be observed at least occasionally if it is a conditioned reflex. Contrary to the observations of Plant and Pierce our dog H1 did not vomit at all during the first four days of the addiction period. This is probably because the dose of morphine was quite small.

Salivation. Our experience with salivation was much the same as that of Plant and Pierce.

Narcosis. "All of our dogs showed marked diminution in the degree of narcosis produced by the daily administration of morphine, but none of them showed complete absence of narcotic effect, even where the administration was continued for more than 300 days."

"With an initial dose of 5 to 10 mgm. per kilogram the animal is deeply narcotized for three to six hours, during which it is difficult to arouse and if partially awakened, immediately sinks back into a relaxed comatose condition." Reference to Table II shows that none of our dogs were given as high as five mg. per kilogram of morphine sulphate at the start of the experiment. Also, Fig. 1 shows that the low initial dosages were continued for a period of eight days, until some tolerance had developed, before they were raised.

So, in complete contrast to the symptoms noted by Plant and Pierce our dogs were never narcotized, and the depressing effect after each injection did not manifest itself after a short time had elapsed. The condition observed by us simulates more closely the behavior of human addicts. The human addict often does not sleep well even at night.

Constipation. Both our dogs and those of Plant and Pierce showed varying degrees of constipation. Our dogs did not become so constipated as some of theirs did. We observed diarrhea on several occasions; Plant and Pierce do not mention this.

General Behavior. "All of our dogs were friendly and responsive to petting and easy to handle before the administration of morphine was begun. Three of them became somewhat cross and showed tendency to snap after tolerance was developed, but in none of these was the change sufficiently marked to make handling them difficult; the attendant was never bitten and in no case was a muzzle necessary. Two became quarrelsome with other dogs and had to be watched to prevent fighting in the runway. The majority were friendly, active, and responsive in the morning before the injection, but never as much so as before addiction was begun. Two became shy and seemed to avoid all contact with the attendant and with the other dogs but were not cross and could be handled without difficulty. The tolerant dogs seldom evidence any marked interest in other animals and although they occasionally played together in the runway, they more often held aloof. We never saw any evidence of heat in the females during addiction."

Our dogs were easy to handle at all times with the exception of C1. C1 was never cross or mean. With the exception of C1 our dogs were friendly and responded to petting throughout the study. None of our dogs became quarrelsome with other dogs. Like two of the dogs mentioned above, C2 became shy. B3 was always interested in all of the other dogs except during the first week of withdrawal. C1 showed an interest defect at all times.

Appetite. The appetites of our dogs were not so good as those of Plant and Pierce.

Hypersensitiveness and skin rashes. In avoiding most of the phenomena that Plant and Pierce report under this heading we more nearly approached the conditions observed in human beings. The skin of the human addict is very often decidedly hyposensitive. H1 and C1 developed slight hypersensitiveness.

Withdrawal symptoms will be compared now.

Tremors, twitching and rigidity in voluntary muscles. "The symptoms most frequently observed during withdrawal consisted in fine, fibrillary twitching in the muscles of the legs, back and head." These symptoms were not observed by us in H1, B1, B2 and C1, the dogs that were protected by sodium rhodanate. C2 and B3, not being protected by sodium rhodanate, exhibited both a gross head tremor and fibrillary twitching.

Groaning, howling and whining. Except for a little whining on the part of C1 these symptoms were not seen in our dogs.

Restlessness. Many of the dogs that Plant and Pierce worked on exhibited restlessness of varying degrees of intensity. C2 and B3 were slightly restless and nervous at times. The restlessness was not accompanied by noisiness, but was rather intermingled with depression and disinterestedness. The dogs protected by sodium rhodanate did not appear restless or nervous.

Gnawing at objects within reach. This phenomenon probably can be classified as nervousness. C1 exhibited it before and during the time that the dosage of morphine was being increased most rapidly. Several dogs showed slight tendencies to gnaw during withdrawal, especially B3, which dog was not protected by sodium rhodanate.

Change in temperament and behavior. Our dogs did not become irritable and cross in contradistinction to some of those of Plant and Pierce. C2 showed a distinct desire for the drug as did one of theirs. There were marked changes in the behavior of C1; these will be considered separately.

Before abrupt withdrawal and while sodium rhodanate was being administered, B1 and B2 became somewhat disinterested and quiet. Since the withdrawal symptoms are due to the slow return of the nerves to normal after stopping morphine and a consequently protracted period of irritability, we can, if necessary, describe the behavior of B1 and B2 as due to withdrawal. Morphine was given in increasing dosage during this time. If the sodium rhodanate only partially overcame the effect of the morphine, partial peptization would occur with a consequent irritability of the nerves which can be manifested by depression and disinterest. In this manner the actions of B1 and B2 can be accounted for.

Hiccough. None of our dogs showed this symptom.

Photophobia. With the possible exception of C1 during the time that he did not have enough sodium rhodanate, this symptom was not noticed.

Salivation. Plant and Pierce noted that salivation became less marked during withdrawal. We found the same thing in the cases of B3, C2, and C1. On the other hand B2, the protected dog, stopped salivating entirely for about eight days immediately after withdrawal. B1, the other dog receiving sodium rhodanate salivated less than before withdrawal. After eight days these two dogs began to salivate more profusely than any of the others.

Vomiting. While Plant and Pierce observed vomiting in many of their dogs, only C1 vomited during withdrawal; this was reflex in nature.

Muscular weakness, respiratory distress, panting, and sleepiness were not observed in any of our dogs.

Diarrhea. Plant and Pierce observed this in eight of their dogs. We observed it only in the two dogs that were not protected by sodium rhodanate.

Weight changes and pupillary reactions have already been described and discussed. Plant and Pierce observed only one dog that exhibited a desire for the drug. Schübel,[1] and Tatum, Seevers, and Collins,[2] have not observed a desire on the part of addicted dogs for the drug. The detailed study of this group of dogs presents many instances that can be interpreted as a desire for the drug. There seems to be no question but that the dogs liked the injections that they were given. A close study of the actions, reactions and habits of this group of dogs convinces us that most of them wanted, needed, and liked the drug after they became addicted.

The reactions of C1 provide an exceptionally interesting behavior study. Not long before he came to us he was subjected to trauma, his right hind leg being injured. The effect of trauma is agglomeration. Before the start of the experiment he was observed to be a highly excitable, scatter-brained dog. He was hard to control, although not in any sense mean. When approached he tended to be suspicious. He showed no desire or care for human company or affection. He barked at the sky senselessly for long spells at a time. This is akin to the hypomanic state which consists of a condition of unstable irritability, poor discrimination, in which there is a quick reaction on the part of the stimulus response mechanism. The external and internal stimuli are reacted to more promptly than normal, but less thoroughly.

Eleven days on morphine quieted C1 down. He was calm and less nervous; he was slightly more approachable, less wild, and ceased barking at the sky. He remained quiet for eight days. This stage is designated as "sedated hypomanic." In the manic depressive psychoses the sympathetic nervous system and its central correlations are agglomerated. Morphine acts first on the central nervous system. It can cause agglomeration in the central nervous system that will therefore mask the hypomania. Continued administration of morphine will finally agglomerate the affected sympathetic system intensifying the psychosis. In other words, the hypomania was masked

---

[1] Archiv exp. Path. Pharm., 88, 1 (1920).

[2] J. Pharm. Exp. Ther., 36, 460 (1929).

by the narcotic effect of the morphine, just as acute mania can be controlled, but not cured, by sodium amytal. The depressing effect of the morphine was noticeable during more than half of this period.

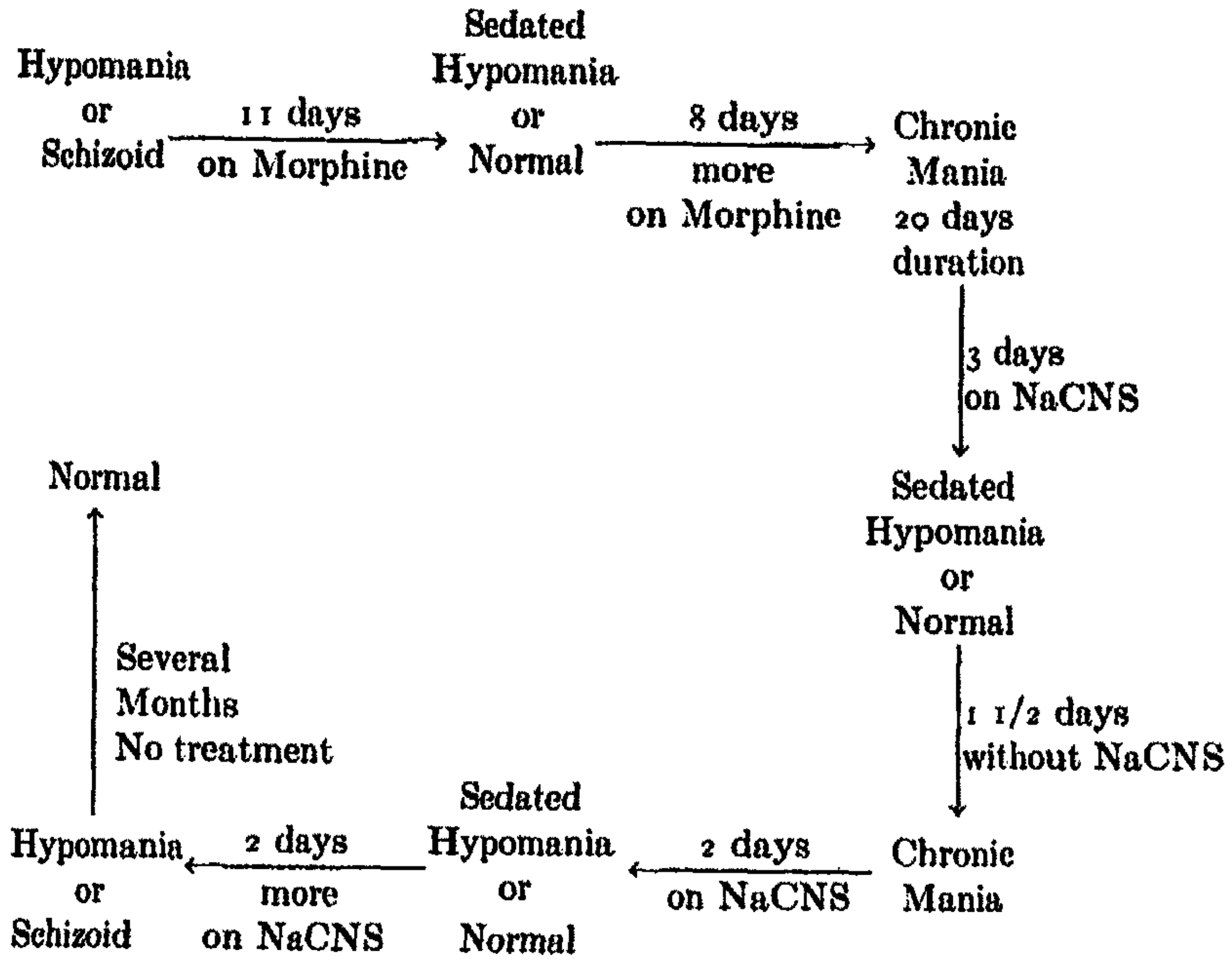
At the end of nineteen days a new condition became manifest. The dog was somewhat restless, and very unapproachable. He tended to stand faced away from human beings; sometimes with his head in the corner of his cage. There was an obvious hunted, maniacal look in the eyes of the dog during this period. It was difficult to give him injections during this time because he was so excitable. Upon soothing him the task was sometimes easier. This stage corresponds to the chronic mania stage of the manic depressive, manic psychosis, a more agglomerated condition than hypomania. The dog stayed in this stage for 20 days.

After withdrawing the morphine, sodium rhodanate was given for three days. This brought the dog back by peptization to a sedated hypomanic condition. The maniacal bearing disappeared and the dog quieted down. This is probably because the morphine was more rapidly eliminated from the sympathetic nervous system than from the central giving rise to a condition much the same as the original sedated hypomanic condition.

Sodium rhodanate was discontinued for one and one-half days. The maniacal bearing returned, and with it the state of chronic mania. Sodium rhodanate was administered for two days, and the dog returned to the sedated hypomanic condition. Two more days brought him into the original hypomanic state. Several months later the colloids of his nervous system returned to a normal degree of dispersion, having recovered from the trauma and the drug addiction. In this condition the dog persistently sought human affection, and cared for human company. He was easily approachable, and acted in every way like a normal dog.

On the other hand the dog may have been in a schizoid state, and over-dispersed, trauma not being an etiological factor. Injections of morphine for eleven days, under this interpretation, returned the dog to normal due to the agglomerating action of morphine. Eight days more brought him into a condition resembling chronic mania, a condition which is due to agglomeration of certain of the protein colloids of the brain and sympathetic nervous system. Then, three days on sodium rhodanate peptized the colloids back to normal. The chronic mania reappeared when the sodium rhodanate was discontinued for a day and a half. Upon resumption of the administration of the peptizing agent the dog again returned to normal. He was then over-dispersed by the sodium rhodanate, going into the schizoid condition. Some months after the sodium rhodanate was stopped, the over-dispersed condition disappeared, and the dog returned to normal.

It does not seem necessary to insist that one or the other of these explanations is the correct one; the important thing is that there was a cycle of changes in behavior of the dog which paralleled the colloidal changes that were induced. The following diagram illustrates the cycle that this dog went through.



The object of this work has been realized because the dogs, C2 and B3, that were not given sodium rhodanate developed definite withdrawal symptoms. Whereas, C1, B1, and B2 being protected by sodium rhodanate exhibited no withdrawal symptoms. It is regrettable that the effect of sodium rhodanate on the post-withdrawal craving can not be studied satisfactorily in animals for that is probably the most important part of the problem of drug addiction.

General Conclusions

1. Dogs can be addicted to small, increasing amounts of morphine; the picture produced is much the same as when larger amounts of the drug are used.

2. By using small doses of morphine the systemic upset produced is not so profound.

3. The behavior of the dogs during addiction and withdrawal indicates strongly that the demand of addicted tissue for morphine is reflected in a desire for the injected material.

4. As in human beings, some of the dogs were retarded by the drug. Likewise on dull, damp days the dogs were apparently depressed as many human addicts are.

5. Most of the phenomena observed by others during addiction were manifested by our dogs.

6. The theory requires that sodium rhodanate shall forestall or diminish greatly the withdrawal symptoms in addicted tissue because it should peptize rapidly the protein colloids that are agglomerated by morphine.

7. Sodium rhodanate was administered to addicted dogs one week prior to the abrupt withdrawal of morphine. During this time morphine was administered in ever-increasing doses.

8. These dogs were somewhat depressed at first. This may have been due to a disturbed condition brought about by the rapid peptization of the agglomerated colloids.

9. The dogs protected by sodium rhodanate exhibited no withdrawal symptoms upon the abrupt withdrawal of morphine. They gained a little weight.

10. The dogs not protected by sodium rhodanate were nervous, listless, lost weight, exhibited head and body tremors, had diarrhea and dilated pupils.

11. Sodium rhodanate does, in fact, prevent withdrawal symptoms in dogs addicted to small amounts of morphine, thus bearing out the theory.

12. One dog exhibited definite psychic changes as his protein colloids became more or less agglomerated; these changes were reversed. The dog went from one state of dispersion to another, and back again.

13. Withdrawal symptoms appeared in the dog just mentioned when sodium rhodanate was stopped. Resumption of the administration of the drug obliterated the symptoms.

14. Gnawing is not necessarily a withdrawal symptom.

15. It is to be expected from these experiments that the effects of morphine will be counteracted at least partially in the case of human beings by the use of sodium rhodanate.

Cornell University.

THE CATALYTIC ACTIVITY OF REDUCED COPPER CHROMATE AND OF VANADIUM OXIDE IN THE REDUCTION OF NITROCOMPOUNDS*

BY H. A. DOYAL[1] AND O. W. BROWN[2]

Introduction

The ability of finely divided platinum to promote certain oxidations was discovered by Davy and Doebereiner at the beginning of the nineteenth century. Near the latter part of the same century Sabatier and his co-workers began an extensive investigation of catalysis in the field of organic chemistry. Since that time numerous experiments have been carried out in many different laboratories, showing that a great number of diversified chemical reactions can be promoted by the use of suitable catalysts.

Since 1920, a series of investigations have been made in this laboratory, concerning the ability of finely divided metals and oxides to catalyze the reduction of nitrocompounds by hydrogen. This article gives the results of an investigation of the catalytic activity of reduced copper chromate and of vanadium oxide in the reduction of nitrobenzene to anilin. The activity was measured by the yields of amines and by the impurities which were present in the anilin.

Apparatus and Method of Procedure

The catalytic furnace used in this investigation was a horizontal type with an electrically heated bath consisting of lead-tin eutectic alloy, 75 atomic per cent of tin. The catalyst tube was an iron pipe, thirty inches in length and one inch in diameter. The design of the furnace and the method of operation are described in a previous publication[3] from this laboratory.

The ends of the catalyst tube were covered with a thick layer of asbestos to retard the leakage of heat and to prevent the condensation of the products in the delivery tube. The products were condensed in an air-cooled glass condenser. The excess hydrogen passed downward through a condenser drain tube and bubbled through 100 cc. of 1 : 1 HCl in a graduated liter flask. This was to prevent the escape of uncondensed anilin.

The catalyst was introduced into the furnace through an opening made by unscrewing the delivery tube. By means of a metal boat with a calibrated handle, a catalyst column ten inches long was placed inside the furnace. The outer end of this column was five and one-half inches inside the heating jacket of the furnace.

---

*This paper is constructed from a dissertation presented by H. A. Doyal to the Faculty of the Graduate School of Indiana University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[1] Assistant in Chemistry, Indiana University.

[2] Professor of Chemistry, Indiana University.

[3] J. Phys. Chem., **34**, 2651-2665 (1930).

The temperature was measured by means of a copper constantan (advance) thermocouple which was inserted in a well surrounded by the metallic bath. This was calibrated against a standard thermocouple whose tip was placed inside the catalyst tube, five and one-half inches inside the heating jacket. During the calibration, air was passed through the furnace at the rate of 14 liters per hour.

Two cubic centimeter samples, measured by means of a calibrated pipette, were introduced into the furnace through a glass capillary. This capillary extended far enough into the catalyst tube to insure that the nitrobenzene was vaporized and would be carried over the catalyst by the hydrogen. The rate of flow of the nitrobenzene was regulated by means of a variable pressure which was obtained by changing the height of a mercury column, as described by Brown and Henke.[1] The rate of flow of hydrogen was measured by a calibrated flowmeter.

While the furnace was being heated to the desired temperature before an experiment and during the cooling which followed the completion of a series of runs, a current of hydrogen was continually passed through the furnace.

The hydrogen was allowed to flow for forty minutes, at the same rate as that used during the experiment, after the last of the nitrobenzene had entered the furnace. The amount of material still remaining in the furnace was very small and practically constant. Since the experiments were carried out without a time interval between them, this error was eliminated from all except the first run of a series.

After the furnace was "washed" with hydrogen 1:10 HCl was used to wash the products from the condenser into the graduated liter flask containing the 100 cc. of 1:1 HCl. This sample was then diluted to one liter and 100 cc. aliquot portions were titrated with tenth molar sodium nitrite solution. (This solution was standardized against pure catalytic ortho amido phenol.) Twenty cubic centimeters of conc. HCl were added before titrating. Starch iodide paper was used as an external indicator.

At room temperature the reaction is as follows:

$$C_6H_5NH_2 + HNO_2 \longrightarrow C_6H_5OH + N_2 + H_2O$$

If the temperature is low the following reaction occurs:

$$C_6H_5NH_2\cdot HCl + HNO_2 \longrightarrow C_6H_5N_2Cl + 2H_2O$$

Since both reactions use the same amount of nitrous acid per mol of anilin the titration can be made at room temperature. Any other amines present would produce an error but this would be less than that introduced by purifying the anilin and weighing it.

All the yields given in this article are the average of from two to four consecutive experiments. The first run of each series is not included since it is generally either high or low, depending upon the previous history of the catalyst. The maximum variation of yields from these consecutive experiments is within one-half of one per cent.

---

[1] J. Phys. Chem., **26**, 161, 272 (1922).

The quality of the anilin was investigated by collecting one run at each point of investigation. Part of this was let stand exposed to light for several days and the color changes noted. Part was placed on a watch glass in a drying oven at about 80°C. After the anilin had evaporated the glass was examined for solid residue.

In order to purify the nitrobenzene, it was shaken with sodium carbonate solution, removed from the mixture by steam distillation, separated from the water in the distillate by decantation and dried with anhydrous calcium chloride. It was then distilled while in contact with fresh drying agent. The central constant boiling portion was redistilled. The middle portion of this distillate was used in this investigation.

The commercial hydrogen was purified by passing over red-hot copper, bubbling through concentrated sulphuric acid, passing through a caustic tower and then through a glass-wool filter.

PART I

Reduced Copper Chromate as a Catalyst

Preparation of the Catalyst

One hundred grams of Mallinckrodt's potassium dichromate were dissolved in about three liters of distilled water. Enough potassium hydroxide was added to convert the salt to potassium chromate. One hundred fifty grams of J. T. Baker's C. P. copper nitrate were dissolved in one and one-half liters of water. This solution was added to the potassium chromate solution while stirring rapidly. The precipitate was washed three times by decantation and then washed well on a Büchner funnel. It was then dried in an oven for about two days at 80°C. The lumps were then ground into a coarse powder (through a ten mesh screen) and stored in a stoppered bottle until needed.

All copper chromate catalysts were prepared in the following manner unless otherwise specified. Fifteen grams of copper chromate were placed in the catalyst tube and reduced at 360°C. for one hour with a rate of flow of hydrogen of 14 liters per hour.

Experimental Part

The data given in Table I show the effect of the rate of flow of nitrobenzene on the yield of amines.

Twenty runs were made before the above data were taken. Nitrobenzene was fed into the furnace at the rate of 3.55 grams per hour in these preliminary experiments. A new catalyst does not give constant yields during the first few runs.

Slow rates of flow of nitrobenzene produced a red-colored product. Tar-like substances condensed in the furnace exit-tube. The red color of the product and the tar gradually disappeared as the rate of flow of the nitrobenzene was increased.

TABLE I

Catalyst—reduced copper chromate.
Rate of flow of hydrogen—14 liters per hour.
Temperature—310°C.

Nitrobenzene Gms. per hr.	Hydrogen in per cent of theory	Yield of amines in per cent of theory. Calculated as anilin
2.4	975	96.6
2.9	820	97.0
3.55	660	97.5
4.75	495	97.4
7.3	320	97.2
10.8	220	96.6

The best yields and the best products were obtained when 3.5 to 4.75 g. per hour of nitrobenzene were fed into the furnace. This anilin was clear with only a faint green color. Only a faint trace of solid residue remained when a small portion was evaporated on a watch glass. The sample which was titrated remained water white after titration. Many of the impurities gave colored products with sodium nitrite in the presence of hydrochloric acid. This showed that these substances were absent.

A deep green color replaced the green tint as the rate increased beyond 4.75 g. of nitrobenzene per hour. This color seemed to appear when the catalyst was being overloaded. This could be done either by feeding the nitrobenzene into the furnace too rapidly or by shortening the time of contact by increasing the rate of flow of the hydrogen. Anilin which had this deep green color reddened rapidly on standing in the light. The conditions under which the green appeared indicate that it was probably due to some intermediate reduction compound of nitrobenzene.

The figures given in Table II show the effect of the rate of flow of hydrogen on the yield of amines.

TABLE II

Catalyst—reduced copper chromate.
Rate of flow of nitrobenzene—3.55 g. per hour.
Temperature—310°C.

Hydrogen in liters per hour	Hydrogen in per cent of theory	Yield of amines in per cent of theory. Calculated as anilin
25	1180	96.7
20	940	97.7
14	660	98.3
10	470	98.8
5	235	98.7
3	140	98.3

Fifteen runs were made before the above data were taken.

The best yields and products were obtained when the rate of flow of hydrogen was ten liters per hour. When slower rates were used, the anilin had a reddish tint which darkened to a deep red on standing over night. When faster rates were used, the product had a deep green color. Here, again, this color appeared when the catalyst was overloaded.

The results given in Table III show the effect of temperature on the yield of amines.

TABLE III

Catalyst—reduced copper chromate.
Rate of flow of nitrobenzene—3.55 g. per hour.
Rate of flow of hydrogen—10 liters per hour.

Temperature °C.	Yield of amines in per cent of theory. Calculated as anilin	Temperature °C.	Yield of amines in per cent of theory. Calculated as anilin
381	86.4	297	98.4
349	94.3	282	98.1
333	96.9	246	96.0
310	98.8	237	80.9
		217	43.2

The product had a burnt orange color at high temperatures. This color gradually disappeared as the temperature was lowered. After four runs at 310°C., the product was clear and the only color was a faint tinge of green. Below 310°C., the green gradually darkened.

Below 310°C., the yield of anilin decreased as the temperature became less. Two things indicate that this was due to a decrease in the activity of the catalyst. The first was the appearance of the green color. The second was the appearance of nitrobenzene in the products. One method of detecting its presence was by its odour. Another was by the characteristic taste of nitrobenzene that one obtained from the vapors while pipetting aliquot samples for titration. Below 246°C., a black tarry amorphous precipitate appeared in the hydrochloric acid solution. It also appeared in the delivery tube of the furnace. Nitrobenzene, highly colored with impurities, collected at the bottom of the solution of anilin-hydrochloride.

Above 310°C., the yield of anilin also decreased. Apparently, since no nitrobenzene was found in the products, this decrease in yield was not due to too little activity but rather to too much activity on the part of the catalyst. Above 400°C., the volume of the condensed liquid products decreased rapidly. When operating at these high temperatures, a white smoke poured out of the delivery tube of the furnace. This smoke condensed neither in the air-cooled glass condenser nor in the *1 : 1* HCl in the graduated liter flask but was carried out into the air by the excess hydrogen.

Traces of products, probably due to consecutive reactions, increased with the temperature (above 310°C.). At 381°C. enough diphenylamine was produced to give a slight precipitate when the anilin-hydrochloride solution was diluted to one liter. At temperatures below 381°C., there was enough of the secondary amine present to give the solution a purple color after titration with sodium nitrite. After two or three runs were made at 297 to 282°C., no test for diphenylamine could be obtained. After running at temperatures in the neighborhood of 400°C., several runs were necessary before the product failed to give a test for this secondary amine when the temperature of the furnace was maintained at 310°C.

The curves in Fig. 1 show the relation between the temperature and the yield of amines with a reduced copper chromate, a copper and a chromium catalyst. The data for the copper and chromium were obtained from previous publications[1] from this laboratory.

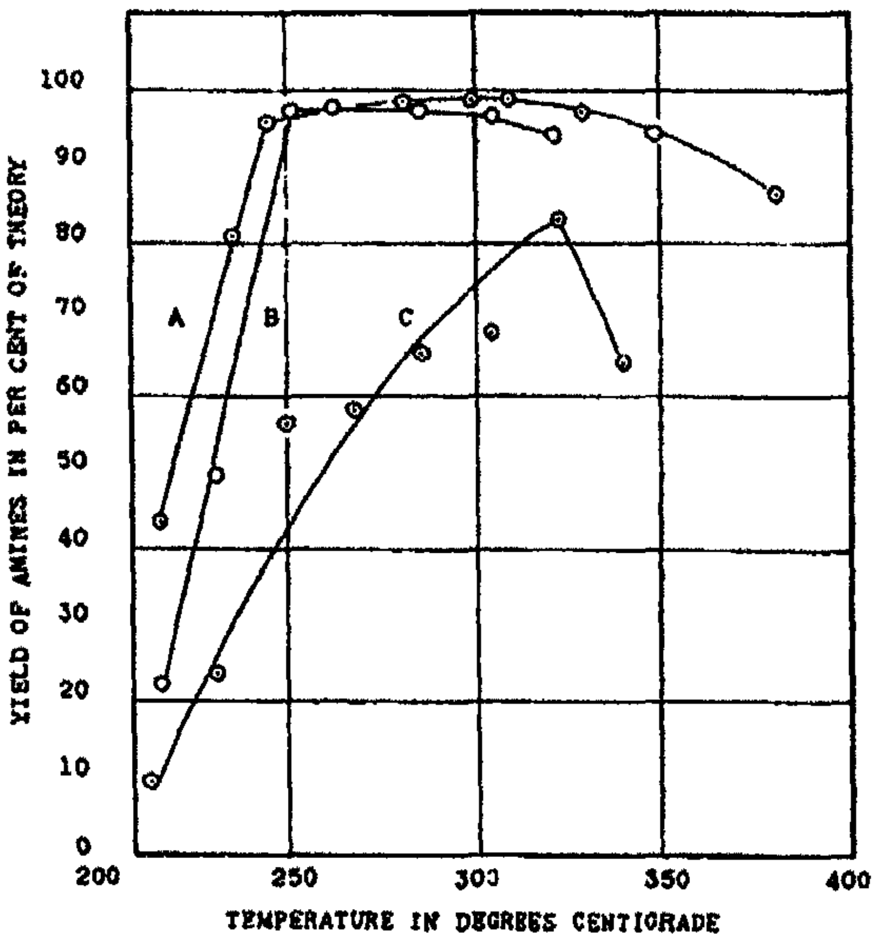


Fig. 1

Curve A shows the yields obtained over a reduced copper chromate catalyst. The yields for a copper catalyst are plotted in curve B and for chromium in curve C.

It is seen, from the curves, that the action of the reduced copper chromate catalyst more closely resembles that of copper than of chromium. The products also indicated this.

Three catalysts were prepared from copper chromate. Fifteen grams were used in each case. The first was heated in a current of hydrogen, 14 liters per hour, at 360°C. for one hour. The second was heated in a current of hydrogen, 14 liters per hour, at 460°C. for one hour. The third was first heated in a current of air at 460°C. for two hours and then heated in a current of hydrogen, 14 liters per hour, at 360°C. for one hour. The three catalysts

---

[1] J. Phys. Chem., 26, 161, 272 (1922).

were run at 310°C. until constant yields were obtained. The rate of flow of nitrobenzene was 3.55 g. per hour. The rate of flow of hydrogen was 14 liters per hour. The first catalyst produced 98.7 per cent of anilin. The second gave yields which averaged 96.5 per cent and the third produced 99 per cent of anilin. This shows that the yield of anilin can be decreased by heating the catalyst in hydrogen at 460°C. The anilin produced by such a catalyst is opaque. Previous heating in air at 460°C. seemed to have little effect on the yield and quality of the anilin. The products obtained by the use of the first and third catalysts were clear and almost white. The only color was a faint trace of green. There was only a slight trace of solid residue remaining after the anilin was removed by evaporation at about 80°C. The solution of anilin-hydrochloride remained water white after titration with sodium nitrite. The anilin, without purification by distillation, when protected from the light would remain without any appreciable color change for three or four days. At the end of three weeks, it was still clear but had acquired a light red color.

Anilin produced under unfavorable conditions was opaque and not clear. This was due to finely divided impurities in suspension. The addition of two drops of nitrobenzene to 2 cc. of anilin will produce a red color in a few minutes. This explains why the anilin which contained traces of nitrobenzene was red. Other impurities were produced at high temperatures which also gave the product a red color.

PART II

The Catalytic Activity of Vanadium Oxide in the Reduction of Nitrocompounds

A few experiments, using a lower oxide of vanadium as a catalyst, were carried out[1] in this laboratory in 1922. The maximum yield of anilin obtained by the reduction of nitrobenzene was 88 per cent of theory. The following experiments were carried out to investigate the activity of this catalyst.

The catalysts were prepared by the ignition of ammonium meta-vanadate, C. P., purchased from the S. W. Shattuck Chemical Co., Denver, Colorado.

The effect of the rate of flow of hydrogen on the yield of amines is shown by the results given in Table IV.

TABLE IV

Catalyst—15 g. V_2O_5 reduced in hydrogen (é).
Rate of flow of nitrobenzene—3.55 g. per hour.
Temperature—403°C.

Hydrogen in liters per hour	Hydrogen in per cent of theory	Yield of amines in per cent of theory. Calculated as anilin
20	940	80.8
14	660	83.9
10	470	79.5

---

[1] J. Phys. Chem., 26, 283 (1922).

(6) *Preparation of the catalyst.* Ammonium meta-vanadate was placed in a porcelain dish and ignited in an electric muffle at 275°C. for three hours. During the heating the catalyst was stirred frequently. The muffle was provided with two openings for the circulation of air. The resulting black powder was placed in a cold catalytic furnace. The temperature was gradually raised to 460°C. where it was maintained for two and one-half hours. During this time, hydrogen was passed through the furnace at the rate of 14 liters per hour. The catalyst was probably a lower oxide of vanadium.

Fifteen runs were made with this catalyst at 403°C. before the data for Table IV were taken. Constant results were not obtained during the first runs. The product from these first runs was green and no precipitate could be detected in the anilin-hydrochloride solution. The color became lighter after the first few runs and a precipitate containing diphenylamine appeared in the 1:1 HCl in the liter flask. No precipitate appeared in the glass condenser since this secondary amine is somewhat soluble in anilin.

The diphenylamine was identified by the following properties:

1. It was almost insoluble in dilute acids and its solubility increased with the concentration of the acid. It was soluble in concentrated hydrochloric or concentrated sulphuric acid.

2. When sodium nitrite or some other oxidizing agent was added to its solution in concentrated sulphuric acid an intense blue color appeared. At lower concentrations, varying shades of color from blue to light purple appeared.

3. The crystals were flat plates. The melting point was not sharp but was from 55° to 65°C. This was due to impurities and to decomposition products caused by the exposure of the amine to the air and to traces of HCl which was used to remove the anilin.

4. When the crystals were moistened with dilute hydrochloric acid they turned blue on exposure to the air for a few hours.

The presence of this secondary amine introduced an error in the determination of amines, since one mol of diphenylamine combines with the same amount of nitrous acid as one mol of anilin. When the solution of anilin in 1:1 HCl was diluted to one liter, part of the dissolved diphenylamine precipitated. Most of the precipitate was in a state of fine division and remained in suspension. Since part of the secondary amine was still in solution no attempt was made to remove the rest by filtration. Even under the most favorable conditions for the production of diphenylamine less than five per cent of it was produced. When the conditions were favorable for the production of anilin this error was less than one-tenth of one per cent. The presence of the precipitate made the end point of the titration rather slow since more of the precipitate dissolved as that in solution was removed by the titration. In acid solution, the following reaction takes place during titration.[1]

$$(C_6H_5)_2NH + HNO_2 \longrightarrow (C_6H_5)_2N\cdot NO + H_2O$$

---

[1] Bernthsen and Sudborough: "Text-book of Organic Chemistry," 404 (1930).

The best yield of amines was obtained with this catalyst when hydrogen was passed into the furnace at the rate of 14 liters per hour. When a rate of ten liters per hour was used the precipitate of diphenylamine increased. When samples of the anilin were taken most of this secondary amine was dissolved in the solvent, but part of it remained in suspension. This caused the solution to be opaque. The sample darkened rapidly. This was more noticeable when it was exposed to a strong light.

The production of diphenylamine seems to be a consecutive reaction and not a side reaction. If a catalyst promotes consecutive reactions, then increasing the time of contact with the catalyst should increase the amount of the substances which are formed by the consecutive reactions. This fact and the results shown in Table IV and Table V lead the authors to believe that the production of the diphenylamine is a consecutive reaction. It probably takes place in the following manner.

$$2\ C_6H_5NH_2 \longrightarrow (C_6H_5)_2NH + NH_3$$

Diphenylamine was produced in all of the experiments listed in Table IV. When the rate of flow of hydrogen was increased to twenty liters per hour the yield of both anilin and diphenylamine decreased.

The effect of nitrogen on the activity of vanadium oxide is shown in the results given in Table V.

TABLE V

Catalyst—15 g. of reduced V_2O_5, prepared in the same manner as described following Table IV

Rate of flow of nitrobenzene—3.55 g. per hour.
Rate of flow of gas—14 liters per hour.
Temperature—403°C.

Nitrogen Liters per hour	Hydrogen Liters per hour	Hydrogen in per cent of theory	Yield of amines in per cent of theory. Calculated as anilin
0	14	660	83.8
4	10	470	80.8
10	4	190	73.7

In this case, the rate of flow of the gases was kept constant and the partial pressure of the hydrogen was varied. The effect which the nitrogen had on the adsorption of the hydrogen and the nitrobenzene is not known. This should be specific and should depend on the nature of the catalyst used and on the other substances present. The yield of amines was decreased by the presence of the nitrogen. If the variation in the amount of hydrogen made any change in the amount of diphenylamine produced, this difference was too small to be detected by inspection of the precipitate.

The data given in Table VI show the effect of temperature on the activity of a vanadium oxide catalyst.

TABLE VI

Catalyst—15 g. of reduced V_2O_5, prepared as previously described.
Rate of flow of hydrogen—14 liters per hour.
Rate of flow of nitrobenzene—3.55 g. per hour.

Temperature °C.	Yield of amines in per cent of theory. Calculated as anilin	Temperature °C.	Yields of amines in percent of theory. Calculated as anilin
489	35.1	403	81.3
442	61.0	393	75.0
425	66.9	368	54.7
413	75.1	336	30.2

Fifteen runs were made with this catalyst at 403°C. before the data for Table VI were taken. All anilin produced above 393°C. contained diphenylamine. The amount increased as the temperature increased. No clear aniline was produced with a vanadium oxide catalyst prepared in this manner. The opacity of the aniline was due to impurities which were in suspension.

The anilin was black when the temperature was allowed to drop a few degrees below 403°C. A tarry product condensed in the delivery tube of the furnace. It was this substance which produced the color in the anilin. Tests showed that this tar was only slightly soluble in alcohol, ether or gasoline, but was fairly soluble in anilin. When several runs were made at lower temperatures the formation of this tar decreased rapidly but never ceased entirely. This was very similar to the action of reduced copper chromate at temperatures below 246°C. As the amount of tar produced decreased the black color of the product gradually changed to red. The red color was probably due to traces of nitrobenzene in the product. The amount of nitrobenzene increased as the temperature decreased. When the catalyst was used at temperatures as low as 336°C. large drops of nitrobenzene collected at the bottom of the anilin-hydrochloride solution. The catalytic activity of this catalyst, at temperatures below 403°C. seems to decrease as the temperature decreases. The red color of the anilin produced at low temperatures is similar to the color produced when nitrobenzene is added to anilin.

Although nitrobenzene was found in the products at lower temperatures, none was detected in the mixture at higher temperatures. Products from consecutive reactions, such as diphenylamine appeared at higher temperatures but they did not appear when the catalyst was used at lower temperatures.

Experiments were conducted to determine the effect of heating the V_2O_5 in air at 400°C. before it was reduced in hydrogen. After the V_2O_5 was heated in a current of air at 400°C. for one hour, 15 g. of the material were placed in the catalyst tube and reduced by heating in hydrogen for two and one-half hours at 460°C. The rate of flow of hydrogen was 14 liters per hour. Fifteen runs were made before the data were taken. The yields from this catalyst are shown in Table VII.

TABLE VII

Catalyst—15 g. of reduced V_2O_5.
Rate of flow of nitrobenzene—3.55 g. per hour.
Rate of flow of hydrogen—14 liters per hour.

Temperature °C.	Yield of amines in per cent of theory. Calculated as anilin	Temperature °C.	Yield of amines in per cent of theory. Calculated as anilin
415	80.8	398	86.8
408	87.7	378	77.2
403	89.3	360	67.9

The results in Table VII show that heating to 400°C. in air increased the production of anilin. Less diphenylamine was produced by this catalyst than by the ones prepared by heating in air to only 275°C. The anilin produced by the use of this catalyst was opaque due to impurities in suspension.

A catalyst was prepared by heating ammonium meta-vanadate in air at 450°C. for one hour. Fifteen grams of the V_2O_5 produced were placed in a catalytic furnace and heated in a current of hydrogen, fourteen liters per hour, at 460°C. for two and one-half hours.

A study of the effect of the rate of flow of nitrobenzene on the yield of amines was made with this catalyst. Table VIII shows the results obtained. Fifteen runs were made before the data for this table were taken.

TABLE VIII

Catalyst—reduced V_2O_5.
Temperature—403°C.
Rate of flow of hydrogen—14 liters per hour.

Nitrobenzene Gms. per hour	Hydrogen in per cent of theory	Yield of amines in per cent of theory. Calculated as anilin
2.37	970	90.9
2.85	805	91.3
3.55	660	91.7
4.90	480	91.8
7.10	330	88.3

The color of the anilin was a cherry red when slow rates of feed of nitrobenzene were used. The purple color due to the reaction of diphenylamine and sodium nitrite, appeared in the solution of anilin-hydrochloride after the titration had been made. Tarry substances condensed in the delivery tube of the furnace.

As faster rates were used, the product gradually lost its red color. When 7.1 g. per hour of nitrobenzene were fed into the furnace the product was a yellowish green. The color as'well as the decrease in the yield of amines indicates that the catalyst was overloaded.

The anilin produced when 3.5 to 4.9 g. per hour of nitrobenzene were fed into the furnace was almost clear. A test for diphenylamine could be obtained by evaporating the anilin at about 80°C. and dissolving the solid residue in a few drops of concentrated sulphuric acid. The addition of a drop of sodium nitrite solution produced a deep blue color.

Discussion of Results

When the flow of nitrobenzene was kept constant, the furnace maintained at the most favorable temperature and the rate of flow of hydrogen was varied, an intermediate rate was found to give the highest yield of amines in per cent of theory. A high velocity of the hydrogen seemed to cause incomplete reduction. In the horizontal furnace, the contact between the reacting gases and the catalyst is brought about by the diffusion of the gases and convection currents. The heat of reaction and, possibly, the heat of adsorption cause the temperature of the catalyst to become higher than that of the rest of the furnace. The heat of reaction in the reduction of nitrobenzene to anilin is 98.8 Calories per mol. The vapors in contact with the wall of the furnace also become hotter than the rest. This difference in temperature causes the convection currents. The concentration of the nitrobenzene vapor in the original gaseous mixture is decreased next to the catalyst since it, in addition to part of the hydrogen, is continually being removed by the chemical reaction. This would cause diffusion of the nitrobenzene toward the catalyst. Probably, a high velocity would carry some of the nitrobenzene vapor through the furnace without its being in contact with the catalyst.

When the velocity of the vapors was too low there was too long a contact with the catalyst, which reduced the yield of anilin. The red color and the opacity of the products, neither of which was due to nitrobenzene or anilin, indicate that the decrease in yield was due to the formation of other compounds. When a vanadium oxide catalyst was used one of these compounds was shown to be diphenylamine.

In addition to velocity, the ratio of nitrobenzene to hydrogen is a factor which must be considered in the production of anilin. When the rate of flow of hydrogen was kept constant and the amount of nitrobenzene was varied an intermediate rate of flow of nitrobenzene was found to be the most favorable for the production of anilin. (See Tables I and VII). When low rates of flow of nitrobenzene were used, the product was red and opaque. A tar-like substance with a high boiling point condensed in the delivery tube of the furnace. When sufficiently high rates were used nitrobenzene could be detected in the products. Thus, low rates favor the formation of impurities in the anilin while high rates cause incomplete reduction of the nitrobenzene. The most favorable rate of flow of nitrobenzene and of hydrogen depends upon the amount and the nature of the catalyst used.

The effect of the temperature has been described following Tables III and VI.

When these catalysts, which had been working under favorable conditions for the production of anilin, were used at sufficiently low temperatures a large quantity of tarry substances appeared in the products. However, the amount of tar decreased with each successive run until only a trace remained. In the case of reduced copper chromate, the temperature drop required was about 70°C. below the most favorable temperature for the production of anilin. When vanadium oxide was used a drop of about 15°C. was sufficient to promote the formation of these tars.

Conclusion

I. The highest yield of amines obtained with a reduced copper chromate catalyst was 99 per cent of theory. This yield was obtained at 310°C. with a flow of hydrogen of 14 liters per hour and a rate of flow of nitrobenzene of 3.55 g. per hour. The catalyst used was prepared by heating copper chromate in air at 460°C. and then reducing it in a current of hydrogen, 14 liters per hour, at 360°C.

II. The highest yield of amines obtained with a reduced vanadium oxide catalyst was 91.8 per cent of theory. This yield was obtained at 403°C. with the rate of flow of nitrobenzene 4.9 g. per hour. The rate of flow of hydrogen was 14 liters per hour. The catalyst was prepared by igniting ammonium meta-vanadate in air at 450°C. for one hour. Fifteen grams of the vanadium pentoxide produced were placed in a cold catalytic furnace and heated in a current of hydrogen, 14 liters per hour, at 460°C. for two and one-half hours.

III. Diphenylamine was shown to be one of the products which was produced by both catalysts. Vanadium oxide was shown to be a better catalyst than reduced copper chromate for the production of diphenylamine.

IV. The substitution of nitrogen for part of the excess hydrogen was shown to decrease the yield of amines when a vanadium oxide catalyst was used.

V. Reduced copper chromate was shown to be a better catalyst for the production of anilin than vanadium oxide. The ability of reduced copper chromate to promote the production of a high grade anilin was shown.

VI. The relative amounts of nitrobenzene and hydrogen, the velocity of the gases as they passed over the catalyst and their temperature were shown to be important factors in the production of secondary products.

Laboratory of Physical Chemistry,
Indiana University, Bloomington.

ENERGY EXCHANGE IN UNIMOLECULAR REACTIONS

I. The Decomposition of Mixtures of Dimethyl and Diethyl Ether

BY E. W. R. STEACIE

Introduction

In a homogeneous unimolecular gas reaction, the reacting molecule undoubtedly acquires the energy of activation by a redistribution of energy between molecules at collisions. It is a fundamental characteristic of such reactions that the velocity constants decrease at low pressures. At such pressures the time required for an activated molecule to react becomes comparable with the time between collisions. At low partial pressures of the reactant, collisions with inert gases would naturally be expected to be effective in maintaining the rate of reaction. It is an experimental fact, however, that the effect of inert gases is highly specific. Hydrogen and the reaction products are usually highly effective in maintaining the rate, while other foreign gases are usually quite ineffective.

The highly specific nature of the effect is somewhat puzzling, although the question has received considerable attention from the point of view of quantum mechanics.[1] If statistical redistribution of energy occurred during a single collision between a molecule of inert gas and an activated molecule of reactant, then, since almost all activated molecules have energy only slightly in excess of the energy of activation, deactivation should result in virtually every collision. This should be the case even with comparatively simple inert gases with a small number of degrees of freedom.[2] Since this is not the case with the majority of inert gases, it is necessary to assume a high specificity of energy transfer during collisions of the second kind.

It would naturally be expected that complex molecules with a number of internal degrees of freedom comparable to that of the reactant would be more effective in maintaining the rate than would simple gases. It would also be expected that statistical redistribution would be more easily established between molecules which resemble one another in structure and in chemical properties, since such redistribution is apparently easily established between molecules of the reactant itself. Up to the present, however, all investigations of the effect of foreign gases on unimolecular reactions have been confined to comparatively simple gases.

The decompositions of the various aliphatic ethers which have been investigated by Hinshelwood and his co-workers,[3] offer ideal material for the

---

[1] Kallmann and London: Z. physik. Chem., **B2**, 207 (1929); Zener: Phys. Rev., (2) **37**, 556 (1931); O. K. Rice: Chem. Reviews, **10**, 125 (1932).

[2] O. K. Rice: Réunion internationale de chimie physique, Paris, Oct. **1928**, p. 305; Kassel: "Kinetics of Homogeneous Gas Reactions," 111 (1932).

[3] Hinshelwood: Proc. Roy. Soc., **114A**, 84 (1927); Hinshelwood and Askey: **115A**, 215 (1927); Hinshelwood and Glass: J. Chem. Soc., **1929**, 1804.

investigation of the mutual influence of similar complex molecules. An investigation has therefore been commenced on the thermal decomposition of mixtures of various ethers, as announced in a preliminary communication.[1] The present paper deals with the first pair which has been investigated, viz. dimethyl and diethyl ether.

Experimental Procedure

The reaction velocities were followed in the usual way by admitting the reactant, or reactants, to a heated silica bulb connected to a capillary manometer and noting the change in pressure with time. The apparatus was identical with one which has been previously described.[2]

Temperatures were measured with a chromel-alumel thermocouple in conjunction with a Cambridge "Workshop Pattern" potentiometer. The temperature was controlled by the hand regulation of rheostats, and could be maintained constant to within 0.5°C.

Methyl ether was prepared from sulphuric acid and methyl alcohol in the usual way. The gas was freed from unchanged methyl alcohol by bubbling through sulphuric acid saturated with methyl ether. It was then dried by passage through tubes containing phosphorus pentoxide, and fractionally distilled. During the course of the experiments it was stored as a liquid in a bulb immersed in a carbon dioxide-acetone mixture.

Ethyl ether was purified by shaking with sulphuric acid. It was then dried over sodium and fractionally distilled (B. P. 34.5°C). It was stored in a bulb over sodium. To prevent contamination by tap grease this bulb was also immersed in a carbon dioxide-acetone mixture.

Experimental Results

Since the falling off in rate at low pressures is only very slightly influenced by temperature, it was not considered worth while carrying out experiments over a range of temperatures. Accordingly all experiments were made at 478°C, at which temperature both ethers decompose at convenient rates.

According to the mechanisms postulated by Hinshelwood, the reactions are mainly as represented by

$$CH_3OCH_3 = CH_4 + CO + H_2,$$

and

$$C_2H_5OC_2H_5 = C_2H_6 + CO + CH_4.$$

Hydrogen is the only reaction product which has any effect in maintaining the rate. This introduces a certain complication when dealing with mixtures, inasmuch as the hydrogen formed in the decomposition of methyl ether will influence the rate of decomposition of ethyl ether. In order to minimize this effect all measurements were made in the early stages of the reaction, the rates of reaction being inferred from a comparison of the times for a 25 percent increase in pressure of the reactant or reactants.

---

[1] Steacie: J. Am. Chem. Soc., 54, 1695 (1932).

[2] Steacie: Can. J. Research, 6, 265 (1932).

The Effect of Surface.

In agreement with the results of Hinshelwood, it was found that the decomposition of both ethers is predominantly homogeneous. Experiments in a bulb packed with short lengths of silica tubing showed that the surface reaction was negligible.

The results which follow were obtained in random order. A few runs were made with methyl ether alone, then with ethyl ether, the mixture, and so on. In each series the runs were also made in random order as regards pressure.

(*a*). *Pure Ethyl Ether.*

The values of T_{25} for pure ethyl ether at 478°C are given in Table I.

TABLE I

Pure Ethyl Ether

Pressure, cms.	6.30	6.82	8.54	8.75	10.01	11.16	11.80
T_{25}, mins.	29.5	29.5	27.0	26.8	24.2	24.5	24.4
Pressure, cms.	14.39	16.15	16.60	16.88	17.83	17.98	
T_{25}, mins.	23.1	21.4	22.5	21.9	21.5	20.5	
Pressure, cms.	20.29	22.18	25.80	28.02	28.30	31.05	31.20
T_{25}, mins.	20.6	20.1	17.6	16.3	17.0	16.7	15.8
Pressure, cms.	32.07	32.75	37.06	37.55	38.40	53.80	
T_{25}, mins.	16.8	16.0	15.0	14.8	15.6	13.3	

The results given in Table I are plotted in Fig. 1. In order to obtain a convenient curve for interpolation, it is desirable not to have too great curvature. Fig. 1, therefore, gives T_{25} plotted against $1/p$, rather than against p.

The falling off in rate shown in Table I and Fig. 1 is in practically exact agreement with that previously found by Hinshelwood. The absolute value of the velocity is slightly greater than that of Hinshelwood. We may calculate the rate at infinite pressure to a fair approximation by a linear extrapolation of Fig. 1. Treating Hinshelwood's data in a similar way for 504°C, and using his value for the heat of activation, we obtain about 11.4 mins. for T_{25} at 478°C. The value from Fig. I is about 9.0 mins. The difference may in part be due to the uncertainty in extrapolating to infinite pressure. In any case it corresponds to a discrepancy of only about 2° in temperature between the two investigations.

(*b*). *Pure Methyl Ether.*

The results for pure methyl ether at 478°C are given in Table II.

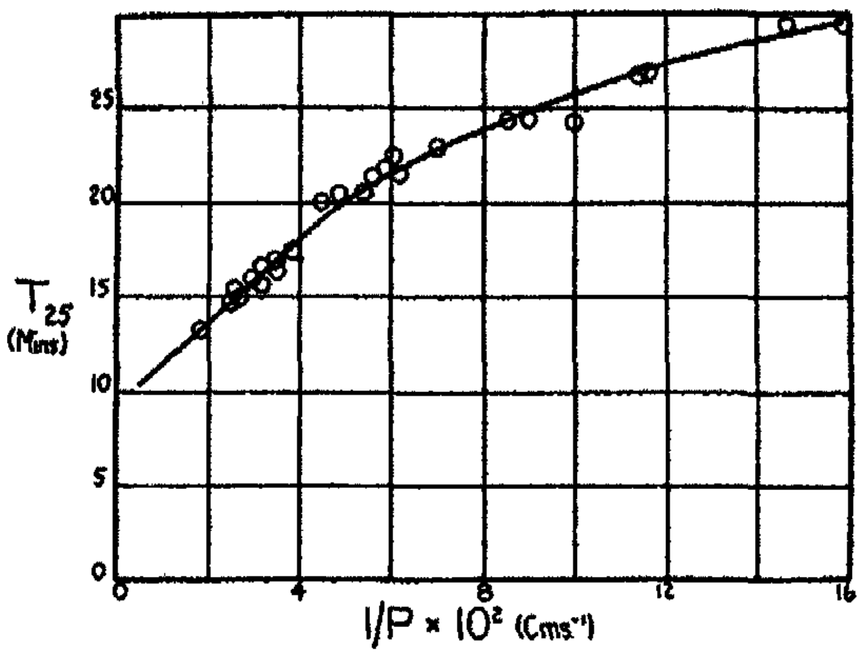


FIG. 1
Ethyl Ether

TABLE II

Pure Methyl Ether

Pressure, cms.	6.31	8.45	10.37	12.03	13.32	17.85	18.25	18.70
T_{25}, mins.	45.6	36.3	33.7	30.0	27.5	25.0	25.0	23.5
Pressure, cms.	28.30	30.90	38.10	39.34	46.40	50.30	59.40	
T_{25}, mins.	21.4	20.6	19.9	19.5	19.1	17.8	16.8	
Pressure, cms.	63.35	65.30						
$T_{,25}$ mins.	16.8	16.7						

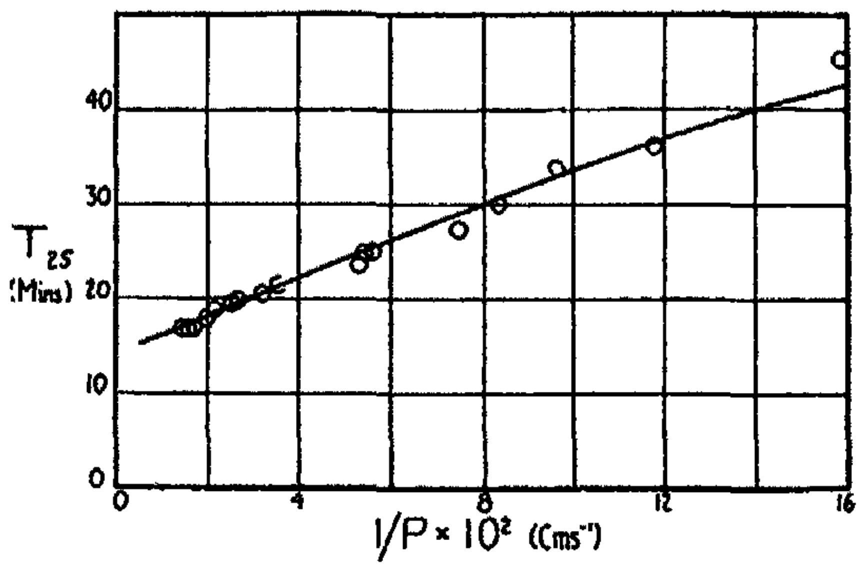


FIG. 2
Methyl Ether

The data of Table II are plotted in Fig. 2 in the same way as those for ethyl ether. As with ethyl ether, the falling off in rate with decreasing pressure is similar to that found by Hinshelwood. A comparison of the calculated high pressure rates at 478°C gives 13.5 mins. from Fig. 2, as against about 14.2 minutes from Hinshelwood's data. The discrepancy is within the experimental error, since it corresponds to a temperature difference of about 0.5°C.

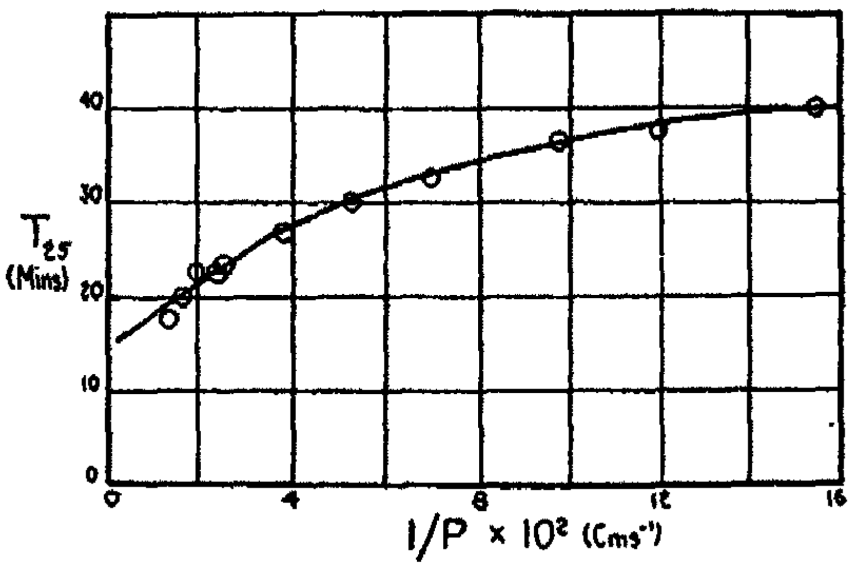


Fig. 3
1 $C_2H_5OC_2H_5$ + 0.980 CH_3OCH_3

(c). *Mixtures of Methyl and Ethyl Ether.*

Having established the rates for the separate ethers over the range of pressure, a series of runs were made with a mixture consisting of 1 $C_2H_5OC_2H_5$ + 0.980 CH_3OCH_3. The times for the total pressure of the mixture to increase by 25 percent are given in Table III.

TABLE III

1 $C_2H_5OC_2H_5$ + 0.980 CH_3OCH_3

Total pressure, cms.	6.44	8.33	10.20	14.95	18.95	26.05
T_{25}, mins.	39.7	37.5	36.6	32.5	30.0	26.8
Total pressure, cms.	38.26	40.05	50.58	58.83	71.10	
T_{25}, mins.	23.2	22.6	22.7	20.0	17.3	

The results are plotted as before in Fig. 3.

In Table IV the observed results for the mixture are compared with those calculated from the rates of decomposition of the separate reactants on the assumption (a) that the two substances have zero efficiency in so far as mutual activation is concerned, and (b) on the assumption that the efficiency is 100 percent. The manner in which the values in Table IV are arrived at may be illustrated by a sample calculation, using the figures given in the first line of the table.

TABLE IV

Total pressure, cms.	T_{25}, mins.	T_{25} for pure methyl ether at a pressure equal to the partial pressure in the mixture.	T_{25} for pure ethyl ether at a pressure equal to the partial pressure in the mixture.	Percent increase in total pressure in the time given in column 2, due to methyl ether.	Percent increase in total pressure in the time given in column 2, due to ethyl ether.	Calculated fractional change in the time given in column 2.	Ratio $\frac{\text{calculated change,}}{\text{observed change}}$ assuming zero efficiency.	T_{25} for pure methyl ether at a pressure equal to the total pressure of the mixture.	T_{25} for pure ethyl ether at a pressure equal to the total pressure of the mixture.	Percent increase in total pressure in the time given in column 2, due to methyl ether.	Percent increase in total pressure in the time given in column 2, due to ethyl ether.	Calculated fractional change in the time given in column 2.	Ratio $\frac{\text{calculated change,}}{\text{observed change}}$ assuming 100 per cent efficiency.
71.10	17.3	20.2	15.5	10.5	14.3	24.8	0.99	16.8	11.2	12.7	19.5	32.2	1.29
58.83	20.0	21.2	17.0	11.5	15.0	26.5	1.06	17.4	12.5	14.1	19.1	33.2	1.33
50.58	22.7	22.5	18.1	12.3	16.0	28.3	1.13	18.0	13.4	15.6	21.3	36.9	1.48
40.05	22.6	24.3	20.1	11.4	14.0	25.7	1.02	19.2	14.8	14.5	19.4	33.9	1.36
38.26	23.2	25.0	20.4	11.4	14.5	25.9	1.03	19.5	15.0	14.6	19.6	34.2	1.37
26.05	26.8	29.5	23.3	11.2	14.6	25.8	1.03	22.0	18.1	15.0	18.8	33.8	1.35
18.95	30.0	35.5	27.7	10.5	14.0	24.5	0.98	24.6	20.5	15.0	18.6	33.6	1.34
14.95	32.5	40.8	28.3	0.8	14.7	24.5	0.98	27.5	22.5	14.5	18.3	32.8	1.31
						mean =	1.03					mean =	1.36

It is found experimentally that when the total pressure of the mixture is 71.10 cms. the value of T_{25} is 17.3 minutes. The partial pressure of methyl ether in the mixture is 35.21 cms., that of ethyl ether is 35.89 cms. From Figs. 1 and 2, the values of T_{25} for the pure substances at these pressures are 20.2 and 15.5 mins., respectively. If we assume zero efficiency in mutual activation, the substances will decompose at rates corresponding to these values when mixed. In the time required for a 25 percent increase in pressure of the mixture, viz. 17.3 mins., the methyl ether present will therefore decompose to an extent corresponding to a time equal to 17.3/20.2 of T_{25}. From a typical rate curve for methyl ether, this corresponds to 21.3 percent increase in pressure. Similarly, in 17.3 mins. the percent pressure increase for ethyl ether will be 28.0. Hence, taking into consideration the relative quantities of the two substances, we find that the increase in total pressure due to the decomposition of methyl ether will be 10.5 percent in 17.3 minutes, while that due to ethyl ether will be 14.3 percent. Hence, the calculated pressure increase in 17.3 mins. is 24.8 percent, as against an observed increase of 25 percent.

The calculations for 100 percent efficiency are carried out in the same way, except that it is assumed that each reactant will decompose at a rate corresponding to a pressure of the pure substance equal to the total pressure of the mixture.

It will be seen that the average value of the ratio

$$\frac{\text{percent change calculated}}{\text{percent change observed}},$$

assuming zero efficiency in mutual activation, is 1.03. Considering the number of different experimental values involved in the calculation, this certainly constitutes an agreement within the experimental error. The difference of 0.03 found is actually in the wrong direction, i.e. the mixture decomposes more slowly than the calculated rate.

On the assumption of 100 percent efficiency, the average value of the above ratio is 1.36. In other words, if 100 percent efficiency in activation occurred the mixture should decompose at a rate nearly 40 percent faster than the observed value.

It may therefore be concluded that if either of the reactants has any effect in keeping up the rate of the other, the effect is smaller than the experimental error of the present investigation, and is probably not more than 5 percent of the effect due to collisions between molecules of the same kind.

Discussion

The work of Zener, Kallmann and London, and Rice, previously referred to, has given indications of a theoretical basis for the high specificity of energy transfer during collisions of the second kind. This gives at least a partial explanation of the high efficiency of hydrogen compared with nitrogen, helium, etc. It offers no explanation, however, for the high specificity when dealing with molecules of a foreign gas whose complexity is of the same order of magnitude as that of the reactant.

There is, however, some indication of a similar specific energy transfer between complex gas molecules and a solid surface. Thus there appears to be a high efficiency of energy transfer in producing activated molecules by collisions of acetone and diethyl ether with platinum.[1] On the other hand, collisions of propionaldehyde and of dimethyl ether with platinum are comparatively inefficient in establishing statistical distribution of energy.[2] In such cases, however, we are dealing with collisions between two substances of a quite different nature.

The low efficiency of energy transfer in the case of the two ethers is, however, very surprising. The chemical and physical properties of the two substances are very similar. Their modes of decomposition are almost identical, in each case involving the splitting off of a hydrocarbon, followed by the loss of carbon monoxide by the resulting aldehyde, viz.

$$CH_3OCH_3 = CH_4 + HCHO = CH_4 + CO + H_2,$$

and

$$C_2H_5OC_2H_5 = C_2H_6 + CH_3CHO = C_2H_6 + CO + CH_4.$$

The activation energies of the two processes are also of the same order of magnitude, being 58,500 and 53,000 calories, respectively. The falling off in rate with pressure is slightly different for the two substances, and leads to the conclusion that 15 squared terms are required to account for the decomposition of dimethyl ether, and 8 for diethyl ether. If the number of squared terms were a measure of the efficiency of energy transfer, we might not expect ethyl ether to be effective in maintaining the rate of decomposition of methyl ether, but it would certainly be expected that methyl ether would be effective in preventing the falling off in rate of ethyl ether.

We are therefore led to the conclusion that the efficiency of energy transfer must be governed by the actual groups participating in the collision, rather than by the general nature of the molecule as a whole. Presumably collisions between methyl groups or ethyl groups are effective, but not collisions between a methyl group and an ethyl group. From this point of view, considerable information might be gained from the investigation of mixtures of methyl ethyl ether with dimethyl ether, and with diethyl ether. Such experiments are under way.

Summary

The homogeneous unimolecular decomposition of mixtures of dimethyl and diethyl ether has been investigated. The efficiency of energy transfer between molecules of the two substances is zero (within the experimental error), in so far as the production of activated molecules is concerned. The rates of decomposition of the separate reactants are therefore additive, and they have no mutual activating effect.

Physical Chemistry Laboratory,
McGill University,
Montreal, Canada.

---

[1] H. A. Taylor: J. Phys. Chem., **33**, 1793 (1929); Steacie and Campbell: Proc. Roy. Soc., **128A**, 451 (1930).

[2] Steacie and Morton: Can J. Research, **4**, 582 (1931); Steacie and Reeve: unpublished.

THE BEHAVIOUR OF THE GLASS ELECTRODE IN AQUEOUS SOLUTIONS OF SODIUM AND BARIUM ACETATE

BY MALCOLM DOLE

Freundlich and Rona[1] first investigated the glass electrode in solutions whose ions were multi-valent. They showed that although the electrokinetic potential of the glass aqueous solution boundary was changed considerably by changing the valence of the positive ion in the solution, the thermodynamic potential did not change at all or only with a change of the hydrogen ion concentration. It seems of interest to extend this study of the effect of multivalent ions upon the thermodynamic potential of the glass electrode to solutions of high alkalinity because in this pH range, the potentials are functions of the concentration of ions such as lithium or sodium ions in addition to the hydrogen ion.

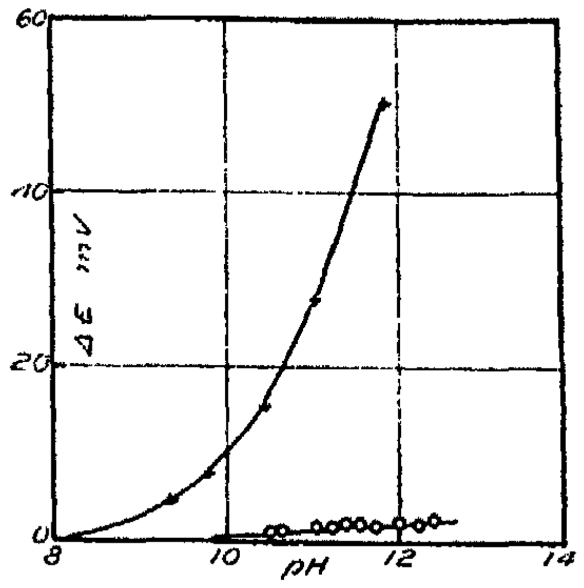


FIG. 1
Errors of the Glass Electrode
Top Curve 1.0 N Sodium Acetate
Bottom Curve 1.0 N Barium Acetate

The author has recently advanced the hypothesis[2] that the mobility of the ions across the glass aqueous solution boundary may be influenced by the Helmholtz double layer. Since the large errors in alkaline solutions have been shown by him to be due to the relative mobilities of the ions across the boundary, it was thought that a study of the glass electrode errors under different boundary conditions might indicate if any connection between the Helmholtz double layer and the mobilities across this layer existed or not. The glass electrode shows a marked difference of behaviour in solutions of univalent and bivalent ions. In Fig. 1 the errors of the glass electrode in 1 normal sodium solutions are plotted along with the errors in 1 normal barium solutions. The barium solution errors are nearly within the experimental errors of measurement in contrast to those for the sodium ions which are very large. This difference has been experimentally demonstrated by a number of investigators.[3] Now the question which may be asked is, are the low errors of the glass electrode in barium solutions due to a low mobility of the barium ion across the boundary or are they due to a change in the Helmholtz double layer

---

[1] H. Freundlich and P. Rona: Sitzb. preuss. Akad. Wiss., 20, 397 (1920).

[2] M. Dole: J. Am. Chem. Soc., 53, 4260 (1931).

[3] K. Horovitz: Sitzb. Akad. Wiss. Wien., Abt. II a, 134, 335 (1925); W. S. Hughes: J. Chem. Soc., 1928, 491; M. Dole: J. Am. Chem. Soc., 53, 4260 (1931). The data plotted are taken from this paper.

caused by the double positive charge on the barium ion? To solve this problem it was decided to carry out experiments in mixed barium and sodium solutions. If the barium acted solely through its mobility across the boundary, one would expect that the sodium ions would cause just as large an error in the presence of the barium as by themselves (except for a possible change in the activity of the sodium ion due to a change in the ionic strength), but if the effect of the barium ions is to change the mobility due to a change in the Helmholtz double layer, one might expect the mobility of the sodium ion also to be changed and with this change in mobility a change in the error of the glass electrode.

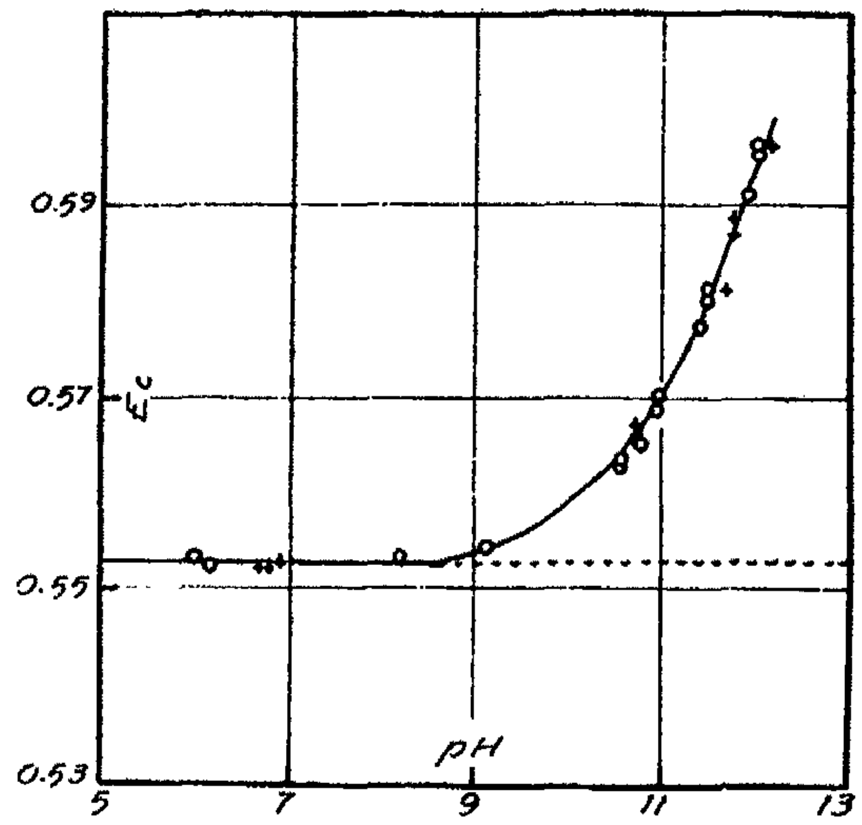


FIG. 2

Potential of the Glass Electrode in Sodium Acetate 0.5 N, circles; and in 0.5 N Sodium Acetate, 0.5 N Barium Acetate, crosses.

Measurements were made of the following cells exactly in the manner already described;[4]

A. Hg | HgCl | Sat. KCl || Sodium or barium acetate solution || glass || acetate buffer + sodium chloride | AgCl | Ag

B. Hg | HgCl | Sat. KCl || Sodium or barium acetate solution | H_2 | Pt

From measurements of cells A and B, the potential of the cell C may be obtained by difference.

C. Ag | AgCl | Acetate buffer + sodium chloride || glass || Sodium or barium acetate solution | H_2 | Pt

---

[4] Ref. (2).

Cell C should have a potential of 0.553 v. as long as the glass electrode shows no error; i.e., as long as it behaves as a perfect hydrogen electrode. The first experiments were made with 0.5 N NaAc solution, adding 0.5 N NaOH to increase the pH. Having obtained consistent results with this solution, a solution having the composition 0.5 N NaAc, 0.5 N $BaAc_2$ was then substituted and the measurements repeated. The results are recorded in Table I and are plotted in Fig. 2.

Table I

Potentials of the cell at 25°

Ag | AgCl | Acetate buffer + sodium chloride || glass || Sodium + barium acetate | H_2 | Pt

0.5 N Na^+			0.5 N Na^+, 0.5 N Ba^{++}		
pH	Glass Electrode No.	ΔE	pH	Glass Electrode No.	ΔE
5.98	F-3	0.5536	6.68	F-34	0.5524
	F-4	.5526		F-35	.5522
8.23	F-27	.5538	6.79	F-34	.5530
9.16	F-27	.5549	10.73	F-34	.5672
10.59	F-3	.5639		F-35	.5662
	F-4	.5630	11.76	F-34	.5813
10.81	F-27	.5655	11.84	F-34	.5888
10.99	F-3	.5690		F-35	.5873
	F-4	.5704	12.22	F-34	.5965
11.48	F-27	.5773			
11.55	F-3	.5814			
	F-4	.5801			
12.03	F-27	.5911			
12.11	F-3	.5965			
	F-4	.5953			

From a study of the data and the figure it is evident that there is no significant difference between the two solutions; hence we can conclude that the barium ion has no influence upon the errors due to the sodium ions. If the barium ions do change the nature of the Helmholtz double layer by their presence, this change of the Helmholtz double layer has no influence on the mobility of the sodium ions across the glass aqueous solution boundary. In this connection it is interesting to point out that this experiment indicates that mixtures of barium and sodium ions could be analysed for their sodium content in much the same way that Urban and Steiner[5] analysed mixtures of sodium and potassium.

---

[5] F. Urban and A. Steiner: J. Phys. Chem., 35, 3058 (1931).

Experiments to be reported elsewhere have also been carried out in acid solutions in order to find out if the acid solution errors recently discovered by MacInnes and Belcher[6] are at all affected by change in valence of the ions present. These experiments likewise gave negative results.

Summary

The glass electrode behaves in mixtures of sodium and barium as if no barium were present. This indicates that the barium ion does not affect the mobility of ions across the glass aqueous solution interface due to any effect its double positive charge might have on the Helmholtz double layer.

Chemical Laboratory,
Northwestern University,
Evanston, Illinois.

---

[6] D. A. MacInnes and Donald Belcher: J. Am. Chem. Soc., **53**, 3315 (1931).

ABSORPTION SPECTRA OF LIGNIN SOLUTIONS[1,2]

BY A. J. STAMM, JOS. SEMB AND E. E. HARRIS

Synopsis

The absorption spectra of a number of lignin solutions were determined, using the photographic method of Hilger and also a direct method in which the intensity of transmitted monochromatic light was measured with a thermopile. The results of the two methods agree satisfactorily. The hardwood lignins studied all gave characteristic absorption bands with maxima at 2740 to 2760 Å. The softwood lignins gave characteristic absorption bands with maxima at 2810 to 2850 Å. The different methods used for isolating lignin from wood had substantially no effect upon the absorption spectra. The lignin from partially chlorinated wood, or previously isolated lignin that was only partially chlorinated, when dissolved in a solution of sodium sulfite gave absorption bands that have extinction coefficients somewhat smaller than those of lignin solutions prepared from completely chlorinated wood or lignin. A thermal reaction product of cellulose, which is insoluble in 72 per cent sulfuric acid and which has been shown to have other characteristic chemical properties of lignin, gave an absorption band practically identical with that of lignin, except that the corresponding extinction coefficients were smaller.

Herzog and Hillmer[3] have shown that lignin solutions give a characteristic light absorption band in the ultraviolet. Cellulose and other carbohydrates, on the other hand, show no characteristic light absorption even in the short wave length ultraviolet.[4] These facts suggest that absorption spectra measurements should be of value in studying lignin, even in the presence of carbohydrate material. Further, absorption spectra measurements should aid not only in determining the molecular structure of lignin but also in determining the purity of lignins isolated by various processes. This preliminary paper deals primarily with the purity phase of the study.

The earlier absorption spectra measurements of Herzog and Hillmer[3] were made with the rather qualitative photographic method of Hartley-Baly. Their results show in a semiquantitative way the position of the absorption bands, but give only relative values for the extinction coefficients.

When the research reported here was under way, recent papers by Hägglund and Klingstedt[5] and Herzog and Hillmer[6] on the absorption spectra of

---

[1] Presented before the Division of Cellulose Chemistry at the eighty-third meeting of the American Chemical Society, New Orleans, La., March 28, 1932.

[2] Forest Products Laboratory; maintained at Madison Wis., in cooperation with the University of Wisconsin. Forest Service U. S. Department of Agriculture.

[3] Herzog and Hillmer: Ber., 60B, 365 (1927); Z. physiol. Chem., 168, 115 (1927).

[4] Kwiecinski and Marchlewski: Bull. Inter. Acad. polonaise, (A) 1928, 271.

[5] Hägglund and Klingstedt: Z. physik. Chem., 152A, 295 (1931).

[6] Herzog and Hillmer: Ber., 64B, 1288 (1931); Papier Fabrikant, Fest und Ausland Heft, 1931, 40.

lignin were brought to the authors' attention. The results obtained by these investigators, using the photographic method of Henri which is more accurate than that of Hartley-Baly, are summarized in Table II for comparison with the results obtained in this investigation.

Experimental Methods

The absorption spectra measurements were made by two different methods, that of Hilger[7] and also a direct light-absorption one. A double cell, made by cementing matched quartz windows over two holes 1.0 cm. in diameter and 1.8 cm. apart that were drilled in a piece of plate glass 0.927 cm. thick, was used in both methods. A small slot, ground on one surface of the plate glass at the top of each hole and extending beyond the quartz plates, served in filling the cells. The spectrophotometer, which was of the Cornu prism type, gave a dispersion of 4 cm. over the range in wave length of 2500 to 2900 Å. An iron arc was used as the source of illumination.

Slight variations in the intensity of the light source have no effect upon the results obtained by the Hilger method, since the photographs of the solution and of the solvent are taken simultaneously. Further, the effect of any slight light absorption by the solvent is eliminated because of the comparative nature of the method. Another advantage is that absolute values of the extinction coefficient are obtained. The formula for the calculation required is

$$\epsilon = \frac{f}{cd} \log \frac{S}{S_o} \qquad (1)$$

where ϵ is the extinction coefficient in grams per liter, c is the concentration in grams per liter, d is the depth of the cell in centimeters, f is the correction for photographic density, S_o is the angle of the sector wheel opening[7] for the solvent, and S is the angle for the solution. The method used to obtain f will be given later in this paper.

In the direct light-absorption method, light from a mercury vapor lamp was focused upon a constant-deviation quartz monochrometer consisting of two 30° prisms. The monochromatic light was in turn focused upon an 11-junction platinum-iridium thermopile. The thermopile was connected to a sensitive suspension galvanometer, the deflections of which were read on a glass scale at a distance of 3 meters. A galvanometer deflection of 1 cm. was produced by 19 ergs of energy. The thermopile was carefully protected from stray light effects and the electrical parts of the apparatus were all grounded. The holder built for the cell permitted bringing either the solvent or the solution part into proper alignment in front of the monochrometer slit by merely pulling or releasing a cord.

With the conditions under which the measurements were made the galvanometer deflections are directly proportional to the intensity of the immergent light. The absolute extinction coefficient for any wave length

---

[7] Weigert: "Optische Methoden der Chemie," 230 (1927).

can be readily calculated by making the measurements alternately upon the solvent and the solution. Then

$$\epsilon = \frac{1}{cd} \log \frac{I_0}{I} \qquad (2)$$

where I_0 is the intensity of the light beam after passing through the solvent, I is the intensity after passing through the solution, and the other symbols have the same significance as in equation (1). The transmissive power of the two parts of the double cell were found to differ by 2 per cent when measurements were made at several different wave lengths, using distilled water; the necessary corrections were made in the calculations. Depending upon the intensity of the respective spectral lines, the light of the different wave lengths at which measurements were made caused the galvanometer deflections, for the solvent, to range from 2 to 16 centimeters.

The direct light-absorption method gives absolute values of the extinction coefficient directly, while the Hilger method involves the correction f for photographic density. This proportionality factor was obtained by making measurements on the same solution by both methods and then determining the shift along the extinction coefficient axis that would make the two curves identical. For determination No. 1, Table I, f was found to be 0.532. This value was used in all of the following calculations on measurements made by the Hilger method.

Solutions studied

A 2 per cent solution of sodium sulfite was used as the solvent in a large number of the measurements. Baly and Bailey[8] have shown that these solutions cause an appreciable absorption of light below a wave length of 2800 Å. In this investigation a fresh 2 per cent solution of sodium sulfite gave complete absorption below 2550 Å. The sodium sulfite solutions undergo a change on standing even when kept in sealed flasks. After several days of standing they transmitted light down to 2320 Å. When the lignin solutions in sodium sulfite solution were made up several days before the measurements were made, the light-absorption effect of the solvent was found to be negligible above a wave length of 2500 Å. For this reason all of the lignin solutions in sodium sulfite solution that were investigated were several days old.

The lignin solutions were prepared directly from wood and also from isolated lignin. Those from wood were prepared by the Cross and Bevan method; 2 grams of wood were treated with chlorine and the lignin dissolved in 100 cc. of 2 per cent sodium sulfite solution or water. The solutions of isolated lignin were prepared by chlorinating 0.2 gram samples and then dissolving them in 50 cc. of sodium sulfite solution. The solution of isolated lignin in ethyl alcohol (determination No. 13, Table I) was prepared by extracting a sulfuric acid lignin with the alcohol in a Soxhlet extractor for two days. At the end of this time no more lignin went into solution. The isolated lignins were prepared according to recognized procedures. The time

---

[8] Baly and Bailey: J. Chem. Soc., 121, 1813 (1922).

and the temperature of treatment with 72 per cent sulfuric acid, for the sulfuric acid lignins, are given in parentheses in Table I. The sulfite liquor was obtained from a normal sulfite digestion in which lime was used as the base.

The thermal reaction product of cellulose was obtained by heating maple Cross and Bevan cellulose containing 5.25 per cent of moisture in a sealed glass tube to 138° C. for 8 days. The brown product thus obtained gave, upon chlorination and treatment with sodium sulfite solution, a solution that showed many of the chemical characteristics of lignin.[9] Treating the heated cellulose with 72 per cent sulfuric acid caused an appreciable residue corresponding to that of lignin. This residue after chlorination is soluble in sodium sulfite solution, in acetic acid or glycol containing a small amount of hydrochloric acid, and in strong alkali. The solution used for the absorption measurements was obtained by chlorinating the 72 per cent sulfuric acid residue and dissolving the result in sodium sulfite solution. Only one chlorination was made, whereas several are required for complete solution of the lignin-like material. The results should thus be comparable with the partially chlorinated lignins.

The total concentration of organic matter was taken to represent the lignin concentration, except for determination No. 1 of Table I, for which the pentosan content (15.3 per cent) was deducted. This inclusion of the pentosan content with the lignin concentration makes the extinction coefficients from 6 to 10 per cent too low for determinations Nos. 3, 4, 5, and 6.

Discussion of Results and Conclusions

Figs. 1 and 2 give the absorption spectra curves for all of the measurements and Table I summarizes the measurements. The numbers on the curves correspond to the numbers of the determinations given in Table I.

The results for determinations Nos. 1 and 2 showed that the presence of pentosans in the solution had no effect upon either the position of the absorption band or the values of the extinction coefficients when the concentration of pentosans present is subtracted from the total concentration in making the calculations. This not only substantiates the findings that carbohydrates show no appreciable light absorption but also indicates that the dilute alkali treatment used to extract the pentosans has no effect upon the characteristic light-absorbing part of the lignin molecule.

The light-absorption curves for chlorinated lignin dissolved in sodium sulfite solution and dissolved in water are practically identical above a wave length of 2500 Å (determinations Nos. 4 and 5). Below this wave length the absorption of the sulfite solution, even though several days old, is appreciable, as shown in the foregoing.

Lignin solutions prepared from only partially chlorinated wood or lignin (determinations Nos. 3 and 7) give the same absorption band as the solutions prepared from the completely chlorinated material (determinations Nos. 4

---

[9] Hawley and Wiertelak: Ind. Eng. Chem., 23, 184 (1931); Hawley and Harris, Paper presented before the Division of Cellulose Chemistry at the eighty-first meeting of the American Chemical Society and to be published soon.

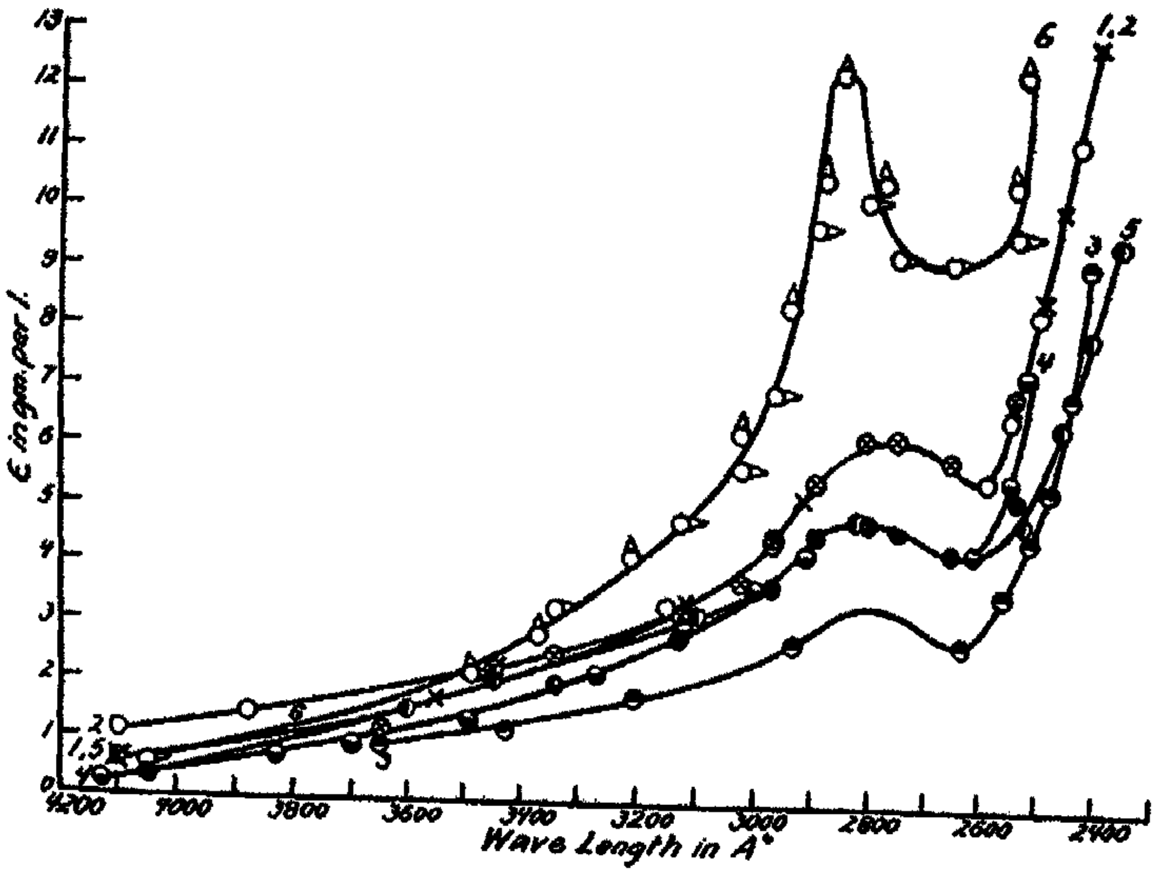


Fig. 1

× 1. Hilger method
⊗ 1. Direct method
○ 2. Hilger method
◓ 3. Hilger method
◒ 4. Hilger method
● 4. Hilger method
◐ 5. Hilger method
△ 6. Hilger method
⊳ 6. Direct method

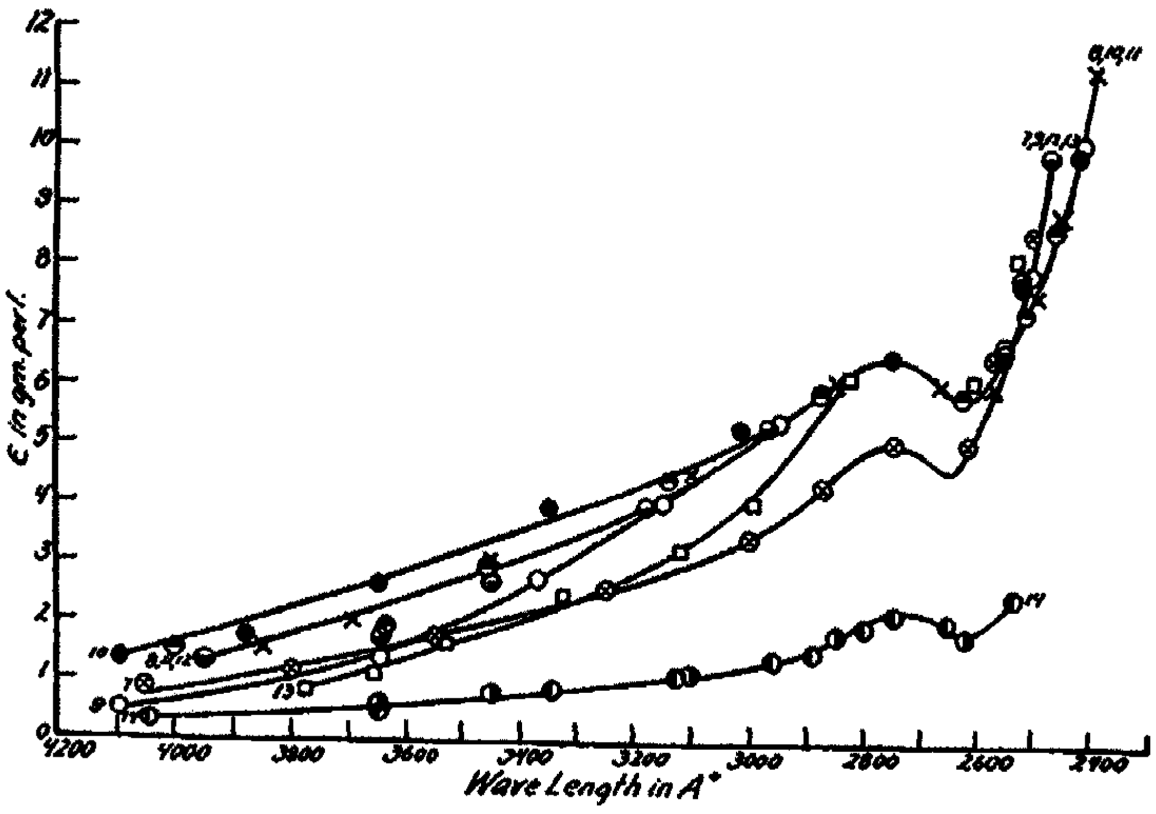


Fig. 2

⊗ 7. Hilger method
× 8. Hilger method
○ 9. Hilger method
● 10. Hilger method
◓ 11. Hilger method
◒ 12. Hilger method
□ 13. Hilger method
◑ 14. Hilger method
◐ 14. Direct method

Table 1 carries the key to the determination numbers.

and 8) except that the corresponding extinction coefficients are smaller. This is similar to the effect reported by Hägglund and Klingstedt.[5] They found that amyl lignin prepared by partial solution in amyl alcohol containing 1 per cent hydrochloric acid gave smaller extinction coefficients than when the lignin was almost completely dissolved (Table II). This shift in the extinction coefficients they reported can be due to differences in solubility of the constituents of a mixture made up either of molecules of the same molecular weight but containing different proportions of the characteristic absorbing group, or of different molecular-weight species each containing the same characteristic group. Further study will be necessary to determine the facts. The measurements indicate strongly, however, that lignin is not a simple monomolecular substance.

The measurements show a definite displacement in the absorption-band maxima between hardwoods and softwoods. This same displacement was noted by Hägglund and Klingstedt[5] and by Herzog and Hillmer[6] (Table II). The maxima for hardwoods were found to be within the narrow range of 2740 to 2760 Å in all of the investigations. Softwoods, on the other hand, showed a range for the position of the maxima from 2800 to 2870 Å. This variation is surprisingly small for measurements made upon such widely different lignin preparations as those studied by different investigators, using different experimental methods. The exact nature of this difference between lignin preparations obtained from the two types of wood is still unknown. Differences in the chemical reactions and in the methoxyl content have been recognized for years, but the shift in the absorption spectra band can hardly be due to differences in the number of methoxyl side chains. The difference must be due to a variation in the characteristic absorption group.

Isolated lignins prepared by several modifications of the sulfuric acid method, by the Willstätter hydrochloric acid method, and by the Freudenberg cuprammonium method all gave practically identical absorption bands, with the extinction coefficients differing appreciably only for the longer wave lengths. These results show that the lignins prepared by these different methods do not differ in the characteristic absorbing groups. Differences in the methoxyl content that do exist among the different lignin preparations can affect the results only in so far as they shift the extinction coefficients because of differences in molecular weight.

A solution of isolated lignin prepared by complete extraction with alcohol in a Soxhlet extractor showed an absorption band virtually identical with that obtained by chlorinating and dissolving the same lignin preparation in sodium sulfite solution. Differences in the extinction coefficients occurred only in the longer wave lengths.

The measurements on the calcium salt of lignin sulfonic acid, the only solution studied that was also studied by either of the other groups of investigators, gave results in good agreement with those obtained by Hägglund and Klingstedt[5] (Tables I and II). In both investigations these were the sharpest maxima obtained, a fact that may have some significance.

Table I
Absorption Spectra of Lignin Solutions

Determination No.	Species	Nature of lignin solution	Solvent	Concentration	Method of measurement	Position of maximum	ε at maximum	Position of minimum
				Grams per liter		Å	Grams per liter	Å
1	Sugar maple	Cross and Bevan; complete chlorination	2 per cent Na_2SO_3	0.125	Direct	2760	6.3	2610
				.0669	Hilger	2760	6.3	2610
2	"	Cross and Bevan; complete chlorination (pentosans extracted from wood)	2 per cent Na_2SO_3	.102	"	2760	6.3	2610
3	White spruce	Cross and Bevan; chlorinated 1 minute in desiccator filled with Cl_2.	2 per cent Na_2SO_3	.1265	"	2810	3.4	2640
4	"	Cross and Bevan; complete chlorination	2 per cent Na_2SO_3	.157	Direct	2820	4.8	2630
				.157	Hilger	2820	4.8	2630
5	"	"	Water	.0717	"	2820	4.8	2630
6	Spruce	Sulphite liquor	$CaSO_3$ solution	.1095	Direct	2850	12.3	2650
				.0547	Hilger	2850	12.3	2650
7	Sugar maple	H_2SO_4 lignin (16-hour treatment at 10°C.); chlorinated 1 minute in desiccator filled with Cl_2	2 per cent Na_2SO_3	.133	"	2750	5.1	2640

Table I (Continued)

Adsorption Spectra of Lignin Solutions

Determination No.	Species	Nature of lignin solution	Solvent	Concentration	Method of measurement	Position of maximum	ε at maximum	Position of minimum
				Grams per liter		Å	Grams per liter	Å
8	Sugar maple	H_2SO_4 lignin (16-hour treatment at 10°C.); complete chlorination	2 per cent Na_2SO_3	.0756	Hilger	2760	6.7	2610
9	"	H_2SO_4 lignin (3-hour treatment at room temperature); complete chlorination	2 per cent Na_2SO_3	.0834	"	2760	6.7	2610
10	"	H_2SO_4 lignin (16-hour treatment at room temperature); complete chlorination	2 per cent Na_2SO_3	.0854	"	2760	6.7	2610
11	"	HCl lignin; complete chlorination	2 per cent Na_2SO_3	.0768	"	2760	6.7	2610
12	"	$CuNH_3$ lignin; complete chlorination	2 per cent Na_2SO_3	.0848	"	2760	6.7	2610
13	"	H_2SO_4 lignin (16-hour treatment at room temperature); complete extraction in Soxhlet	Ethyl alcohol	.1375	"	2760	6.7	2610
14	"	Synthetic lignin (Cross and Bevan cellulose heated eight days at 138°C in a sealed tube); partial chlorination	2 per cent Na_2SO_3	.231	Direct	2740	2.2	2620
				.180	Hilger	2740	2.2	2620

TABLE II

Absorption Spectra of Lignin Solutions by Other Investigators using the Method of Henri

Investigators	Species	Nature of lignin solution	Solvent	Position of maximum	ϵ at maximum	Position of minimum
				Å	Grams per liter	Å
Hägglund and Klingstedt	Spruce	Amyl lignin	Alcohol	2840	18.8	2575
"	Pine	"	"	2830	18.8	2570
"	Birch	"	"	2760	12.5	2590
"	Beech	"	"	2755	12.5	2590
"	Spruce	Amyl lignin, 10-minute extraction	"	2810	14.9	2560
"	"	Amyl lignin, 30-minute extraction	"	2810	15.9	2580
"	"	Amyl lignin, 6 hour extraction	"	2810	21.1	2600
"	Birch	Amyl lignin, 10-minute extraction	"	2750	8.0	2585
"	"	Amyl lignin, 30-minute extraction	"	2740	9.4	2695
"	"	Amyl lignin, 6-hour extraction	"	2750	13.9	2610
"	Spruce	Amyl lignin	Dilute alkali	2870	17.5	2680
"	"	Metholated amyl lignin	Alcohol	2830	22.7	2600
"	Beech	"	"	2755	14.0	2610
Herzog and Hillmer	Spruce	Glycol lignin	Dilute alkali	2820	19.5	2630
"	Beech	Ethyl lignin	Alcohol	2750	5.4	2630

TABLE II (Continued)

Absorption Spectra of Lignin Solutions by Other Investigators using the Method of Henri

Investigators	Species	Nature of lignin solution	Solvent	Position of maximum	ε at maximum	Position of minimum
				Å	Grams per liter	Å
Hägglund and Klingstedt	Spruce	Ethyl lignin	Alcohol	2830	18.9	2575
"	"	Methyl lignin	"	2815	19.1	2585
"	"	Calcium salt of lignin sulfonic acid	Water	2830	13.8	2630
"	Birch	Calcium salt of lignin sulfonic acid	"	2760	11.4	2610
"	Spruce	Lignin sulfonic acid	Alcohol	2840	13.8	2640
Herzog and Hillmer	"	"	Water	2800	6.5	2630
"	Basswood	"	"	2740	4.1	2610
"	Rye straw	"	"	2780	3.8	2590
"	Pine	Alkali lignin	Alcohol	2800	21.4	2700
"	Basswood	"	"	2740	20.0	2590
"	Rye straw	"	"	2760	20.4	2590
"	Jute	"	"	2750	9.8	2620
"	Flax	Pectin lignin	"	2790	19.1	2600
"		Polymer of coniferol alcohol[1]	"	2780	25.0	2540

[1] For values on related aromatic compounds see Herzog and Hillmer, reference No. 6 in the present report.

The thermal-reaction product of cellulose that shows a number of chemical characteristics of lignin also gave an absorption band similar to that of lignin except that the extinction coefficients were smaller. The fact that this solution corresponded to a first fraction may account in part for the low extinction coefficient. The material, however, may consist of lignin together with an impurity that has either a slight or no absorption band, or the material may have the characteristic light-absorption band of lignin although necessarily having then a different molecular weight. The similarity of this synthetic product to natural lignin is being investigated further.

Although Herzog and Hillmer[6] have shown the similarity in light absorption of lignin and certain aromatic organic compounds, notably coniferyl alcohol and its polymers, the structure of lignin has never been definitely proven to be aromatic. A hydro-aromatic structure, which can best account for what appears to be a thermal synthesis of lignin, has not been eliminated as a possibility. Further investigation will be necessary for the drawing of definite conclusions.

The authors wish to thank the staff of the Physical Chemistry Department of the University of Wisconsin for the use of the spectrophotometer, and the staff of the Physics Department for the apparatus used in the direct-measurement method.

THE CONDUCTANCE OF SOME SODIUM OLEATE SOLUTIONS IN RELATION TO INTERFACIAL ADSORPTION.*

BY RALPH F. NICKERSON AND PAUL SEREX

Introduction

In a recent investigation Johlin[1] has found that the relative values of surface tension of sodium oleate solutions between concentrations .0019 N and .059 N are much greater than those obtained by other investigators. Leeten[2] and Dennhardt[3] studied the conductivity of these solutions and reached the conclusion that the hydrolysis constant of sodium oleate is comparatively small. Hahne[4] studied the effect of benzene on the properties of the soap in aqueous solution, but the magnitude of the interface benzene/sodium oleate was unknown. The present investigation was undertaken for the purpose of redetermining the conductances of sodium oleate solutions in the range of concentrations stated, to compare the results with surface tension data, and to measure the relative interfacial adsorption between these solutions and various oils, in order that the function of the interface in emulsification of oil-in-aqueous sodium oleate solution might be more clearly defined.

Apparatus and Materials

The conductivity bridge was essentially the same as that described by Hall and Adams[5] except that a two-stage audio frequency amplifier was interposed between the bridge output and the head phones. The alternating current used had a frequency of 1000 cycles/sec.

The bridge circuit was calibrated according to the method suggested by Wark.[6]

The procedure described by Popoff[7] was followed in the preparation of the platinum black surfaces on the electrodes of the conductivity cell. The cell constant was about 0.3595. (Subject to the calibration curve of Wark's method.)

"Equilibrium" water with a specific conductance of about $.9 \times 10^{-6}$ mhos was used throughout the investigation.

Kahlbaum's "Purest" sodium oleate was recrystallized twice from absolute alcohol, and dried in a vacuum oven. The purified product was used to make a stock solution from which various concentrations were obtained by dilution.

---

* Condensed from the thesis submitted by Ralph F. Nickerson at Massachusetts State College, 1932, in partial fulfillment of the requirements for the degree of Master of Science.

[1] Johlin: J. Biol. Chem., **84**, 534 (1929).

[2] Leeten: Z. deut. Öl-Fett-Ind., **43**, 50, 65, 81 (1923).

[3] Dennhardt: "Handbuch der Chemie u. Tech. der le Öu. Fette." Goldschmidt, **3**, 417 (1910).

[4] Hahne: Z. deut. Öl-Fett-Ind., **45**, 245-8, 263-64, 274-76, 289-90, 308-10 (1925).

[5] Hall and Adams: J. Am. Chem. Soc., **41**, 1515-25 (1919).

[6] Wark: J. Phys. Chem., **34**, 885-6 (1930).

[7] Popoff: "Quantitative Analysis," 2d Ed., 450 (1927).

Benzene, toluene and carbon tetrachloride were high grade, obtained from the Eastman Kodak Company. Meta-xylene, hexane and heptane were technical grade from the same company.

Experimental

Conductivities of the several concentrations of sodium oleate were obtained by placing the solutions in the cell and allowing them to stand in the thermostat at 25°C for half an hour before measurements were taken. Aliquots were transferred carefully to prevent frothing. Contamination by CO_2 was minimized as much as possible. The data are presented in Table I.

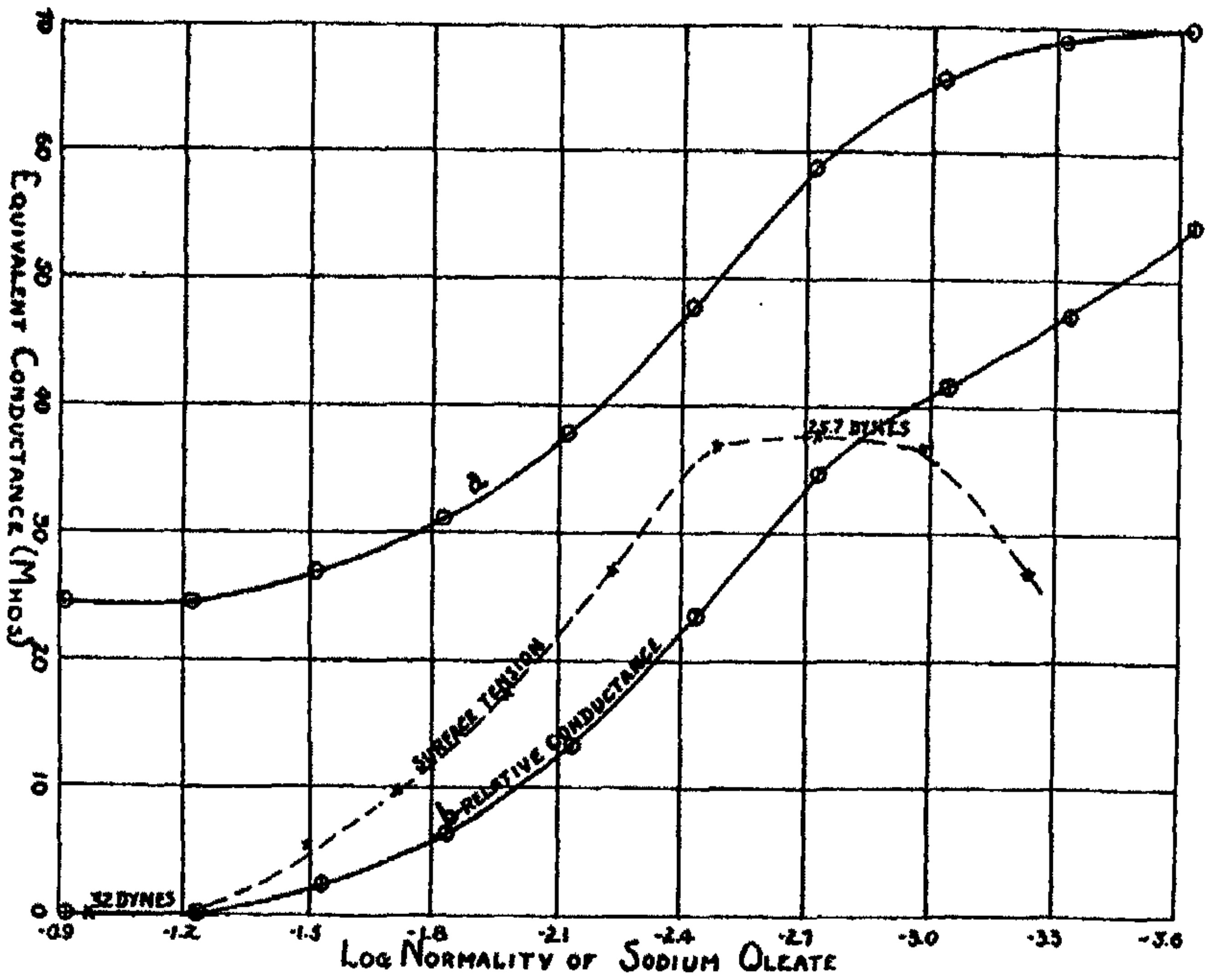


Fig. 1

The variation of equivalent conductance (a) and relative conductance (b) with logarithm of concentration of sodium oleate. The dotted line is Johlin's surface tension data.

Table I

Equivalent Conductance of Sodium Oleate at 25°C

Normality Sodium Oleate H_2O	Equivalent Conductance (Mhos) at 25°C $.83 \times 10^{-6}$	Normality Sodium Oleate H_2O	Equivalent Conductance (Mhos) at 25°C $.83 \times 10^{-6}$
.1216	24.75	.0019	58.65
.0608	24.47	.00095	66.00
.0304	26.87	.00048	69.03
.0152	31.05	.00024	69.90
.0076	37.88	.00024 (13 hrs. later)	72.20
.0038	47.80		

The curve (Fig. 1-a) represents graphically the conductivity-log. concentration relationship. A decided break in the trend of the curve may be seen at about .002 N. Leeten fails to point out this "break" although his data show it.

To eliminate the possibility that the change of trend of the conductance curve was due to the less highly conducting salt, Na_2CO_3, which could result from the interaction of NaOH, a consequence of the hydrolysis of sodium oleate, and the CO_2 of the "equilibrium" water, conductances of sodium oleate and NaOH of the various concentrations were determined simultaneously on the same water. Subtraction of the specific conductance of the NaOH solution from the corresponding figure for the sodium oleate solution gave a curve which showed the same effect (Fig. 1-b). The curve (Fig. 1-b) was taken, therefore, as the graphical representation of pure *increases* of mobility and hydrolysis with dilution.

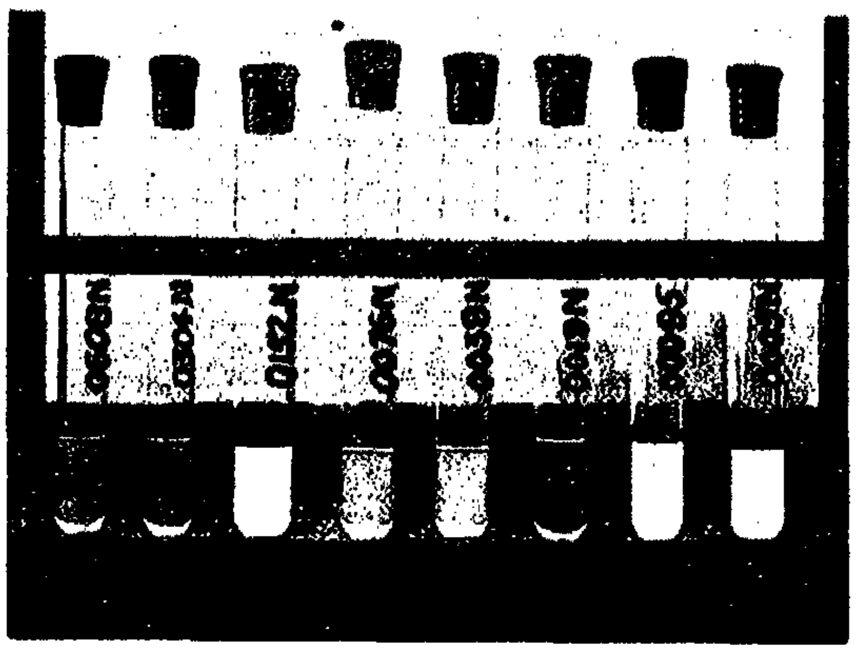


FIG. 2
The effect of dilution on the appearance of sodium oleate solutions. Photograph taken nine days after the dilutions were made.

An intense turbidity developed almost immediately in solutions of concentrations less than .002 N, but very gradually and much fainter in concentrations greater than .002 N. The photograph (Fig. 2) clearly illustrates this phenomenon. The conductances of the highly turbid solutions fall in the "break" of the conductance-log. concentration curve.

A small quantity of dilute alkali solution quickly removed this turbidity. Solutions of concentration .002 N or greater produced stable foams when shaken, whereas concentrations less than .002 N did not.

A number of investigators have shown that the minimum surface tension of aqueous sodium oleate solutions corresponds to about .002 N.

Discussion

From the photograph (Fig. 2) and the conductance-log. concentration relationship (Fig. 1) together with Johlin's surface tension data (Fig. 1) which have been plotted for comparison it is evident, first, that surface tension decreases as conductance increases from a .059 N solution down to a concentration of .002 N; second, that both surface tension and conductance are constant above .059 N at least as high as .120 N; and third, that the appearance of an intense turbidity is coincident with abrupt changes in the trends of the conductance and surface tension curves. In solutions of concentration .02 N or greater the colloidal material flocculates and settles on standing. McBain[1] and his students find that "acid soap" results from hydrolysis. If increasing conductance be taken as a criterion of increasing hydrolysis it is apparent that surface tension decreases as hydrolysis proceeds between the limits .059 N and .002 N. The lowering of the surface tension over this interval must be attributed to the hydrolytically formed "acid sodium oleate" and increases of mobility of the conducting particles.

Adsorption at the Oil/Sodium Oleate Interface

In order to inquire into the mechanism of oil-in-water stabilization by sodium oleate, the following studies were carried out on sodium oleate solutions with varying interfacial conditions.

Experimental

The first series of experiments consisted of varying the concentration of the sodium oleate solution under constant interfacial conditions. For each of the various concentrations of sodium oleate the procedure was as follows: 10 cc. of the solution were placed in the conductivity cell and permitted to reach surface and thermal equilibrium at 25°C. The conductance of the solution was then determined. A 2 cc. portion of benzene was then carefully layered on the surface of the solution in the cell and after 23 hours the conductance redeter-

TABLE II

The Effect of a Surface Layer of Benzene on the Conductance of Sodium Oleate in 23 Hours at 25°C

Concentration	Equivalent Conductance	Equivalent Conductance after 23 hours	Δ Equivalent Conductance
.0608 N	26.89	27.29	.40
.0304 "	28.85	30.07	1.22
.0152 "	32.85	37.22	4.37
.0076 "	38.81	53.53	14.72
.0038 "	49.16	73.14	23.98
.0019 "	59.16	82.99	23.83
.0010 "	73.21	86.95	13.74
.0005 "	73.48	87.37	13.89
	Controls		
.005 N NaOH	235	229.5	−2%
.001 "	216	210.	−3
.0005 "	205	197.5	−3.5

---

[1] McBain: J. Soc. Chem. Ind., Jubilee Number, 1931, 238.

mined. Controls consisting of benzene layered on dilute solutions of sodium hydroxide were determined in the same way. The data obtained are presented in Table II.

These data have been plotted (Fig. 3) together with the surface tension measurements of Johlin for reference.

It was observed, also, that the layer of benzene caused the colloidal turbidity to dissolve in a few hours with the result that the aqueous layer was clear and transparent.

The second series of experiments consisted of varying the oil while the other conditions were kept constant. The procedure was the same as that just outlined except that 10 cc. portions of a .0118 N sodium oleate solution were used in each case, and 2 cc. portions of different oils were layered on the surface. The rate of change of conductance was obtained by noting the time. Oil-NaOH controls were determined also. The experimental error, as manifested by the controls, is taken into consideration in the graphical representation of this data (Fig. 4).

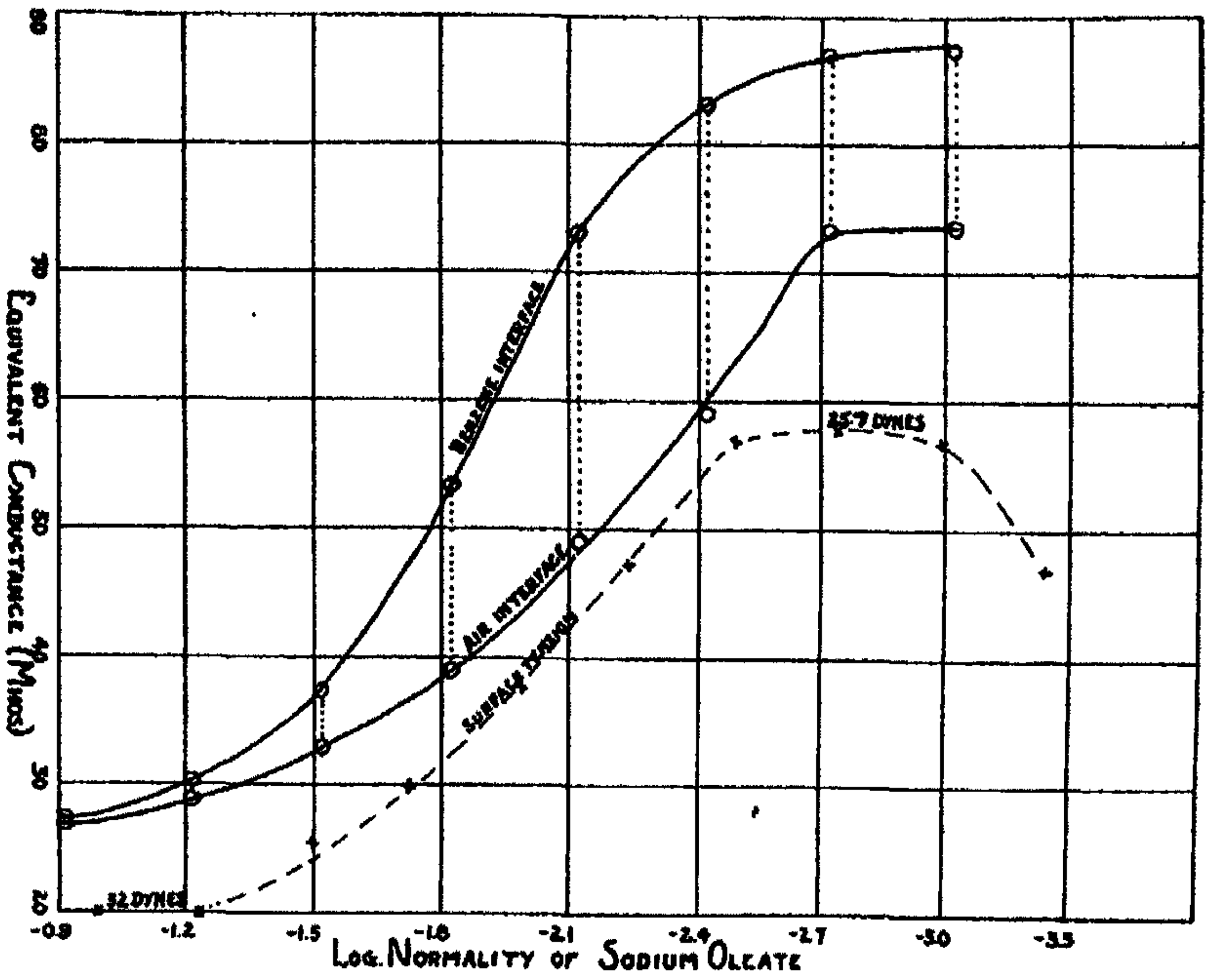


Fig. 3

A diagram showing the increases of equivalent conductance of various concentrations of sodium oleate in contact with benzene for 23 hours. The surface tension curve after Johlin.

The third series of experiments was concerned with a varying interfacial area, while the other conditions were held constant. Pyrex vessels, which gave different areas of the benzene/solution interface with the same volumes of sodium oleate solution and benzene, were set up in the thermostat. A 25 cc. aliquot of the same sodium oleate solution was placed in each container. A

25 cc. portion of benzene was then layered on the interface in each vessel. After 30 hours an aliquot from the aqueous layer of each vessel was transferred to the conductivity cell and the measurement taken. Toluene, carbon tetrachloride, and m-xylene were determined in the same way. The data are plotted (Fig. 5).

Discussion

A layer of benzene on sodium oleate solutions whose concentrations varied from .059 N to .001 N brought about increases in the conductances of these solutions. In the case of concentrations .002 N or greater the more turbid the solution, the smaller was the increase of conductance. Under the conditions of the experiments the increments of conductance were negligible in concentrations greater than .059 N. The experimental errors due to the diffusion of CO_2 through the benzene layer and its subsequent interaction with the NaOH resulting from the hydrolysis of sodium oleate, and to the distribution of impurities in the benzene layer between the two liquid phases, were negative with respect to the increments of conductance. The results with sodium oleate solutions are, therefore, probably slightly low.

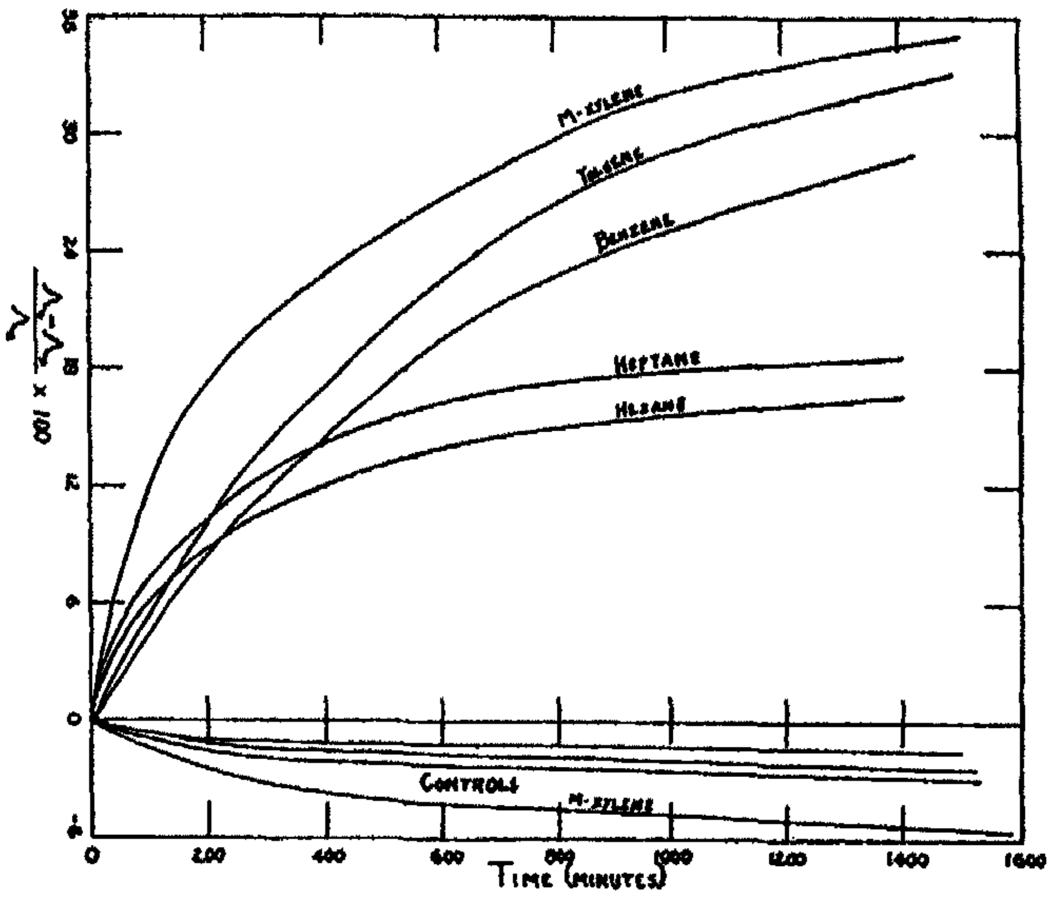


Fig. 4

The rate of percentage increase of conductance of .0118 N sodium oleate solution due to surface layers of various oils. The controls consist of the same oils on dilute sodium hydroxide.

The colloidal "acid sodium oleate" which was present as a finely divided white solid when the interface of the aqueous sodium oleate solution was in contact with its saturated vapor, went into solution when benzene was layered on the surface. This transition from a turbid to a clear solution was not observed when the concentration was less than .0005 N. The addition of a small quantity of dilute alkali had the same action on any of these solutions, namely, a clarification.

The areas of the vessels used in the surface variation experiments could not be measured with precision and the errors involved in transferring aliquots to the conductivity cell are certainly not negligible, but the data taken under the same conditions show that the conductance increases with larger and larger areas of contact oil/sodium oleate solution.

Conclusions

The presence of benzene on the surface of sodium oleate solutions under the conditions already mentioned brings about increases of conductance of these solutions. The shifts in conductance increase with time. The magnitude of the increment in any specific case is limited by the amount of "acid sodium oleate" which is present as a colloidal suspension in the solution when benzene is absent from the interface. As the conductance increases, the solution clears.

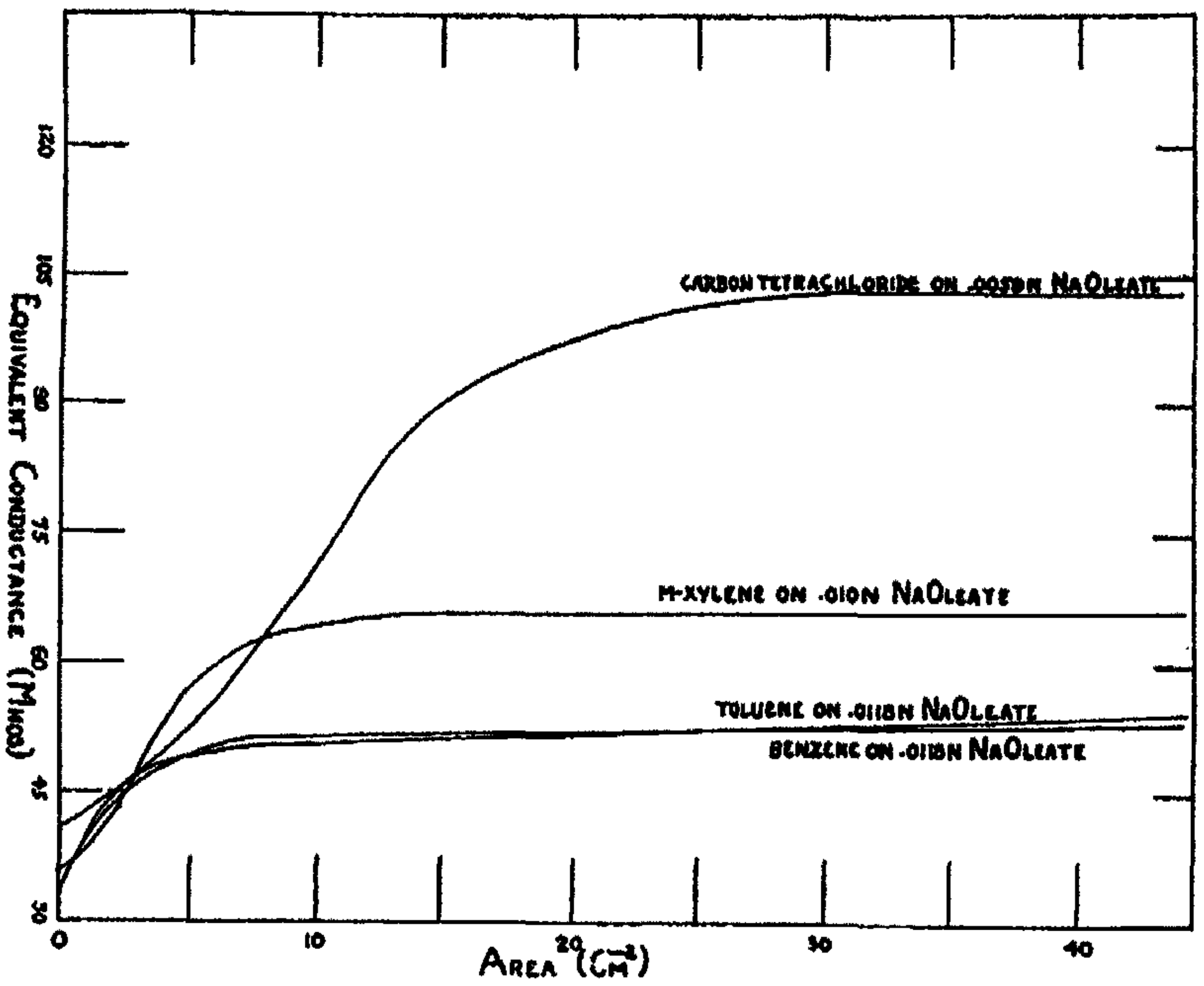


FIG. 5
The changes of equivalent conductance of sodium oleate solutions caused by varying the interfacial area between the oil and the solution.

From the assumption that .002 N is the minimum concentration of sodium oleate for which the interface against air is saturated[1] and that all solutions of this soap of greater concentration than .002 N have saturated interfaces, it is evident that the surface activity of these sodium oleate solutions is determined to a great extent by the "acid sodium oleate" which results from hydrolysis of the neutral salt. The surface tension is a minimum at .002 N and

---

[1] Harkins, Davies and Clark: J. Am. Chem. Soc., 39, 54 (1917).

the solution is clear (Fig. 2) which indicates a maximum concentration of the "acid sodium oleate" in the interface. The surface tension increases as hydrolysis decreases because the ratio of the *more water soluble* component sodium oleate to the less soluble "acid sodium oleate" in the surface becomes larger and larger until the surface becomes saturated with sodium oleate and the surface tension as well as the conductivity becomes constant.

The result of the presence of benzene in the interface is the displacement of sodium oleate from the interfacial film and the substitution[1] of "acid sodium oleate" which exists largely in colloidal suspension in the case of the solution/vapor interface. The exchange takes place until the colloidal excess becomes exhausted. The removal of the excess "acid sodium oleate" from the solution is followed by further hydrolysis of the sodium oleate which is recorded as increments of equivalent conductance (Fig. 3). A study of the changes in the equivalent conductance that take place as the interfacial area is increased (Fig. 5) leads to the conclusion that hydrolysis of the sodium oleate induced by the presence of the oil ceases when the concentration of alkali reaches a "suppressing value." Further adsorption must remove from the solution both sodium oleate and "acid sodium oleate."

The various oils used in this investigation show marked differences in the induction of hydrolysis (Fig. 4). Such differences may be interpreted as meaning that the interfacial energy between the oil and the sodium oleate solution determines the quantity of "acid sodium oleate" adsorbable and hence the concentration of alkali which is capable of suppressing further hydrolysis.

Increments of conductance of these sodium oleate solutions due to the influence of an oil layer on the interface indicate that the surface active material is in equilibrium with that dissolved in the main bulk of the solution. The "acid sodium oleate" is more highly adsorbed at the oil/solution interface than it is at the vapor/solution interface for the same solution of sodium oleate because its fugacity from the aqueous phase is determined by its solubility in the interface. The solubility in the interface, in turn, is conditioned by the interfacial energy.

In discussing the results of Briggs[2], Clayton[3] says: "This assumption may not be strictly true, as possibly the difficultly-soluble acid sodium oleate produced by hydrolysis may be a factor in emulsification." It is hoped that this investigation clarifies the action of "acid sodium oleate" in emulsoid systems.

Frothing is observed only in those solutions which have a saturated surface and an excess in colloidal suspension or as a crystalloidal precipitate. Stable foams may be obtained, therefore, on solutions in which there is an excess in equilibrium with the surface and the hydrolytic system.

Further investigations along this line are being carried on at this laboratory.

---

[1] Nonaka: J. Soc. Chem. Ind. Japan, **32**, 115-20 (1929) reaches essentially this conclusion from cataphoretic studies.

[2] Briggs: J. Phys. Chem., **19**, 210-31 (1915).

[3] Clayton: "Theory of Emulsions," 2d Ed., 84 (1928).

Summary

1. At concentration .002 N sodium oleate shows an abrupt change in the trend of the concentration-conductivity relationship. This change of trend is coincident with minimum surface tension and loss of frothing power.

2. Surface tension of sodium oleate solutions varies inversely with hydrolysis between the limiting concentrations .059 N and .002 N.

3. More "acid sodium oleate" is adsorbed at the oil/solution interface than at the vapor/solution interface of the same sodium oleate solution.

4. Various oils have differing capacities to adsorb "acid sodium oleate."

5. The mechanism of the buffer action of sodium oleate in solution has been demonstrated.

6. The rôle of "acid sodium oleate" in emulsification has been much underated.

7. Frothing is attributed to a hydrolytic system in equilibrium with a saturated surface and an excess, colloidal, or colloidal and crystalloidal, depending on the concentration.

Goessmann Chemistry Laboratory,
Massachusetts State College,
Amherst, Mass.
February, 1932.

THE SYSTEM:—$CuSO_4$—$CoSO_4$—H_2O

BY H. D. CROCKFORD AND D. J. BRAWLEY

A search of the literature fails to reveal any data on the system: $CuSO_4$ — $CoSO_4$ — H_2O. In this paper are given the solubility data for the 0° and 25°C isotherms.

Experimental Procedure. CP grade of J. T. Baker Chemical Co. copper sulphate and cobalt sulphate were used. These were subjected to recrystallization before use. A series of bottles holding approximately 100 ml were prepared from saturated solutions of the sulphates. To some of the bottles an excess of one of the sulphates was added. In other cases saturation was carried out at a higher temperature than that of the isotherm to be determined and the solid phase was thus secured upon cooling. For the 25° isotherm the bottles were placed in a constant temperature bath constant to plus or minus .03°. For the zero isotherm the bottles were immersed in a container filled with crushed ice and water. This in turn was placed in a large refrigerator. A temperature very close to zero was thus secured. Equilibrium was rapid. This was especially true in the cases where supersaturated solutions were employed in the production of the solid phase. Only a few hours were necessary for equilibrium in these cases.

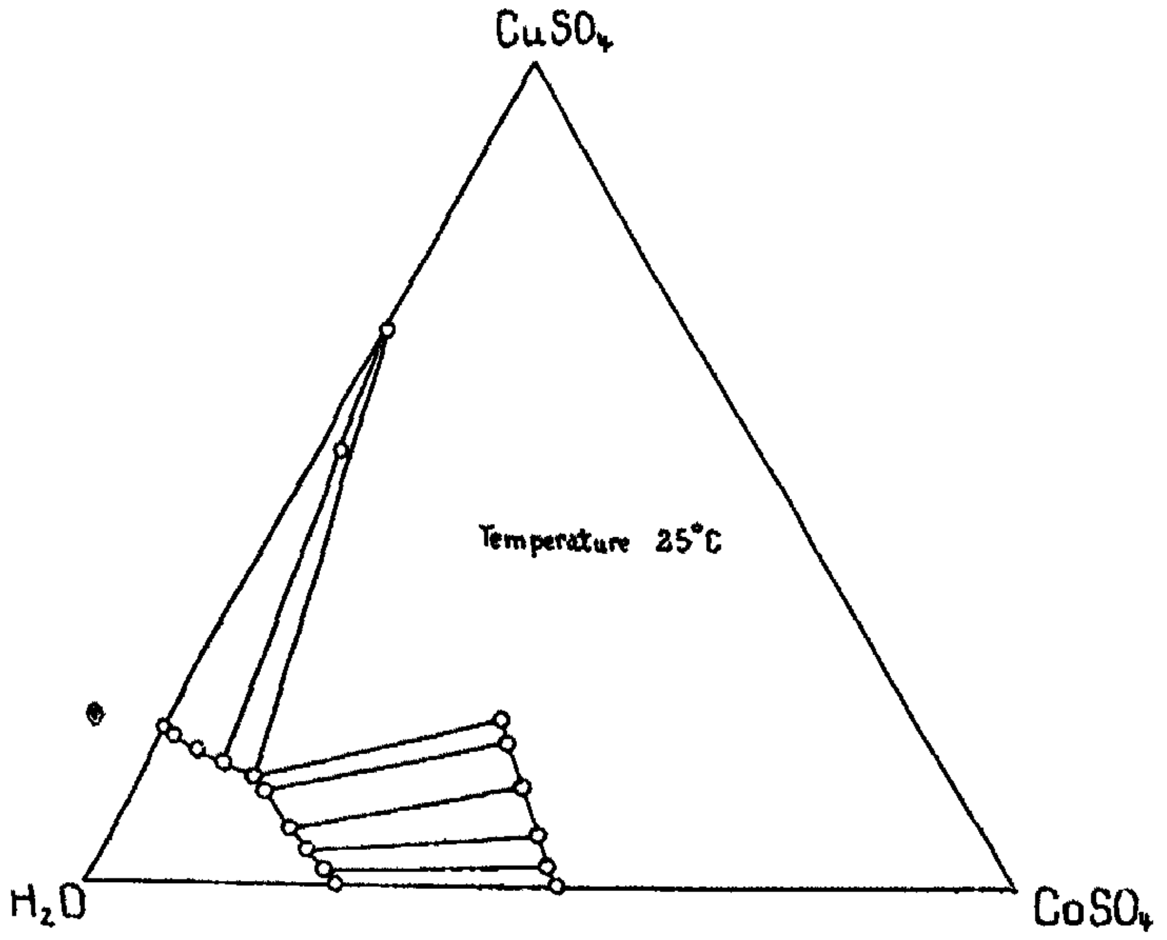


FIG. 1

Both the copper and cobalt were determined electrolytically. After removal of the copper and before the removal of the cobalt the solutions were treated with ammonium hydroxide, sodium bisulphite, and ammonium sulphate according to the procedure of Dorothy H. Brophy.[1] Most excellent results were obtained with this procedure.

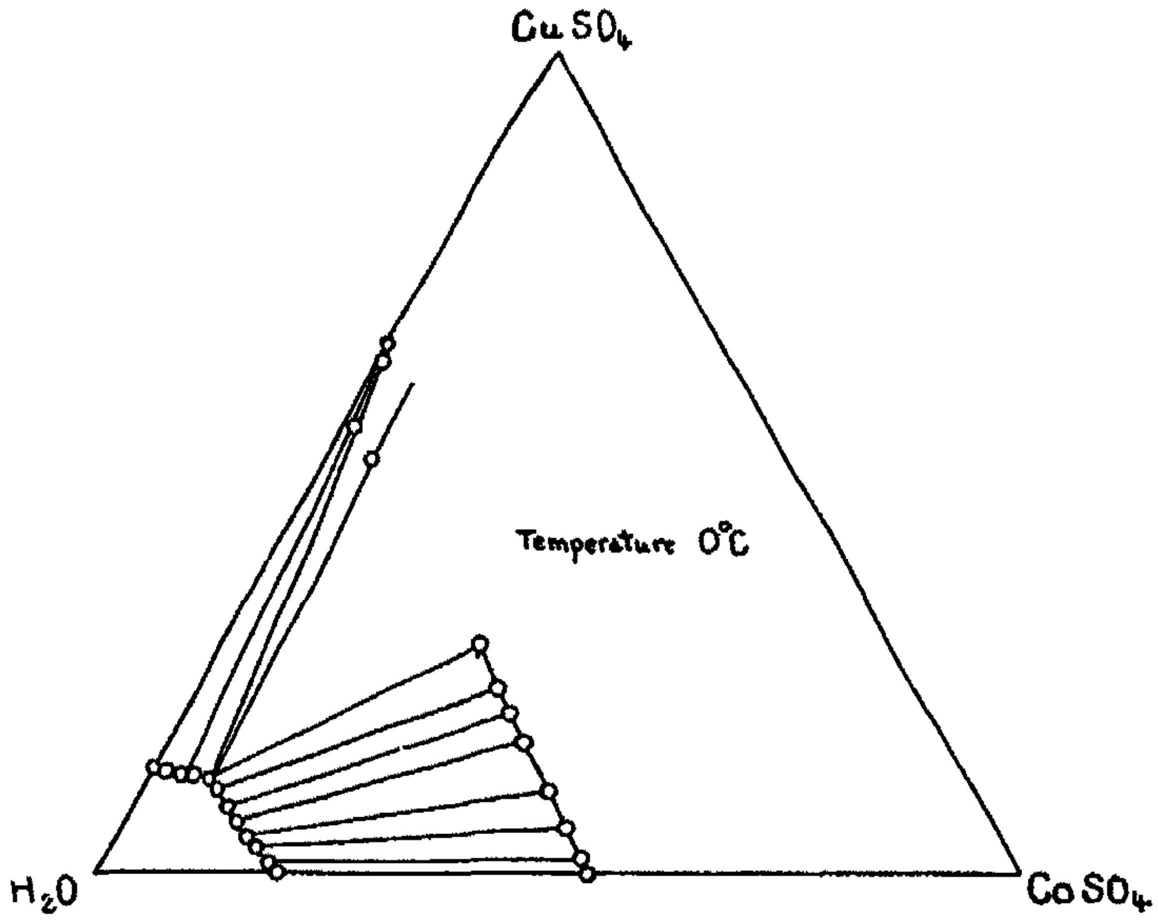


Fig. 2

TABLE I

25° Isotherm

Bottle No.	Liquid Percent $CuSO_4$	Liquid Percent $CoSO_4$	Solid Percent $CuSO_4$	Solid Percent $CoSO_4$	Composition of Solid
1	18.45	—	—	—	$CuSO_4.5H_2O$
2	18.18	1.14	—	—	"
3	16.66	5.07	—	—	"
4	14.68	9.70	51.82	2.58	"
5	12.91	13.80	63.30	trace	$CuSO_4.5H_2O$ and
5	"	"	19.88	35.77	Solid Solution
6	11.61	15.03	17.04	37.52	Solid Solution
7	7.45	18.55	13.04	41.88	"
8	3.71	23.25	6.66	48.20	"
9	1.76	25.24	2.99	51.78	"
10	—	27.16	—	—	$CoSO_4.7H_2O$

---

[1] Electrolytic Determination of Cobalt, Ind. Eng. Chem., Anal. Ed., 3, 363 (1931).

In all cases the compositions of the solids were determined by removing some of the wet residue and freeing it as far as possible of the mother liquor before analysis. In the case of the solid solutions the crystals were usually large enough to make this procedure very easy.

Results. The data are given in Tables I and II and plotted in Figs. 1 and 2.

TABLE II
0° Isotherm

	Liquid		Solid		
Bottle No.	Percent $CuSO_4$	Percent $CoSO_4$	Percent $CuSO_4$	Percent $CoSO_4$	Composition of Solid
1	12.87	—	—	—	$CuSO_4.5H_2O$
2	12.78	1.00	—	—	"
3	12.55	2.80	51.53	0.80	"
4	12.33	4.05	—	—	"
5	11.90	5.93	62.19	0.69	$CuSO_4.5H_2O$ and Solid Solution
5	"	"	49.46	4.39	"
6	12.01	5.96	27.92	26.73	"
7	9.53	7.89	21.99	28.00	Solid Solution
8	6.66	10.67	18.26	36.61	"
9	5.03	12.34	15.26	39.14	"
10	3.14	15.02	10.45	43.48	"
11	1.57	17.64	5.41	49.08	"
12	.59	19.08	1.38	53.57	"
13	—	19.82	—	—	$CoSO_4.7H_2O$

It is seen that the solid phases consist either of copper sulphate pentahydrate or a solid solution in which part of the cobalt in the cobalt sulphate heptahydrate is replaced by copper. The limiting solid solution in the 25° isotherm has the composition 19.88% $CuSO_4$ and 35.77% $CoSO_4$. In the 0° isotherm the composition is 27.92% $CuSO_4$ and 26.73 $CoSO_4$. The crystals of the solid solutions were always well-formed and showed the same crystalline shape as the cobalt sulphate heptahydrate. As the copper content increased an increasing bluish color appeared. The fact that cobalt and copper have so nearly the same atomic weight caused all the solid solutions to fall on the same straight line. The intersection of the solution curves was established by separation and analysis of the two phases present and by the fact that the further addition of copper sulphate pentahydrate to the bottles resulted in no change in composition of the liquid. It was not considered necessary to analyze all the solid phases.

Summary. The 0° and 25° isotherms for the system: $CuSO_4-CoSO_4-H_2O$ have been determined. In both cases the solids consist of copper sulphate pentahydrate and a series of solid solutions in which copper partially replaces the cobalt in cobalt sulphate heptahydrate.

NEW BOOKS

A Comprehensive Treatise on Inorganic and Theoretical Chemistry. *By J. W. Mellor. Vol. XI. 24 × 17 cm; pp. xii + 909. London and New York: Longmans, Green and Co., 1931. Price: $20.00.* This volume deals with tellurium, chromium, molybdenum, and tungsten. It was published last year; but the review copy for the Journal of Physical Chemistry either went astray, which is not likely, or was not sent until now.

"Tellurium occurs combined with gold, silver, bismuth, and many other metals. It is rather a nuisance in certain auriferous districts where the gold and silver ores are unfit for amalgamation, etc., because the telluride ores do not give up their gold to mercury, to cyanide, or to chlorine; the ores also concentrate badly; they are difficult to roast on account of their low melting-point and gold is lost during the removal of the tellurium. The telluride ores are smelted either with lead or copper ores which act as a flux. Large amounts of tellurium enter the copper matte. The mattes are then bessemerized,and the copper refined by electrolysis. The copper contains not far from 0.04 per cent of tellurium. The slimes contain most of the tellurium, antimony, caesium, and bismuth together with silver and gold. The chief tellurium minerals are the tellurides; and the oxidized minerals are represented by tellurous acid, the tellurites and the tellurates," p. 2.

"Tellurium is insoluble in a normal solution of potassium hydroxide from which oxygen is excluded. In a 10 N solution, however, it dissolves at 100° to form a red solution, from which it separates on cooling or dilution. This points to the simultaneous presence of positive and negative tellurium ions," p. 20. The author seems to have said too much or too little.

"According to Auerbach, tellurium in accord with its metallic character dissolvesin pyrosulphuric acid as monatomic molecules, and, in coagulation, the colour changes from red through violet to blue. . . . Fenaroli found that, as in the case of selenium, the oxidized element does not colour glass; but, if reducing conditions are present, blue, brown, and red glasses are obtained," p. 27.

"On account of some industrial applications, tellurium is beginning to acquire some technical importance. It has a very limited application in the glass industry; it is used in the preparation of organic dye-stuffs; in the manufacture of electrical equipment; high resistance alloys and ultramarine; in the coloring of lithopone; the staining of silver; as a delicate test of sterilization in bacteriology; and as a toning agent in photography. A compound of tellurium has been used as an anti-knock constituent of motor fuels, and its use is said to lead to greater efficiency. Remarkable properties are shown by the alloys of tellurium; the tin alloys are extremely hard and have very great tensile strength; and the aluminium alloys are very ductile. The silver alloys have been used. The element is poisonous, and is fairly readily adsorbed—*e.g.* from gold dental stoppings. F. C. Mathers and J. Papish used solutions of salts of tellurium for staining metals; C. Dickens used colloidal tellurium as an insecticide, germicide, fungicide, and wood preservative," p. 30.

"According to F. W. Aston, the mass spectrum of tellurium gives lines corresponding with isotopes of the the atomic weights 126, 128, and 130, the intensities of the latter two being equal, and double that of the first. All the mass numbers of tellurium probably form members of isobaric pairs," p. 35.

"Whilst β-sulphur retains two percent of tellurium in solid solutions, α-sulphur retains only 0.5 percent; but the separation of the excess occurs only under the influence of light," p. 111.

"Müller and Soller said that chrome alum dissolved in N H_2SO_4 is not appreciably oxidized to chromic acid by the use of an anode of smooth platinum; but a trace of lead in the solution is precipitated on the anode as lead dioxide, and this brings about oxidation; traces of chlorine also favour the oxidation," p. 131.

Nobody would guess from the author's account, p. 136, that Placet and Bonnet exhibited in Paris metallic chromium obtained by electrolyzing chromic acid, that the Germans questioned the possibility of obtaining chromium in this way, and that Carveth showed that it could be done.

"One of the most important applications of chromium is in the production of various alloys, principally ferrochromium alloys for the manufacture of special steels many of which contain about 2 per cent of chromium and a small proportion of other metals—*vide* the alloys of iron. The chrome-alloy steels are hard and tough. They are used in making armour-plate, armour-piercing projectiles, burglar-proof safes; tyres, axles, springs for railways and motor-cars, stamp-mill shoes, crusher jaws, the so-called rustless cutlery, stellite—an alloy containing chromium, cobalt, and molybdenum and tungsten—for high speed tools which require their cutting edge at temperatures approaching redness; nichrome—nickel, chromium, iron (60:14:15), a high-temperature resistance alloy; chromium-vanadium steel; chromium magnet steel; heat-resisting and acid-resisting steels; etc. Chromium plating as a protective coating for steel is much employed—*vide supra*, the electrodeposition of chromium. Perhaps the largest demand for chromium is in the form of chromite used as a refractory in certain parts of open-hearth and other furnaces. Chromium compounds are used in tanning certain leathers—chrome leathers; as a mordant for dyeing; it is used for impregnating wood, paper, etc., with chromic hydroxide; and in the preparation of filaments for incandescent lamps. Chromates are used for making gelatine insoluble—for a mixture of gelatine and potassium dichromate becomes insoluble when exposed to light—in color printing, block printing, heliography, photolithography, photozincography, etc. Chromium compounds are used in making safety matches; as antiseptics; in bleaching oils; in the purification of wood vinegar; as a component of certain galvanic cells; an oxidation agent in the preparation of some aniline dyes and in a number of analytical and chemical processes; as a catalytic agent in the preparation of sulphur trioxide (*q.v.*), and, according to H. W. Underwood, in the hydrogenation of organic compounds.

"Chromic oxide is employed as green pigments for paints—chrome-green, emerald-green, Cassel's green, etc.—and it may be associated with other substances—*e.g.* boric oxide, phosphoric oxide, zinc oxide, etc., to produce special tints, there are yellow chromates of lead, etc.—*e.g.* chrome yellow, lemon yellow, Paris yellow, royal yellow, etc.; red basic lead chromates—*e.g.* chrome-orange, chrome-vermilion, etc.; and brown, manganese chromate. Chromic oxide is employed in producing on-, in-, and underglaze green colours in enamel, pottery and glass manufacture; on-glaze yellows employed for on-glaze work, and in enameling are derived from lead chromate, the on-glaze reds and orange colours, from basic lead chromate. A crimson or pink colour for pottery decoration is based on the result of calcining stannic oxide with one or two percent of chromic oxide; for the coloration of alumina with chromium to form artificial rubies—*vide* alumina. C. J. Smithells described the manufacture of articles from chromium," p. 165.

On p. 177 the author says: "A very thin sublimate of chromic oxide is red, and this probably explains the colour of chrome-tin pink and of the ruby." This cannot be true unless the sublimate is an instable form. This statement is the more remarkable because the author cites Stillwell's experiments on the same page. One is also puzzled over the statements in regard to the dialysis of hydrous chromic oxide, p. 190. "It is hence calculated that the colloidal chromium particle consists of 1000 chromium atoms and carries 30 free charges. The number of chromic oxide molecules in a colloidal particle is about 240." This apparently means Cr_4O_6 for chromic oxide. "Wintgen and Rinde gave 580 for the number of chromic oxide molecules in a colloidal particle aged by boiling and 750000 for the case of an aged ferric oxide colloidal particle." The reviewer endorses the author's remark that "these numbers are of doubtful accuracy."

"Ferrous and magnesium chromites form solid solutions; so also do ferrous chromite and ferrous aluminate. There is also evidence that some ferrites and chromites form solid solutions," p. 202. Simon and Schmidt find Cr_6O_{13} and Cr_6O_{12} as definite chemical compounds between CrO_3 and Cr_2O_3, p. 206.

"Reese observed that, in the absence of a catalytic agent, a solution of chromic acid, alone or in the presence of 1-15 percent by volume of sulphuric acid, is not reduced by hydrogen below 50°; and only very slowly below 100°. After 116 hours exposure, 70 percent of hydrogen is oxidized; and at 156°, after 7 hours exposure, 11 percent of hydrogen is oxidized and much oxygen is evolved owing to the decomposition of the chromic acid. The oxidation is not dependent on the thermal decomposition of chromic acid because it occurs at a temperature below that at which oxygen is evolved," p. 229.

"When potassium dichromate is added in the theoretical quantity to a solution of stannous chloride in the absence of acid, brownish- and greenish-blue gelatinous masses are formed, which dissolve and form a clear deep olive-green solution when the whole of the dichromate has been added. These solutions appear red by transmitted light," p. 237. Berzelius observed that the lemon-yellow potassium chromate becomes bright red when heated, p. 253.

"According to Antony and Paoli, if excess alkali hydroxide be added to a solution containing a chromium and a manganese salt in the proportion Mn : 8 Cr, no precipitate is obtained, but the liquid is coloured emerald green and must be regarded as a colloidal solution of the hydroxides of chromium and manganese, since this behaviour is exhibited only when the salts are present in exactly the above ratio. [This last statement is of course an error.] Chromium being tervalent and having both an acid and a basic function, whilst the manganese is bivalent and decidedly metallic in its properties, it is inferred that they exist in this solution in the form of a salt, an electrolyte, which must be either a manganous chromite or polychromite," p. 308. Whatever else we may have, it is pretty certain that we do not have a dissolved manganous chromite or polychromite.

"The extraordinary confusion in the use of the terms plumbago, graphite, galena, and molybdena, which prevailed from the time of Aristotle, *circa* 350 B.C. to the 18th century, has been discussed in connection with carbon, and with galena. It is very difficult to pick out from the various references those which in all probability refer to molybdena. The term molybdaena is the Latinized form of the Greek μολύβδαινα, which is derived from μόλυβδος, lead. The term μολύβδαινα appears to have been applied by Aristotle, Dioscorides, Galen, Pliny, etc., to various things associated with lead—plummets, sinkers for fishing nets, bullets for catapults, etc.—to lead oxide obtained as a by-product in cupellation, and to natural lead ores," p. 484.

"Langmuir found that higher values for electron emission are obtained from filaments containing one to two percent thoria. With an ordinary thoriated filament, the thorium is present as the dioxide, and the electronic emission is the same as for tungsten alone; but if the temperature is raised above 2600°K., the thoria reacts with the tungsten to form thorium. This reaction was studied by C. J. Smithells. Langmuir found that the thoriated filament heated to 2600°K. gives the normal value for tungsten at 1500°K. since the thorium metal will have evaporated from the surface. It is therefore necessary after flashing the thoriated filament at 2800°K. for, say, 3 min. to lower the temperature to about 2000°K. to allow the thorium to diffuse to the surface from the interior. The emission at 1500°K. is then 100,000 times the value for tungsten alone—*vide supra*. If the temperature is kept below 1900°K., this high value is retained indefinitely, but it is destroyed above 2200°K. owing to the volatilization of the thorium," p. 712.

"The passivity of tungsten is due to oxide films, ranging in colour from brown, blue and green to yellow. The colours are pronounced and can be followed as the electrolysis proceeds. The films are independent of the dissolved cation or anion. They are due to the OH-ions reacting with the tungsten. The passivity is a function of the colour of the film, the colour varying with the amount of oxygen present. The passivity varies directly with the current, time and temperature, and inversely with the solubility of the film, the volume of electrolyte and the diffusion velocity. If the film dissolves as rapidly or more rapidly than it is formed, the tungsten will remain active. The films can be dissolved and the passivity destroyed. Solutions of potassium hydroxide and ammonia render passive tungsten active. Solutions of acids and salts make passive tungsten active if allowed to react for some time on it. Passive tungsten has been made active overnight in distilled water," p. 720.

"Some unique properties of tungsten have important industrial applications. It has a high density exceeding that of lead. Its melting-point is higher than that of any known metal; its tensile strength exceeds that of iron and nickel; it is paramagnetic and elastic so that it has been tried in electrical meters, and non-magnetizable watch-springs. It can be drawn into thinner wires than any other metal, and this fact, coupled with its chemical stability, offers possibilities in making suspensions for galvanometer needles, and cross-hairs for telescopes; and for thin wires in surgical operations in place of gold or silver wires. The greatest use of tungsten is in the preparation of iron or steel alloys, *e.g.* in the preparation of high-speed tool steels (*q.v.*). Tungsten forms alloys with many of the metals, and some of them have valuable properties although in many cases the cost of the alloy is out of proportion with its usefulness. The stellite alloy described by E. Haynes is an alloy of cobalt, chromium, and tungsten (75:20:5) with or without additions of other metals. It is a competitor for some high-speed cutting steels. J. T. Bottomley proposed an alloy called *platinoid*, composed of nickel, zinc, copper, and tungsten for conductivity wires. E. Weintraub patented an alloy with 40 to 80 percent of platinum for use in electrical contacts, jewelry, etc. *Partinium* is an alloy of aluminium and tungsten employed in automobile construction; *sideraphite*, an alloy of iron with nickel, copper, aluminium and tungsten; minargent, an alloy of copper, nickel, and tungsten; and *backford*, an alloy of copper, tin, and tungsten. F. A. Fahrenwald discussed the use of alloys of tungsten and molybdenum as substitutes for platinum for contact points in sparking coils, voltage regulators, and other electrical instruments. Gold-coated tungsten dental pins are also used in place of platinum," p. 735.

"A solid solution of copper tungstate in calcium tungstate is as luminous as scheelite; manganous tungstate acts like the copper salt. The tungstates of sodium, potassium, strontium, barium, and zinc; wolframite, ferberite, and the different tungstate bronzes, are not luminous when exposed to X-rays," p. 785.

"W. Ducca, and W. Löwinthal studied the action of luminophores—*e.g.* traces of manganese, copper, or bismuth salts—in enhancing the fluorescence of calcium tungstate when exposed to X-rays. The presence of 1/12,000th part of a bismuth salt gave the best results. The spectrum of the blue fluorescence of calcium tungstate containing a trace of a bismuth, manganese or copper salt shows feeble spectral bands in the blue violet; and when the tungstate contains a trace of a silver, gold, nickel, cadmium, antimony, or lead salt, the fluorescence is green. Calcium tungstate exhibits no thermoluminescence at room temperature; but when it is cooled to −192°, exposed to X-rays, and its temperature allowed to rise, it becomes luminescent, the glow is then extinguished, and as the temperature still continues to rise, a second luminescence appears. A small amount—say 0.1 gram.—shows only one thermoluminescence. The luminescence of calcium tungstate in cathode rays resembles that produced by X-rays," p. 785.

"R. Tronquoy found that powdered hübnerite is sulphur yellow, and with plates of decreasing thickness the colour changes in different directions are: *a*, dark red to brown to pale brick-red to olive-green; *b*, bright red to orange-red to greenish-yellow; and *c*, orange-red to bright yellow with a faint green tinge. Usually the higher the proportion of ferric oxide, the blacker the colour; but the black mineral from White Oaks has only 0.55 percent of ferrous oxide, whereas lighter coloured hübnerite may contain more ferrous oxide. The cause of the dark colour is unknown. Hübnerite may be pleochroic with *b* yellowish-brown, and *c* green. Ferberite is described by F. L. Hess as a black, opaque mineral which under the microscope may appear red by light transmitted through very thin edges—say 0.0001 to 0.0002 inch thick. Ferberite may occur coated with hydrated iron oxide, or be so intergrown with it that both the outside, and the parts exposed by fracture or cleavage may be brown. Some specimens are iridescent owing to thin films of oxide," p. 799.

Wilder D. Bancroft

EXPERIMENTS WITH A HIGH-TEMPERATURE OZONIZER

BY RAYMOND P. ALLEN

Introduction

It has been stated by Bancroft[1] that "the chemical effect of light is merely to eliminate, if possible, the substance absorbing the light. Whether that elimination takes place as a result of oxidation or of reduction is a matter which is quite independent of the light and which depends on the nature of the depolarizer. . . . We distinguish between chemical depolarizers or sensitizers and optical ones. The action of the chemical depolarizers is quite simple. If we take a ferric chloride solution and expose it to light, we might hope to get ferrous chloride and chlorine; but the two could not co-exist and therefore would be formed only to a slight extent, if at all. If we take an alcoholic solution of ferric chloride, the chlorine can react with the alcohol. It therefore takes less energy to reduce or decompose ferric chloride in alcoholic solution." Actually, there is a photochemical change under these conditions.

This principle can be extended in a general way to include other depolarizers which are not ordinarily considered as such. We are particularly concerned here with the effect of the photo-sensitivity of a substance when the temperature of that substance is changed. If we have a substance which we wish to decompose by means of light, we may find that an ordinary source of energy decomposes the compound very slowly, or not at all. If the temperature is raised, however, it should be possible for the same radiant energy to cause the reaction to occur more rapidly because the compound has been raised to a temperature closer to its thermal decomposition point; the molecule has become more instable and consequently the light has less work to do. In this case the effect of raising the temperature is similar to the action of a depolarizer or sensitizer. This appears to contradict the idea which has been held that the temperature coefficient of photochemical reactions is almost unity.[2] By temperature coefficient of a reaction the physical chemist means something quite different from what his words should mean. He means the ratio of the velocities at ten-degree intervals. If a reaction velocity is independent of the temperature, the ratio of the velocities at ten-degree intervals is unity. The real temperature coefficient is zero. While the ratio of the reaction velocities for ten-degree differences may be almost unity over certain ranges of temperature, it must be true that at temperatures approaching the point of thermal decomposition, the so-called temperature coefficient of photochemical decomposition increases rapidly.

The converse of this principle should also be true. If a given system becomes more stable at lower temperatures, it should be less photo-sensitive and

---

[1] J. Phys. Chem., 32, 531-2 (1928).

[2] Taylor: "Treatise on Physical Chemistry," 2, 1241 (1924).

the temperature coefficient should be smaller. But there is some reason to believe that it may also become larger at lower temperatures. Chlorine and hydrogen unite explosively in sunlight at ordinary temperatures but Amato[1] reports that at –12° the reaction does not occur even when the mixture is kept in bright sunlight for several hours. The temperature coefficient of this reaction is given as 1.0–1.04,[2] but it is evident that if Amato's result is correct, the coefficient must be much higher than this in the temperature range from –12° to about +15°.

Dewar conducted some interesting experiments on photographic paper and plates. He found that paper[3] becomes insensitive to ordinary light when held at liquid air temperatures but the photographic action of ultra-voilet light is not entirely prevented. This might mean that the temperature coefficient is different for different wave-lengths but the result is probably more related to the greater sensitivity to ultra-violet light. In 1896 Dewar reported at the Royal Institution that at a temperature of –180° certain sensitive films were reduced in sensitiveness to less than a quarter of that which they possess at ordinary temperatures. If the so-called temperature coefficient were uniform over this entire range (from 20° to –180°) it would have a value of about 1.07. He found also in experiments with liquid hydrogen, at –252°, that the loss in sensitiveness becomes asymptotic as absolute zero is approached, which points to a different coefficient in the extreme lower range.

From Abney's work[4] it appears that the coefficient for a certain photographic plate may be higher than that found by Dewar. In 1893 Abney found that a plate often required double the exposure when the temperature decreased from 33° to –12°, a drop of about 40°. This corresponds to a so-called temperature coefficient of approximately 1.19 as compared with Dewar's result of 1.07.

The general conclusion at which we must arrive is that the temperature coefficient does vary in different regions of temperature, and the general curve showing the relation between temperature coefficient, sensitivity or reaction velocity and temperature must be like this:

In the specific case of hydrogen and chlorine, for example, the portion of the curve BC must be very short if Amato's results are correct.

In the case of acetaldehyde our work has confirmed the portion BCD. Acetaldehyde begins to decompose thermally at about 400°. If at temperatures approaching this thermal decomposition point, the molecule becomes more instable, light should have less work to do in decomposing the molecule of acetaldehyde and we should expect an increase in the rate of decomposition and in the so-called temperature coefficient. In order to investigate this question it was first necessary to devise an apparatus in which photochemical reactions could be brought about at temperatures up to 350°–400°. It seemed to us that an ozonizer would be a convenient source of photochemical

---

[1] Amato: Gazz., 14, 57 (1884).
[2] Taylor: 1242.
[3] Collected Papers: 2, 1030.
[4] Proc. Royal Soc., 1893.

energy, but to use the ordinary type of ozonizer containing sulfuric acid or any other conducting liquid at a high temperature would be entirely out of the range of practical possibility. The danger of breakage and the difficulty of making the necessary gas and electrical connections made it appear unprofitable to spend any time on the ordinary type of apparatus. We devised, therefore, an entirely new ozonizer for the specific purpose which we wanted it to serve. It consisted essentially of two concentric glass tubes, of suitable size and length. The center portion only of these tubes was made conducting by means of a metallic coating on the outside of the outer tube and the inside of the inner tube. The gases or vapors in which the reaction was taking place passed through the space between the tubes.

Because the metallic coatings in the center extended for only one-third of the total length of the tubes, and the Tesla discharge passed between these coatings, it was necessary to heat only this portion, together with a short length on either end of the coating. Thus the ends of the tubes remained cool and enabled the proper connections to be made with the greatest ease. A more detailed description of the apparatus will be given later.

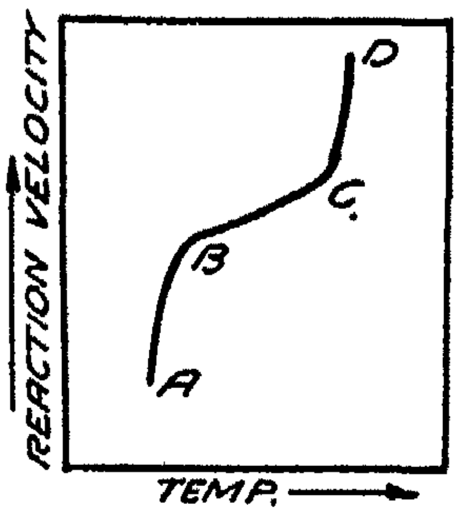


Fig. 1

In addition to investigating depolarization by heat, it seemed to us that certain organic compounds offered an attractive field for photochemical work because of the possibility of carrying out reactions similar to those obtained by the use of catalysts. Alcohol can be decomposed in two ways catalytically. If alumina is used, alcohol is dehydrated, forming ethylene and water, while with nickel as a catalyst dehydrogenation occurs, with the formation of hydrogen and acetaldehyde. To duplicate these reactions photochemically seemed an attractive possibility and our second object in this work was to discover, so far as possible, the course of the photochemical reactions in the decomposition of certain organic compounds.

Grotthuss, in 1818, formulated the law that only that light which is absorbed by a substance can cause chemical change. In 1912 Bancroft proposed the following improved generalization: "All radiations which are absorbed by a substance tend to eliminate that substance. It is entirely a question of chemistry whether any reaction takes place or what the reaction products are." We may go further and say that any particular reaction tends to take place photochemically if the right wave-length is absorbed. But the wave-length which will be absorbed and cause a particular reaction must be provided and in photochemical work its presence becomes our first concern. In our work we elected to use the Tesla discharge as a convenient source of radiant energy. The question immediately arose whether its action is strictly comparable to that of a source of pure photochemical energy such as the quartz mercury lamp. Several separate pieces of evidence seemed to show that it is. Berthelot and Gaudechon, Maquenne, de Hemptinne, Jackson and Northall-Laurie, and Löb used as sources of radiant energy a quartz mercury lamp, an ordinary ozonizer, or a high-frequency discharge. With these sources they effected the decomposition of some of the organic compounds with which we proposed to work and their results with different sources on the same compound showed that in so far as the nature or amounts of the products is concerned, the energy sources are more or less comparable.

The following results are typical as an example from which this conclusion is reached. These figures give the percentage of decomposition products from methyl alcohol:

	CO	CO_2	H_2	CH_4	C_2H_2 or C_2H_4
Berthelot and Gaudechon[1] (quartz mercury lamp)	8.0	5.0	87.0	—	—
Maquenne[2] (silent discharge)	19.6	—	42.9	36.7	—
de Hemptinne[3] (silent discharge)	30.4	4.2	30.5	32.9	small
Jackson and Northall-Laurie[4] (high frequency discharge)	35.5	—	61.1	2.4	1.8

The products are in general the same. The percentages are different in some cases, which may show that a different point of equilibrium is attained, or that some decomposition of the initial product occurs.

It is evident that if photochemical decomposition occurs when an electric discharge is passed through a gas or vapor, then the radiation which causes this reaction must be formed in the gas itself. We would therefore expect some relation between the emission and absorption bands of a gas. The question then is this: will the radiation which is formed in the vapor be absorbed by the vapor? In order to determine that point a Tesla discharge was passed through bromine vapor and the spectrum photographed (Fig. 2a). Then a spectrophotograph was made of the discharge in air (Fig. 2b). Next, between the spectrograph and the discharge tube (with air) was placed a 3 mm. layer of bromine vapor; the spectrophotograph thus made is shown in Fig. 2c. It is observed that the bromine vapor has absorbed those bands in the air spectrum in the same general region where it itself emits radiation in the Tesla discharge.

This does not prove that the absorbed radiation causes any photochemical action; it shows only that a substance can absorb light in the same general region in which it itself emits light in the Tesla discharge. This absorbed light will tend to decompose the vapor which absorbs it and for that reason we

---

[1] Compt. rend., 151, 479 (1910).

[2] Bull., 40, 60 (1883).

[3] Z. physik. Chem., 25, 285 (1898).

[4] J. Chem. Soc., 89, 1192 (1906).

shall, at least for the present, treat the reactions which take place in the Tesla discharge as purely photochemical.

It is, of course, true that the spectrum for every gas is characteristic. That this is true limits very definitely the reactions which can take place. No primary photochemical reaction can be made to occur if the necessary wavelength is absent. Conversely, any photochemical reaction tends to occur if the proper wave-length is present. The photochemical reactions which tend to take place are therefore limited first of all by the radiation which is produced by the passage of the discharge through the gas. Whether the reactions actually do take place and the extent to which they occur depends on the energy relations. Considering a specific case, it might be true that the passage of the Tesla discharge through ethyl alcohol produces only the wave-length which is necessary to dehydrogenate the alcohol and does not produce the necessary radiation for dehydration. Hence, hydrogen and acetaldehyde would be formed, but no ethylene and water. It is more likely, of course, that both wave-lengths or bands are produced. As a matter of fact, both reactions do occur in ethyl alcohol, although the dehydrogenation occurs to the greater extent, probably because it requires less energy.

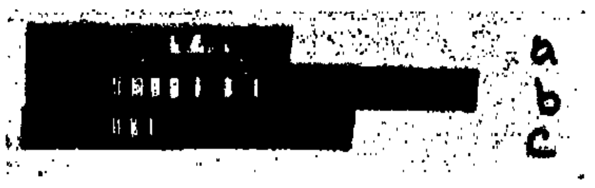


FIG. 2

To be so limited in possible reactions by the almost accidental presence of the proper radiation, or in the extent to which a given reaction can occur by the almost fortuitous quantity of energy produced is a condition which could with advantage be changed. One possibility lies in the variation of pressure or voltage, or frequency. There is another possibility which is very attractive. It is based on the work of Cario and Franck.[1] When hydrogen is illuminated by a quartz mercury lamp there is no evidence of the formation of hydrogen atoms. But Cario and Franck showed that if mercury vapor is introduced into the hydrogen, it gives out radiation, under the influence of the ultraviolet light, which is capable of forming and does form hydrogen atoms from the molecules of hydrogen which are present.

If this principle is of general application, then there is a wide field for using it in connection with the Tesla discharge. Unfortunately, we have not yet been able to obtain any positive results. But there is still reason to believe that by the use of the proper substance in the discharge tube, a desired reaction could be made to occur. In the case of ethyl alcohol, which has already been cited, excitation of the alcohol molecule by the proper second substance, which in turn is influenced by the discharge itself, might result in a high yield of ethylene instead of a high yield of hydrogen, as at present.

That the Tesla discharge proved to be a convenient source of photochemical energy for our high-temperature ozonizer was the chief reason for using it. We hoped, however, that the rate of decomposition would be high, and our

---

[1] Z. Physik, 12, 162 (1922).

experiments showed that it is high. A comparison with some of the results obtained by other workers will show its advantage in this respect.

Berthelot and Gaudechon[1] used a quartz mercury lamp. The organic liquid undergoing decomposition was contained in a quartz vessel which was held in close proximity to the lamp. The decomposition products, under these conditions, amounted to a few cubic centimeters per hour at the most. With some substances it was a fraction of a cubic centimeter per hour. Maquenne,[2] who used a silent discharge, obtained forty to fifty cubic centimeters of gas per hour. Jackson and Northall-Laurie[3] evidently obtained larger amounts of gas in the same length of time than any of the other investigators, although the exact amount is not stated. They used a high-frequency discharge.

With our apparatus we were able to obtain from ten to several hundred cubic centimeters of gas per minute. This made the analysis easier and more accurate. More important still, if one of the products happened to be present in a small percentage, it was detected more readily.

Literature

The compounds which were studied in this work were acetone, methyl alcohol, acetic acid, ethyl alcohol, acetic aldehyde, a mixture of sulfur dioxide and oxygen, and a mixture of ethylene and acetylene. The literature shows that a considerable amount of investigation had already been made on these substances. To some of this work reference has already been made and it has been stated that the investigators who have been mentioned above used different sources of radiant energy. In general there are three classes: the quartz mercury lamp, the silent electric discharge, and the high-frequency electric discharge. It has not been possible in every case to find out in detail what kind of apparatus was used in the experimental work but the references given below provide information sufficient for our purpose.

Berthelot and Gaudechon were the only investigators, of those to be mentioned, who used a quartz mercury arc. In their description[4] they say:

"The chemical action of ultra-violet rays, recognized for a long time in photography, can be now produced with great intensity by means of a quartz mercury vapor lamp.

"We have employed either an Heraeus lamp of 110 volts consuming 2.5 amperes in normal operation and of which the arc is 4 cm. long, or a Westinghouse lamp of 220 volts, consuming 5 to 6 amperes and with an arc 5 to 6 cm. long. The carefully dried gases, subjected to the rays, were enclosed in a quartz tube about 0.6 mm. thick. The pressure was in the neighborhood of 75 cm. Under these conditions, the gases were ionized and became conductors, and remarkable chemical effects were produced."

---

[1] Compt. rend., 150, 1169 (1910).

[2] Bull., 39, 307 (1883).

[3] J. Chem. Soc., 89, 1192 (1906).

[4] Compt. rend., 150, 1169 (1910).

In a subsequent paper of the series[1] the authors continue the description of the use of their apparatus. "In the study of organic compounds we have preferred the small lamp of 110 volts, of which the action is more manageable; in most cases the temperature was allowed to mount to 80° or 90°; in certain cases it did not exceed 50° or 60°. In general the evolution of gas stopped in-increasing at the end of about ten hours, and the state of equilibrium appeared established, for sensibly the same proportion of gas was found in many successive experiments."

Jackson and Northall-Laurie[2] used the high-frequency discharge, with several well-defined objects in mind. "Many experiments have been made on the behavior of various gases and vapors under the influence of electrical discharges, but so far as we know no experiments have been published dealing directly with the first change and not with the accumulated changes which occur when such vapours as those of methyl alcohol and acetaldehyde are subjected to the rapid oscillations of a high frequency discharge. . . .

"Qualitative experiments on the action of electric discharges on various saturated and unsaturated compounds led one of us to the conclusion that as a general rule the former were broken down to simpler molecules, whilst the latter were converted into complex polymerized substances.

"In the case of methyl alcohol and acetaldehyde, it was thought worth while to study the reaction quantitatively and to use the high-frequency current for the source of oscillation, as it would be possible in this way to avoid the effect of heat to the greatest extent.

"Moreover, by employing this form of current, relatively large volumes of the vapours could be used and the immediate, not the accumulated, effect on them could be studied."

Their apparatus "is a high-frequency machine similar to those used for therapeutical purposes, and consists of two Leyden jars with spark gap, the length of which can be adjusted, and a large solenoid on a drum which can be revolved and the length of wire in use adjusted by the position of the side terminal. This enables the apparatus to be 'tuned' to give the best results with the current and size of bulb used. One jar is connected to earth, and the two jars are connected on the inside with the secondary poles of a large induction coil capable of giving a spark of 50 cm. in length in air, and on the outside with each end of the solenoid. A current of 2 amperes at 100 volts was used in the primary coil."

The "bulb in which the decomposition took place" was round, and "about 12 cm. in diameter, with two side tubes joined" respectively to a vacuum pump and a manometer. "The platinum electrode . . . was made about 6 cm. long and 1.5 cm. in diameter, shaped like a small nutmeg grater. The pierced and roughened surface assisted in spreading the discharge." It was hung in the middle of the decomposition bulb. The bulb itself was hung inside a "large beaker, round the outside of which was fixed a strip of tin foil 7

---

[1] Compt. rend., **151**, 479 (1910).

[2] J. Chem. Soc., **89**, 1190 (1906).

cm. wide, connected to earth. The action of the tin foil caused the discharge from the electrode" (in the middle of the bulb) "to spread all around and completely fill the bulb with a glow."

"The purified and dried liquid required was contained" in a bulb connected to the manometer side of the apparatus.

The idea which Jackson and Northall-Laurie expressed of being able to determine the initial reaction has been mentioned by others. Maquenne, who used a silent discharge on various vapours, had the same end in view.[1]

"One can observe that the decompositions effected by the silent electric discharge are ordinarily similar to those which heat produces. The analogy is evident for most of the gaseous binary compounds; I have tried to extend it to the more complex compounds by studying the decomposition of the first members of the fatty acid series in the discharge apparatus of Berthelot. One knows that, in that case, electricity, as well as heat, tends to produce secondary reactions which each time mask, by their importance, the initial reaction. I have succeeded in partially overcoming that difficulty by effecting the decomposition in a vacuum, maintained constant by an outflow of mercury; one thus removes the gases evolved by the action away from the discharge almost as soon as they are freed and before they have had time to react together. This method permits in addition the production of a vigorous discharge free from sparks, and the discovery of some of the most important secondary reactions, by studying the variations in composition of the gas obtained under a high or low vacuum.

"The apparatus employed was composed of a discharge tube according to M. Berthelot connected by a three-way stopcock to a mercury manometer and to the pump. The liquid to be studied is introduced at the bottom of the discharge tube and its vaporization is effected rapidly enough, for the moderately volatile substances, so that one obtains, at the pump, about 40 to 50 cc. of gas per hour. The decomposition is more rapid as the internal pressure is lower."

It seems as if what the pressure really measures must be the velocity of flow of the vapor through the apparatus. For different substances the pressure will have no relation unless it happens that the vapor pressure at the temperature of operation, and the rate of decomposition are the same. "The silent discharge tube of Berthelot" which Maquenne used was illustrated and described by Berthelot several years before.[2]

Dilute acid was used in the concentric tubes surrounding the reaction tube, as in the ordinary ozonizer and the discharge was furnished by[3] "a Ruhmkorff coil, the largest possible, operated with five or six large Bunsen cells. If more are used, the tube may be pierced; that inevitably happens when more than eight are used. . . .

"The discharge which is produced is silent and invisible in broad daylight; but at night, the tube or, more correctly, the annular space which contains the gas, appears illuminated by a phosphorescent glow, in which the alternations

---

[1] Bull., 39, 306 (1883).

[2] Ann. Chim. Phys., (5) 10, 75; 12, 463 (1877).

[3] Loc. cit., 10, 81.

can be perceived by turning the head rapidly; these correspond to the interruptions of the Ruhmkorff coil."

Poma and Nesti increased the yield by connecting several ozonizers in parallel as shown in a sketch of their apparatus.[1] The nature of the discharge is similar to the ordinary silent discharge. They used a high-voltage alternating current, whereas most people use usually the oscillating current obtained from a Ruhmkorff coil. "We used[2] a small converter which ... gave an alternating current of 46 cycles and 96 volts. This was raised to a maximum of about 10,000 volts by a small oil-cooled transformer. The conversion ratio was varied from 1 to 100, 1 to 75, and 1 to 50.

"The ozonizers of two coaxial glass tubes had an internal armature consisting of a light silver mirror deposit, formed by one of the usual reduction methods. The external armature consisted of a fixed net of fine iron wire.

"As shown in the diagram, the organic substance was placed in a glass flask and heated in a water bath or an oil bath. Reflux condensers on top of the ozonizers were connected with the flasks by side arm tubes so that the condensed vapors did not flow back through the apparatus.

"In order to have sufficient quantities of the reaction products for experimental studies, we made the apparatus in batteries of three or six units as shown in the diagram, electrically connected together. The condensers were connected with a gas sampling bulb so the uncondensed vapors could be withdrawn for analysis."

de Hemptinne was the first to use, so far as we know, anything approaching a high-frequency discharge when he used Lecher's apparatus[3] as a source of current. By using this apparatus he was enabled to secure a wide variation in wave-lengths.

"The vapors[4] of a series of substances were subjected to the influence of electric oscillators and the decomposition products analyzed according to the usual methods. The apparatus, in which the decomposition was accomplished, consisted of a wide glass tube about 75 cm. long and 4 cm. in diameter; at one end was the three-way stopcock R, at the other a graduated tube B, 75 cm. long, which is connected by means of a long rubber tube with the mercury reservoir C." Through the three-way stopcock, the decomposition tube could be pumped out and then "the gas being studied can be led in until the desired pressure is reached, e.g., 10 mm. On the two opposite sides of the decomposition tube is pasted tin foil which is connected with the wires of the Lecher apparatus. The interior of the tube may in this way be subjected to oscillations of the desired wave-length."

"The course of the reaction can be followed by observing the position of the mercury" in the tube connecting the mercury reservoir and the decomposition tube. When the decomposition is finished the apparatus is connected with a Hempel burette and the gas is drawn over for analysis.

---

[1] Gazz., 51 II, 89 (1921).

[2] Loc. cit. p. 83.

[3] Wied. Ann., 41, 850 (1890).

[4] Z. physik. Chem., 25, 284 (1898).

Losanitsch and Jovitschitsch[1] used a "Berthelot" apparatus, while Losanitsch[2] alone, ten years later, used practically the same ozonizer.

"I have used[3] here the same Berthelot ozonizer which I used in my first experiments. On this apparatus I have provided only two changes, namely: on the inlet tube I placed a stopcock, with which I could hermetically seal the gas in the apparatus; and I have bent the exit tube down so that when it is immersed in mercury I can measure the pressure of the gases in the apparatus with it. In this way I have been able to appraise the velocity of the reaction so far as it is connected with condensation."

Losanitsch also mentions means of running experiments at higher temperature, and by using steam, goes to 100° or slightly higher. "When I wished to conduct this reaction at a higher temperature, I filled the apparatus with warm conducting acid. Or if a more intense heat was necessary, I covered the cylinder in which the ozonizer rested, with rubber tubing and through this led in steam."

Löb[4] used an ozonizer similar to that of Poma and Nesti to study the effect of the silent discharge on organic liquids. He, however, allowed the condensed vapor to flow back through the reaction chamber, whereas Poma and Nesti led them back into the vaporizing flask by means of a side tube. Löb studied the effect of both alternating and direct current. He gives[5] a detailed description of his apparatus, in order that no essential factor be neglected.

The essential features of the apparatus of several investigators have been described. We shall now review their results on methyl alcohol, ethyl alcohol, acetic aldehyde, acetic acid, and acetone, and attempt to classify and coordinate them, and harmonize them with the conditions of the experiment.

Methyl Alcohol

A summary of the results which have been obtained with methyl alcohol shows only slight concordance at first glance:

	CO	CO_2	CH_4	H_2	C_2H_2	C_2H_4
Berthelot and Gaudechon[6]	8.0	5.0	—	87.0	—	—
Maquenne[7] (3-4 mm.)	24.3	0.0	51.0	20.4	4.3	
(50 mm.)	21.8	0.9	43.2	33.7	0.9	
(100 mm.)	19.6	0.0	36.7	42.8	0.9	
Poma and Nesti[8]	10.8	—	15.5	73.3	—	—
de Hemptinne[9] (weak oscillations)	30.4	4.2	32.9	30.5	—	—
(strong oscillations)	28.0	3.0	35.0	32.0	—	—
Jackson and Northall-Laurie[10]	35.5	—	2.4	61.1	1.2	0.6

---

[1] Ber., 30, 135 (1897).

[2] Ber., 40, 4656 (1907); 41, 2683 (1908); 42, 4394 (1909).

[3] Ber., 40, 4656 (1907).

[4] Z. Elektrochemie, 12, 282 (1906).

[5] Loc. cit. p. 285.

[6] Compt. rend., 151, 479 (1910).

[7] Bull., 40, 60 (1883).

[8] Gazz., 51 II, 84 (1921).

[9] Z. physik. Chem., 25, 285 (1898).

[10] Loc. cit.

Of their results Berthelot and Gaudechon[1] say that "the photolysis of the primary functional alcohol group, CH_2OH is marked by the predominance of hydrogen, associated with carbon monoxide, and by the absence of carbon dioxide. Furthermore, in the first members of the fatty acid alcohols, of the type RCH_2OH, one finds in the gaseous state the hydrocarbons R_2 coming from the doubling of the radical R from two contiguous molecules.

"The essential feature[2] of the photolysis of alcohols is an abundant evolution of hydrogen (70% approximately of the total gas) with the formation of the corresponding aldehyde: $CH_3CH_2OH = H_2 + CH_3COH$. . . .

"We have verified likewise the formation of methyl aldehyde in methyl alcohol exposed to the rays. . . . The alcohol group,[3] CH_2OH, is split up, H_2 forming 60 to 70 volumes; and the residues, OH and C, react to give H_2O and the gas CO, which forms 10 to 20 volumes. The gas CO_2 appears only accidentally in the case of methyl alcohol, without doubt as a result of the secondary formation of a little formic acid, which decomposes in its turn. (The action of oxygen upon alcohol gives a notable quantity of formic acid, as we have ascertained directly)."

In other words, the primary reaction, according to them, is:

$$HCH_2OH = H + CH_2OH$$

which is followed by:

$$2H = H_2$$

and

$$2OH + C = H_2O + CO.$$

It is a little difficult to see just how they make these quantities balance.

The same considerations evidently cannot apply to the results of Maquenne,[4] who does not speculate on details. "The composition of the gas varies with the interior pressure because of the secondary reactions which take place between the products of the initial decomposition. These secondary reactions give birth to resinous bodies, less volatile, which consequently escape the analysis, and which one finds, at the end of the experiment, dissolved in the excess of methyl alcohol. These polymerizations take place with the liberation of hydrogen, as one observes ordinarily in pyrogenic reactions."

Maquenne here hints at a reaction which Poma and Nesti[5] discuss in some detail. It will be worth while to find out what they say before Maquenne's results are discussed.

"In order to free the gas from the alcohol and formaldehyde which were inevitably present, the first portions were washed in salt water. . . . The result of our experiments is interesting in view of the large proportion of hydrogen compared to methane and even more so because of the high ratio to carbon monoxide, indicating that in all probability under the conditions of our experiment, methyl alcohol is dehydrogenated to form a large proportion of formaldehyde or perhaps one or more of the polymers.

---

[1] Compt. rend., 151, 1349 (1910).
[2] Compt. rend., 153, 383 (1911).
[3] Compt. rend., 151, 480 (1910).
[4] Bull., 40, 61 (1883).
[5] Gazz., 51 II, 84 (1921).

"In short, in order to explain the formation of the gas which we obtain, the following equations may be assumed:

$$(1)\quad CH_3OH = CO + 2H_2$$
$$(2)\quad 2CH_3OH = 2CH_4 + O_2$$
$$(3)\quad CH_3OH = HCHO + H_2$$

"The presence in our system of methane and the absence of oxygen and carbon dioxide indicate that the oxygen probably combines with the hydrogen to form water. Since our analysis showed two volumes of carbon monoxide to three volumes of methane, equations (1) and (2) may be combined to give equation (4):

$$(4)\quad 5CH_3OH = 2CO + 3CH_4 + 3H_2O + H_2.$$

"As it appears from this equation that the volume of hydrogen given off in accordance with equations (1) and (2) should be equal to one-half the volume of carbon monoxide, it follows that in our experiments, the hydrogen should have been 5%. Consequently the hydrogen liberated exclusively in accordance with equation (3) should be approximately 68% of the total volume of gas and indicated that about two-thirds of the alcohol vapor loses hydrogen to form formaldehyde or its polymers.

"We combined the liquid from three flasks—from three ozonizers—this being the residue from about fifty hours' action. This was a clear alcoholic liquid, colored slightly yellow and having a strong formaldehyde odor, and giving a copious precipitate with bisulphite, indicating the presence of free formaldehyde in the alcoholic liquor.

"Most of the alcohol was distilled off on the water bath, leaving an oily yellow liquid of high density. A second distillation was made over a Wood's metal bath; the liquid distilled at 100° to 109° but most of it decomposed, giving off suffocating vapors of formaldehyde. A small residue was left of a liquid which rapidly turned brown and resinified without distilling.

"A part of the distillate congealed to a white crystalline mass which when redistilled, decomposed mostly to formaldehyde."

de Hemptinne[1] is quite positive that the primary reaction in the decomposition of methyl alcohol is: $CH_3OH = CH_4 + O$, but his explanation does not seem sound. "The molecule is decomposed into oxygen and methane, $CH_3OH = CH_4 + O$, and the oxygen reacts in turn on methane and forms carbon dioxide, carbon monoxide, and water, while at the same time methane itself decomposes into hydrogen and other hydrocarbons. The presence of carbon dioxide is surprising at first glance because there is an excess of methane over oxygen; one can, however, easily explain the appearance of CO_2. Maquenne[2] has shown that a mixture of carbon monoxide and water vapor gives carbon dioxide under the influence of electric oscillations. I can myself confirm this fact: a mixture of CO at 20 mm. pressure and H_2O at 6 mm. pressure gives after ten minutes 4% of CO_2. Since the action of oxygen on

---

[1] Z. physik. Chem., 25, 286 (1898).

[2] Compt. rend., 96, 65 (1883.)

methane certainly yields water, one should not wonder about the presence of CO_2. Since the action of electric oscillations is a very complicated process, it is very difficult to explain the facts correctly, and any contingent assertions can be advanced only with much reserve. Meanwhile, I believe that one has a good basis for the assumption that, in the decomposition of methyl alcohol, the molecule first breaks down into oxygen and methane: $CH_3OH = CH_4 + O$; other explanations are not permissible. The two usual ones are as follows:

"1. One can assume a decomposition into carbon monoxide and hydrogen, which is, however, very unlikely, since the analysis shows a large amount of methane, the presence of which is difficult to explain. The equation would read: $CH_3OH = CO + 2H_2$, and the methane would have to be formed from its elements. This is improbable, for according to the experiments of Berthelot a mixture of carbon monoxide and hydrogen, under the influence of electric oscillations, gives, besides carbon dioxide, a solid substance with the approximate composition $C_4H_6O_3$: $5CO + 3H = CO_2 + C_4H_6O_3$. The gas contains, also, traces of acetylene and unsaturated hydrocarbons, while in our experiments about 35% of methane is formed.

"2. One could assume that the hydroxyl is split off from the molecule and since it is only slightly stable, decomposes into oxygen and hydrogen, which in their turn react with the CH_3 group and give carbon monoxide, water, and methane. This hypothesis is slightly probable. In this case there must be as much carbon monoxide as methane, which is not the case. Moreover, how could the formation of so large an amount of methane be explained when this gas itself is decomposed by electric oscillations? One could still assume the formation of polymerized hydrocarbons from CH_3, but this assumption again does not explain the presence of methane and the other end-products."

Poma and Nesti also agree with a primary decomposition of the molecule into CH_4 and O as an explanation for the presence of methane. They assume three primary reactions as follows:

$$(1)\quad CH_3OH = CO + 2H_2$$
$$(2)\quad 2CH_3OH = 2CH_4 + O_2$$
$$(3\quad CH_3OH = HCHO + H_2$$

The first undoubtedly occurs under the proper conditions. Jackson and Northall-Laurie offer some results which show that reaction (1) occurs under their conditions, almost to the exclusion of any other.

Poma and Nesti have shown that reaction (3) occurs, and Maquenne's results point in the same direction, since he undoubtedly had polymerized formaldehyde in the residue.

Neither of these reactions, however, explains the presence of methane, for which Poma and Nesti, and de Hemptinne offer equation (2). That this is a primary reaction seems unlikely. The formation of methane and the splitting off of oxygen with the subsequent decomposition of the methane to form other hydrocarbons and the reaction of the methane and oxygen to form carbon monoxide, water, and carbon dioxide is improbable for several reasons. In the first place, the action of the discharge as shown by reactions (1) and (3) is quite analogous to the action of some reagents, while reaction (2) is not effected by any chemical reagent. In the second place, methane is very stable and it is unlikely that it reacts with oxygen, in the electric discharge, to form carbon monoxide in more than traces. And thirdly, if methane could be as easily decomposed in the discharge as de Hemptinne would lead us to believe, it is very unlikely that it would ever be formed. It seems as if de Hemptinne reasons too much in a circle.

A more plausible explanation would be to assume that one primary action in the discharge is the splitting off of the hydroxyl group:

$$CH_3OH = CH_3 + OH$$

two of which combine to form water and free oxygen:

$$2OH = H_2O + O$$

The CH_3 group then might react with hydrogen which has just been set free and form methane:

$$\begin{aligned} CH_3OH &= 2H + HCHO \\ CH_3 + H &= CH_4 \end{aligned}$$

while the oxygen combines with the formaldehyde, giving water and carbon monoxide:

$$O + HCHO = CO + H_2O$$

We would assume that there are three primary reactions:

$$CH_3OH = CO + 2H_2 \tag{a}$$

$$CH_3OH = 2H + HCHO \tag{b}$$

$$CH_3OH = CH_3 + OH \tag{c}$$

and if (b) and (a) are combined in the manner just described, we have

$$\begin{array}{rcl} CH_3OH & = & 2H + HCHO \\ 2CH_3OH & = & 2CH_3 + 2OH \\ \hline 3CH_3OH & = & 2CH_4 + 2H_2O + CO \end{array} \tag{d}$$

The results of Maquenne, Poma and Nesti, and de Hemptinne can be explained quantitatively on the basis of equations (a), (b), and (d). It will be noted that Maquenne obtains at each pressure approximately half as much CO as CH_4. Equation (d) gives this relation also. This equation plus (b) is a quantitative representation of Maquenne's results.

Maquenne expected his results at low pressures to be more exclusively those due to the primary reaction, and not to secondary reactions. While in some cases this may be true, it cannot be wholly true with methyl alcohol where there are probably three primary actions. There enters not only the question of primary reactions but also the concentration, in the vapor phase, of the products of the reaction. Acetylene is probably formed because of dehydration of the alcohol.

From the results of Poma and Nesti, reactions (a), (b), and (d) probably all took place, while in de Hemptinne's apparatus, reactions (a) and (d) occurred. Jackson and Northall-Laurie showed quite conclusively that reaction (a) occurred almost exclusively in their high-frequency ozonizer.

"Preliminary experiments and a number of analyses of the gaseous products showed that if these were allowed to accumulate by continuing the discharge for any length of time, the results obtained showed such variety as to be of little value for interpretation. If, however, the discharge were passed for a few seconds only, comparable results could be obtained. The vapours were under a pressure of about 100 mm. for methyl alcohol and 180 mm. for acetaldehyde and the discharge passed for from one to ten seconds. The products were then pumped out of the apparatus, separated from the vapours, and analyzed. Working in this way no solid or heavy liquid products were obtained, although these were observed if the discharge were continued for a long time.

"Several analyses were made of the gaseous products obtained in this way, and it was found that the shorter the time the current was allowed to pass, the more nearly did the composition of the products (from methyl alcohol) approximate to carbon monoxide and hydrogen, the volume of the hydrogen being very nearly double that of the carbon monoxide. By working with mere flashes of the discharge and pumping out the products after each flash, gases were obtained which, when freed from the vapour of methyl alcohol and traces of water, gave the following results as the mean of several determinations of the main products:

CO	H	CH_4	C_2H_2	C_2H_4
32.5	61.1	2.4	1.2	0.6

(percentage by volume)

"We conclude that the immediate action on the vapour of methyl alcohol of such oscillations as are obtained in high frequency discharge is represented by the simple change

$$CH_3OH = CO + 2H_2."$$

Maquenne, and Poma and Nesti used somewhat the same kind of discharge and their results show a similarity. Reaction (a) giving $CO + H_2$ probably did not occur in Maquenne's apparatus and only slightly in Poma and Nesti's . Reaction (b) giving formaldehyde, occurred in both, while reaction (d), giving $CH_4 + CO$ occurred in both.

Reaction (a) was the chief one in the experiment of Jackson and Northall-Laurie and probably the principal one for de Hemptinne, although in the latter's experiment reaction (d) also occurred because of the longer duration of the discharge.

Ethyl Alcohol

Ethyl alcohol has been subjected to photochemical decomposition in the same apparatus used for methyl alcohol by most of the investigators who worked with methyl alcohol. The following table is a summary of the results:

	CO_2	CO	H_2	C_nH_{2n}	$2\ C_2H_4$
Berthelot and Gaudechon[1]	—	22.0	63.0	15.0*	—
Maquenne[2] 2 mm	2.2	11.0	42.6	30.0*	14.0**
" 100 mm	0.5	15.4	55.2	26.6*	2.3**
Poma and Nesti[3]	2.2	4.4	59.0	26.0***	9.0**
de Hemptinne[4]	2.0	22.0	25.0	48.0***	—
Löb[5]	1.0	5.5	68.2	22.1***	3.2

*C_2H_4
**C_2H_2 and C_2H_4
***CH_4 and C_2H_6

The experiments of Berthelot and Gaudechon[6] proved conclusively the formation of acetaldehyde.

"A quartz flask of 40 cc. filled with ethyl alcohol and cooled by means of water, was exposed for 4 hours at 6 cm. from the 110 volt lamp, functioning in a moderate fashion (3.6 amp. with 45 to 50 volts at the terminals). We then ascertained the reducing action on ammoniacal silver nitrate. The following reactions showed the presence of ethyl aldehyde: instantaneous recoloration with Schiff's reagent (fuchsine decolorized with sulfurous acid); yellow coloration after several minutes of boiling with concentrated soda and a little water; orange color upon contact with Hehner's reagent (water + a drop of phenol solution + concentrated H_2SO_4). All of these reactions tried on the original alcohol, before exposure, were negative."

Berthelot and Gaudechon, it will be remembered, stated that the essential feature of the photolysis of alcohols is an abundant evolution of hydrogen with the formation of the corresponding aldehyde. They obtained also some carbon monoxide and ethane.

Maquenne[7] detected aldehyde but concluded that the primary reaction in the discharge tube is the formation of ethylene.

"Ordinary alcohol (99.5) decomposes rapidly in the discharge tube. The evolved gas has a strong odor of aldehyde and acetylene. The gases were washed with water before analysis. . . . "Ethylene, relatively abundant when the pressure is very low, diminishes very rapidly; at a pressure of 100 mm. it is no longer found.

"It appears then that the alcohol, under the influence of the discharge, is separated into ethylene and water in an initial decomposition which is immediately followed by the secondary reaction. The ethane has a similar origin. It is in its turn decomposed little by little. The hydrogen then increases in a continuous fashion. Also in that case, it forms the polymerized products, of resinous appearance, which remain in solution in the undecomposed alcohol."

---

[1] Compt. rend., **151**, 479 (1910).
[2] Bull., **40**, 61 (1883).
[3] Gazz., **51**, 86 (1921).
[4] Z. physik. Chem., **25**, 288 (1898).
[5] Z. Elektrochemie, **12**, 308 (1912).
[6] Compt. rend., **153**, 383 (1911).
[7] Bull., **40**, 61 (1883).

Poma and Nesti considered the reaction with ethyl alcohol to be similar to that with methyl alcohol but "as may be seen, the greater complexity of ethyl alcohol makes the reaction also more complex but still there is a predominance of hydrogen. . . . "In this case, also, the residue was clear and yellow and gave a copious precipitate with bisulphite, i.e., the bisulphite compound of acetaldehyde. The distillation residue was a complex mixture which decomposed and resinified in part, liberating acetaldehyde."

de Hemptinne used the same experimental conditions as with the methyl alcohol.

"The analysis shows the absence of those hydrocarbons which are absorbed by fuming sulfuric acid; the remaining hydrocarbons belonged, therefore, to the C_nH_{2n+2} group. . . . Through calculations one can easily find the quantity of ethane and be convinced that it is not unimportant. The exact knowledge of the quantity relations of ethane to methane is not considered important for theoretical considerations but the fact itself that a considerable quantity of ethane is formed, is important. (Here, as later, the hydrocarbon richest in carbon continually appears in considerable quantities. I did not especially make a note of this quantity because it is different according to the experimental conditions.)

"Methane is formed through a secondary reaction from ethane, just like a series of more solid and resinous decomposition products. If one does not consider these side reactions, considerations similar to those obtaining with methyl alcohol lead to the conclusion that the molecule of ethyl alcohol will split up according to the equation: $C_2H_5OH = C_2H_6 + O$. One can scarcely explain in any other way the large amounts of ethane which appear. The assumption that decomposition into $CO + CH_4 + H_2$ occurs is not valid because ethane cannot be formed from methane and carbon monoxide. In order to meet all objections which would be raised against this explanation, we wish to allow the electric oscillations to act on alcohol vapor in the presence of phosphorus. If free oxygen is formed, part of it would have to be absorbed and the quantity of carbon monoxide would have to become smaller.

"This experiment had to be made in one of the earlier, somewhat different apparatus. Since the relative amounts of decomposition products depended on the dimensions of the apparatus, I made two preliminary experiments without phosphorus:

CO_2	2 %	
C_nH_{2n}	0.5	II
CO	15	
H_2	20	
$C_2H_6+CH_4$	62.5	

"The second analysis gave essentially the same result as the first.

"The action of the electric oscillations on alcohol vapor at the pressure and under the same conditions as above but in the presence of phosphorus gave:

CO	7%
C_nH_{2n}	1
H_2	65
$C_2H_6+CH_4$	27

"The action took place in the same time and with the same intensity as above. One sees that the quantity of carbon monoxide is smaller and of free hydrogen much greater. This phenomenon is easily explained, if one assumes that oxygen set free from the molecule becomes bound to the phosphorus. The disappearance of the carbon monoxide is not complete because it is impossible to expose every part of the vapor of the reaction to the phosphorus; and since the latter can absorb only that immediately surrounding, a part of the oxygen molecules withdraw themselves from this action and react with C_2H_6.

"My conclusions are confirmed under the experiment to be described with acetone. It was shown that acetone decomposes according to the theory into C_2H_6 + CO and that the quantity of carbon monoxide does not decrease in the presence of phosphorus, so that no free oxygen is therefore formed.

"Suppose we assume that the alcohol molecule decomposes according to $2C_2H_5OH = 2C_2H_6 + O_2$; if we now mix oxygen and ethane in this proportion, subject the mixture to the influence of electric oscillations for the same length of time and under the same conditions as before, then we obtain:

carbon dioxide	6%
carbon monoxide	15
hydrogen	34
ethane and methane	45

"These proportions of quantities approach those of experiment II; the same quantity of carbon monoxide appears but more carbon dioxide, which is easy to explain on the ground that the gas mixture is really always richer in oxygen than when the molecule decomposes into $2C_2H_6 + O_2$, because in the latter case the oxygen is still surrounded by alcohol vapor which it can oxidize in turn.

"A question now involuntarily obtrudes itself: how is it possible that oxygen splits away from the C_2H_6 group, in order to react with it again later?

"One can answer to this question, that in the molecule C_2H_5OH the grouping of C_2H_6 is not the same as that of the molecule C_2H_6, consequently the oxygen can separate completely from the molecule C_2H_5OH, whereupon the hydrogen atoms assume a new equilibrium position relative to the carbon and form a new ethane nucleus which can be attacked by oxygen. In other words, nothing else is to be said than that molecular nuclei of the same composition but different atom grouping have different affinity to one and the same element and will be attacked by this element in different ways. This is a well-known phenomenon in chemistry and to give only one of the many examples, let us consider that normal butyl alcohol gives butyric acid upon oxidation, while the secondary alcohol goes over to the methyl-ethyl ketone and the tertiary alcohol or trimethylcarbinol yields acetone, acetic acid, and carbon dioxide."

This explanation is ingenious but de Hemptinne entirely overlooked the presence of acetaldehyde in the decomposition of ethyl alcohol. The primary reaction probably being $C_2H_5OH = H_2 + CH_3CHO$, had the phosphorus then inhibited the decomposition of the acetaldehyde, the results would be just what he obtained, i.e., a larger relative amount of hydrogen and smaller amounts of the hydrocarbons and carbon monoxide but essentially the same ratio of hydrocarbon to carbon monoxide. The fact that this ratio is fairly close indicates that this explanation is reasonably possible:

	Without P	With P
$C_2H_6+CH_4/CO$	4.17	3.86

It would be interesting to know the relative rates of decomposition with and without phosphorus.

Löb[1] believed that Maquenne obtained methane and not ethane. "Methane is not specified; yet, it seems to me unquestionable, according to de Hemptinne's experiments and my own, that the saturated hydrocarbons consisted for the most part of methane, which Maquenne did not expect among the decomposition products and therefore overlooked. In any case the occurrence of the reaction $CH_3.CH_2OH = CH_3CHO + H_2$ is to be seen with certainty from his experiments, since otherwise the presence of aldehyde cannot be explained. Since aldehyde itself yields principally methane and carbon monoxide and the latter is copiously formed in the gas mixture, so must the former also be present in the gas mixture as experiment with pure acetaldehyde shows. If one considers this as a secondary synthetic product, however, which is very improbable, its components still remain methane and carbon monoxide."

Löb[2] described his purpose as follows: "The results heretofore obtained are not comparable with my results as they stand, since they were obtained under different experimental conditions. Maquenne and de Hemptinne worked with reduced pressures, Berthelot in the presence of nitrogen. From that it appeared important to me to obtain next a picture of the decomposition of alcohol under atmospheric pressure in the absence of other substances in order to find out the influence of water and some gases. In accordance with the discussion given in the theoretical part, it was necessary to investigate acetaldehyde and acetic acid also; the behavior of the other substances formed by the action of the discharge on alcohol has already been called to notice in the first part of this work.

"The decomposition of absolute alcohol was undertaken in the electrisator provided with an inner condenser and a ground-polished little flask which had already served for the formaldehyde and formic acid experiments.

---

[1] Z. Elektrochemie, **12**, 302 (1906).

[2] Z. Elektrochemie, **12**, 308 (1906).

"The results of several analyses of the gases are as follows:

TABLE I

No.	Current	Amp.	Gases obtained from Reaction in cc.				
			CO_2	CO	H_2	C_nH_{2n+2}	C_nH_{2n}
1	Alternating	6.5	0.2	1.6	27.8	7.9	3.2
2	"	8.6	0.2	—	11.9	4.0	1.4
3	Direct	2.5	0.6	3.4	42.5	13.8	2.0

TABLE II

No.	Composition in Volume Percentage				
	CO_2	CO	H_2	C_nH_{2n+2}	C_nH_{2n}
1	0.5	3.9	68.3	19.4	7.9
2	1.1	—	68.0	22.9	8.0
3	1.0	5.5	68.2	22.1	3.2

"With alternating operation about 50 cc. were formed in two hours, while with direct current about 70 cc. in one hour were developed. In every case copious amounts of acetaldehyde were formed, so that, as the gas analyses further proved, the principal decomposition to occur was according to the equation: $CH_3CH_2OH = CH_3CHO + H_2$. The hydrocarbons C_nH_{2n+2} consisted chiefly of methane and ethane; the hydrocarbons C_nH_{2n} were nearly exclusively ethylene. The splitting of acetaldehyde remained secondary. The small amounts of carbon monoxide were easily explained from the large excess of hydrogen, which reduced the carbon monoxide for the most part to hydrocarbons.

"For comparison with the chief experiments it was necessary to find out the behavior of alcohol vapor at ordinary temperatures also. A difficulty existed therein in that most gases react with alcohol or with its decomposition products under the influence of the discharge. I finally chose nitrogen, which according to Berthelot's statement is absorbed only slowly, and made the experiment in the manner described in the electrisator for moist gases, in which I used 50% alcohol as the filling liquid, which also was used for the other combinations. The discharge space was filled completely with nitrogen and several cubic centimeters of the dilute alcohol were placed in the spherical enlarged part of the electrisator. This and all of the following experiments were carried out in a closed electrisator.

"The results of a two-hour experiment made with direct current of 2.5 amp. are as follows:

CO_2—1.6; CO—2.0; H_2—17.2; hydrocarbons—5.1 cc. and in volume percentage:

CO_2	6.2
CO	7.7
H_2	66.4
hydrocarbons	19.7

"The reaction liquid contained, detected at once by odor, acetaldehyde.

"In this and the last experiment of Table I the presence of formaldehyde was established. The carbohydrate reaction failed to appear in every case.

"The decomposition picture is essentially the same at ordinary temperatures as at the boiling point of alcohol. Only the presence of water leads to the more copious appearance of carbon dioxide from carbon monoxide whose reduction becomes less at the lower temperatures. The hydrocarbon consisted predominantly of methane, so that both typical reactions stood out sharp."

It seems probable that there are two primary reactions in the photochemical decomposition of ethyl alcohol: one, the formation of hydrogen and acetaldehyde; the other the dehydration of the alcohol to give ethylene and water. The photochemical decomposition of the aldehyde then follows with the formation of carbon monoxide and methane. Because of this primary decomposition of alcohol into aldehyde, the photochemical reactions of these should be considered together. Before proceeding with any further discussion of the alcohol reactions, those of acetaldehyde will, therefore, first be described.

Acetic Aldehyde

The following table shows the results which have been obtained in the photochemical decomposition of acetic aldehyde:

	CO_2	CO	H_2	C_nH_{2n+2}	C_2H_4
Berthelot and Gaudechon	5.0	39.0	33.0	23.0*	
Losanitsch	—	high	low	high**	low
Löb (25% solution)	6.7	33.0	32.5	27.8**	
de Hemptinne		41.0	20.0	39.0**	
Jackson and Northall-Laurie		45.2	0.4	44.2**	8.6***

*C_2H_6
**CH_4
***C_2H_2

Berthelot and Gaudechon[1] conclude that the photochemical reaction with acetaldehyde is

$$2CH_3CHO = C_2H_6 + 2CO + H_2.$$

"The photolysis of the primary aldehyde group COH is characterized by the predominance of carbon monoxide. It is accompanied by hydrogen. One also finds a few cubic centimeters of carbon dioxide. That corresponds actually to the point of view of oxidation, the aldehyde stage being intermediate between the alcohol stage and the acid stage.

"In the evolved gaseous mixture, with the first members of the fatty acid series RCOH, we have detected the hydrocarbons R_2 formed by the doubling of the radical R; with the higher members of the normal chain series, the hydrocarbons R_2 are no longer formed, they not being gaseous."

Losanitsch[2] concluded that the principal reaction results in the formation of carbon monoxide and methane, but claimed to have found also hydrogen,

---

[1] Compt. rend., 151, 1351 (1910).

[2] Ber., 42, 4397 (1909).

ethylene, and formaldehyde. "Acetaldehyde[1] condenses under the action of the silent electrical discharge with strong liberation of gas (up to 20 bubbles per minute), whereby about 80% of the aldehyde used is decomposed and only 20% condenses. This gas consists of equal volumes of carbon monoxide and methane, besides a small amount of hydrogen and ethylene. The principal decomposition of acetaldehyde is therefore:

$$CH_3CHO = CO + CH_4.$$

"Moreover, a considerable amount of formaldehyde is formed which further polymerizes.

"That portion of the acetaldehyde condensed by the discharge is a greenish yellow, mobile liquid which has an aldehyde odor and also shows aldehyde reactions. It is easily soluble in alcohol and ether, but only partially in water.

"The crude product boils from 70° to 190°; the distillate has a greenish yellow color and pungent odor. The fresh distillate does not act on litmus paper, but with standing the reaction becomes strongly acid, which in any case is to be attributed to oxidation of the aldehyde. By distillation I have obtained the following products:

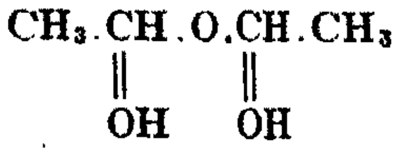
B.P.	70-90°	100-120°	130-150°
C	45.31	45.51	49.02
H	9.75	8.62	8.12
O (diff.)	44.94	45.87	42.86

		Corresponding formula	
	$C_4H_{10}O_3$	$C_8H_{16}O_6$	$C_9H_{18}O_6$
C	45.28	45.71	48.65
H	9.44	8.58	8.11
O	45.28	45.71	43.24

"According to their composition these compounds are all aldehyde-like polymers of acet- and formaldehyde:

$C_4H_{10}O_3$ is $2C_2H_4O.H_2O$
$C_8H_{16}O_6$ is $2CH_2O.3C_2H_4O.H_2O$
$C_9H_{18}O_6$ is $3CH_2O.3C_2H_4O$

"The diacetaldehyde hydrate, $2C_2H_4O.H_2O$, is in any case the first anhydride of acetaldehyde hydrate."



$$\underset{\displaystyle OH}{\overset{}{CH_3.CH}}.O.\underset{\displaystyle OH}{CH}.CH_3$$

Löb's results cannot be compared directly with the others because he used an aqueous solution of aldehyde. "In the absence of water the vapor of acetaldehyde decomposed into methane and carbon monoxide; the methane yielded free hydrogen. In the presence of water a partial conversion of the carbon monoxide occurred into carbon dioxide and hydrogen, whereby the content of the latter is increased. The results of an experiment of three hours' duration with a 25% aqueous solution under an atmosphere of nitrogen, with direct current, were as follows:

	cc	%
CO_2	1.4	6.7
CO	6.9	33.0
H_2	6.8	32.5
CH_4	5.8	27.8"

de Hemptinne obtained these same gases in different proportions.

"Under the same conditions as with the other substances aldehyde gives:

carbon monoxide	41%
hydrogen	20%
methane	39%

"Aldehyde therefore decomposes according to this equation: $CH_3CHO = CO + CH_4$. It is interesting to compare aldehyde with acetic acid, which gives $C_2H_4O_2 = C_2H_4 + O_2$ and shows us how the mutual attraction of the elements can be changed through the introduction of an atom of oxygen in the molecule."

Jackson and Northall-Laurie found evidence of two distinct reactions.

"In the case of acetaldehyde a double reaction apparently takes place. Analyses of many samples of the gaseous products showed the presence of methane, carbon monoxide, and acetylene in large quantities, together with a very little hydrogen and other hydrocarbons. The proportions of these gases varied somewhat, but by working with discharges of very short duration it was possible to prove that the vapors of acetaldehyde decomposed partly into carbon monoxide and methane and partly into acetylene and water.

"The average composition of the gas freed from water and the vapor of aldehyde and obtained with discharges of short duration is shown by the following numbers:

CO	CH_4	C_2H_2	H_2
45.2	44.2	8.6	0.4

(percentage by volume)

"The presence of water as one of the products was ascertained in each experiment, but it was found difficult to obtain concordant results for the small amounts formed. From these numbers it will be seen that about eighty percent of the vapor of the aldehyde yielded carbon monoxide and methane, whilst the remainder was converted into acetylene and water. The changes took place apparently simultaneously and were the primary reactions, whilst the formation of any hydrogen and other hydrocarbons was probably due to secondary changes, as the amounts of the gases only became appreciable when the discharge was continued for a minute or two. A relatively considerable quantity of the main products was obtained by a mere flash of the discharge.

"The reaction giving rise to acetylene and water is apparently a reversible one, as when steam and acetylene were subjected to the discharge it was found possible by removing the products quickly to detect an aldehyde readily and to prove that it was acetaldehyde. An aldehyde was also obtained from carbon monoxide and methane treated similarly, but the quantity was small and there was certainly some formaldehyde produced. It is possible that the greater readiness of acetylene and water to form aldehyde may well account for the observed fact that the proportion of acetylene and water to carbon dioxide and methane was greater the shorter the duration of the discharge.

"We conclude, therefore, that the immediate action of high frequency discharges on the vapor of acetaldehyde is represented by the equations:

$$CH_3.CHO = CO + CH_4$$
$$CH_3.CHO = C_2H_2 + H_2O."$$

From the results so far reviewed, of the action of the electric discharge on ethyl alcohol, there is every reason to believe that the chief primary decomposition is into acetaldehyde and hydrogen. Occurring, also, but to a less extent, is the decomposition into ethylene and water. Every investigator, with the exception of de Hemptinne, detected the presence of large amounts of acetaldehyde. It is inconceivable that among his decomposition products, this compound was not also found, particularly since the analysis of his gaseous product shows substantially the same composition as that obtained by the others.

Furthermore, with regard to his results, it was shown (p. 1619) that in his experiments in the presence and absence of phosphorous, the ratio of carbon monoxide to hydrocarbon remained essentially the same, which would lead to the conclusion that the effect of the phosphorus is to retard the decomposition of the aldehyde which is first formed.

Because ethyl alcohol is decomposed first into acetaldehyde and hydrogen, it follows that any other gaseous products, with the exception of ethylene, probably come from subsequent decomposition of the acetaldehyde. The first photochemical action on the acetaldehyde is the splitting off of the CO group:

$$CH_3CHO = CH_3 + H + CO$$

which explains the relative abundance of this gas in the evolved products.

After this first separation there are two possibilities: either the formation of CH_4 from the CH_3 and H or the formation of C_2H_6 and H_2. Leaving out for the moment the decomposition into acetylene and water, acetaldehyde may therefore be decomposed photochemically in two ways:

$$2CH_3CHO = C_2H_6 + H_2 + 2CO \qquad (1)$$

$$CH_3CHO = CH_4 + CO \qquad (2)$$

In whichever way the decomposition occurs, the amount of CO should be equal to the total amount of C_nH_{2n+2} and H_2. But only Jackson and Northall-

Laurie (and possibly Losanitsch) obtained this result, and it must be concluded that the CO first formed, disappeared by some subsequent reaction or dissolved in the condensed liquid.

If ethyl alcohol goes first to acetaldehyde and the latter then decomposes as just shown, it would be expected that the ratio of CO to C_nH_{2n+2} will be the same for alcohol and aldehyde in any given apparatus. Only two sets of results are available to test this hypothesis:

		Vol. CO	Vol. C_nH_{2n+2}	CO/C_nH_{2n+2}
Berthelot and Gaudechon	C_2H_5OH	22	15	1.5
	CH_3CHO	39	23	1.7
de Hemptinne	C_2H_5OH	22	48	0.46
	CH_3CHO	41	39	1.05

It must be concluded that some other reaction occurs in order to give such divergent results as those of de Hemptinne. Those of Berthelot and Gaudechon are close enough to lend some support to the hypothesis.

Acetone

A consideration of the results which have been obtained show that the photochemical decomposition of acetone is not a simple breakdown into CO and C_2H_6:

		CO_2	CO	H_2	C_nH_{2n+2}	C_2H_4
Berthelot and Gaudechon		—	49.0	—	51.0*	—
Maquenne	low pressure	1.1	37.5	24.7	32.4**	4.3
"	50 mm.	1.1	40.0	25.7	29.7**	3.5
"	100 mm.	0.6	42.1	24.4	30.0**	2.9
de Hemptinne		2.0	48.5	11.0	37.0	1.5
Poma and Nesti		1.6	38.1	—	55.3	5.0***

*5% CH_4; 46% C_2H_6
**C_2H_6
***$C_2H_2 + C_2H_4$

Berthelot and Gaudechon find the photochemical decomposition of acetone very simple. "Ordinary acetone decomposes in a few minutes and gives 49 volumes of CO and 51 volumes of a mixture which is composed of 46 volumes of ethane and 5 volumes of methane. The aqueous solution of acetone gives 1 volume of CO_2, 44 volumes of CO, and 55 volumes of a mixture which comprises 46 volumes of C_2H_6 and 9 volumes of CH_4.

"The high proportion of carbon monoxide as well as the rapidity of evolution is a conspicuous characteristic of the ketone group and has already been pointed out for levulose. . . .

"In no case does the decomposition of a ketone give hydrogen. That distinguishes them from the aldehydes and corresponds entirely to the difference in the formulas CO and CHO."

---

[1] Compt. rend., 151, 1351 (1910).

Again they say:[1] "The photolysis of the secondary aldehydes (ketones) give carbon monoxide, as those of the primary aldehydes, but are distinguished by the absence of hydrogen. The type of decomposition of ordinary acetone, which decomposes very rapidly into carbon monoxide and ethane

$$CH_3COCH_3 = CO + C_2H_6$$

appears to again take place in the higher chain ketones, such as methylnoylketone, $C_{11}H_{22}O$ (liquid), and palmitone, $C_{31}H_{62}O$ (solid), but the hydrocarbons which are formed being liquids or solids, the evolved gas, of which the quantity is moreover very small, is composed solely of carbon monoxide."

Maquenne appears to completely overlook the hydrogen which is evolved when he says: "The ease with which CO is produced in all of the preceding decompositions makes us think that acetone would double its volume, by the discharge, into CO and C_2H_6; the experiment has completely verified that prediction.

"One could not measure the low pressure because of the enormous pressure of the acetone at the temperature of the experiment. The composition of the gas varies little with the pressure, moreover, CO and C_2H_6 always dominating."

de Hemptinne found that the composition of the evolved gases is the same in the presence and in the absence of phosphorus. "This other isomer of allyl alcohol gives under the same conditions:

carbon dioxide	2
hydrocarbon C_nH_{2n}	1.5
carbon monoxide	48.5
hydrogen	11
hydrocarbon $C_2H_6+CH_4$	37

"Acetone appears therefore to decompose first into carbon monoxide and ethane, whereby secondary methane is formed

$$CH_3-CO-CH_3 = C_2H_6 + CO$$

"According to the analysis, allyl alcohol appears to decompose in an entirely different manner than the two isomers, acetone and propyl alcohol, which both decompose in about the same way.

"The constitutional formula of allyl alcohol is $CH_2=CH-CH_2OH$; the hydrocarbon nucleus which contains a double bond, seems therefore to better withstand a physical stress than the analogous nucleus of propylaldehyde C_2H_5-CHO and of acetone $CH_3-CO-CH_3$, in which the oxygen appears to be more tightly bound.

"From the chemical standpoint a nucleus with a double bond is less stable in the sense that it reacts more easily with other elements; moreover, experience teaches that with energetic oxidation, the hydrocarbon splits at the place where the multiple bond occurs. One can therefore draw here the same conclusion as before, namely, that the chemical constitutional formula does not necessarily tell the location of the strongest bond considered from the mechanical standpoint.

"In order to be able to meet all objections, I made several other experiments in another apparatus in the presence of phosphorus and without phosphorus.

	Without Phosphorus	With Phosphorus
carbon dioxide	1.5	2
hydrocarbons C_nH_{2n}	1	1.5
carbon monoxide	30	28
hydrogen	20	17
ethane and methane	47.5	51.5

"One can see from these experiments that the carbon monoxide splits off from the molecule as an entity, because otherwise one would have to find much less carbon monoxide, as was the case with alcohol, in the presence of phosphorus because of the absorption of oxygen."

It would have been interesting if de Hemptinne had given the relative rates of decomposition in the presence and absence of phosphorus.

Poma and Nesti's results are valuable because they showed a complex residue after the decomposition. "We then proceeded to study the effect of the discharge on acetone vapor. In this case the conductivity of the acetone vapor was comparatively high compared with the preceding cases. Keeping all other conditions constant, the intensity of the current which passed was comparatively high. At the same time the luminosity in the ozonizer was also relatively high. On the other hand, the volume of gas produced was small.

"The analysis of the gas was:

CO_2	1.6%
$C_2H_2+C_2H_4$	5.0
CO	38.1
$CH_4+C_2H_6$	55.3

"The reaction proceeds in the vapor phase according to the equation:

$$CH_3COCH_3 = CO + C_2H_6$$

"The distillation residue when redistilled left an oily yellow residue of high density which may contain acetonyl-acetone. Using Knorr's γ diketone reaction, we treated a small portion of the liquid with excess glacial acetic acid and ammonia, boiled for one minute, added dilute sulfuric acid and dipped a pine splint in the boiling solution. The wood was colored deep red. The Ehrlich test also was positive, indicating that the reaction products formed from acetone by the silent discharge contain appreciable quantities of a γ diketone, probably acetonyl-acetone."

The results of Poma and Nesti show that the decomposition of acetone in the discharge is not as simple as Berthelot and Gaudechon found with the quartz mercury lamp. While the principal reaction may result in the formation of CO and C_2H_6, other reactions also occur which give not only different gaseous products but also new compounds in the liquid residue.

Acetic Acid

In the photochemical decomposition of acetic acid, there is fair agreement among the results, with the exception of those of de Hemptinne:

	CO_2	CO	H_2	C_nH_{2n+2}	C_2H_4
Berthelot and Gaudechon	41	14	13	32*	—
Maquenne 2 mm.	20.7	33.9	4.5	38.5**	2.4****
" 50 mm.	11.6	42.6	24.9	19.5**	1.3
" 100 mm.	9.6	44.6	34.4	11.5**	0.3
Poma and Nesti	35.4	18.5	28.3	17.3	—
de Hemptinne	22	10		18***	50

*13% CH_4; 19% C_2H_6
**CH_4
***Includes H_2
****C_2H_2 and C_2H_4

In the fatty acid series and in passing from the alcohols to the acids, Berthelot and Gaudechon[1] point out the relation between the gaseous product obtained to the composition of the compound.

"The photolysis of the acid group CO_2H is characterized by the predominance of carbon dioxide; it is accompanied by hydrogen and carbon monoxide. In the first members of the normal fatty acid series, $R.CO_2H$, we have pointed out some of the hydrocarbons composed of R_2 as well as methane. That characteristic is found again in the higher chain acids, butyric $C_4H_8O_2$, heptylic $C_7H_{14}O_2$, caprylic $C_8H_{16}O_2$, capric $C_{10}H_{20}O_2$, palmitic $C_{16}H_{32}O_2$, and stearic $C_{18}H_{36}O_2$. As before, when one advances in the series, the evolution of gas decreases while the quantity of gaseous hydrocarbons decreases, then disappearing completely."

They also say:[2] "The acid radical CO_2H is characterized by an abundance of CO_2 which forms 40 to 60 volumes; to this is added 15 to 20 volumes each of CO and H_2.

"When one passes from alcohols to aldehydes and to acids the quantity of hydrogen decreases and that of carbon dioxide increases."

Maquenne[3] postulates two successive reactions to explain his results, although it is simpler to conclude that there are two primary reactions.

"Glacial acetic easily decomposes in the discharge. . . .

"One sees that this body gives birth in the first reaction, to carbon dioxide and methane. These two gases react immediately with each other, as in the experiments of Thenard, and one sees appear a large quantity of carbon monoxide and hydrogen. There are formed also some of the non-volatile polymers which remain at the bottom of the discharge tube."

---

[1] Compt. rend., 151, 1351 (1910).
[2] Compt. rend., 151, 479 (1910).
[3] Bull., 40, 62 (1883).

Poma and Nesti[1] do not explain the presence of carbon monoxide in the decomposition products. "We also repeated this experiment with acetic acid and obtained a gas with the composition:

CO_2	35.4%
CO	18.5
CH_4, C_2H_6	17.3
H_2	28.3
	99.5%

". . . Since the reaction is more complex, two different causes of the reaction may be considered corresponding to the equations:

$$(1)\quad 2CH_3CO_2H = 2CO_2 + C_2H_6 + H_2$$

$$(2)\quad CH_3CO_2H = CH_4 + CO_2$$

"The liquid remaining in the flask distilled without residue."

Another possible reaction is a breakdown into CO and H_2:

$$CH_3COOH = 2CO + 2H_2$$

According to this, a volume of hydrogen equal to the volume of carbon monoxide will be formed. If, then, this amount of carbon monoxide is subtracted from the total quantity of hydrogen, there will be left $28.3 - 18.5 = 9.8\%$. The volumes of gases remaining then have a striking relation to the volumes in equation (1).

	% Remaining	Corrected %	% in Equation (1)
CO_2	35.4	56.6	50
$CH_4 + C_2H_6$	17.3	27.7	25
H_2	9.8	15.7	25

de Hemptinne obtained results far different from anyone else. He gives a simple but inadequate explanation.

"Acetic acid gives

carbon dioxide	22%
hydrocarbon C_2H_{2n}	50
carbon monoxide	10
hydrogen and hydrocarbon C_nH_{2n+2}	18

"Acetic acid, $C_2H_4O_2$, appears to give as the first decomposition product $C_2H_4 + O_2$; other explanations are scarcely admissible, because the presence of a large amount of ethylene does not agree with the assumption that CO_2 is separated as an entity."

In the experimental work in this laboratory on methyl alcohol, ethyl alcohol, acetaldehyde, acetone, and acetic acid, results have been secured which in several cases show more clearly the course of the reactions than the results in the work which has been reviewed.

---

[1] Gazz., **51** II, 87 (1921).

Apparatus

It has already been pointed out that the apparatus which we used was unique in allowing photochemical reactions with the Tesla discharge to be carried out at high temperatures, although in not every case was this feature utilized.

Our apparatus consisted essentially of four parts; the electrical circuit which generated the high-frequency current; the ozonizer which was comprised of concentric glass tubes through which the vapors and high frequency discharge passed; the flask containing the boiling liquid; the receiving apparatus for collecting the undecomposed vapor and the liquid and gaseous decomposition products.

The electrical circuit is shown in Fig. 3. B represents a 10,000 volt transformer for use on 110 volt A.C. and with a capacity of 250 watts. A represents an A.C. ammeter and C a single-pole switch. Three Leyden jars, 15 cm. in diameter and with tinfoil 16 cm. high, are shown at L. S represents a variable spark gap, with zinc terminals. This was placed in a wooden box, tightly covered to confine the ozone and permit less noisy operation. I represents a variable inductance for tuning the primary with the secondary Tesla circuit.

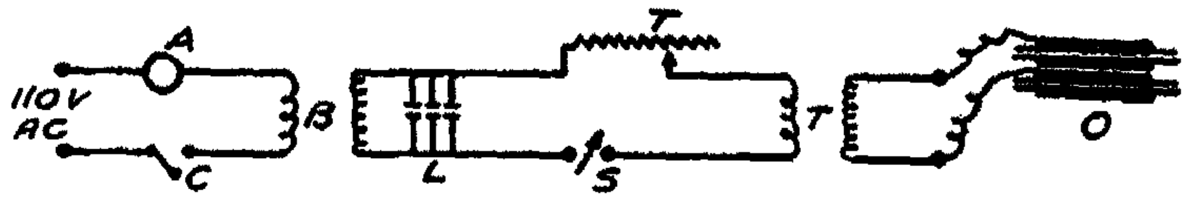


Fig. 3

T represents the Tesla coil. There were two turns in the primary and 65 in the secondary. The secondary coil was wound on a wooden frame approximately 22 cm. in diameter and 50 cm. long. This combination of turns was used because it was found by trial to work best with the rest of the circuit. It will be well to emphasize here the importance of correct tuning; it will no doubt be sufficient to state that the number of turns in the Tesla coil and the number of Leyden jars can be selected by trial so that a good discharge will be obtained in a particular discharge tube. If the number of turns is not quite correct, or too many or too few condensers are used, the discharge will be weak. In this regard it is interesting to note the remark of Jackson and Northall-Laurie on tuning (p. 1607).

It was found that the best results were secured by using sufficiently large wire in all parts of the circuit. From the wall plug to the primary of the transformer, ordinary heater cord, No. 18 wire, was used; from the secondary to the Leyden jars, No. 20 bare copper wire; from these condensers to the primary of the Tesla, No. 14 bare copper wire was used. In this part of the circuit conduction is mostly on the surface of the wire and a large diameter is necessary. The secondary of the Tesla coil was of No. 20 annunciator wire, while the primary was No. 14. From the secondary of the Tesla to the discharge tube, No. 22 bare copper wire was used.

All of the electrical apparatus was elevated so that it could not be touched accidentally and the only wires near the apparatus were those from the secondary of the Tesla circuit. Since they carried high frequency current, they were not dangerous.

During operation the terminals of the variable spark gap were from 5 to 8 mm. apart; the current in the 110 volt circuit usually remained at 3.6 amperes, although it varied occasionally from 3.4 to 3.8 amperes.

O represents the ozonizer. The type which was finally found most satisfactory was designed after trials with several different types.

The first ozonizer was something like Fig. 4. Both tubes were of pyrex glass. The diameter of the outer tube was 35 mm. inside, and the outer diameter of the inner tube was 20 mm.

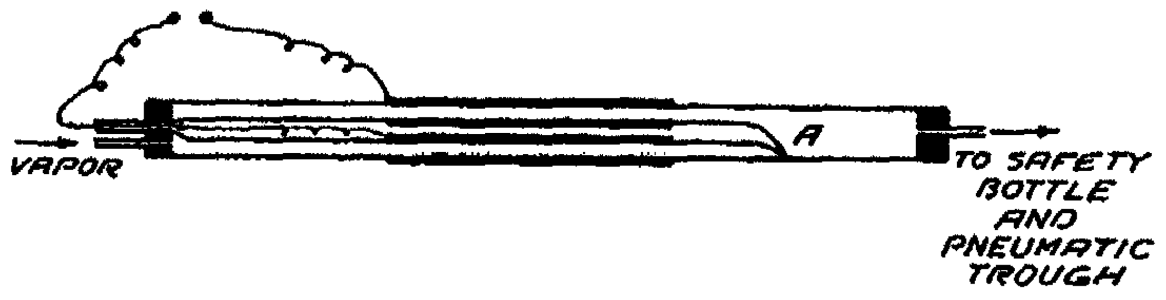


FIG. 4

At A the inner tube was drawn out and sealed and the end was bent down so that it supported the tube exactly in the center of the outer tube.

The coatings (30 cm. long) on the outside of the outer tube and on the inside of the inner tube consisted of copper electroplated on silver. The silver was deposited by Brashear's method, the tubes being first cleaned with a solution of stannous chloride, then rinsed, and then treated with nitric acid, and given a final rinsing with distilled water.

This ozonizer was not perfectly satisfactory because the tubes were too large and the discharge space or distance too great. For that reason, the next ozonizer was constructed with smaller tubes. The new outer tube was 20 mm. outside, and 17 mm. inside. The inner tube was 9 mm. outside. The distance through which the discharge passed was now 4 mm., whereas in the first ozonizer it was 6 mm. The cross sectional area of the discharge space was also smaller, being now about 1.65 sq. cm., where before it had been 3.65 sq. cm. The use of these smaller tubes was satisfactory from the standpoint of having a more restricted space through which the discharge passed. It was actually found that the discharge was more constant and even than before, and that the vapors and gases were swept along better. The rate of decomposition was also higher.

The small size of the tubes, however, made it impossible to use the same arrangement for the entrance of the vapor and for the electrical connection with the coating of the inner tube. A new design was therefore used: At the point where the wire connecting the inner tube passed in there was a free opening so that no difficulty arose from sealing the wire in glass. This arrangement had the distinct advantage of allowing the freest possible passage to the vapor and gases. It had the disadvantage of being somewhat difficult to construct and of being rather fragile. In the next type these disadvantages were overcome, but before describing the next design, some special problems which were encountered with the small tubes but not encountered when using the big tubes, should be discussed.

Since the new inner tube was so small (only 7 mm. inside) it was almost impossible to first deposit silver on the inner wall and then plate copper on electrolytically. Recourse was had to another method which proved very simple and satisfactory. The method depends on the decomposition of copper formate by heating:

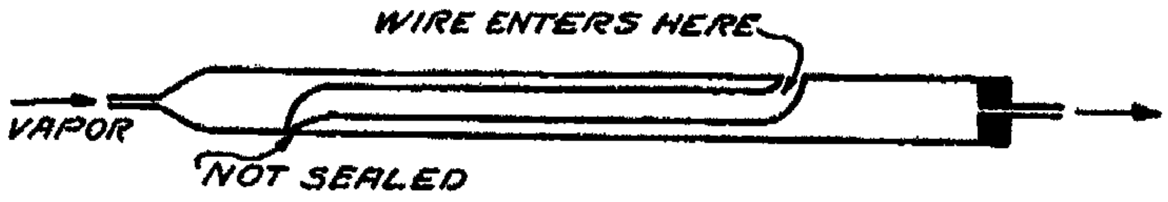


FIG. 5

$$Cu(HCO_2)_2 = Cu + H_2O + CO + CO_2.$$

The tube to be plated was filled with copper formate which had been dried at 105° and then powdered in a mortar. The tube so filled was held oblique and heated slowly and carefully over a Bunsen burner. The tube was heated from the top downward to prevent the evolved gases from blowing out the copper formate. If the operation is carefully performed, an even, adherent film of copper is obtained on the glass. The coating on the outer tube was also changed. The tightly adherent silver-copper coating was replaced by a thin copper foil wound on and secured with wire. It is scarcely proper to call this a coating, since it was not in optical contact with the glass. It appeared to work as well as the first coatings and was subsequently changed only by substituting aluminum foil for the copper. The aluminum lasted indefinitely without oxidizing or melting at the operating temperatures.

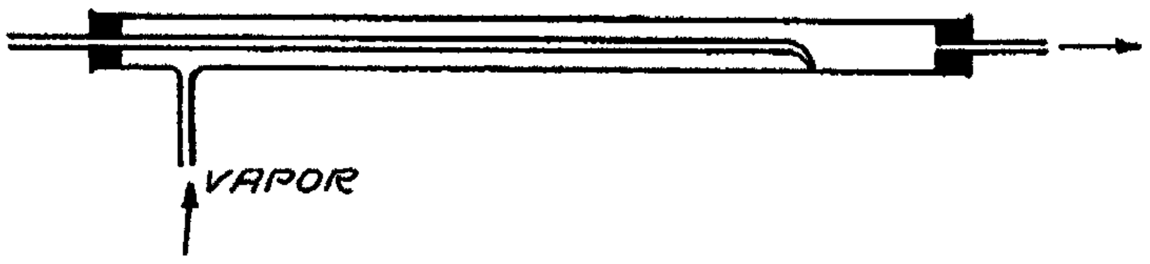


FIG. 6

The next type of ozonizer was somewhat simplified because it was not necessary to seal the inner tube into the outer tube, Fig 6. The end of the inner tube was drawn out and bent as before to hold the tube in the center. The vapor entered through a side arm and the gases had a free exit. This type proved very satisfactory. It was easily made and assembled and quite readily replaced in case of breakage. However, since the breakage in service was rather high, one change was made. A separate tube, 30 cm. long and of the same diameter as the other tube, was provided with a side arm. This short tube was connected to the discharge tube by means of rubber tubing: In case of breakage of the discharge tube, this short tube could be used again. It eliminated sealing a side arm on each new discharge tube.

With this new design of ozonizer, the copper coating on the inside of the inner tube was abandoned in favor of a bare copper wire, about 7 mm. in diameter, just small enough to slide in the inner tube. This was satisfactory in operation and replacement was very easy.

The side arm from the ozonizer was connected directly to the flask containing the boiling liquid. To provide a steady flow of vapor through the discharge tube and prevent spasmodic boiling, an ebullator tube was always used in the flask, an electric coil was used for heating, and the flask was protected from drafts with an asbestos cylinder.

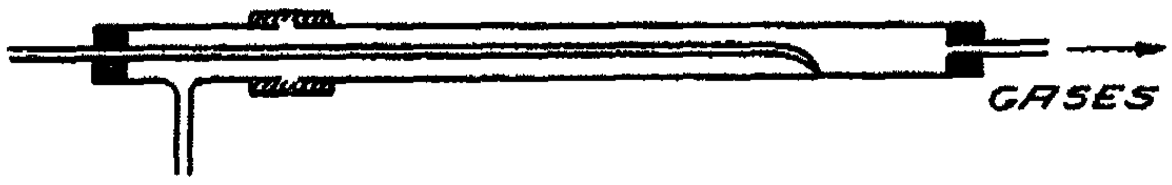


Fig. 7

For heating the ozonizer a 20-burner gas combustion furnace was used and to insure even heating the outer tube was laid on a layer of asbestos paper. The temperature was measured by means of a thermometer secured to the top of the tube and insulated with several layers of asbestos paper to prevent loss of heat by radiation.

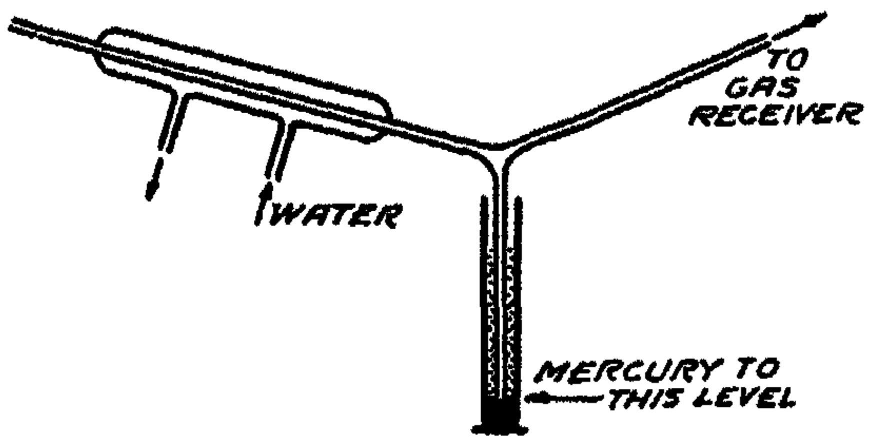


Fig. 8

The receiving end of the apparatus was made as follows:

This arrangement permitted the continuous collection of the gases and liquid without the admission of air. The gases were collected in bottles in a pneumatic trough.

Method of Analysis

The analyses of the gas were made according to the directions given in Dennis' "Gas Analysis," and were briefly as follows:

Gas removed	Solution in Gas Pipette
CO_2	NaOH 1:2
Olefines	15-20% fuming H_2SO_4
SO_3	NaOH 1:2
O_2	alkaline pyrogallol
CO	ammoniacal Cu_2Cl_2
NH_3	5% H_2SO_4

The hydrogen was next taken out by combustion over CuO at a temperature of 270°, and the residue was then burned in a Dennis combustion pipette.

The olefines were treated several times in a pipette containing ammoniacal silver solution in order to remove the acetylene without taking out the ethylene, although Ross and Trumbull[1] have shown that this method is only approximate.

Experimental Results

Methyl Alcohol

Methyl alcohol was decomposed at a temperature of 75°. The outer tube was 18 mm. outside, 15 mm. inside; the inner tube was 6 mm. outside; the coating was 40 cm. long.

The gaseous product consisted only of carbon monoxide and hydrogen in the following proportions:

CO	7.5%
H_2	92.5

This result indicates that the principal reaction is:

$$CH_3OH = HCOH + H_2$$

The original alcohol contained only a trace of formaldehyde as determined by the method of Georgia and Morales.[2] It was found that the condensate always contained a relatively large amount, and in one particular experiment it contained between 0.5 and 1.0% of formaldehyde. From the volume of hydrogen obtained in this experiment, it was calculated that the condensate should contain 0.75% of formaldehyde. Considering the limit of accuracy of this method of determining formaldehyde, the check of the amount of formaldehyde with the equivalent amount of hydrogen is sufficiently good to conclude that the principal reaction with methyl alcohol is its decomposition into formaldehyde and hydrogen.

It is not difficult to account for the formation of 7.5% of carbon monoxide. It may either be formed from formaldehyde as follows:

$$HCHO = CO + H_2$$

or from methyl alcohol:

$$CH_3OH = CO + 2H_2$$

The second reaction was concluded by Jackson and Northall-Laurie to be the principal reaction of methyl alcohol in the decomposition by the high frequency discharge. On the other hand, Russ[3] showed that formaldehyde is decomposed at 150° by the silent electric discharge into CO and H_2, and it was further shown by Löb[4] that formaldehyde plus water vapor under the influence of the silent discharge gives CO and H_2.

Jackson and Northall-Laurie operated under reduced pressure and it is easily possible that, even with the brief discharges which they used, the amount

---

[1] J. Am. Chem. Soc., 41, 1180 (1919).

[2] Ind. Eng. Chem., 18, 304 (1926).

[3] Z. Elektrochemie, 12, 412 (1906).

[4] Z. Elektrochemie, 11, 751 (1905).

of energy was so great for the quantity of alcohol present that the primary reaction product, formaldehyde, decomposed into CO and H_2 before the discharge ceased.

It may be concluded, therefore, that the primary photochemical reaction with methyl alcohol is the formation of formaldehyde and hydrogen in every case. A secondary reaction is the formation of carbon monoxide and hydrogen from the formaldehyde.

Our results agree with those of Berthelot and Gaudechon except that they obtained 5% of CO_2. They ascribe this to the reaction between formic acid formed from the alcohol with a small amount of oxygen present in the reaction tube.

The formation of methane found by Maquenne, de Hemptinne, and Jackson and Northall-Laurie is the result of still another reaction. It was found by Brodie[1] that carbon monoxide and hydrogen would give methane and water under prolonged action by the silent discharge. This undoubtedly happened with these investigators. de Hemptinne operated his tube for long periods of time. It has already been shown that Jackson and Northall-Laurie probably had a very high concentration of photochemical energy acting on a small amount of vapor, while Maquenne found that as the pressure in his apparatus decreased, and the amount of energy per unit of weight of vapor thereby increased, the relative amount of methane became greater. It may be concluded, therefore, that one reaction, under suitable conditions, in the discharge tube can be:

$$CO + 3H_2 = CH_4 + H_2O$$

Ethyl Alcohol

Ethyl alcohol was decomposed at temperatures just above the boiling point and at nearly 400°. The results of several experiments checked closely at the same temperature; also at these widely different temperatures very little difference in composition was found:

	85°	380°
$C_2H_2 + C_2H_4$	10.4	10.3
CO	21.6	22.7
H_2	53.8	52.9
C_nH_{2n+2}	14.2	14.1

The mixture of unsaturated hydrocarbons was about 25% ethylene and 75% acetylene.

The outer tube used with ethyl alcohol was 17 mm. outside and 14 mm. inside; the inner tube was 6 mm. outside. The coating was 40 cm. long.

The condensed liquid had the odor of acetaldehyde and readily reduced an ammoniacal silver solution. No quantitative determination of the amount of aldehyde was made.

In the review of the literature on ethyl alcohol, it has been pointed out that probably the chief primary reaction is the formation of acetaldehyde and hydrogen. Another primary reaction is the dehydration of the alcohol to form ethylene and water.

---

[1] Ann., 169, 270 (1873).

It is probable that the formation of carbon monoxide and the saturated hydrocarbons results from the decomposition of the acetaldehyde, and for that reason it will be more interesting to discuss together the reactions of alcohol and aldehyde after giving the results obtained with acetic aldehyde.

The rates of decomposition of ethyl alcohol at 100° and 380° were 16.7 and 83.3 cc. per minute, respectively. The ratio of the reaction velocities over this range is therefore 1.06 per 10°.

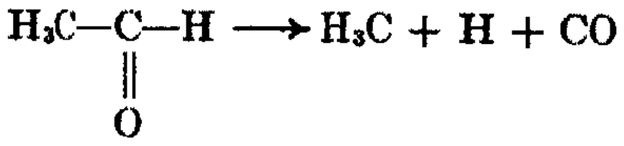
Acetaldehyde

Acetic aldehyde was decomposed at several temperatures, ranging from 40° to 340°. The outer tube had a diameter of 19.5 mm. outside and 17.0 mm. inside. The inner tube was 6.1 mm. outside and 4.7 mm. inside. The coating on the outer tube was 27 cm. long, except in the experiment at 40°, where it was 25 cm. The tube was water-jacketed in the experiments made at 40°, 70° and 80°.

Because of some solution of the gases, particularly carbon monoxide, in the condensate on the walls of the reaction tube in the experiments at 40° and 70°, the results cannot be considered to give an accurate picture of the gaseous products at these temperatures. (This probably happened also in some of the previous work where the percentage of carbon monoxide was low—see p. 1625). The results at 40° and 70°, however, do help to show a trend in the proportions of the constituents and for that reason are included here:

	40°	70°	210°	320°
CO_2	2.3	—	—	—
C_2H_2 or C_2H_4	0.0	3.5	1.3	0.3
CO	35.5	46.2	49.8	49.3
H_2	39.4	27.7	16.7	10.8
$CH_4 + C_2H_6$	22.8	22.6	32.1	39.6

At the higher temperatures carbon monoxide comprises about one-half of the gaseous product. It may be concluded that the primary action of the discharge on aldehyde is to split off the CO group in this fashion:



$$H_3C-\underset{\underset{O}{\|}}{C}-H \longrightarrow H_3C + H + CO$$

From the H and CH_3 there is either the possibility of the formation of ethane and hydrogen:

$$2CH_3 \longrightarrow C_2H_6$$

$$\text{and} \quad 2H \longrightarrow H_2$$

or the formation of methane:

$$CH_3 + H \longrightarrow CH_4$$

Acetaldehyde may therefore be decomposed in two ways photochemically:

$$2CH_3CHO \longrightarrow C_2H_6 + H_2 + 2CO \qquad (1)$$

$$\text{or} \qquad CH_3CHO \longrightarrow CH_4 + CO \qquad (2)$$

It will be observed that the proportion of the products is not the same at all temperatures, but it is interesting to note that at 210° the volume ratio of $CO:H_2:C_nH_{2n+2}$ is very close to 3:1:2, a condition which would be true if reactions (1) and (2) occurred to an equal extent:

$$\begin{array}{c} 2CH_3CHO = C_2H_6 + H_2 + 2CO \\ CH_3CHO = CH_4 + CO \\ \hline 3CH_3CHO = C_2H_6 + CH_4 + H_2 + 3CO \\ \text{or } 3 \text{ vol } CH_3CHO = 3 \text{ vol } CO + 1 \text{ vol } H_2 + 2 \text{ vol } C_nH_{2n+2} \end{array}$$

When discussing ethyl alcohol it was pointed out that some of the gaseous decomposition products probably came from the acetaldehyde which was first formed from the alcohol. An interesting relation between the products formed from aldehyde and alcohol may now be observed. Because the first reaction in the decomposition of alcohol is the formation of acetaldehyde, it would be expected not only that the products obtained would be the same but that the ratio of CO to C_nH_{2n+2} when decomposing alcohol would be the same as when decomposing pure acetaldehyde. The relation is actually close if the results at 210° are used:

	CO	C_nH_{2n+2}	CO/C_nH_{2n+2}
CH_3CHO (210°)	49.8	32.1	1.55
C_2H_5OH (85°)	21.6	14.2	1.53
C_2H_5OH (380°)	22.6	14.1	1.60

The hydrogen cannot be included in this ratio because there is not complete decomposition of the aldehyde which is formed from alcohol. Because reaction (2) of acetaldehyde begins to predominate at higher temperature, this ratio will of course change as the temperature rises.

One of the most interesting features in the photochemical decomposition of alcohol and acetaldehyde is that the composition of the gaseous decomposition product of alcohols is practically the same at low and high temperatures, while with acetaldehyde it is different. With acetaldehyde, two reactions occur to more or less equal extent at low temperatures, while at high temperatures, one reaction tends to predominate. There are two explanations but we believe that this fact is most probably evidence of depolarization by heat.

The first explanation is that when decomposing alcohol, the alcohol vapor in the discharge tube may absorb most of the photochemical energy in the wave-lengths which are necessary to decompose aldehyde. The fact that the rate of decomposition of alcohol is only one-third that of aldehyde shows that the total energy required for decomposition is greater for alcohol than for aldehyde.

If the wave-lengths absorbed by the alcohol are those which would decompose the aldehyde, a close connection between these photochemical reactions and contact catalysis can be pointed out. Bancroft[1] has cited a case which may be considered an interesting analogy.

---

[1] J. Phys. Chem., 27, 853 (1923).

"Copper and nickel do not behave alike towards alcohol at the same temperature. Though both tend to convert alcohol into acetaldehyde and hydrogen, nickel is much more likely to decompose the aldehyde into carbon monoxide and methane. . . . . The specific effect occurs also during hydrogenation, though the difference is not so marked. . . . . Armstrong and Hilditch consider that both alcohol and water are adsorbed selectively by copper, thus decreasing the adsorption of the aldehyde and protecting it from decomposition."

That alcohol may absorb the wave-lengths which are needed for the decomposition of aldehyde would explain the slower rate of decomposition of aldehyde and might explain the change in the proportion of gaseous products of aldehyde as the temperature changes.

The second explanation of the change in products seems more nearly true. Bone and Smith[1] found that at 400°, acetic aldehyde rapidly decomposes almost completely into methane and carbon monoxide. That the photochemical reaction also tends to go this way as the temperature is raised indicates very clearly that the molecule becomes more instable in this direction. In the introduction it was postulated that the action of heat as a depolarizer would be shown by an increased rate of reaction and a higher so-called temperature coefficient as the temperature of thermal decomposition is approached. We are now able to conclude that the action of heat as a depolarizer in a photochemical reaction may be demonstrated in two ways.

First, at higher temperatures, one reaction tends to predominate; this reaction will be that one in the direction of which the higher temperature has brought about the more instable molecule.

Second, the rate of reaction increases as the temperature rises.

It has already been shown that as the temperature rises, the change in the composition of the gaseous decomposition products indicates depolarization by heat. The rates of reaction also show clearly that depolarization occurs with acetaldehyde; that at temperatures approaching the thermal decomposition point, light has less work to do in decomposing the molecule.

Temperature	80°	210°	320°	340°
cc./min.	156	168	194	236

(A blank run at 380° without the discharge gave 7.5 cc./min; there was no evolution at 340° or below).

A calculation of the ratio of the reaction velocities at 10° intervals shows the same effect:

Temperature	Rate in cc./min.	K
80°	156	
210°	168	1.006
320°	194	1.010
340°	236	1.10

---

[1] J. Chem. Soc., 87 II, 910 (1905).

A corollary of these conclusions is that if the temperature of thermal decomposition is not approached, the composition of the gaseous decomposition products will not change over a wide change in temperature. This may be demonstrated by both ethyl alcohol and acetic acid. These two substances begin to decompose thermally at 500°[1] and about 800°,[2] respectively, or at temperatures not approached in our tube. The fact that alcohol gives the same products at 85° and at 380° is an indication of the truth of this corollary; on the other hand, this evidence cannot be considered as absolute proof because in a heated glass tube alcohol decomposes in the same two ways in which it decomposes photochemically. The thermal decomposition products of acetic acid are not mentioned. Further work should be carried out in connection with this interesting question.

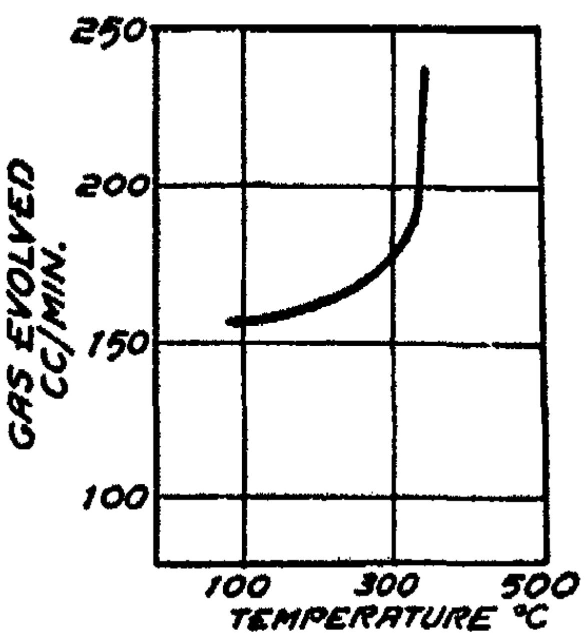


Fig. 9

Acetone

The decomposition of acetone was carried out in one of the early tubes. The diameter of the outer tube was 35 mm., of the inner tube 20 mm., and the length of the coating 25 cm. Because the tubes were larger than in the later designs, the rate of decomposition can not be directly compared with the other substances which have already been discussed.

At 80°, 22 cc. of gas were formed in 5 minutes, or at a rate of 4.4 cc. per minute. The gaseous products analyzed as follows:

Acetylene and olefines	4.1
CO	49.6
H_2	19.1
C_nH_{2n+2} (principally CH_4)	27.2

This result is most nearly like that of de Hemptinne. All investigators have agreed that the primary reaction is the splitting off of CO, but only Berthelot and Gaudechon and Poma and Nesti have explained the reaction further. The former obtained only ethane and carbon monoxide in essentially equal amounts, hence the explanation is simple; the latter obtained no hydrogen but found the condensate to be complex.

In the present work, no analysis was made of the condensate. Because CO comprises one-half of the gaseous product and methane and hydrogen both are formed from the CH_3 group, it must be true that either free carbon or a carbon-rich compound is formed in the decomposition of acetone. Since

---

[1] Berthelot and Jungfleisch: "Traite elem. de Chimie Org.," 2nd Ed., 1, 256 (1886).

[2] Berthelot: Ann. Chimie, (3) 33, 300 (1851).

no free carbon was observed, it must therefore be concluded that a carbon-rich compound is formed. It is possible that this compound is a polymerized olefine.

Sabatier and Senderens[1] found that acetone is decomposed in the presence of nickel at 270° to give a little carbon monoxide, ethane and ethylene, but principally methane, hydrogen and carbon.

Acetic Acid

In the decomposition of acetic acid the gaseous products, as with ethyl alcohol, have practically the same composition at low and high temperatures:

Temperature	118°	320°
CO_2	13.3	15.3
C_2H_2 or C_2H_4	3.5	3.1
CO	36.4	35.8
H_2	26.7	23.5
$CH_4 + C_2H_6$	20.1	22.3

These results do not conform to those obtained in any previous work except in that of Maquenne. Berthelot and Gaudechon obtained a predominance of carbon dioxide; so also did Poma and Nesti. de Hemptinne found a large amount of ethylene.

The significance of obtaining the same products at low and high temperatures has already been pointed out when discussing acetaldehyde.

It seems quite evident that in our apparatus the principal reaction cannot be:

$$CH_3COOH = CH_4 + CO_2$$

$$\text{or}\quad 2CH_3COOH = C_2H_6 + 2CO_2 + H_2$$

Because of the large amount of carbon monoxide, it is more probable that the principal primary reactions are:

$$2CH_3COOH = 2CO + C_2H_4 + 2H_2O$$

(with polymerization of the excess ethylene)

$$\text{and}\quad CH_3COOH = 2CO + 2H_2$$

The so-called temperature coefficient of the photochemical decomposition of acetic acid is higher than that of ethyl alcohol. At 118° the rate of decomposition is 31 cc. per minute; at 320° it is 200 cc. per minute. The so-called temperature coefficient is therefore 1.10 for 10°. Although the curve for the change in rate of decomposition was not obtained with acetic acid, one might judge from this rather high coefficient that the slope might change even more rapidly than with acetic aldehyde when the temperature of thermal decomposition is approached.

Ethylene and Acetylene

It seemed possible that in several of our photochemical decompositions there occurred a polymerization of ethylene or acetylene because after con-

---

[1] Ann. Chim. Phys., (8) 4, 474 (1905).

tinual use of a discharge tube, there was some deposit of a gummy or semi-hard, brown or black substance. Other workers have described polymerization products of acetylene or ethylene.

Berthelot and Gaudechon[1] placed acetylene in a "tube subjected to the action of the lamp of 110 volts for 1 hour at 2 cm. distance, 1 hour at 5 cm., 1 hour at 8 cm. Initial volume 2.6 cc. Final volume 2.18 cc. Contraction 16%. At the end of some moments, one observes a fog appear in the tube, which is then desposited on the surface of the mercury, and a solid layer on the walls of the tube, the thickness increasing progressively, which shows the colorations of thin plates. The chemical action, at first very rapid, soon slows down, as a result of the non-transparency of the deposit to ultra-violet rays.

"The deposit is of a brownish yellow color, and has the particular odor of the polymers of acetylene obtained by the action of the silent discharge on the gas.

"There is no liquid benzene. The residual gas is entirely absorbed by ammoniacal copper chloride. Polymerization has therefore occurred without decomposition.

"The preceding chemical action, like those which are related to the ionization of the gas, is assisted by the diminution in pressure which renders the gases better conductors. This is equalized by the addition of an inert gas, which diminishes the partial pressure of the active gas in the mixture."

In another experiment Berthelot and Gaudechon[2] used ethylene alone in a "tube subjected to the action of the 220 volt lamp at 4 cm. distance, during 2 hours. Initial volume 2.72; final volume 2.42. Contraction 11%. One part of the residual gas is analyzed by combustion, then by the addition of alkaline pyrogallol.

	Total Gas	CO_2 Formed	Contraction	O Consumed	Residue
Observed	1.25	2.48	2.50	3.74	0.01
Calculated for C_2H_4	1.24	2.48	2.46	3.72	0.00

"The residual gas is therefore pure ethylene. There is formed a waxy liquid polymer which gives off a rancid fat odor, and boils at a little above 100°. It is a substance which recalls caprylene or the homologous compounds obtained in the pyrogenic decomposition of wax.

"In another experiment, after 3 hours exposure at about 5 cm. distance from the 110 volt lamp, ethylene contracted 13% with the formation of the same polymer. The residual gas, analyzed as before, is pure ethylene.

"The ease and simplicity of the reaction caused by ultra-violet rays contrasts with the previous negative results of Goriarnoff and Bontleroff, who state in their paper 'Sur les polyolènes': 'We have endeavored to polymerize ethylene but without succeeding.'"[3]

---

[1] Compt. rend., **150**, 1170 (1910).

[2] Loc. cit. p. 1171.

[3] Ann., **169**, 147 (1873).

When Berthelot and Gaudechon[1] subjected a mixture of acetylene and ethylene to the action of their ultra-violet lamp, they imply that the two gases polymerized separately.

"The tube was exposed for 2 hours to the rays from the 220 volt lamp at a 4 cm. distance. Initial volume 3.22, composed of 1.55 cc. C_2H_2 plus 1.70 cc. C_2H_4. Final volume 2.36 cc. Contraction 26%.

"The quartz tube is coated with a solid brownish yellow layer, of identical appearance to the polymer of acetylene, and besides, some of a fatty layer which can be distilled off above 100°, in the form of a heavy vapor of rancid odor and having an odor similar to the product of the condensation given by ethylene alone."

Several attempts have been made to polymerize acetylene and ethylene separately by the silent discharge. P. and A. Thénard[2] found that in the silent discharge ethylene alone condenses to a powerfully odorous liquid, soluble in ether, insoluble in water. M. Berthelot[3] reported that ethylene gives a little acetylene, some hydrogen and resinous condensation products. Wilde[4] condensed ethylene to a liquid and acetylene finally to a brown, brittle solid.

M. P. E. Berthelot[5] found that ethylene condenses rapidly but since the time of action in his apparatus was generally 24 hours, it is not clear just how rapidly the condensation occurs. During the action of the silent discharge a little acetylene and benzene are formed and considerable hydrogen. The condensed liquid had the formula $C_2H_{3.4}$. He reported also that acetylene condenses very rapidly, first to a liquid and then to a solid. In the residual gas he found hydrogen, ethylene and a trace of benzene.

Losanitsch and Jovitschitsch[6] stated that under the action of the silent discharge, ethylene polymerizes into a yellow, viscous liquid with a very strong, somewhat pleasing odor. The liquid boils above 200° and its formula is $(C_2H_4)_n$.

Jovitschitsch[7] later published more work on the probable structure of the polymerization products of acetylene and ethylene. He concluded that the probable formula of the first is $C_{30}H_{26}$ and of the second, $C_{30}H_{54}$.

Collie[8] subjected a mixture of ethylene and carbon monoxide (80:20) to the silent discharge and after several hours obtained 2.5 grams of liquid. He separated three fractions boiling from 50° to 180° and the fourth fraction, boiling above 180°, was a brown, sticky substance resembling burnt india-rubber, and when heated, it smelled like rubber. Some of the residual gas was hydrogen. Collie concluded that the ethylene was condensing more easily than the carbon monoxide, although aldehyde were formed to a slight extent, so his next experiment was with ethylene alone. After submitting

---

[1] *Loc. cit. p. 1171.*

[2] Compt. rend., **76**, 1513 (1873).

[3] Bull., (2) **26**, 103 (1876).

[4] Ber., **7**, 357 (1874).

[5] Compt. rend., **126**, 567 (1898).

[6] Ber., **30**, 135 (1897).

[7] Monatshefte, **29**, 1, 5 (1906).

[8] J. Chem. Soc., **87**, 1540 (1905).

ethylene to the discharge for several hours, he found the residual gas to be hydrogen. He collected four fractions, boiling from −100° to 250° and a resin boiling above 250°. He found the maximum amount of distillate between 133° and 170° and another increase above 200°. The resin represented two-fifths of the whole of the substances produced.

Collie found that the percentage of hydrogen gradually fell from 16.0% (C = 83.4) in the first fraction to 12.3% (C = 87.7) in the distilled resin. He concluded "that ethylene gas under the influence of the silent electric discharge at the ordinary temperature not only unites with carbon monoxide, but also polymerizes, yielding a series of complicated hydrocarbons having a boiling point approximating to that of hydrocarbons having the formula $C_{10}H_{20}$; moreover, this molecule loses hydrogen and in its turn polymerizes, yielding a substance possessing properties somewhat like those of india-rubber and a composition very near to $(C_5H_8)_x$."

From all of these results it may be concluded that both ethylene and acetylene do polymerize to form gummy substances. It seemed to us particularly an interesting question whether a mixture of acetylene and ethylene in polymerizing formed two polymers of the separate gases or a polymer which would have the formula $(C_4H_6)_n$.

Experimental Work

We found that, when ethylene alone is run through the discharge tube, there is gradually formed on the walls of the tube a liquid which is at first colorless, then yellow, then brown. Most of this substance can be removed with benzene, but there still remains a more or less hard, yellow or brown substance which becomes soft under the benzene treatment but does not dissolve immediately. Most of this hard substance is on the inner tube of the ozonizer.

No quantitative determination was made of the composition of these polymers of ethylene.

In the first experiments with a mixture (50-50) of acetylene and ethylene a tube with a coating 45 cm. long was used. The rate of flow of gas was 50 cc. per minute. The formation of the yellow or brown polymer could be observed after a few minutes of operation and after building up continually for an hour the deposit on the inside of the outer tube was about 1 mm. thick. The maximum thickness was at a distance of about 30 cm. from the front end of the coating.

If the discharge continued much longer than one hour, the thickness of the deposit became so great at this point that the discharge began to concentrate here and became more intense. The brown polymer then started to carbonize, the discharge concentrated still more and very soon the tube cracked or a hole formed in it and a spark discharge occurred.

It is not perfectly clear why the deposit reached a maximum at 30 cm. from the front end of the coating. The distribution of the deposit was like this:

at 20 cm. the deposit began,
at 30 cm. the deposit was thickest,
at 40 cm. the deposit ended.

It is believed that polymerization starts in the first part of the discharge and continues as the gases pass through the tube with the formation of higher boiling point polymers. The polymers with a sufficiently high boiling point are probably formed after traveling about 30 cm. through the tube and therefore condense at this point. This decreases, at this particular place, the distance which the discharge has to travel and the discharge gradually becomes a little more intense here, although it was perfectly uniform in the beginning. Once started, the effect becomes more pronounced as the experiment continues.

If the rate of flow of the gas mixture was made less, e.g., 30 cc. per minute instead of 50, the deposit occurred over a longer portion of the tube and a maximum was not so evident. As a practical means of overcoming this difficulty when measuring the amount of contraction, the coating was shortened from 45 to 15 cm.

It was found that either a very intense discharge or a combination of the discharge and heat would cause decomposition of the polymerized substance. On the inside of the outer tube, the deposit was a thick, yellow, sticky liquid. On the other side of the inner tube where the discharge per unit of area was greater than on the outer tube (17:7), the liquid deposit gradually blackened and charred. If the temperature of the tube was raised above 200°, the polymer began to carbonize very rapidly on the outer tube also. It was found that if no external heat were applied, the temperature naturally rose to about 190° and remained at that point.

Rate of Flow versus Contraction

In this experiment, the inner tube was 7 mm. (outside), the outer tube was 17 mm. (inside), and the coating was 15 cm. long. The temperature was 190°. A 50-50 mixture of acetylene and ethylene was passed through.

Rate, cc./min.	% Contraction
32	68
36	67
51	56
65	55
254	23
448	6

If these are plotted, the curve indicates that maximum contraction with zero flow will be somewhat less than 100%. In other words, some gas other than the original ethylene and acetylene is formed to the extent of about 10-20%. This is interesting because the exit gases were found to contain hydrogen to the extent of about 8% at the lower rate of flow.

The ratio of acetylene to ethylene was quite different in the exit gases from their ratio at the beginning. Before passing through the tube, they were present in equal parts. After passing through the discharge tube, there was present three to four times as much ethylene as acetylene. This fact seems to indicate that the two gases polymerize separately and that acetylene polymerizes more readily than ethylene.

However, analysis of the resinous, gummy, semi-liquid deposit which appeared to be a mixture of polymers having boiling points from about 150° to 250°, showed the formula to be very close to $(C_4H_6)_n$.

Several attempts were made to further polymerize this thick liquid.

(1) A small amount of the liquid was treated with a few drops of quinoline. There was no change either in the cold or on heating. After remaining at 140° for five days there was no change in the consistency.

(2) The liquid was kept in a sealed tube at 140° for 5 days. There was no change.

(3) The liquid was kept in a sealed tube with sodium amalgam at 50°. The amalgam was introduced in an atmosphere of nitrogen and had a clean surface. There was no change in two days, but after five days there were flecks of a brown solid on the side of the tube with unchanged liquid still remaining.

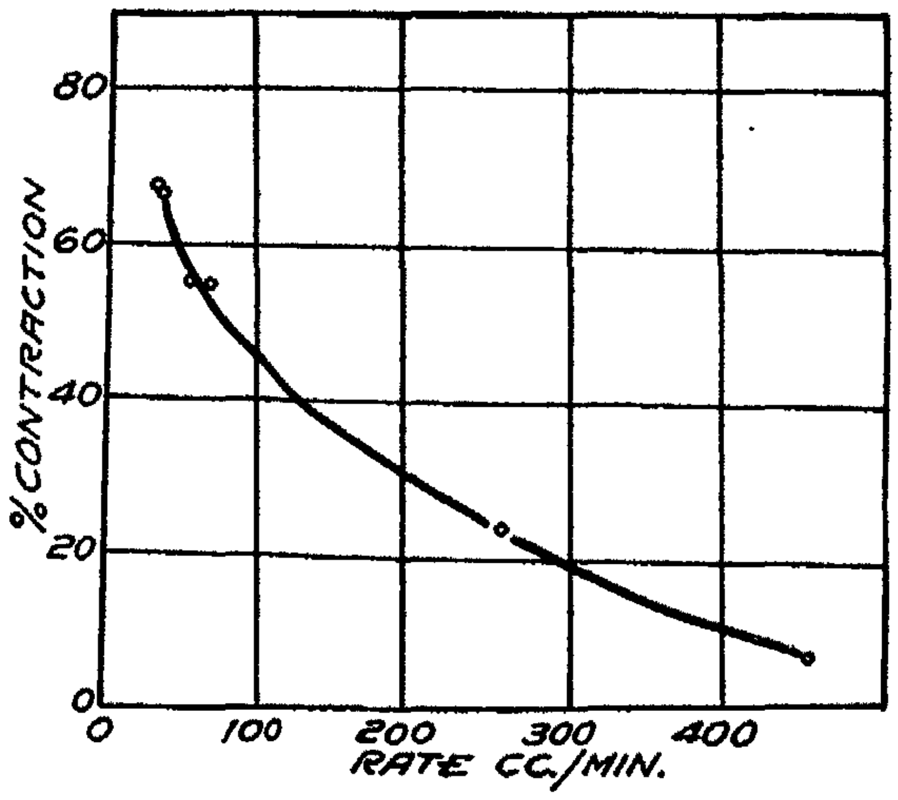


Fig. 10

(4) There was no change in the liquid kept in contact with the clean surface of sodium for two days at 50°.

In this report on the action of the Tesla discharge on ethylene and acetylene, the curve showing the relation of contraction to rate of flow is probably the most interesting material presented. It suggests at once the possibility of obtaining and isolating in a fairly pure condition the separate fractions of the polymers by using a short discharge space and a suitable rate of flow.

Sulfur Trioxide

An interesting photochemical synthesis seemed to us to be the formation of sulfur trioxide from sulfur dioxide and oxygen. Findlay[1] stated that a

---

[1] Z. Elektrochemie, 12, 129 (1906).

mixture of SO_2 and O_2 will give some SO_3 under the influence of the Tesla discharge. Losanitsch[1] using the silent discharge, found that SO_2 alone gives SO_3 and free sulfur quite rapidly. Berthelot[2] and Wilde[3] also studied the action of the silent discharge on the oxidation of SO_2 by O_2.

According to the experiments of Coehn[4] and Coehn and Becker,[5] SO_2 is split by ultra-violet light into SO_3 and S, and SO_2 and O_2 give SO_3. They later concluded after further work with a quartz mercury lamp that a definite photochemical equilibrium exists. At 160°, for example, the equilibrium mixture contains 65% SO_3. They found the temperature coefficient to be 1.2 per 10° between 50° and 160°.

Moser and Isgarischeff[6] studied the action of the silent discharge on a mixture of SO_2 and O_2 and on SO_3 alone. They operated at temperatures from 50° to 70° in order to prevent the condensation of SO_3. In the experiment on SO_3 alone, they used nitrogen saturated with about 20% of SO_3. They could detect no decomposition into SO_2 and O_2 but concluded that free sulfur and a superoxide, S_2O_7, are formed. They concluded that the reaction $SO_2 + \frac{1}{2}O_2 = SO_3$ is irreversible:

"By the use of stoichiometric mixtures of SO_2 and O_2 (2:1) the formation of the superoxide by condensation of the SO_3 occurs only after the necessary union of the gases to form SO_3.

"In the presence of an excess of oxygen occurs the further oxidation of the SO_3 which has been formed, to sulfur peroxide in the sense of the Berthelot equation:[7]

$$2SO_3 + \frac{1}{2}O_2 = S_2O_7$$

"In the presence of an excess of SO_2 occurs a condensation of that substance with the separation of sulfur and the formation of SO_3 according (compare Losanitsch and Jovitschitsch:)[7] to the equation:

$$3SO_2 = 2SO_3 + S$$

"As soon as the sulfurous acid is used up according to this equation there occurs, with a further separation of sulfur, the formation of sulfur peroxide."

Some of their results are given in the following table. Their maximum yield in grams per KWH was 14.3.

Apparatus 2. Composition of gas: 61.5% SO_2, 32.4% O_2; 6.1% N. T 67°.

Volts	Milli-amps	Watts	Speed of Flow, cc./min.	SO_3 Formed, Grams	Time, Minutes	SO_3, Gm./KWH
12500	1.92	11	0	0.0102	15	3.5
12500	2.9	16.5	7.3	0.0560	27	7.4
12500	2.8	16	21.8	0.0298	8	14.3

---

[1] Ber., 40, 4657 (1907).
[2] Compt. rend., 86, 20 (1878).
[3] Ber., 7, 357 (1874).
[4] Z. Elektrochemie, 13, 545 (1907); Chem. Ztg., 31, 541 (1907).
[5] Z. physik. Chem., 70, 88 (1910).
[6] Ber., 40, 4656 (1807).
[7] Compt. rend., 86, 20 (1878).

Experimental Work

In our apparatus we used a considerably higher rate of flow than Moser and Isgarischeff and obtained higher yields per KWH. The outer tube used for this experiment was 18 mm. outside and 15 mm. inside; the inner tube had a diameter of 6 mm. outside. The coating on the outer tube was 40 cm. long.

A mixture of 2 volumes of sulfur dioxide and 1 volume of O_2 was passed through the tube with the following results:

Rate	Average	In Exit Gas		SO_2 oxidized × 100	Yield
cc./min.	Temp.	gms. SO_2	gms. SO_3	SO_2 original	gms./KWH
329	300°	2.220	0.773	21.8	23.4
1218	300°	4.480	0.982	14.9	59.5

It is unfortunate that these experiments could not have been carried further. It is probable that if several other values had been obtained, varying the rate of flow, a curve which would indicate the point of equilibrium would have resulted. One thing is worth while noting in these two experiments. The difference in the rate of flow is large but the difference in the percentage of SO_2 oxidized to SO_3 is rather small. Also, with the faster rate of flow, the yield per KWH is higher. Both of these facts indicate that the reaction takes place very rapidly. An apparatus in which the discharge would pass only through the unchanged mixture, or in other words, an apparatus in which the discharge would be used most efficiently, would probably give higher values for the amount of SO_2 oxidized and very much higher yields per unit of energy used.

Summary

(1) An apparatus has been designed in which photochemical reactions can be carried out by means of a Tesla discharge at temperatures up to 350° to 400°. The range could be extended by using quartz or glazed porcelain tubes instead of pyrex glass.

(2) The reactions in the Tesla discharge give essentially the same products as other photochemical energy sources. Exactly the same results are not obtained, possibly because any given wave-length or band may not be present to the same extent.

(3) There has been obtained evidence that a compound can be made photosensitive by means of heat. That a compound is made photosensitive is shown by the increased rate of reaction and the higher temperature coefficient.

(4) Regardless of the photochemical reactions which occur at low temperatures, the predominant photochemical reaction at temperatures approaching the thermal decomposition point is that reaction which results from the instability of the molecule brought about by the high temperature.

(5) The developed apparatus seems a good one in which to try out the possibilities of influencing the reactions by using a second substance, e.g., mercury, in the discharge tube.

(6) The gaseous and some of the liquid decomposition products of methyl alcohol, ethyl alcohol, acetone, and acetic acid have been determined. Some of them have been of service in drawing the conclusions just mentioned under (2) and (3).

(7) A gummy resin has been obtained in the polymerization of a mixture of acetylene and ethylene. This appears to be a mixture of polymers of the two separate gases and not polymers of a combination of the two. Several methods of further polymerizing this resinous mass were tried but in none of these trials was there any further polymerization.

This work was suggested by Professor Bancroft. It is a pleasure and a privilege to be able to thank him, in this way, for his constant interest, criticism, suggestions and inspiration.

Cornell University.

26.

A NEW EQUATION FOR THE RATE OF FORMATION OF THE PHOTOGRAPHIC LATENT IMAGE*

BY JULIAN M. BLAIR AND PHILIP A. LEIGHTON

Introduction

An equation which, based upon theoretical postulates, would correctly express the relation between the rate of formation of a developable image and the time and intensity of exposure on photographic emulsions would be of value for the information it might give regarding the nature of the process forming the latent image.

Several equations which express a relationship between these quantities have been presented, and have been excellently summarized by Ross,[1] who has also added one of his own. However, these equations either do not fit the experimental data closely, or are not based on theoretical postulates, or both. The research here reported was undertaken with the view of finding an equation which would overcome these difficulties. In the earlier equations, trouble has been caused by the "reciprocity failure," or lack of inverse proportionality between intensity and time of exposure. In order to avoid this complication we have, in the present work, considered the effect of time of exposure only, while using a uniform light intensity.

The Rate of Formation of the Latent Image in Very Thin Emulsions

Hurter and Driffield[2] showed that the density of a photographic plate is proportional to the mass of silver per unit area. Accordingly, the density of a plate, when developed under such conditions that all developable silver halide grains have been reached and reduced by the developer, will be a measure of the extent to which the reaction forming the latent image has progressed.

Ordinary commercial photographic plates are so opaque, due to the concentration of silver salts, that grains of silver halide on the side of the emulsion facing the incident light receive greater exposure than grains buried deeper in the emulsion.[3]

If after exposure and development the density of such a plate is determined it will not be an accurate measure of the degree of developability at any layer of the emulsion, but rather a summation of the different degrees of developability at the various levels.

In order to overcome this difficulty, we used in this research a special thin emulsion in which the amount of silver halide was so small that the plates

---

* Contribution from the department of Physics, University of Colorado, and the department of Chemistry, Stanford University.

[1] F. E. Ross: "The Physics of the Developed Photographic Image," Eastman Kodak Co. Monograph No. 5, p. 48 (1924).

[2] F. Hurter and V. C. Driffield: Photography, 1890, August 30.

[3] Ross: Loc. cit., p. 40.

were quite transparent before development, and grains at different levels of the emulsion could be exposed very nearly equally.

Measurement of the density of the special plates before development showed that the amount of silver halide per unit area was constant along lines parallel to the shorter dimensions of the plate, but along lines parallel to the longer dimensions there was a uniform increase in density from one end of the plate to the other. In order to avoid error from this source, the plates were cut into two longitudinal strips, which were reversed in the plate holder so that whenever the dense portion of a strip was given a certain exposure the correspondingly less dense portion of the other strip was given the same exposure. The average density of the two was accepted as the true value of the density.

In order to expose the strips, tungsten lamps burning at constant voltage, were placed behind a ground glass in a ventilated box. On the opposite side of the ground glass an opening in the box was covered with a No. 50 Wratten laboratory filter. This filter transmits a band between 4000 and 5000 Å, with a maximum transmission around 4550 Å.

Two and one-half meters in front of the box an ordinary camera plate holder was rigidly mounted in this beam of uniform blue light. As stated, the strips were mounted with ends reversed in this plateholder. The slide of the plateholder was then drawn so that one half inch of the ends of the strips were exposed. After 15 seconds the slide was drawn an additional half inch. This was repeated until the whole of the plate was exposed, each half inch of plate receiving 15 seconds more exposure than the next. On some plates, part of the exposures were of still greater duration, so that the whole range of sensitivity of the plates was explored.

Different plates were found to be coated with slightly different amounts of silver halide. Error from this source was avoided by making the greatest exposure on one pair of strips and the least exposure on the next pair of strips. This permitted the densities of all plates to be determined in terms of the amount of silver halide on the first plate.

The strips were developed for 20 minutes at a temperature of 19°C. in the Ferrous Oxalate Developer described by Hurter and Driffield,[4] then fixed, washed, and dried in the usual manner. This developer was chosen because it gives a high density, i.e., develops a maximum number of exposed grains, yet has very little tendency to spread and affect unexposed grains. It should be pointed out that some later publications in giving the formula for this developer leave out the bromide, which was described by Hurter and Driffield, and the use of which is essential.

The densities of the various parts of the plates were measured with a Burt photoelectric cell. This cell was mounted in one end of a dark box, separated by a partition from a tungsten lamp operated at constant voltage in the other end. The plates to be measured were placed over an opening in the partition, the size of which could be adjusted to the size of the section of plate to be measured. A water cell was placed between the lamp and the plate.

---

[4] F. Hurter and V. C. Driffield: Phot. J., 38, 76 (1898).

The photoelectric cell was connected in series with a 45 volt battery, a condenser, and a charge and discharge key. The key was placed in the charge position for a measured interval of time, then it was thrown into the discharge position and the accumulated charge passed through a ballistic galvanometer of high sensitivity. Comparisons between this photoelectric method and a surface thermopile method gave concordant results for density.

The circles on Fig. 1 represent the developable densities produced by various times of exposure under the conditions described. The abscissa is time of exposure rather than the conventional log time. No correction is made for "fog." The distance along the time axis for the points t = 805; 1305; 1740; 2175; and 2610 seconds, respectively, are shortened to avoid extension of the graph.

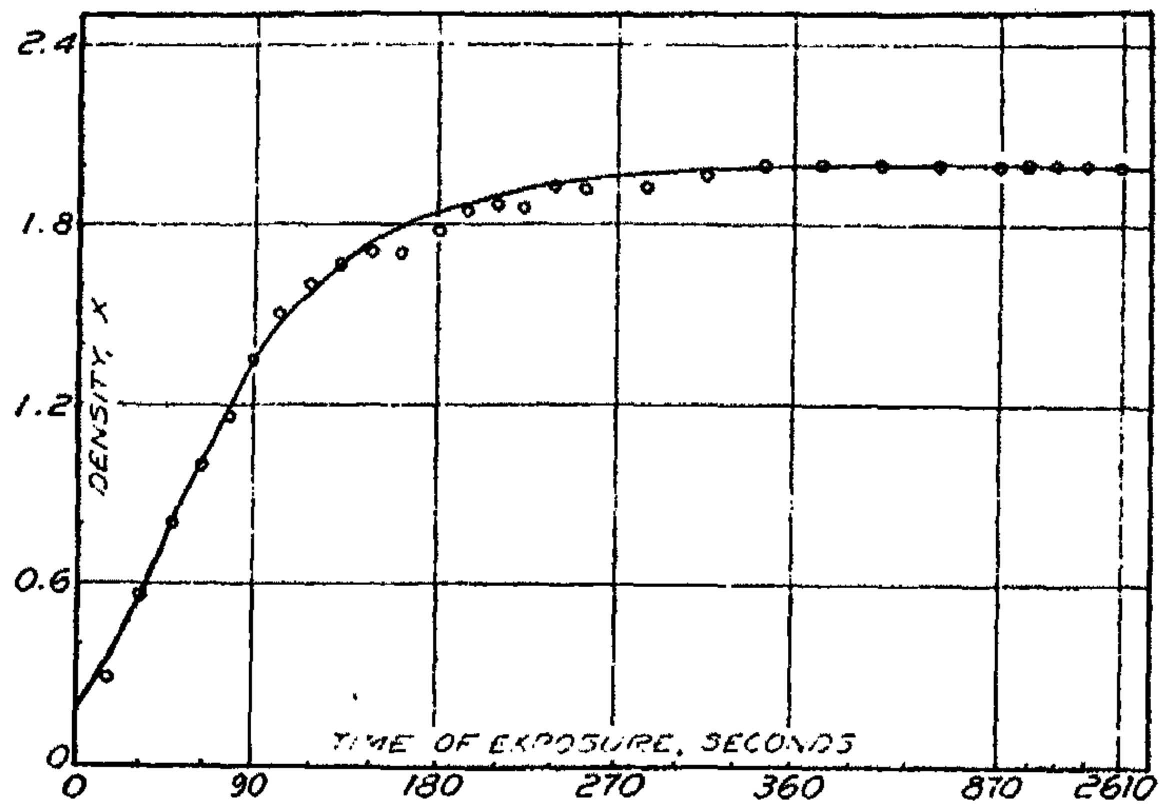


FIG. 1
Time-Density Relations for Thin Emulsions
Circles = observed; Solid line = calculated

The Ideal Maximum Density

In the analysis which is to follow we use a concept which we shall call the ideal maximum density. By this we mean the density that the plate would attain if all of the silver halide present in the plate had been converted during development into metallic silver.

Jones and Hall[5] have shown that even at optimum exposure to light of moderate or low intensity this value is never attained. However, by assuming the relation as demonstrated by Hurter and Driffield[6] that the density of a plate is proportional to the mass of silver per unit area, it is possible to determine the ideal maximum density by chemical means.

In the determination of this value, a plate was cut into four longitudinal strips of precisely equal area. Two alternate strips were exposed to the blue

---

[5] L. A. Jones and V. C. Hall: Proc. Int. Cong. Phot., 7, 115 (1928).

[6] F. Hurter and V. C. Driffield: Photography, loc. cit.

light previously mentioned long enough to produce the maximum developable density for this light. These two strips were then developed with the standard developer, fixed, and washed. Without drying, they were immersed in hot sodium hydroxide solution for 24 hours. The residual silver was then filtered off and washed free from gelatine, dissolved in nitric acid, and the silver precipitated as the chloride and weighed in the usual manner.

The two remaining strips of the plate were, without any previous treatment, immersed in hot sodium hydroxide solution for 24 hours. At the end of that time the silver oxide was filtered off and the silver content determined as before. From the relative amounts of silver chloride produced in the two cases the ratio between the ideal maximum density and maximum developable density was determined. The ratio found was 1.095. When applied to the maximum developable density shown in Fig. 1, the ideal maximum density for the plates and development conditions used is found to be 2.19.

Derivation of An Equation for Developable Density

In attempting an analysis of the rate of formation of the latent image, as indicated by the developable density produced, we have been led to five basic postulates, as follows:

1. *The process of formation of the latent image is chemical.* The idea that it probably consists of the photochemical liberation of minute amounts of free metallic silver has received support from the work of many investigators.[7]

2. *Two processes are involved, one a forward reaction, tending to produce the latent image, and the other a reverse reaction, tending to destroy it, or to change the developable grains into their original condition.*

The phenomenon of reversal or solarization is an old and well established fact. The new aspect here presented is that reversal begins as soon as the first grains have been rendered subject to development, and is concurrent with the formation of the latent image. We have obtained direct experimental evidence in support of this assumption, which will be presented in another paper.

3. *The forward reaction is autocatalytic.* This is suggested by the shape of the density-time curve, as well as by the effect of "flash" exposures and by the sensitizing effect of silver on emulsions.

4. *The forward reaction is a function of the number of grains in the original state.* This is a general property of photochemical reactions where light absorption is weak.

5. *The reverse reaction is a function of the developable density.* It is reasonable to assume that the rate of the reverse reaction, which decreases the number of developable grains, is some function of their concentration, and therefore a function of the developable density.

---

[7] Abegg: Archiv Wiss. Phot., I, 268 (1899); Brit. J. Phot., 46, 196 (1899); Lüppo-Cramer: "Kolloidchemie und Photographie" (1908); Lorenz and Hiege: Z. anorg. Chem., 92, 27 (1915); Sheppard and Trivelli: Phot. J., 61, 403 (1921); Fajans: Chem. Ztg., 45, 666 (1921).

Proceeding on the basis of these postulates, we can say that the rate of formation of the latent image, dx/dt, will be governed by the relation:

$$dx/dt = f_1(x) \cdot f_2(b-x) - f_3(x) \qquad (1)$$

where x = the developable density, b = the ideal maximum density, and t = time of exposure to light of constant intensity. Accordingly, f_1 (x) represents the autocatalytic term, f_2(b-x) the term expressing the relation between the forward reaction and the number of grains in the original state, b-x, and f_3(x) represents the dependence of the reverse reaction on the number of developable grains.

The autocatalytic reaction appears to be proportional, not to x, but to the square root of x, i.e., $f_1(x) = K_1x^{\frac{1}{2}}$. The other two functions, since the grains are mutually independent, should involve no more than a direct proportionality. Accordingly, we obtain the equation:

$$dx/dt = K_1x^{\frac{1}{2}}(b-x) - K_2x. \qquad (2)$$

This equation is found to predict the slope rather accurately for all values of x. In order to evaluate the constants K_1 and K_2, the ratio K_1/K_2 was found by considering a point on the curve at which maximum density has been attained. At this point dx/dt = 0, x = 2.0 and b = 2.19. This gives the ratio

$$K_1/K_2 = 7.45$$

By employing this ratio, when other measured values for dx/dt and the corresponding values for x are substituted in the equation, the constant values $K_1 = 0.0122$ and $K_2 = 0.00164$ are found.

The differential equation (2) may be integrated, and for the determined values of the parameters it yields the relation:

$$e^{K_1t\sqrt{\left(\frac{K_2}{2K_1}\right)^2+b}} \cdot C = \frac{\sqrt{\left(\frac{K_2}{2K_1}\right)^2+b} + x^{\frac{1}{2}} + \frac{K_2}{2K_1}}{\sqrt{\left(\frac{K_2}{2K_1}\right)^2+b} - x^{\frac{1}{2}} - \frac{K_2}{2K_1}} \qquad (3)$$

where C is the constant of integration, and possesses the value 2.125.

This value of C was determined by substituting corresponding values of x and t for any one point shown in Fig. 1. Using this value of C in the above equation, the values of x predicted for various values of t were determined. The resulting curve is shown by the continuous line in Fig. 1. Within limits of error, it is in agreement with the experimental curve throughout the whole region of exposures we have thus far investigated.

Instead of the usual form of density-time curve, with a considerable "foot" or flat underexposure portion, this curve, both experimental and calculated, has a very short foot, and moreover, strikes the ordinate (zero time) at a density of 0.2.

This is due in part to the fact that no fog correction was made in either the calculation or measurement of x, and in part to the scale of the abscissa, time instead of log time. The thinness of the emulsion must also be a contributory cause of the short foot, since the grains deep in the emulsion receive full exposure and become developable as rapidly as those near the surface. No solarization was observed experimentally and none would be predicted for the values of the parameters found.

Summary

A differential equation, based on definite theoretical postulates, which expresses the relation between density and time of exposure in photographic emulsions, has been presented. Measurement of the density-exposure relationships on very thin emulsions shows that the equation accurately reproduces the experimental values.

THE BEHAVIOUR OF THE TUNGSTIC ACIDS TOWARDS SODIUM HYDROXIDE

BY ARTHUR M. MORLEY

In a previous publication[1] the preparation of four types of tungstic acid has been described. Preparations of each type were subjected to various ageing processes, and from a combined analytical and X-ray study of the original and aged products, deductions were made as to the structure of the various tungstic acids. The present publication describes experiments which were carried out to study the action of solutions of sodium hydroxide upon tungstic acid products of the above mentioned types, with special reference to solubility, and the production of colloidal solutions.

A search of the literature reveals the fact, that although there are many references of a general nature to the solubility of tungstic acids in sodium hydroxide, no systematic work has been carried out on this subject, and no quantitative data are available. It is generally agreed, however, that one of the chief characteristics of tungstic acid is the ease with which it dissolves in solutions of the strong alkalies, giving perfectly clear solutions. Since in the experiments carried out by the author it was desired to study the peptisation of the tungstic acids, the sodium hydroxide solutions employed were, in most cases, of low concentration.

Experimental

Preparations.

All the preparations employed were made from solutions of ammonium tungstate and hydrochloric acid, as described in detail in a separate paper.[1] The analyses and general characteristics of the preparations are as shown in Table I.

A pure primrose-yellow tungsten trioxide was also prepared, by heating a tungstic acid of type A in a platinum basin for three hours at 800°C. in an electric furnace.

All preparations were sieved through a 90 mesh I.M.M. sieve.

In the paper previously referred to, the structures of the tungstic acids employed were shown to be as follows: Type A—H_2WO_4, H_2O; Type B—a hydrated amorphous variety of either H_2WO_4 or H_2WO_4, H_2O; Type C—a mixture, consisting chiefly of an imperfectly crystallised or a condensed acid, with smaller amounts of H_2WO_4 and amorphous tungstic acid; Type D—H_2WO_4.

---

[1] Morley: J. Chem. Soc., 1930, 1987 T.

TABLE I

	Type A I	Type A II
WO_3	85.49(%)	85.48(%)
H_2O	14.39	14.41
NH_3	0.01	0.02
Cl	Nil	Nil
	99.89	99.91

	Type B I	Type B II
WO_3	84.10(%)	84.12(%)
H_2O	15.14	14.67
NH_3	0.01	0.02
Cl	Trace	Trace
Insoluble matter*	0.78	1.07
	100.03	99.88

	Type A	Type B
Colour	Lemon yellow	Greyish white
Appearance under microscope (× 800)	Flat leaflets exhibiting frequent twinning. Largest about 10μ in length, and 4μ across the centre. May be regarded as crystalline	Glassy amorphous particles of irregular shape. Size very variable. Maximum breadth between 2μ and 50μ

	Type C I	Type C II
WO_3	89.69(%)	90.00(%)
H_2O	9.56	9.18
NH_3	0.77	0.74
Cl	Trace	Nil
	100.02	99.92

	Type D
WO_3	91.16(%)
H_2O	8.38
NH_3	0.05
Cl	Trace
	99.87

	Type C	Type D
Colour	Greenish yellow	Deep yellow
Appearance under microscope (× 800)	Amorphous. Very small, almost spherical particles, of average diameter 1 μ	Identical with Type C products

* Matter insoluble in water after fusion with sodium carbonate. Due to absorption of calcium from tap water used for washing the precipitated tungstic acid.

General Method.

The general method employed was to mix suitable quantities of sodium hydroxide solution and tungstic acid, in a flask coated internally with paraffin wax, which was then fitted with a waxed cork and suspended in a large water thermostat at 25° C. ± 0.1°C. The contents of the flasks were shaken periodically, and were examined and analysed at intervals, by determining the total amount of tungsten in the supernatant liquids, and in the liquids after ultrafiltration through collodion membranes. The difference between the values so obtained was regarded as a measure of the amount of tungstic acid present in the colloidal condition. One series of experiments was carried out with tungsten trioxide and tungstic acid D, but two series were performed with products A, B, and C, the separate preparations used being referred to as I and II in the analyses. The second short series served to confirm the first set of results, and in addition, certain other determinations were carried out viz. the determination of the pH values of the solutions, and the examination of the solid phase in a selected number of cases.

Experimental Technique.

(a) *Alkali solutions.* The specially distilled water employed for the experiments had a specific conductivity of ca. 2×10^{-6} reciprocal ohms. The sodium hydroxide solution was prepared by subjecting pure metallic sodium to the action of water vapour in an enclosed space, free from carbon dioxide. The saturated solution produced was diluted with freshly prepared conductivity water in the usual type of enclosed apparatus, waxed internally, and with burette attached. This stock solution was diluted as required to prepare the solutions for the experiments.

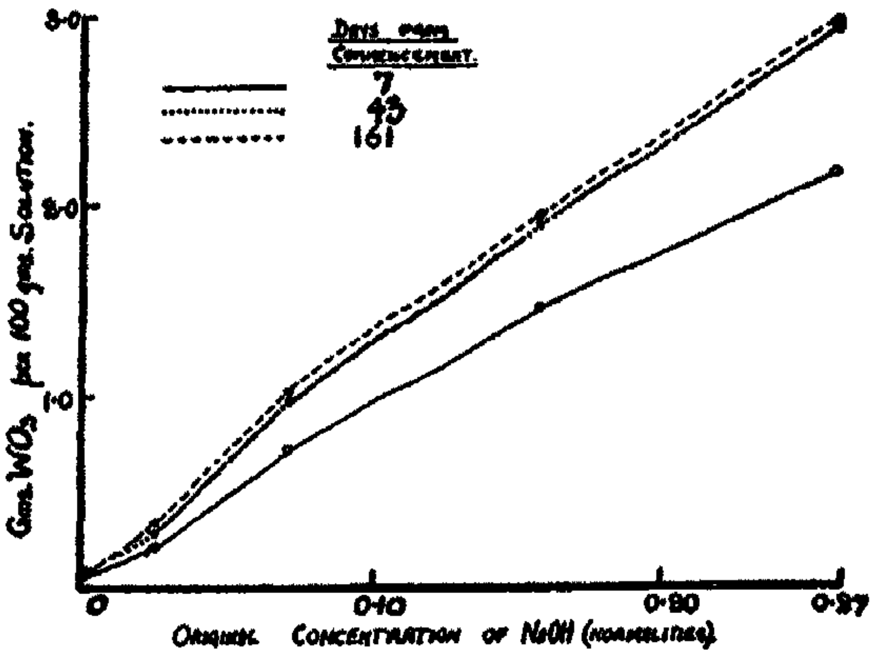


Fig. 1

Tungsten Trioxide in NaOH
Before Ultrafiltration

(b) *Determination of hydrogen ion concentration.* The standard potentiometric method was used. The limit of accuracy of the apparatus employed may be regarded as ± 0.02 of a pH unit. Both the hydrogen and quinhydrone electrodes were used, but since in certain cases at low pH values poisoning of the hydrogen electrode occurred,[1] the values given in the tables are those obtained with the quinhydrone electrode, which behaved normally throughout the investigations.

(c) *Ultrafiltration.* The method of ultrafiltration through collodion membranes was that previously described by Collins and Wood.[2] Tests by Bechold's method[3] showed that the filters held back particles with diameters greater than 1 $\mu\mu$. It was shown by direct adsorption tests with pieces of collodion membrane and solutions containing tungstate, metatungstate, and

---

[1] Cf. Britton: J. Chem. Soc., **1927,** 147(T); **1930,** 1249T.

[2] J. Chem. Soc., **121,** 1122 (1922).

[3] Z. physik. Chem., **60,** 257 (1907).

colloidal tungstic acid, that there is no adsorption of ions or colloidal particles containing tungsten, by the membranes. It was also shown by quantitative tests on the ultrafiltration of optically void solutions of sodium tungstate, and sodium metatungstate of known tungsten content, that at laboratory temperature, with ultrafiltrations carried out up to two hours, the experimental error due to evaporation of the solutions etc. was not greater than 2%. All ultrafiltrations were carried out under the above mentioned conditions.

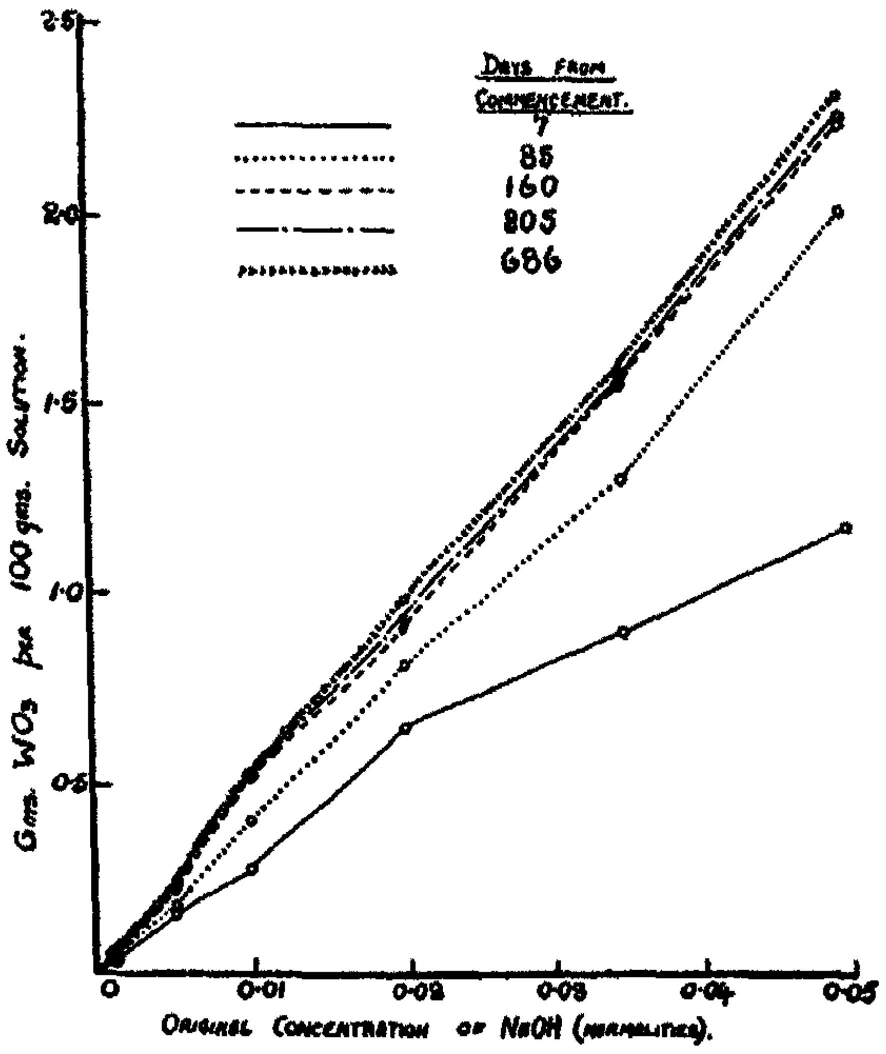


FIG. 2

Tungstic Acid (type A)—in NaOH
Series I—Before Ultrafiltration

(d) *Estimation of Tungsten.* All analyses were carried out by the standard gravimetric mercurous nitrate method. The method was carefully tested, and shown to be accurate with tungsten in the forms of sodium tungstate, sodium metatungstate, and tungstic acid in the colloidal condition. Since small quantities of solutions had to be used in many cases, all portions for analysis were accurately weighed out, and all results were expressed as grams of WO_3 per 100 grams of solution.

All estimations were carried out in duplicate. In all Series I experiments, portions of the solutions were taken for analysis by allowing the solids present to settle for several days and carefully pipetting off the supernatant liquids. Filtration of the solid had been found to be unsatisfactory in many cases, owing to its finely divided nature. The settling method of necessity involved a slight concentration error caused by drops of condensed liquid on the upper portions of the flasks.

This was avoided in the various Series II experiments, a centrifuge then being available. The standard method for obtaining a sample was to shake up the contents of a flask, centrifuge a portion for 30 minutes at 2,000 revs. per minute, and pipette off and weigh part of the supernatant liquid. The centrifuging was carried out in an asbestos box at a temperature of 25° C. ± 0.5° C., so that there was no appreciable change in temperature when the solution was transferred from the thermostat to the centrifuge.

(e) *The solid phase.* Wo. Ostwald[1] and von Buzagh[2] by their work on the "solid phase" rule have shown that generally, in a colloidal system, the amount of substance peptised is dependent on the amount of solid phase present. The author has shown by special tests, that this effect applies to the peptisation of tungstic acid by sodium hydroxide. For this reason, the exact quantities of solution and solid used have been given in the following tables.

Analytical Results

All columns of figures headed WO_3 refer to grams of WO_3 per 100 grams of solution. This also applies to the "Colloid content."

The pH values are those obtained with the quinhydrone electrode on solutions which had been centrifuged in the manner previously described. The ratio WO_3/Na_2O gives an approximate idea of the type of tungstate (e.g. whether normal or metatungstate) present in solution; the WO_3 values are those determined in 100 grams of the final ultrafiltrates, divided by its molecular weight, and the Na_2O values, that present in grams in 100 c.c. of the original sodium hydroxide solution divided by its formula weight. Since the densities of the solutions involved are near unity, it is not necessary to introduce the values for the purpose of these calculations. If sodium be adsorbed by the solid phase, it follows that the WO_3/Na_2O ratio will not accurately represent the composition of the salts in solution.

The colloid contents are given to the second place of decimals. Figures of greater accuracy would be meaningless, as, assuming an ultrafiltration error of 2%, even the figures in the second decimal place may be slightly incorrect.

Graphs are given showing the relation between the concentration of the original sodium hydroxide, and the WO_3 in solution before ultrafiltration, in the tungsten trioxide series, and the Series I experiments for tungstic acids A, B, and C. (Tables I, II, IV, VI).

Tungsten Trioxide

No. of flask	1	2	3	4	5
Conc. or original NaOH (Normalities)	0.001	0.020	0.078	0.157	0.261
Wt. of WO_3 (gms.)	3.0	3.0	5.0	10.0	10.0

In all cases 500 c.c. of alkali were used.

---

[1] Kolloid-Z., 41, 163; 43, 227, 249 (1927).

[2] Kolloid-Z., 41, 169 (1927); 46, 178 (1928).

TABLE I

No. of flask	Days from start	Before ultra-filtration (v. Fig. 1)		After ultra-filtration WO_3	Colloid Content	$\frac{WO_3}{Na_2O}$	Appearance of Solution
		WO_3	pH				
1	7	0.038	5.42	0.017	0.02	—	Faintly opalescent
	4	0.068	5.91	0.046	0.02	—	
	161	0.063	6.28	0.048	0.015	4.1	
2	7	0.215	9.83	0.216	Nil	—	Clear
	43	0.286	6.97	0.284	Nil	—	
	161	0.320	6.85	0.326	Nil	1.4	
3	7	0.733	12.0	—	—	—	Clear
	43	0.987	7.51	—	—	—	
	161	1.020	7.33	—	—	1.1	
4	7	1.482	12.23	—	—	—	Clear
	43	1.905	7.82	—	—	—	
	161	1.934	7.63	—	—	1.1	
5	7	2.146	12.77	—	—	—	Clear
	43	2.920	11.87	—	—	—	
	161	2.972	8.04	—	—	0.98	

No change was observed in the appearance of the solid phase.

Tungstic Acid—Type A

	Series I						Series II		
No. of flask	9	10	11	12	13	14	25	26	27
Conc. of NaOH (N)	0.001	0.005	0.010	0.020	0.035	0.050	0.010	0.020	0.028
Volume of solution (c.c.)	200	200	150	100	100	100	500	500	500
Wt. of tungstic acid (gms.)	1.0	1.0	1.0	1.5	3.0	4.0	5.5	9.5	10.5

TABLE II

Series I

No. of flask	Days from start	Before ultra-filtration (v. Fig. 2) WO_3	After ultra-filtration WO_3	Colloid Content	Appearance of Solution
9	7	0.035	—	—	Solutions 9–13 very slightly opalescent at commencement of experiments, later becoming clear
	85	0.039	0.006	0.03	
	160	0.041	0.030	0.01	
	205	0.049	0.038	0.01	
	686	0.044	0.033	0.01	
10	7	0.160	—	—	
	85	0.187	0.134	0.05	
	160	0.221	0.208	0.01	
	205	0.226	0.212	0.01	
	686	0.228	0.218	0.01	
11	7	0.282	—	—	Solution 14 clear throughout the experiments
	85	0.411	0.388	0.02	
	160	0.518	0.523	Nil	
	205	0.527	0.519	0.01	
	250	0.517	0.519	Nil	
	686	0.518	0.519	Nil	
12	7	0.646	—	—	
	85	0.821	0.782	0.04	
	160	0.919	0.920	Nil	
	205	0.938	0.930	0.01	
	250	0.952	0.939	0.01	
	686	0.979	0.987	Nil	
13	7	0.891	—	—	
	85	1.303	1.267	0.04	
	160	1.565	1.560	Nil	
	205	1.565	1.535	0.03	
	250	1.600	1.604	Nil	
	686	1.594	1.594	Nil	
14	7	1.171	—	—	
	85	2.015	2.031	Nil	
	160	2.238	—	—	
	205	2.262	2.219	0.04	
	686	2.324	2.334	Nil	

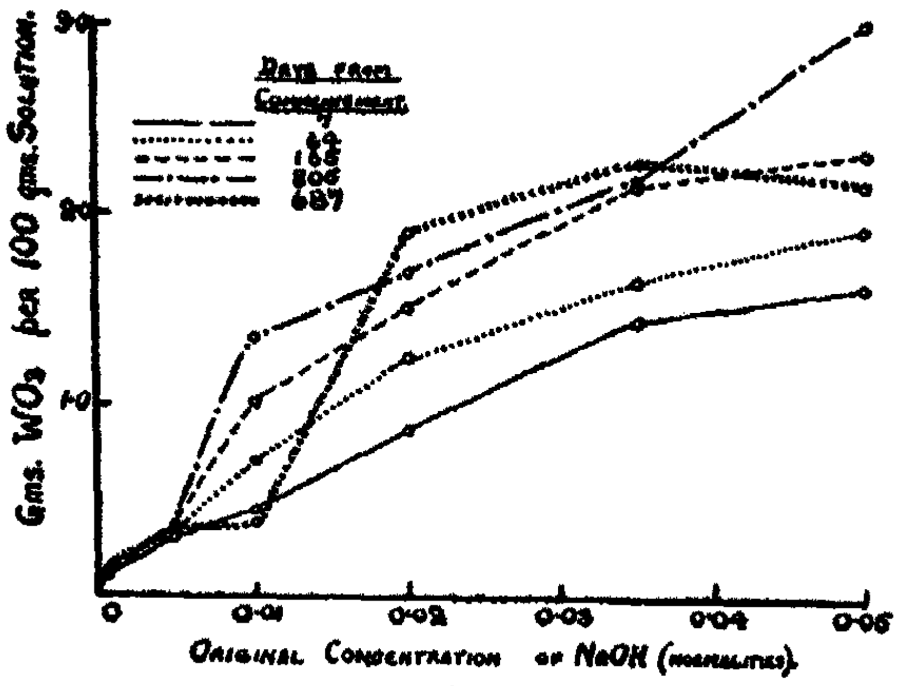


Fig. 3
Tungstic Acid (Type B)—in NaOH
Series I—Before Ultrafiltration

Table III
Series II

No. of flask	Days from start	Before ultrafiltration WO₃	Before ultrafiltration pH	After ultrafiltration WO₃	Colloid Content	$\frac{WO_3}{Na_2O}$	Appearance of Solution
25	91	0.455	5.64	0.424	0.03	—	All solutions resembled 9–13 in Series I
	161	0.469	4.85	0.457	0.01	—	
	218	0.468	4.46	0.477	Nil	4.0	
26	13	0.601	—	0.561	0.04	—	
	63	0.854	—	0.766	0.09	—	
	91	0.922	5.41	0.880	0.04	—	
	161	0.937	4.63	0.939	Nil	—	
	218	0.954	4.29	0.950	Nil	4.1	
27	91	1.156	5.89	1.072	0.08	—	
	161	1.299	4.96	1.239	0.06	—	
	218	1.317	4.59	1.301	0.02	4.0	

No change was observed in the appearance of the solid phase in either series. The final quantitative results were very similar for both series.

Tungstic Acid—Type B

	Series I						Series II		
No. of flask	15	16	17	18	19	20	28	29	30
Conc. of NaOH (N).	0.001	0.005	0.010	0.020	0.035	0.050	0.020	0.035	0.045
Volume of solution (c.c.)	200	200	150	100	100	100	500	400	400
Wt. of tungstic acid (gms.)	1.0	1.5	2.0	3.0	4.0	5.0	10.0	12.0	12.0

Table IV

Series I

No. of flask	Days from start	Before ultra-filtration (v. Fig. 3) WO_3	After ultra-filtration WO_3	Colloid Content	Appearance of Solution
15	7	0.100	—	—	Slight opalescence, decreasing with time
	64	0.105	0.072	0.03	
	165	0.112	0.107	0.005	
	205	0.104	0.091	0.01	
	687	0.125	0.114	0.01	
16	7	0.296	—	—	Same as 15
	64	0.331	0.269	0.06	
	165	0.352	0.337	0.015	
	205	0.346	0.334	0.01	
	687	0.351	0.342	0.01	
17	7	0.456	—	—	Same as 15
	64	0.714	0.612	0.10	
	165	1.007	0.930	0.08	
	205	1.348	1.319	0.03	
	687	0.382	0.371	0.01	
18	7	0.880	—	—	Same as 15
	64	1.250	1.198	0.05	
	165	1.506	1.418	0.09	
	205	1.690	1.569	0.12	
	687	1.900	1.894	0.01	
19	7	1.478	—	—	Clear
	64	1.674	1.644	0.03	
	165	2.129	1.930	0.20	
	205	2.164	1.931	0.23	
	687	2.277	2.250	0.03	
20	7	1.631	—	—	Clear
	64	1.942	1.904	0.04	
	165	2.312	2.173	0.14	
	205	3.018	2.971	0.05	
	687	2.148	2.114	0.03	

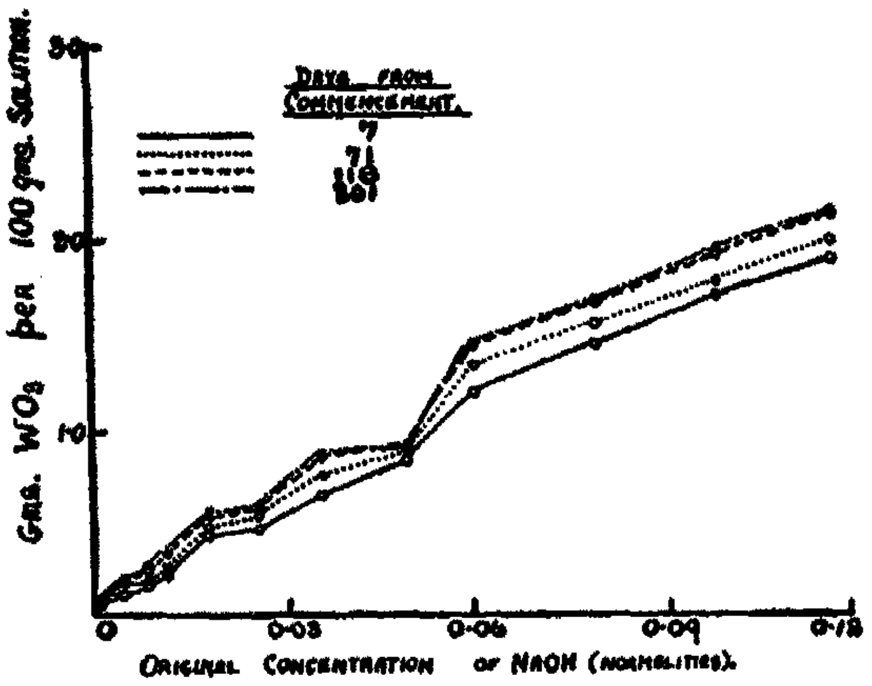


Fig. 4
Tungstic Acid (Type C)—in NaOH
Series I—Before Ultrafiltration

Table V

Series II

No. of flask	Days from start	Before ultra-filtration		After ultra-filtration WO_3	Colloid Content	$\frac{WO_3}{Na_2O}$	Appearance of Solution
		WO_3	pH				
28	87	1.147	3.65	1.107	0.04	—	Clear
	170	1.236	2.73	1.145	0.09	—	
	226	1.244	2.79	1.105	0.14	4.8	
29	15	1.282	—	1.239	0.04	—	Clear
	65	1.377	—	1.354	0.02	—	
	87	1.578	5.42	1.565	0.01	—	
	170	2.057	2.87	1.829	0.23	—	
	226	2.081	2.79	1.873	0.21	4.6	
30	87	1.397	6.41	1.282	0.12	—	Clear
	170	1.888	5.75	1.671	0.22	—	
	226	1.805	5.92	1.761	0.04	2.9	

The following changes in the solid phase were observed: in Series I, solid 15 was definitely yellow after 5 days, the remaining solids being unchanged. As time progressed, solids 16–19 slowly changed to a dull yellow colour, but no change in structure was visible under the microscope. After about 90 days, the solid in flask 20 consisted of small white crystals (hexagonal plates) of Na_2WO_4, $2H_2O$, and unchanged tungstic acid.

These observations were confirmed generally in Series II, e.g., white hexagonal crystals appeared in flask 30.

Tungstic Acid—Type C

Series I

This series actually consisted of three separate short series, the results being combined for convenience. The flasks, therefore, are not numbered consecutively.

No. of flask	44	45	46	39	47	48
Conc. of NaOH (N)	0.001	0.004	0.007	0.010	0.017	0.025
Volume of Solution (c.c.)	200	200	200	150	100	100
Wt. of tungstic acid (gms.)	1.0	1.0	1.0	1.0	1.5	1.5
No. of flask	40	41	21	22	23	24
Conc. of NaOH (N)	0.035	0.049	0.059	0.079	0.098	0.118
Volume of Solution (c.c.)	100	100	50	50	50	50
Wt. of tungstic acid (gms.)	2.0	2.0	2.0	2.0	2.0	2.0

Table VI

No. of flask	Days from start	Before ultrafiltration (v. Fig. 4) WO_3	After ultrafiltration WO_3	Colloid Content	Appearance of Solution
44	7	0.047	—	—	Colloidal in appearance; bluish white by reflected light, reddish-orange by transmitted light
	71	0.058	0.006	0.05	
	118	0.065	0.012	0.05	
	201	0.064	0.026	0.04	
45	7	0.113	—	—	
	71	0.145	0.095	0.05	
	118	0.173	0.120	0.05	
	201	0.186	0.119	0.07	
46	7	0.164	—	—	
	71	0.189	0.155	0.03	
	118	0.229	0.164	0.065	
	201	0.254	0.170	0.08	

TABLE VI (Continued)

No. of flask	Days from start	Before ultra-filtration (v. Fig. 4) WO_3	After ultra-filtration WO_3	Colloid Content	Appearance of Solution
39	7	0.209	—	—	Colloidal in appearance; bluish-white by reflected light, reddish-orange by transmitted light
	71	0.244	0.187	0.06	
	118	0.325	0.238	0.09	
	201	—	—	—	
47	7	0.414	—	—	
	71	0.481	0.398	0.08	
	118	0.529	0.421	0.11	
	201	0.545	0.435	0.11	
48	7	0.472	—	—	
	71	0.523	0.488	0.035	
	118	0.555	0.572	Nil	
	201	0.575	0.563	0.01	
40	7	0.632	—	—	
	71	0.728	0.707	0.02	
	118	0.834	0.843	Nil	
	201	—	—	—	
41	7	0.801	—	—	Clear
	71	0.860	0.849	0.01	
	118	0.900	0.894	0.01	
	201	0.890	0.866	0.02	
21	7	1.185	—	—	Clear
	71	1.352	1.321	0.03	
	118	1.451	1.312	0.14	
	201	1.456	1.420	0.04	
22	7	1.447	—	—	Clear
	71	1.562	1.542	0.02	
	118	1.665	1.525	0.14	
	201	1.677	1.636	0.04	
23	7	1.696	—	—	Clear
	71	1.767	1.747	0.02	
	118	1.910	1.799	0.11	
	201	1.933	1.882	0.05	
24	7	1.881	—	—	Clear
	71	2.000	1.936	0.06	
	118	2.118	2.007	0.11	
	201	2.124	2.040	0.08	

Series II

No. of flask	31	32	33	34
Conc. of NaOH(N)	0.010	0.040	0.060	0.080
Volume of solution (c.c.)	500	400	400	400
Wt. of tungstic acid (gms.)	3.3	8.0	8.0	10.8

TABLE VII

No. of flask	Days from start	Before ultra-filtration		After ultra-filtration WO_3	Colloid Content	$\frac{WO_3}{Na_2O}$	Appearance of Solution
		WO_3	pH				
31	93	0.193	6.32	0.161	0.03	—	Colloidal
	170	0.293	5.95	0.232	0.06	—	
	226	0.324	5.99	0.261	0.06	2.2	
32	93	0.709	6.69	0.707	Nil	—	Very faintly opalescent
	170	0.853	6.67	0.831	0.02	—	
	226	0.890	6.54	0.881	0.01	1.9	
33	14	0.876	—	0.843	0.04	—	Clear
	64	0.957	—	0.933	0.02	—	
	93	0.961	7.10	0.938	0.02	—	
	170	1.139	6.95	1.119	0.02	—	
	226	1.164	6.96	1.161	Nil	1.7	
34	93	1.318	7.10	1.288	0.03	—	Clear
	170	1.499	7.08	1.436	0.06	—	
	226	1.471	7.11	1.439	0.03	1.6	

The solid in flask 44 remained pale greenish yellow; the remaining solids of Series I, and all those of Series II changed rapidly to bluish white products.

In both series, approximately similar quantitative results were obtained up to a concentration of initial alkali of 0.05 N. Above this concentration, the values for the total WO_3 in solution were higher for Series I than for Series II.

Tungstic Acid—Type D

Owing to shortage of time, only one series of experiments was carried out with tungstic acid D.

No. of flask	69	70	71	72
Conc. of NaOH(N)	0.001	0.005	0.010	0.060
Volume of solution (c.c.)	500	500	500	500
Wt. of tungstic acid (gms.)	5.0	5.0	5.0	12.0

TABLE VIII

No. of flask	Days from start	Before ultra-filtration		After ultra-filtration WO_3	Colloid Content	$\frac{WO_3}{Na_2O}$	Appearance of Solution
		WO_3	pH				
69	6	0.038	4.29	0.006	0.03	—	Colloidal in appearance; bright yellow by reflected light, reddish-orange by transmitted light
	27	0.045	4.09	0.014	0.03	1.2	
70	7	0.253	4.19	0.147	0.11	—	
	27	0.270	4.10	0.183	0.09	3.2	
71	7	0.502	4.24	0.370	0.13	—	
	27	0.519	4.14	0.395	0.12	3.4	
72	7	1.915	6.03	1.836	0.08	—	Very slightly opalescent
	27	2.004	6.17	1.980	0.02	2.8	

The solids in flasks 69-71 remained unchanged throughout the experiments. The tungstic acid in flask 72, however, slowly changed to a white solid. The X-ray examination of this product has been described in the previously mentioned publication.

In certain cases, after the final analyses, the solids were taken out of solution, pressed between filter papers to remove excess liquid, and air-dried to constant weight on porous tiles. The following results were obtained:

TABLE IX

Type	No. of flask	Loss on ignition (%)	Loss on ignition (%) of original tungstic acid
A	25	14.41	A. 14.43
	27	14.17	
B	28	11.46	B. 14.69
	29	12.30	
C	31	10.25	C. 9.92
	33	9.78	
D	72	9.24	D. 8.43

Discussion

A study of the pH values of the various solutions, obtained a few minutes after commencing each series, showed that neutralisation of the alkali had taken place, probably producing Na_2WO_4. Thus, the experiments described really record the solubility of the tungstic acids in sodium tungstate solution. With anhydrous tungsten trioxide, the sodium hydroxide was only neutralised slowly, except in the most dilute solution, when immediate "neutralisation" occurred, this suggesting that adsorption was the original cause of the removal of alkali from the solutions. The soluble sodium tungstate produced would then slowly attack the tungstic acid present, forming salts with increasingly large tungsten content.

The peptisation of tungstic acid by alkali may be conveniently explained by the theory of Zsigmondy, which was worked out in detail in connection with the stannic acids. If sodium hydroxide is added to tungstic acid, sodium tungstate will be produced, and if it is assumed that the tungstate ion is strongly adsorbed by the tungstic acid particles, the latter will become negatively charged. If sufficient charging is effected by this process, dispersion of the particles will result, and a sol will be produced. Alternatively, one may assume that tungstate is formed on the surface of the tungstic acid particles. Dissociation of the product so formed may occur, the sodium ions diffusing into the liquid, leaving the particles negatively charged. The final result of such processes is to produce charged micelles containing water, some form of tungstic acid or oxide, and probably sodium, together, of course, with free sodium ions. A study of the colloid contents of the various series shows that with a given tungstic acid, and increasing sodium hydroxide concentration, the colloid content frequently increases from a small value to a maximum, and then decreases. This is particularly well shown in the colloid contents for Types B and D. The effect would be anticipiated, on the following grounds: very small quantities of alkali will produce small quantities of tungstate, and the adsorption of the tungstate ion will charge the particles, but not sufficiently to cause peptisation. Medium quantities of alkali will produce sufficient salt to finally bring about dispersion of the tungstic acid, whilst higher alkali concentrations will finally lead to a coagulation effect on the tungstic acid. It must also be noted that at and above a certain concentration, disintegration of the solid phase occurs, producing molecular tungstate and metatungstate solutions.

The maximum concentration of sodium hydroxide which produced immediate peptisation with the various products was as follows: WO_3, 0.001 N; tungstic acid A, 0.035 N; B, 0.020 N; C, 0.035 N; with D, colloidal matter was present in all solutions tested, i.e. up to 0.06 N. On general grounds, it would be expected that little peptisation would occur with ignited tungsten trioxide, owing to the complex structure and dense nature of the particles. Also, the crystals of tungstic acid A, and the comparatively large glassy particles of tungstic acid B are not suitable products for extensive sol formation. Tungstic acids C and D being of a more finely divided nature and possessing greater adsorptive power than the previously mentioned products (shown e.g. by their ammonia contents), are far more likely to peptise when treated with alkali. These general deductions are in harmony with the observations given in the various Tables under "Appearance of Solution."

During prolonged experiments of the type described in this paper, there are many variable factors, so that the prediction of the possible behaviour in any particular case becomes very difficult. The following possible sources of variation may be considered:—

(a) Change in the dispersion medium may occur owing to the early formed sodium tungstate passing through various intermediate stages to metatungstate, and possibly still higher polytungstates (v. WO_3/Na_2O ratios, Table V, 28 and 29.). This will probably cause varying adsorption of the ion containing tungsten, by the solid phase. This tungstate-metatungstate change is shown by the decrease in the pH values of the solution, and the condition of the final ultrafiltrates is approximately indicated by the WO_3/Na_2O ratios. Solutions of tungstic acid C were exceptional, in that the pH values remained relatively high. This is accounted for by the fact that the solubility of C was rather low, and therefore only incomplete formation of metatungstate would take place.

A study of the solubility "curves" shows that speaking generally, a condition of equilibrium was approached with tungstic acids A and C, and with tungsten trioxide. Abnormalities were observed with product B whilst D had not sufficient time to attain equilibrium. Since A and D are essentially definite compounds, it would be anticipated that the products would easily dissolve in sodium hydroxide, and would finally attain an equilibrium. The much lower solubility of product C is one of the facts which most strongly suggests that it might contain a condensed acid, as previously suggested.[1] Such a product would not readily be attacked by reagents, and one would expect its solubility in sodium hydroxide to be less than the solubilities of H_2WO_4, H_2O or H_2WO_4.

(b) Change in the solid phase. Possible ageing effects are (1) a general coarsening of amorphous particles to larger amorphous particles or (2) crystallisation, either partial or complete.

The evidence (observations and Table IX) shows that such changes were slight with tungstic acids A and C, and not of large extent with D, but were much more pronounced with B. This greyish white product frequently changed to a yellow substance. The author has shown by X-ray analysis[2] that such changes are due to crystallisation into H_2WO_4 or H_2WO_4, H_2O or into a mixture of these products. Also, it was shown by centrifuging, that a tungstic acid B from a solubility experiment contained grey, yellow, and white particles. Since in a solubility series with products of this type, each solid will have assumed a different composition after a short time, and therefore any equilibrium which may have been set up between solid and solution will alter, a smooth solubility curve, and accurately reproducible results would not be expected. Such considerations will account for the irregular results shown in Fig. 3. The large decrease in the tungsten content of solution 17, after 687 days (v. Table IV) may be due to the decomposition of unstable higher tungstates, brought about by the above mentioned causes.

Solutions 20 and 30 were exceptional in that white hexagonal crystalline plates were deposited. This crystallisation accounts for the fact that in the

---

[1] Loc. cit.

[2] Loc. cit.

final ultrafiltrates for 20 and 30, the tungsten contents are less than in 19 and 29, respectively, (Tables IV and V) whilst the pH value of 30 is much higher than for 28 and 29. (Table V).

(c) Change in the particles of the disperse phase. The remarks made under (b) apply in general to the particles of sols; ageing usually produces larger particles with less stability, and which therefore frequently coagulate.

(d) Hydrolysis in the solutions may produce colloidal tungstic acid. If the particles produced were small and heavily hydrated, clear sols may be produced. This was the case in the following experiments: Type B, (Table IV, 18, 19, 20;) Type C, (Table VI, 21, 22, 23, 24). In all these cases, the colloid content of the solution first increased, and then decreased with time; in some cases the value decreased to zero. This effect is probably due to an increase in the size of the particles, accompanied by a change in the degree of hydration, followed by coagulation of the larger particles. In some cases, presumably the whole of the colloidal tungstic acid was removed in this way.

In general, the changes in the amount of tungstic acid present in the colloidal state will be the resultant of the following effects: (a) dispersion of particles of the solid phase, (b) coagulation of aged particles in the sol.

Summary

Tungsten trioxide and four standard tungstic acids whose structures had been previously determined, have been subjected to the prolonged action of solutions of sodium hydroxide of varying concentration. At stated intervals, the amount of tungsten in the solutions was determined before and after ultrafiltration through collodion membranes. The pH values of certain solutions are recorded. Changes in the solid phase have also been studied. The results are discussed.

In conclusion, the author wishes to express his sincere thanks to Dr. J. K. Wood, F.I.C., for the keen interest displayed in the progress of the investigation, and for the helpful suggestions given during the consultations held in connection with the research.

Municipal College of Technology,
University of Manchester,
June 15, 1931.

SOME SOLVENT PROPERTIES OF SOAP SOLUTIONS. II

BY E. LESTER SMITH

In the previous paper of this series, attention was drawn to the extraordinary solvent powers of soap solutions for organic liquids insoluble or slightly soluble in water. The phenomenon was studied by determining the proportion of an organic liquid absorbed by a soap solution in equilibrium with excess of the liquid. In the present paper, the solvent properties of soap solutions will be studied from a different point of view. An organic substance almost insoluble in water—a sterol or an oil for example—may be dissolved to a limited extent in a soap solution; if this solution is then shaken with an organic solvent such as ether, the dissolved substance is by no means completely extracted by the solvent; on the contrary a definite and reproducible equilibrium is set up, the substance being partitioned between the two liquid phases.

Until recently almost the only problems involving the extraction of soap solutions occurred in connection with the analysis of oils, fats and waxes, where determinations of the quantity and nature of the unsaponifiable fraction afford in some instances criteria of genuineness. Very little systematic work is to be found in the literature, dealing with the problems underlying the extraction of soap solutions. Published papers include descriptions of analytical methods for the determination of the unsaponifiable matter in oils, fats and waxes, often unaccompanied by strict evidence as to their accuracy, and some experiments which prove that solvents such as petroleum spirit are less efficient than ethyl ether for the extraction of fish liver oil soap solutions. This work has been reviewed by the author elsewhere.[1]

With the discoveries that the fat-soluble vitamins A, D and E are present in the unsaponifiable fractions of the oils in which they occur, such studies assumed a new importance, particularly in connection with the preparation of concentrates of these vitamins for incorporation into foodstuffs and medicinal preparations. The work here reported was in fact undertaken initially from the point of view of these practical problems, but was continued on account of its own intrinsic interest. The unsaponifiable fraction of natural oils is a complex mixture of substances of ill-defined constitution, and is difficult to estimate with precision; the vitamins are even more difficult to estimate, and it was felt that more useful information might be obtained by studying instead the partition of some pure chemical substances.

p-Dimethylaminoazobenzene and aniline were finally selected, largely on account of the ease with which these basic substances could be extracted with acid from their solutions in organic solvents and estimated colorimetrically or volumetrically.

---

[1] Analyst, 53, 632 (1928).

Partition of p-Dimethylaminoazobenzene between Soap Solutions and Ether

p-Dimethylaminoazobenzene is a yellow dye, almost insoluble in water, but fairly readily soluble in soap solutions and in organic solvents. Dilute solutions of its hydrochloride in hydrochloric acid have a pink colour, very suitable for colorimetric estimation. It was originally desired to study the partition of the natural unsaponifiable matter of cod-liver oil, and the idea was conceived of using this dye as an indicator, in the hope that it would be partitioned in the same ratio as the unsaponifiable matter. This hope received some justification in the fact that it had not proved possible (with rather crude analytical methods) to demonstrate any fractionation between the sterol and liquid portions of the unsaponifiable matter on successive extractions of a soap solution; nevertheless it was not fulfilled, as the dye showed a partition coefficient in favour of the ether phase considerably higher than the corresponding value for the unsaponifiable matter.

Previous experiments had indicated that the addition of methyl or ethyl alcohol increased the partition coefficient for unsaponifiable matter. Accordingly the effect of varying the methyl alcohol concentration on the partition of the dye was investigated, and also the effects of varying the soap concentration, the excess of alkali, and the concentration of the dye itself.

Experimental

The extractions were carried out in 250 cc stoppered separating funnels, into which all solutions were measured by pipette or burette, taking precautions against evaporation of ether. Fatty acids from cod-liver oil stearin were kept as a 50% stock solution in ether, which also contained the p-dimethylaminoazobenzene, in the proportion of 0.01 gm. to the fatty acids from 100 gm. of the oil. In most experiments the fatty acids from 15 gm. of oil were used, being mixed in the separator with the necessary amounts of water, 2 N sodium hydroxide, methyl alcohol and ether. After vigorous hand shaking for several minutes, the separators were allowed to stand at room temperature until complete separation into two layers occurred, noting the time required. The lower and upper layers were then run out separately into graduated flasks of capacity slightly greater than the volumes of the layers, afterwards filling to the mark with water-saturated ether measured from a burette. The volumes of the layers could thus be obtained by difference, with an error probably less than 0.5 cc. The ether layer was then transferred to a separating funnel, and extracted three times with 10% hydrochloric acid using 125 cc in all. The acid solution was warmed on a waterbath to remove ether, made up with water to 250 cc, and compared in a Hellige colorimeter with a standard containing 0.25 mg. of the dye in 100 cc of 5% hydrochloric acid. This gave the weight of dye in the ether layer, and from a knowledge of the total amount present, and the volumes of the layers, the partition coefficient could be calculated. The volume of ether used for an extraction was adjusted after some preliminary experiments, so that approximately half the dye present was extracted since experimental errors in the estimation cause the least error in the calculation of partition coefficients under these conditions.

In the first series of experiments the fatty acids from 15 gm. of cod-liver oil stearin were made up to yield in every case a volume of 150 ccs of alcoholic soap solution (referred to as "10%" soap solution). On adding ether a very appreciable contraction occurred, and the final volume was always less than the sum of the volumes added by 5-10 cc, an amount considerably greater than could be accounted for by evaporation of ether during the measurements

Discussion of Results

Table I records the data for the first series of experiments in which the methyl alcohol concentration was varied, the concentrations of soap, alkali and dye remaining constant. The influence of methyl alcohol on the time required for complete separation of the emulsion is striking; 69 hours were needed in absence of the alcohol, only a quarter of an hour with 15% of methyl alcohol in the soap solution. The use of alcohols for breaking emulsions is of course a familiar procedure in analytical chemistry, but nevertheless it does not seem to be explained by any of the theories of emulsification that have been advanced.

In absence of methyl alcohol, the volume of the soap solution increases on saturation with ether from 150 cc to 187.5 cc. Additions of methyl alcohol up to about 25% cause only small increments in the ether absorption but higher concentrations of methyl alcohol greatly increase the absorption of ether by the alcoholic soap solution.

The partition coefficients after a very slight rise, decrease steadily with increasing methyl alcohol concentration; this point will be discussed later. Slight irregularities in these variations are due partly to experimental error and partly to variations in the room temperature at which the experiments were performed.

TABLE I

Initial Soap Concentration	Excess NaOH over amount required to neutralise Fatty Acids	Methyl Alcohol as % of initial volume of Soap Solution	Time Separate	Volume of Ether-saturated Lower Layer (Initially 150 cc)	Volume of Upper Layer	Partition Coefficient
10%	21.5%	Nil	69 hours	187.5 cc	37 cc	5.8
"	"	2%	?	189.5 cc	36.2 cc	5.8
"	"	5%	7 hours	188.3 cc	35.8 cc	6.0
"	"	10%	45 mins.	191.4 cc	33.2 cc	6.1
"	"	15%	15 "	190.7 cc	33.2 cc	5.6
"	"	20%	11 "	194.5 cc	30.0 cc	5.3
"	"	25%	10 "	199.9 cc	23.8 cc	4.5
"	"	27%	5 "	200.4 cc	43.0 cc	4.2
"	"	33%	5 "	219.0 cc	29.2 cc	3.0
"	"	40%	3.5 "	250.0 cc	57.5 cc	2.15

TABLE II

Initial Soap Concentration	Excess NaOH over amount required to neutralise Fatty Acids	Methyl Alcohol as % of initial volume of Soap Solution	Time to Separate	Volume of Ether-saturated Lower Layer (Initially 150 cc)	Volume of Upper Layer	Partition Coefficient
10%	1%	20%	?	193.0 cc	30.3 cc	5·4
"	21·5%	"	11 mins.	194.5 cc	30.0 cc	5·3
"	42%	"	18 "	198.5 cc	25.0 cc	4·55
"	1%	33%	5 "	212.5 cc	39.7 cc	3·55
"	21·5%	"	5 "	219.0 cc	29.2 cc	3·0

TABLE III

Initial Soap Concentration	Excess NaOH over amount required to neutralise Fatty Acids	Methyl Alcohol as % of initial volume of Soap Solution	Time to Separate	Volume of Ether-saturated Lower Layer (Initially 150 cc)	Volume of Upper Layer	Partition Coefficient
8%	21.5%	20%	7 mins.	184.2 cc	36.0 cc	7.85
10%	"	"	11 "	194.5 cc	30.0 cc	5·3
12%	"	"	6 "	205.5 cc	41.5 cc	3·95
14%	"	"	8 "	221.5 cc	34.8 cc	3·55
16%	"	"	7 "	236.0 cc	48.0 cc	2·9

The second table indicates that for a fixed soap concentration of 10% and methyl alcohol concentration of 20% and 33%, respectively, increasing the free alkali in the soap solution slightly increases the ether absorption and decreases the partition coefficient.

The third table illustrates the effect of increasing soap concentration for a fixed methyl alcohol concentration of 20%. The ether absorption is observed to increase rapidly, while the partition coefficient falls from 7.85 to 2.9 on doubling the soap concentration.

Interpretation of Results

We have seen in the first paper of this series, that the solvent powers of soap solutions can only be accounted for by postulating adsorption of the organic solute on the colloidal soap particles. The resistance which such solutions show towards extraction of the solute by organic solvents favours the same hypothesis. Fortunately also, some of the partition data are amenable to mathematical treatment which enables the hypothesis to be tested.

It is convenient to consider the solute as being distributed between three phases, the organic solvent, the water and the colloidally dispersed soap. The portions of solute in the solvent and in the water, respectively, are in equilibrium according to the law of partition, while the portions of solute in the water and in the soap micelles are in equilibrium according to the adsorption law. It is true that the concentration of solute in the water may be vanishingly small in some cases, and also that solute may pass direct from soap to solvent, but these considerations do not render inapplicable the above equilibrium relationships.

Thus we have:—

Let U = Total weight of solute in system.
X = Weight of solute adsorbed by colloidal soap.
Y = Weight of solute in true solution in aqueous phase (excluding that adsorbed by the soap).
W = Weight of solute in organic solvent phase.
k_1 = Adsorption coefficient.
k_2 = True partition coefficient for solute between organic phase and aqueous phase (without colloidal soap).
K = Measured partition coefficient for solute between organic phase and aqueous plus colloidal soap phases.
v = Volume of organic solvent phase.
V = Volume of aqueous phase.
S = Concentration of colloidal soap in aqueous phase.

Then according to the usual adsorption formula:—

$$(1) \qquad X = k_1 S Y^{1/n}$$

$$(2) \qquad \text{or } Y = \frac{X^n}{k_1^n S^n}$$

According to the partition formula:—

$$(3) \qquad \frac{W}{Y} = \frac{k_2 v}{V}$$

Substituting for Y,

$$(4) \qquad \frac{W}{X^n} = \frac{k_2 v}{k_1^n S^n V}$$

$$(5) \qquad U = X + Y + W$$

But since Y is usually extremely small, it can be neglected in comparison with U giving:—

$$(6) \qquad X = U - W$$

Substituting in (4),

$$(7) \qquad \frac{W}{(U-W)^n} = \frac{k_2 v}{k_1^n S^n V}$$

The ordinary partition formula used for calculating K (in which aqueous and colloidal phases are treated as one phase) is:—

$$(8) \qquad \frac{W}{(U-W)} = \frac{Kv}{V}$$

Whence:—

$$(9) \qquad K = \frac{k_2}{k_1^n S^n} (U-W)^{n-1}$$

If this expression is correct we should expect that the measured partition coefficient K would not remain constant if the amount of solute in the aqueous layer varied over any considerable limits.

It would only remain constant if $n = 1$, when the expression $(U-w)^{n-1}$ reduces to 1. This would be the case if the solute distributed itself between the colloidal soap and the aqueous phases according to the simple law of partition and not according to the usual adsorption law. In a series of experiments, however, it may be taken that small variations in the concentration of solute in the aqueous phase will not affect the value of K, the permissible limits of variation becoming smaller the further the value of n departs from 1.

We should also expect that K would be increased by any factor which would increase the true partition coefficient k_2 and decreased by any factor tending to increase either the adsorption coefficient or the concentration of colloidal soap (not total soap concentration) in the aqueous layer.

Tables I–III provide data which enable some of these conclusions to be tested. Table III shows the pronounced influence of soap concentration of the partition coefficient K; the value of the latter is reduced to much less than half its former value by doubling the soap concentration. This is in agreement with expectations, since according to formula (9) K should be proportional to $1/S^n$; S, the concentration of colloidal soap, would more than double on doubling the total soap concentration, since a relatively greater proportion would be in molecular solution in the weaker solution; also n is greater than 1; both these factors therefore tend to make K decrease more rapidly than the soap concentration increases.

Similarly the effect of excess alkali in the alcoholic soap solution would probably be to increase the proportion of soap in the colloidal state, without much affecting other factors. This is reflected (see Table II) in an increase in the ether absorbed by the soap solution, and a decrease in the partition coefficient K.

Variation in the methyl alcohol concentration has a composite effect. On the one hand, the solubility of the solute in the aqueous phase is likely to increase with increasing alcohol concentration, and since its solubility in the organic phase is not much affected, k_2 the ratio of these solubilities, decreases, so that K tends to decrease. On the other hand, the soap passes more completely into molecular solution as the alcohol concentration is increased, so that S decreases; also the increased solubility of the solute in the aqueous phase is liable to decrease the adsorption coefficient k_1. Both these factors tend to increase K so that the net effect on K cannot be predicted.

Table I shows in the main a decrease in K for increasing methyl alcohol concentration, indicating, if formula (9) is correct, that k_2 decreases more rapidly than $k_1^n S^n$. Neither of these factors can be measured with any degree of accuracy under the conditions of the experiments; it was possible, however, to get a rough measure of k_2 by making the assumption that the solubility of the solute in the aqueous phase (containing methyl alcohol, dissolved ether, and soap in molecular solution) is the same as its solubility in aqueous methyl alcohol of the same strength.

The solubility of the dye in a series of methyl alcohol-water mixtures was therefore determined, by adding the requisite volume of a methyl alcohol solution of the dye to a measured volume of water, allowing the excess dye to crystallise out overnight, and estimating colorimetrically the dye concentration in the acidified filtrate. The solubility of the dye in ether at 15.5° was found to be 2.99 gm. per 100 cc of solution. The ratio of the solubilities in ether and in aqueous methyl alcohol gives k_2 approximately. Since $(U-W)^{n-1}$ was approximately constant for the experiments recorded in Table I, $k_1{}^nS^n$ is proportional to K/k_2. The results obtained are shown in Table IV, a few of the intermediate values for k_2 being read from curves. It will be observed that the solubility of the dye in water increases rapidly with increasing methyl alcohol concentration, so that k_2 decreases in like fashion. The values of k_2/K in the last column, which should be proportional of $k_1{}^nS^n$, also decrease, though less rapidly than does k_2, thus confirming the previous conclusion. In other words, the addition of methyl alcohol has a greater effect in increasing the solubility of the dye in the aqueous phase than it has in decreasing the proportion of soap in the colloidal state and the value of k_1; hence the measured partition coefficient K falls.

TABLE IV

Methyl Alcohol as % of initial volume of soap solution	Solubility of Dye (parts per 10^6)	K_2	K	$k_2/K \propto k_1{}^nS^n$
0%	0.32	93,000	5.8	16,000
5%	0.41	73,000	6.0	12,000
10%	—	43,000	6.1	7,100
15%	1.00	30,000	5.6	5,400
20%	1.95	15,000	5.3	2,900
25%	—	11,900	4.5	2,700
27%	—	10,300	4.2	2,500
30%	3.35	—	—	—
33%	—	6,400	3.0	2,100
40%	10.2	2,900	2.15	1,300

Determination of "n"

A further series of experiments was planned to determine partition coefficients for widely differing concentrations of the dye. This provides data for the calculation of a series of values for the index "n," the constancy of which afford a further test of the validity of formula (9). If all factors except solute concentrations are kept the same in two experiments (for which the subscripts a and b are used) we have:

$$(10) \qquad \frac{K_a}{K_b} = \frac{(U-W)_a^{n-1}}{(U-W)_b^{n-1}}$$

$$(11) \qquad n = \frac{\log \dfrac{K_a}{K_b}}{\log \dfrac{(U-W)_a}{(U-W)_b}} + 1$$

Partition coefficients were measured for the dye p-dimethylaminoazobenzene using a 20% concentration of methyl alcohol, and other concentrations as in the first series of experiments, except that the fatty acids were prepared from cod-liver oil stearin soap solution exhaustively extracted with ether to remove unsaponifiable matter, in case this might interfere. The temperature at which the separations occurred was maintained at 19° ± 1°.

TABLE V

Initial Weight of Dye	K	(U−W)	n
1.0 gm.	6.55	0.574 gm.	
			1.063
0.10 "	5.72	0.0663 "	
			1.065
0.010 "	4.86	0.00563 "	
			1.069
0.0010 "	4.18	0.00063 "	
			1.070
0.00010 "	3.60	0.000072 "	

The results, recorded in Table V, show that the value of n remains constant within the limits of experimental error. Owing to the fact that n is only slightly greater than 1, the partition coefficient is barely doubled for a 10,000 fold increase in initial dye concentration. This means that it would almost be correct to say that the dye is dissolved, rather than adsorbed, by the colloidal soap, a conclusion which is of interest in connection with the further experiments to be described.

Partition of Aniline between Sodium Oleate Solutions and Ethyl Acetate

The experiments described in this section were carried out three years later than those in the preceding section, and in connection with an investigation of the system sodium oleate, water, sodium chloride, ethyl acetate, which will form the subject of a later communication.

Sodium oleate was chosen as a pure soap, of which isotropic solutions could be prepared over a considerable concentration range at room temperature; ethyl acetate because it was one of the few organic solvents known at the date of these experiments which did not form a permanent emulsion when shaken with a soap solution; aniline because it could easily be estimated volumetrically and because it was more soluble in water than other solutes investigated and promised to yield interesting results on this account.

Experimental. Sodium oleate was prepared as described previously. Ethyl acetate was purified by washing repeatedly with calcium chloride solution or brine to remove alcohol, drying over calcium chloride and fractionating. Aniline of C.P. quality was freshly redistilled before use.

To determine a partition coefficient, sodium oleate solution and a solution of aniline in ethyl acetate were weighed into a 100 cc separating funnel, which was stoppered both at the top, and at the bottom of the stem, and then immersed to the neck in a thermostat at 25°. After a period sufficient to ensure temperature equilibrium, the separator was shaken vigorously by hand, and replaced in the thermostat until separation was complete. It was then carefully removed and samples comprising almost the whole of each layer transferred to weighed separating funnels. The aniline was estimated in both samples, so that the concentration of aniline per gram could be calculated for both layers, the ratio of these concentrations being taken as the partition coefficient. This method of calculating partition coefficients needs no apology, for as Hand remarks[1] Nernst's original statement of the partition law was in terms of weight in weight concentrations. Aniline was extracted from the ethyl acetate layer by shaking out thrice, each time with a quantity of 10% sulphuric acid approximately equal in volume to the sample. The bulked acid extracts were boiled down to small bulk to remove ethyl acetate and alcohol resulting from its hydrolysis (acetic acid was found not to affect the estimation) cooled and transferred to a stoppered bottle with enough water to bring the acidity back to about 10% sulphuric acid. Aniline was then estimated volumetrically in this solution by the method of Pamfilov and Kisseleva[2]. About 1 gm. of potassium bromide was added, then a measured excess of N/10 sodium hypobromite solution (usually 50 cc); after standing about 3 minutes, 1 gm. of potassium iodide was added in solution, and the mixture back-titrated with N/10 sodium thiosulphate using starch as indicator. Aniline was extracted similarly from the soap solution after adding a little more ethyl acetate, but it was necessary to filter the acid solution before titrating, in order to remove the trace of oleic acid usually present, which was found to interfere with the aniline estimation. Tested against pure aniline this volumetric method gave results 1-2% too high. No corrections were applied however since the same errors affected the estimations of aniline in both phases, and cancelled out in the calculation of the partition coefficient.

Partition coefficients for aniline were measured over the largest possible range of sodium oleate concentrations, namely from zero to 1.1 N_w. Slightly above the latter concentration a third liquid phase appeared, which was characterised as neat soap on account of its properties, and from a knowledge of the phase diagram which will be described in the next paper in this series. In some experiments the aniline concentration was varied over as wide a range as was practicable, and in others the effect of sodium chloride on the partition coefficient was studied.

The initial sodium oleate concentrations are expressed in weight normalities (mols of soap associated with 1 kilo of water) and also as weight in weight percentages. The weight normality is not affected by saturation with ethyl acetate, and shaking with excess ethyl acetate alters it only very slightly on account of the water abstracted from the soap solution by the upper layer.

Discussion of Results

The results are combined in Table VI. Owing to the moderate solubility of aniline in water, the partition coefficient for this substance between ethyl

---

[1] J. Phys. Chem., 34, 1961 (1930).

[2] Z. anal. Chem., 75, 87 (1928); Analyst, 54, 60 (1929).

TABLE VI

Initial Sodium Oleate		Initial Sodium Chloride N_w	Aniline. Gm. per 100 gm. Solution		Partition coefficient
N_w	Gm. per 100 gm. solution		$(A)_1$ Upper Layer	$(A)_2$ Lower Layer	$K = \frac{(A)_1}{(A)_2}$
0	0	—	0.442	0.0146	30.2 Mean 30.25
”	”	—	0.550	0.0182	30.3
”	”	—	0.0561	0.00182	30.7
”	”	—	4.62	0.157	29.5
”	”	0.5	0.481	0.0146	33.0
0.05	1.50	—	0.542	0.0242	22.4
0.1	2.95	—	0.539	0.0320	16.8
0.1	2.95	0.5	0.399	0.0256	15.6
0.15	4.37	—	0.436	0.0360	12.1
0.2	5.73	—	0.316	0.0303	10.5
0.3	8.36	—	0.396	0.0502	7.9
0.4	10.83	—	0.517	0.0728	7.1 Mean 7.05
0.4	10.83	—	0.528	0.0752	7.0
0.4	10.83	—	3.82	0.534	7.15
0.4	10.83	—	16.90	2.239	7.55
0.4	10.83	0.5	0.422	0.0610	6.9 Mean 6.85
0.4	10.83	0.5	0.439	0.0648	6.8
0.5	13.2	—	0.501	0.0844	5.93
0.7	17.55	—	0.509	0.1106	4.61
0.9	21.5	—	0.649	0.1584	4.10 Mean 4.10
0.9	21.5	—	0.620	0.1507	4.11
1.1	26.7	—	0.469	0.1229	3.82

acetate and water is not abnormally high, like the corresponding value for p-dimethylaminoazobenzene between ether and water.

It will be observed however that 1% of sodium oleate is sufficient to cause a marked decrease in the partition coefficient for aniline, and that the value decreases steadily as the soap concentration increases. Comparison with Table III will show that this decrease in K is of lesser magnitude than in the earlier experiments using the dye as solute. This is largely because the amount of aniline dissolved in the water phase is comparable with the amount dissolved in the colloidal soap phase, a factor which operates in the direction of making K independent of soap concentration. It was hoped that these statements might be expressed mathematically, but although a formula can be derived along the lines of the one used in connection with the earlier experiments, the fact that Y cannot be neglected in comparison with U and X renders the final expression so complicated that it cannot be made to yield any useful information. It will be observed that K is independent of aniline concentration, except when this is so high that the weight of aniline adsorbed by the soap is comparable with that of the ethyl acetate adsorbed. This means that the value of n in the adsorption formula is unity, so that in this case it is hardly correct to speak of adsorption of solute by the soap. Rather must the aniline be regarded as being distributed according to the partition law between the three phases; (1) wet ethyl acetate layer; (2) water (plus dissolved ethyl acetate and soap in molecular solution); and (3) colloidal soap (plus adsorbed ethyl acetate and water of hydration).

The effect of sodium chloride is noteworthy. It *increases*, by the familiar salting-out effect, the partition coefficient for aniline between ethyl acetate and water. When soap is present, however, salt *decreases* the partition coefficient below the corresponding value in the absence of salt. This is attributed to the effect of salt in increasing the proportion of the soap in the colloidal state, thus increasing the size of this phase in relation to the others.

It may be noted in passing that the temporary emulsion produced by shaking 0.9 N_w sodium oleate solution with ethyl acetate is perfectly transparent at 25°.

In general, this series of experiments using aniline as solute confirm the conclusion suggested by the earlier experiments. Both series demonstrate clearly the remarkable solvent powers of colloidal soap. Consideration of the magnitudes of the partition coefficients in conjunction with those of the corresponding soap concentrations indicates that the solubilities of the dye or the aniline in the colloidal soap phase must be comparable with their solubilities in organic solvents. This solvent power of soap is even more in evidence when the solute is the natural unsaponifiable matter of oils, for the available data indicate partition coefficient of ½ to ⅓ the corresponding values for the dye or the aniline.

Partition between Water and Colloidal Soap

When the organic solvent phase is absent, and a small proportion of a solute such as aniline is added to a soap solution, the solute must be distributed between the remaining two phases, water and colloidal soap. Such partition or adsorption phenomena can only be studied indirectly, but two examples of their effects may be cited from the literature. McBain and Bolam[1] and Beedle and Bolam[2] measured the hydrolysis alkalinity of soap solutions by the catalytic effect of the hydroxyl ion on the decomposition of nitrosotriacetonamine. They obtained abnormally low results for the more concentrated soap solutions and ascribed the discrepancy between determinations by this and by electrical methods to adsorption of the amine on the soap micelles. Hampil[3] found that soap had a marked inhibiting effect on the germicidal activity of phenolic compounds towards *B. Typhosus* and other organisms; thus 0.5% of sodium oleate destroyed the activity of hexyl resorcinol at a dilution of 1:1000 which is at least five times the strength necessary to kill the organisms in the same time in aqueous solution. Hampil considered the distribution of the phenolic substance between the water and the colloidal soap, as the most probable explanation of these phenomena.

---

[1] J. Chem. Soc., **113**, 825 (1918).

[2] J. Soc. Chem. Ind., **40**, 27T (1921).

[3] J. Bact., **16**, 287 (1928).

The Extraction of Soap Solutions

We may now consider the bearing of these conclusions on the original problem of how best to extract organic substances dissolved in soap solutions. The first desideratum is evidently that the soap should be as far as possible in true or molecular solution, with the minimum proportion present as colloid. This may be achieved by the use of solvents which tend to render the soap "less colloidal," such solvents being in general those which are appreciably soluble in water, as shown in the first paper of this series.[1]

The same result may be secured by the addition of alcohols. The measurements with p-dimethylaminoazobenzene show, however, that this beneficial effect of alcohol may be counterbalanced by its effect in increasing the solubility of the solute in the aqueous phase. The choice of a solvent of the type suggested, or the use of alcohol, has a second very practical advantage in that the emulsions produced by shaking are relatively impermanent. The value of the adsorption coefficient for the solute by the colloidal soap is usually outside our control. The partition coefficient on the other hand, is evidently proportional to the solubility of the solute in the extracting solvent, if other factors remain unchanged.

In connection with the extraction of unsaponifiable matter from fish liver oil soap, it was sought to utilise this principle by determining the solubility of cholesterol, which constitutes a considerable proportion of the unsaponifiable matter, in a series of solvents. The solubilities decreased in the order ether, benzene, petroleum spirit; the partition coefficients for the same soap concentration decreased in the same order, but not proportionately, because other factors did not remain constant. In practice, the choice of solvents is limited chiefly by the tendency of most solvents to emulsify in the soap solution, and the large proportion of alcohol necessary to break the emulsions so produced. Such solvents as benzene and its homologues, chloroform and chlorinated hydrocarbons generally are unsuitable on this account except in special cases.[2] When mixed with sufficient alcohol to render emulsions unstable, the proportion of solvent absorbed by the soap solution becomes unduly high. Also in some cases (noted particularly in the extraction of unsaponifiable matter with xylene from alcoholic soap solution), the value of n (see formula 9) is large, so that the efficiency of extraction decreases rapidly as the weight of solute remaining behind in the soap solution is reduced. Petroleum spirit does not suffer from these defects, even when the proportion of alcohol in the soap solution is over 50%, but the partition coefficients for unsaponifiable matter are too low to render this solvent serviceable in this connection.[3] Ether is the most generally useful solvent for extracting soap solutions, requiring relatively little alcohol to break its emulsions. Ethyl acetate, however, deserves attention as it does not emulsify even in absence of alcohol and is a good solvent for many organic substances. Its disadvantages are that the soap solution must be neutral in order to avoid

---

[1] J. Phys. Chem., 36, 1401 (1932).

[2] See for example Smith and Hazley: Biochem. J., 24, 1942 (1930).

[3] See Smith: Analyst, 53, 632 (1928).

hydrolysis of the ester, and that more fatty acid is extracted from a neutral than from a slightly alkaline soap solution.

The extraction of soap solutions is no exception to the general rule that the efficiency of extraction increases as a given total volume of extracting solvent is subdivided into smaller portions. In practice however, both in laboratory extractions for the determination of unsaponifiable matter, and in large-scale extractions for the preparation of fat soluble vitamin concentrates, it is found best to give only 3 or 4 extractions. For a given degree of extraction, the solvent saved by giving more extractions with a smaller total volume is more than counterbalanced by the extra time consumed in the operations. The author has shown elsewhere that in general the greatest efficiency is secured by subdivision of the extracting solvent into *equal* portions.[1] The rule applies to the extraction of soap solutions when the value of "n" approximates to unity. When "n" is greater than 1, it can be shown mathematically that it is more efficient to extract with decreasing volumes of solvent.

Summary

Partition coefficients have been measured for the dye p-dimethylaminoazobenzene between ether and soap solution.

The partition coefficients decrease considerably with increasing soap concentration, and slightly with increasing methyl alcohol concentration, and with increasing excess alkali, in the soap solution.

The results are explained by postulating adsorption of the dye on the colloidal soap.

A formula has been derived on the assumptions that the solute is distributed between the colloidal soap and the aqueous phases according to the adsorption law, and between the organic solvent phase and the water according to the partition law.

The formula receives quantitative confirmation in the decrease of the partition coefficients with decrease in the dye concentration.

The addition of methyl alcohol greatly increases the solubility of the dye in the aqueous phase and so decreases the partition coefficients, despite the counterbalancing effect of the alcohol in diminishing the proportion of soap in the colloidal form.

Partition coefficients have also been measured for aniline between ethyl acetate and sodium oleate solutions.

The partition coefficients decrease considerably with increasing soap concentration and decrease slightly on addition of sodium chloride, but are almost independent of aniline concentration.

The system behaves as though the aniline were distributed according to the partition law between the three phases, ethyl acetate, water, and colloidal soap.

The bearing of these experiments on the problem of how best to extract organic solutes, particularly the natural unsaponifiable matter of oils and the attendant fat-soluble vitamins, from soap solutions, is discussed.

Glaxo Research Laboratory, London, N. W. 1.
Research Laboratory, Chelsea Polytechnic, London, S. W. 3.
January 12, 1932.

---

[1] J. Soc. Chem. Ind., **47**, 159T (1928).

THE ACTIVITY COEFFICIENT OF BENZOIC ACID IN SOLUTIONS OF NEUTRAL SALTS AND OF SODIUM BENZOATE*

BY I. M. KOLTHOFF AND WOUTER BOSCH[1]

In previous papers, the authors[2] have studied the influence of neutral salts on the activity coefficients of the anions of weak acids. The hydrogen ion activity of a very dilute buffer mixture of a weak acid and its salt, to which known amounts of neutral salts had been added, was measured and from these data the activity coefficients of the anion of the acid computed. In working with systems containing an undissociated acid and its monovalent anion, the difficulty was encountered that the change of the activity coefficient of the undissociated acid in the presence of neutral salts was not exactly known.[2] For this reason, it was decided to make a more extensive study of the system, benzoic acid-sodium benzoate, in which the activity coefficient of the undissociated acid could be kept constant or be determined in an experimental way.

In the second paper the results of the measurements of the activity coefficient of the benzoate ion in the system benzoic acid (saturated solution in water), 0.01 N sodium benzoate in the presence of various concentrations of neutral salts will be described.

In the third paper of this series the activity coefficient of the silver ions in a saturated solution of silver benzoate in the presence of various concentrations of the same neutral salts will be reported. From the silver ion activity and the solubility product of silver benzoate the activity coefficient of the benzoate ion could be computed and the figures compared with those found in the second paper in solutions of nearly the same ionic strength.

Materials used

Water: Conductivity water was used throughout this work.

Benzoic acid: A U.S.P. product (Eastman Kodak Company) was recrystallized a few times by pouring a concentrated solution in hot alcohol into a large volume of boiling water. After cooling, the crystals were collected by suction and dried over sulfuric acid to constant weight. Various tests (for details see thesis of W. Bosch) showed that the product was chemically pure. In addi-

---

*Contribution from the School of Chemistry, University of Minnesota.

[1] The experimental part of this work was carried out at the University of Minnesota in 1929 and 1930 and presented in the doctor's thesis of Wouter Bosch, submitted to the faculty of the University of Utrecht, in July 1931. After the work was completed papers of E. Larsson and E. F. Chase and M. Kilpatrick Jr., partly covering the same subject, were published. As in the latter's papers a complete discussion of the literature on the activity coefficient of benzoic acid is found, the authors for the sake of brevity omit such a discussion in the present paper.

[2] Comp. I. M. Kolthoff and W. Bosch: Rec. Trav. chim., **46**, 430 (1927); **47**, 558, 819, 826, 861, 873 (1928); **48**, 37 (1929).

tion the normality of a solution of sodium hydroxide was determined according to standard methods with our product, one of the Bureau of Standards and one of Kahlbaum (für kalorimetrische Bestimmungen); all data agreed within 0.02%. In order to test the physical purity (possible presence of another modification) various amounts of solid body (between 0.8 and 6 g. with 200 cc. water) were used in solubility measurements; in all cases the data obtained agreed within 0.1%. If the saturated solution was poured off from the solid body and fresh water added, the same solubility was found. Moreover, Kahlbaum's product, before and after melting, gave exactly the same results as our own product.

Sodium benzoate: A U.S.P. product (Merck) was twice recrystallized from water, washed with small amounts of cold water, finally with a small volume of absolute alcohol, and dried at 150° to constant weight. By qualitative and quantitative tests its purity was established. Moreover, in many of the experiments, solutions of sodium benzoate were prepared from pure benzoic acid and standard base; exactly the same results were obtained as with solutions of the above salt of equivalent concentration.

Neutral salts: C. P. salts were used, some of them recrystallized from water and their purity tested according to standard methods. Very sensitive tests were applied to establish the absence of acidic or basic impurities, (for complete description, comp. thesis of W. Bosch, p. 26-32) moreover, the water content of hydrates was determined in a quantitative way. It may be mentioned that the strontium nitrate was labelled as being a hydrate, whereas it did not contain more than 0.25% water.

Solubility of Benzoic Acid in Water and in Sodium Benzoate

The solubility was determined in a thermostat at 25° ± 0.01°. Weighed samples of benzoic acid with 200 cc. of water or salt solution were rotated in Pyrex glass bottles, closed with paraffined cork stoppers. After saturation had been reached, the bottles were allowed to stand in the thermostat until the supernatant liquid was clear and samples drawn out with the aid of suction with a carefully calibrated pipet at 25°. The tip of the pipet was connected with a piece of glass tubing, the latter being drawn out in the middle and filled with adsorbent cotton. The clear solution was titrated with standard carbonate-free sodium hydroxide, using phenolphthalein as an indicator. As a rule 1.5 g. benzoic acid was used in a volume of 200 cc.; the amount of acid, however, proved to be immaterial. In agreement with M. Kilpatrick Jr. and E. F. Chase,[3] it was found that after five hours' shaking the solution was saturated; as a rule, however, the bottles were rotated over night.

All concentrations are expressed in moles per liter. As an average of thirty determinations with different amounts and products of benzoic acid a solubility of 0.02775 ± 0.00002 moles acid per liter at 25° was found, this

---

[3] M. Kilpatrick Jr. and E. F. Chase: J. Am. Chem. Soc., 53, 1732 (1931).

figure being in close agreement with the data reported in the literature (compare list given byKilpatrick and Chase[3]).

The activity of the undissociated acid is smaller than the saturation value, since a small part of the acid is dissociated into its ions.

$$[aH\ Benz] = 0.02775 - cH^+$$

in which cH^+ represents the hydrogen ion concentration (not the activity) of the saturated solution in water. As will be shown later, the ionization constant of benzoic acid at 25° is equal to 6.60×10^{-5}. From this and the saturation figure, it is found that the hydrogen ion activity in the saturated solution is equal to 1.31×10^{-3}. By applying the simple Debye-Hückel relation:

$$-\log f = 0.5\sqrt{\mu}$$

a hydrogen ion concentration of 1.36×10^{-3} is calculated and the activity of undissociated benzoic acid in the saturated solution in water is found to be $0.02775 - 0.00136 = 0.0264$.

Since this calculation involves the use of some slightly uncertain data, the activity of the undissociated acid was also derived in another way. The solubility of benzoic acid was determined in solutions of sodium benzoate of varying concentrations and the data after correction for the dissociated part plotted in a curve. By extrapolation to a sodium benzoate concentration equal to zero the activity of the acid is found. The correction for the dissociated part of benzoic acid in sodium benzoate is extremely small, as the common ion depresses the ionization of the acid. For example, in 0.01 N sodium benzoate, a solubility of benzoic acid of 0.02670 moles per liter was found, whereas the hydrogen ion activity as determined with the hydrogen electrode was found to be equal to 2.15×10^{-4}, or the hydrogen ion concentration approximately 2.4×10^{-4}. Therefore, the concentration of undissociated acid in 0.01 N sodium benzoate is $0.02670 - 0.00024 = 0.02646$. The correction for the dissociated part decreases with increasing benzoate concentration, which is rather fortunate, as the activity coefficient of the hydrogen ions is not known and the accurate measurement of the hydrogen ion activity in such solutions is extremely hard.

A summary of the results is given in Table I. Sol. benz. acid denotes the experimental value of the solubility of benzoic acid in moles per liter, (cHB) the concentration of the undissociated acid, f_o the activity coefficient of the undissociated acid in the benzoate solutions.

$$f_o = \frac{[cHB]_o}{[cHB]_{Benz}}$$

$(cHB)_o$ is the extrapolated value of the concentration of the undissociated acid at a sodium benzoate concentration equal to zero, whereas $(cHB)_{Benz}$ denotes the same in the benzoate solution of indicated strength.

TABLE I

Solubility of Benzoic Acid in Sodium Benzoate and Inner Complex Constant at 25°

Sodium benzoate m. per l.	Sol. benz. acid moles per liter	[aH⁺]	[cHB]	f_0	[cHB₂⁻]	K
1.00	0.04623		0.04623	0.570	0.01988	1.3
0.75	.03933		0.03933	.671	.0298	1.5
0.5	.03398		.03398	.778	.00763	1.7
0.25	.02934	1.22×10^{-5}	.02933	.989	.00299	2.2
0.1	.02757	2.44×10^{-5}	.02754	.958	.00122	2.1
0.05	.02704	4.57×10^{-5}	.02699	.976	.00069	1.9
0.03	.02682	7.31×10^{-5}	.02674	.985	.00047	1.6
0.02	.02672	1.1×10^{-4}	.02660	.992		
(0.01	.02670	2.15×10^{-4}	.02648	.997)		
0.00			.02635	1.000		

The extrapolated value of the activity of the undissociated acid at an ionic strength of zero corresponds to a concentration of 0.02635, in close agreement with the value of 0.0264 calculated from the solubility of the acid in pure water and that of 0.0265 computed by Kilpatrick and Chase[3] at 25.15°.

As may be seen from the figures in Table I, f_0 decreases with increasing sodium benzoate concentrations, a fact already found by E. Larsson.[4] As a rule the activity coefficient of a non-electrolyte increases with increasing ionic strength (salting-out effect); from other measurements (vide infra), it is evident that sodium ions exert such a salting out effect; therefore, the decrease observed with sodium benzoate has to be attributed to a specific interaction between the benzoate ion and benzoic acid. Larsson[4b] thinks it possible that we are dealing here with the formation of acid benzoate ions, as acid benzoates may crystallize from solutions, saturated with benzoic acid. "Jedoch musz man sehr vorsichtig sein aus der Bildung solcher Verbindungen auf ihre Existenz in Lösung zu schliessen. Hierin können sie vollständig dissoziiert sein." According to the authors' opinion, there seems to be little doubt that the benzoate forms a kind of inner complex with benzoic acid. It is known that benzoic acid in more concentrated solutions has a tendency to associate to give double molecules. This association is facilitated by the formation of the anion of the double molecule:

$$\mathrm{HB} + \mathrm{B}^- \leftrightarrows \mathrm{HB_2}^-$$

the case being somewhat similar to the inner complex formation of boric acid. If the above equation gives a true picture of what is happening, the following expression should hold:

$$[\mathrm{aHB}] \cdot \frac{[\mathrm{aB}^-]}{[\mathrm{aHB_2}^-]} = K$$

Since B– and HB₂– both represent anions of a similar type, it can be approximately written:

$$[\mathrm{aHB}]\ \frac{[\mathrm{cB}^-]}{[\mathrm{cHB_2}^-]} = K$$

---

[4] E. Larsson: Z. physik. Chem., (a) **148**, 148 (1930); (b) **153**, 466 (1931).

The experimental test of this equation meets with some difficulties. [aHB] is equal to 0.02635 at 25° since all solutions were saturated with respect to benzoic acid. It is harder to find the concentration of the associated anion HB_2^-. At first sight, it seems that [cHB_2^-] is equal to the total concentration of the undissociated acid in the benzoate solution ([cHB] in Table I) minus the activity of the benzoic acid (0.02635). This, however, is not true for two reasons: Part of the HB_2^- ions will combine with hydrogen ions to form associated molecules of benzoic acid $(HB)_2$. Since the concentration of the later is negligibly small in a saturated solution of benzoic acid in water at 25°, it is assumed here that its concentration is equally negligible in the benzoate solutions which would mean that the associated benzoic acid behaves as a much stronger acid than the single molecules. A similar relation is found again with boric acid.

The values of [cHB_2^-] in Table I have been calculated on the assumption that the associated acid is entirely present in the anion form. Even if this assumption holds rigorously an absolute constant value of K cannot be expected as the salting-out effect is neglected. It is quite certain that sodium ions decrease the solubility of benzoic acid, whereas it may be expected that the benzoate ions also exert such a salting-out effect which in the present case is masked by the complex formation. Since the salting-out effect is not a linear function of the ionic strength ($-\log f_0$ is a straight line function of μ) a deviation from constant values can be expected at increasing sodium benzoate concentrations. Moreover, it should be added that if instead of sodium benzoate another alkali benzoate had been used, say potassium, a different value for K would have been found since the salting-out effect of potassium is less than that of sodium.

The values of K in Table I have been calculated on the assumption that [cHB_2^-] = [cHB] − 0.02635, and [cB^-] = [cNa benzoate] − [cHB_2^-]. In a similar way the value of K has been calculated at 18° from data of E. Larsson.[4a]

TABLE II

Solubility of Benzoic Acid in Sodium Benzoate and Inner Complex Constant at 18° (Larsson)

Sodium benzoate moles per liter	[cHB]	f_0	[cHB_2^-]	K
1.000	0.0351	0.61	0.0135	2.05
0.930	0.0341	.628	0.0125	2.22
0.698	0.02946	.724	0.00786	2.08
0.500	0.0268	.800	0.0052	2.06
0.465	0.02638	.813	0.00478	1.90
0.2325	0.02383	.900	0.00223	1.59
0.1032	0.02265	.947	0.00105	1.58
0.000	0.02160	1.00		

Although no strict constant value for K is found, which theoretically is not to be expected, there seems to be little doubt that the increase of the solubility of benzoic acid in sodium benzoate must be attributed to the formation of anions of the associated benzoic acid molecules. Comparing the values by Larsson at 18° (Table II) with those in Table I reveals that the complex ions become less stable at higher temperatures, a behavior similar again to that of the inner complexes of boric acid.

The Activity of Benzoic Acid in Neutral Salt Solutions

The solubility of benzoic acid was determined in 0.01 N sodium benzoate as a solvent in the presence of various amounts of neutral salts. As before concentrations are expressed in moles per liter. The results are given in Table III. f_0 has been calculated by dividing the solubility of the acid in 0.01 N sodium benzoate by that found in the presence of neutral salts. A correction for the dissociated part of the acid does not have to be considered, as it is about the same in all solutions and very small as the ionization of the acid is suppressed by the excess of benzoate.

Table III

Activity Coefficient f_0 of Benzoic Acid in Salt Solutions in the Presence of 0.01 Molar Sodium Benzoate at 25°

Salt added to 0.01 molar Na benzoate	Ionic strength salt	Normality salt	Normality benzoic acid	f_0	+ log f_0
—	0.01	0.01	0.02676	1.000	.000
KCl	.09	.09	.02588	1.033	.0142
"	.25	.25	.02456	1.089	.0370
"	.50	.50	.02266	1.180	.0718
"	1.00	1.00	.01938	1.380	.1398
NaCl	.09	.09	.02568	1.042	.0179
"	.25	.25	.02408	1.111	.0457
"	.50	.50	.02170	1.232	.0906
LiCl	.09	.09	.02558	1.045	.0192
"	.25	.25	.02394	1.127	.0480
"	.50	.50	.02160	1.238	.0928
KNO_3	.05	.05	.02658	1.006	.0027
"	.09	.09	.02640	1.013	.0058
"	.25	.25	.02610	1.022	.0095
"	.50	.50	.02558	1.045	.0192
"	1.00	1.00	.02432	1.097	.0402
$NaNO_3$	.05	.05	.02648	1.010	.0042
"	.09	.09	.02634	1.025	.0066
"	.25	.25	.02658	1.041	.0176
"	.50	.50	.02452	1.091	.0378
$LiNO_3$	.05	.05	.02642	1.012	.0053
"	.09	.09	.02618	1.022	.0094
"	.25	.25	.02552	1.048	.0204
"	.50	.50	.02470	1.083	.0345

TABLE III (Continued)

Activity Coefficient f_o of Benzoic acid in Salt Solutions in the Presence of 0.01 Molar Sodium Benzoate at 25°

Salt added to 0.01 molar Na benzoate	Ionic strength salt	Normality salt	Normality benzoic acid	f_o	+ log f_o
KBr	.09	.09	.02608	1.025	.0108
"	.25	.25	.02562	1.068	.0285
"	.50	.50	.02364	1.132	.0537
KI	.09	.09	.02642	1.012	.0053
"	.50	.50	.02528	1.058	.0244
K_2SO_4	.09	.060	.02620	1.021	.0090
"	.50	.333	.02412	1.119	.0450
$NaClO_4$	.09	.09	.02630	1.027	.0072
"	.25	.25	.02590	1.033	.0141
"	.50	.50	.02554	1.060	.0253
$BaCl_2$	.09	.060	.02614	1.023	.0098
"	.50	.333	.02376	1.126	.0516
$CaCl_2$	.091	.061	.02608	1.025	.0108
"	.506	.337	.02348	1.139	.0564
$SrCl_2$	.0914	.061	.02604	1.026	.0113
"	.508	.339	.02346	1.140	.0568
$Ba(NO_3)_2$	.09	.06	.02650	1.009	.0040
"	.25	.168	.02608	1.025	.0110
"	.50	.333	.02564	1.043	.0182
$Ca(NO_3)_2$	.0912	.0608	.02646	1.010	.0045
"	.253	.169	.02624	1.019	.0084
"	.507	.338	.02582	1.036	.0154
$Sr(NO_3)_2$	.120	.080	.02640	1.013	.0058
"	.334	.223	.02580	1.037	.0157
"	.668	.445	.02506	1.067	.0283
$Mg(NO_3)_2$	.0896	.0597	.02646	1.010	.0045
"	.249	.166	.02594	1.031	.0131
"	.498	.333	.02534	1.055	.0234

In Figs. 1 and 2, log f_o is plotted against the ionic strength μ of the salt added. In all cases (except with magnesium nitrate and barium nitrate) a straight line is found as may be expected from the relation:

$$\log f_o = k\,\mu$$

In practically all cases a close agreement was found with the data of E. Larsson[5] with the exception of potassium bromide, for which salt Larsson gives a

---

[5] E. Larsson: Z. physik. Chem., **153**, 299, 466 (1931).

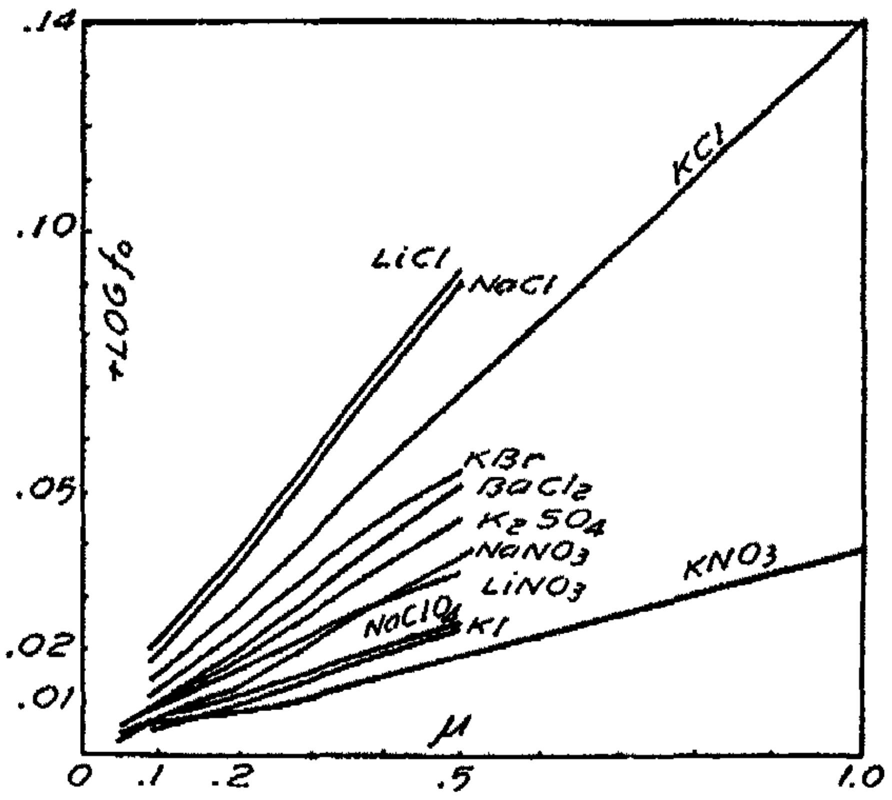


Fig. 1
Salting-out Effect upon Benzoic Acid

value of k equal to 0.07, whereas in the present investigation a value of 0.11 was derived. For salts of divalent cations, Larsson gives the expression: log f_0 = kc, where c represents the salt normality. If his figures are recalculated on the basis of ionic strength, the following values of k are found:

	$BaCl_2$	$SrCl_2$	$CaCl_2$	$MgCl_2$
Larsson	0.10	0.11	0.11	0.11
K. and B.	0.10	0.11	0.11	

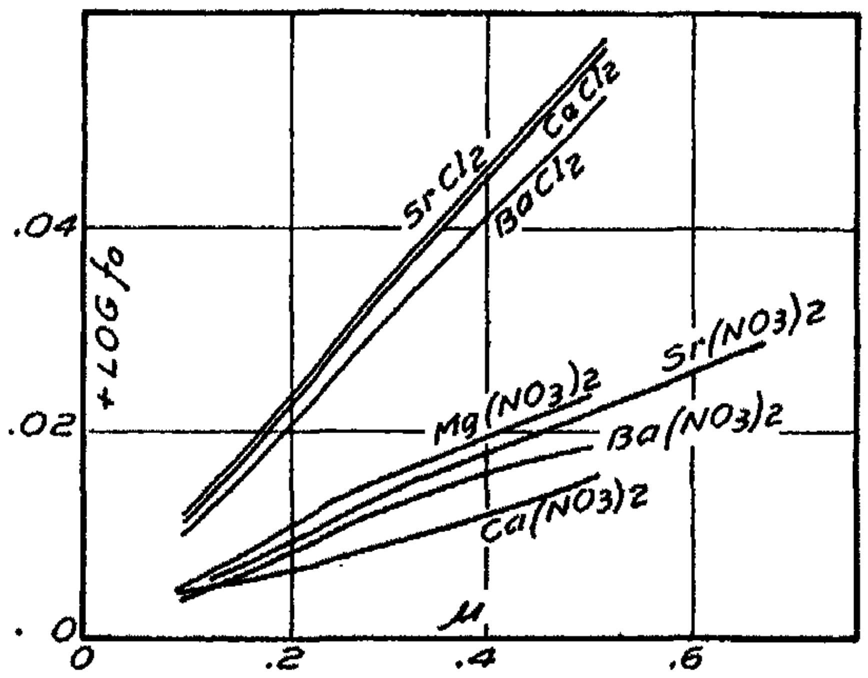


Fig. 2
Salting-out Effect upon Benzoic Acid

A comparison of our figures with others reported in the literature is omitted here (compare, however, thesis of W. Bosch), since E. F. Chase and M. Kilpatrick, Jr.[6] have recently given a complete review of the published data. Our values are in agreement with the results of other reliable investigations.

In the present investigation, it is found that the salting-out effect of the cations decreases in the order:

$$\text{Li} > \text{Na} > \text{K} > \text{Ca} > \text{Sr} > \text{Mg} > \text{Ba}$$

A simple relation between ionic size and salting-out effect as suggested by E. F. Chase and M. Kilpatrick, Jr.[6] does not exist. For the anions, the following order is found:

$$\text{Cl}^- > \text{Br}^- > \text{SO}_4^= > \text{J}^- > \text{NO}_3^- > \text{ClO}_4^-$$

The interpretation of the salting-out effect of cations seems to be fairly well in agreement with the theory of P. Debye and McAulay;[7] greater difficulties, however, are encountered in the interpretation of the anion effect. In the present study it is found that the nitrate and perchlorate ion have an increasing influence on the solubility of benzoic acid. More striking examples of a negative salting-out effect are found in studies of K. Linderström-Lang[8] and especially of H. R. Kruyt and C. Robinson.[9] Kruyt and Robinson[8] attribute the tendency of electrolytes to increase the solubility of non-electrolytes or undissociated organic molecules entirely to a definite orientation of the dipoles of the water molecules around the ions, by which the solvent effect should be increased. The polar organic molecules of the solute, however, also exert an orienting effect on the water molecules, therefore, a most favorable orientation can be expected in a solution of the substance in pure water as a solvent. Any change of the orientation will result in a decrease in the solubility (salting-out effect) and it is hard to see how Kruyt's and Robinson's explanation accounts for the opposite effect observed. In the presence of electrolytes (and especially of cations), the latter will compete with the organic molecules with regard to orientation of the water, resulting in a less favorable orientation of the water molecules around the organic substance or in an increase of the latter's activity. This is the true salting-out effect which decreases in the order Li > Na > K > Rb > Cs. Moreover, it seems necessary to assume a direct interaction between the ions in the solution and the dipoles of the solute; resulting in a mutual polarization and deformation. In extreme cases this may lead to a definite complex formation as is the case with benzoate and benzoic acid and otherwise to a decrease of the activity of the solute or increase in solubility. From the studies of Kruyt and Robinson, it seems that the salting-out effect is more likely to be determined by the kind of cations, whereas the deforming effect is governed by the kind of anions present.

---

[6] E. F. Chase and M. Kilpatrick: J. Am. Chem. Soc., 53, 2589 (1931); see also Haessler: Thesis, Columbia University, 1929.

[7] Debye and McAulay: Physik. Z., 24, 185 (1923).

[8] K. Linderström-Lang: Compt. rend. trav. lab. Carlsberg, 15, 4 (1924); 17, No. 13 (1929).

[9] H. R. Kruyt and C. Robinson: Proc. Acad. Amsterdam, 29, 1244 (1926).

More extensive studies with different types of organic substances, in which the change of the activities of the ions in the presence of the organic solute are also measured, are necessary before a good understanding of the influence of neutral salts on the activity of undissociated molecules can be obtained.

Summary

1. The solubility of benzoic acid in water at 25° was found to equal to 0.02775 ± 0.00002 mols per liter, whereas the activity of the acid to be 0.02635 to 0.0264.

2. The solubility of benzoic acid in sodium benzoate solutions has been determined. The increase in solubility with increasing salt content is attributed to the formation of anions of double molecules of benzoic acid. The stability constant of this complex ion has been approximated.

3. The influence of various neutral salts on the activity of benzoic acid has been determined. In the interpretation of the experimental data it is assumed that electrolytes exert two effects: (a) a true salting-out effect, mainly governed by the type of cations and resulting in an increase of the activity of the solute. (b) a mutual deforming effect, mainly governed by the type of anions and resulting in a decrease of the activity of the solute.

Minneapolis, Minn.

THE IONIZATION CONSTANT OF BENZOIC ACID AND THE ACTIVITY COEFFICIENT OF THE BENZOATE ION IN PRESENCE OF NEUTRAL SALTS*

BY I. M. KOLTHOFF AND WOUTER BOSCH[1]

The hydrogen ion activity was measured in dilute solutions of benzoic acid and sodium benzoate and from the results obtained the ionization constant of the acid was computed by application of the limiting Debye-Hückel expression.

Measurement of the Hydrogen Ion Activity

The activity of the hydrogen ions was measured with the hydrogen electrode. A simple cell was used as described in a previous paper,[2] the quinhydrone electrode in a mixture of 0.01 N hydrochloric acid and 0.09 N potassium chloride served as standard half cell. The cell was refilled every day after cleaning the electrode. The connection between the two half cells was made by a saturated potassium chloride bridge in 3% agar, and no correction has been applied for the liquid junction potential. The measurements have been made in a thermostat at 25° ± 0.05°. The type of hydrogen electrode used in this work gives constant readings with ordinary buffer solutions within two to three minutes. Peculiar difficulties were encountered in the measurement of benzoic acid-benzoate solutions. There was a continuous drift in potential with time, the electrode becoming less and less noble. This irregular behavior could not be attributed to impurities in the hydrogen, as the latter was carefully purified and finally passed over red hot copper or nickel wire. Special experiments were made in order to see whether the effect could be attributed to a hydrogenation of benzoic acid, but no indication of such an action was found. Therefore, it seems that benzoic acid or benzoate exerts a polarizing effect upon the electrode. It was found that the rate of change of the E. M. F. was proportional to the thickness of the layer of platinum black on the electrode, and for this reason the platinum spiral electrodes were covered with a very thin coat of platinum. A 1% solution of pure chloroplatinic acid[3] was used for platinizing, with a current of 20 milliamperes during five minutes. After polarization in 1 N sulfuric acid, the electrode had a grayish appearance. Cleaning and recoating were often necessary, but with the type of electrode described, it was usually possible to obtain constant readings within 15 minutes, although, it should be mentioned, that the final reading was not made unless the potential had been constant for a few hours. In the presence of large concentrations of sodium benzoate (0.25 N or higher) no reliable results

---

* Contribution from the School of Chemistry, University of Minnesota.

[1] Comp. Note 1 in the previous paper; J. Phys. Chem., 36, 1685 (1932).

[2] I. M. Kolthoff and Wouter Bosch: Rec. Trav. chim., 46, 434 (1927).

[3] E. Wichers: J. Am. Chem. Soc., 43, 1268 (1921).

could be obtained. Owing to the difficulties described, at least three sets of independent measurements with each solution were made; the results are accurate to within 0.01 pH. It may be mentioned that the sluggishness of the electrode is more pronounced in the absence of neutral salts; the latter exert a decidedly favorable effect.

Since the quinhydrone electrode assumes a constant potential very readily, all measurements have also been made with such an electrode. It was found, however, that sodium benzoate changes the activity of the components of the quinhydrone in the solution causing an uncertainty in the calculation. At small benzoate concentrations (below 0.01 N), the effect is small, but at higher benzoate concentrations the figures are no longer reliable. Neither E. Larsson[4] nor M. Kilpatrick and E. F. Chase,[5] who applied the quinhydrone electrode in their work, mention the specific effect of benzoate on the quinhydrone.

The majority of measurements were made in solutions, containing only 0.01 N benzoate in the presence of neutral salts. Quite generally the readings with the quinhydrone electrode gave slightly higher pH values than those with the hydrogen electrode. As a rule the differences were not larger than 0.02, but in the presence of larger amounts of nitrates they were much greater. The differences are partly accounted for by the salt error of the quinhydrone electrode in presence of large concentrations of neutral salts. A special study has been made of this error under the experimental conditions; the work is not completely finished and will be described later.

In Table II the results are given of measurements with the hydrogen as well as the quinhydrone electrode; the figures obtained with the former are used in the calculation of the activity coefficient of the benzoate ion.

The calculation of paH was based on the classical Sörensen equations. The relation between the Sörensen value and the negative logarithm of the hydrogen ion activity paH is given by:

$$\mathrm{paH} = \mathrm{pH} + 0.037$$

Ionization Constant of Benzoic Acid at 25°

The hydrogen ion activity was measured in dilute mixtures of sodium benzoate and benzoic acid. After correction for the dissociated part of the acid

$$\mathrm{p}K' = -\log \frac{[\mathrm{H}^+][\mathrm{cB}^-]}{[\mathrm{aHB}]}$$

in which $[\mathrm{H}^+]$ represents the Sörensen value of the hydrogen ion concentration, $[\mathrm{cB}^-]$ the benzoate concentration (concentration sodium benzoate plus dissociated part of the acid), and $[\mathrm{aHB}]$ the activity of the undissociated acid, pK' was calculated. From this value $\mathrm{p}K_0 = -\log \dfrac{[\mathrm{H}^+]\,[\mathrm{aB}^-]}{[\mathrm{aHB}]}$ was computed

---

[4] E. Larsson: Z. physik. Chem., **148**, 304 (1930).

[5] M. Kilpatrick and E. F. Chase: J. Am. Chem. Soc., **53**, 1732 (1931).

with the assumption that in the very dilute solution the simple Debye-Hückel expression holds:

$$\log f_{B^-} = -0.5\sqrt{\mu}$$

log f_B being the logarithm of the activity coefficient of the benzoate ion. Finally, pK represents the acid exponent after correction for the difference between the Sörensen exponent and paH:

$$pK = pK_o + 0.037$$

The data are given in Table I.

TABLE I

Ionization Constant of Benzoic Acid at 25°

Concentration sodium benzoate in moles p. l	Concentration benzoic acid in moles p. l	pH	pK′	pK_o	pK
0.05	0.025	4.349	4.047	(4.172)	
0.025	0.025	4.092	4.089	(4.169)	
0.025	0.0125	4.365	4.062	4.141	4.178
0.01	0.01	4.107	4.101	4.151	4.188
0.01	0.005	4.400	4.094	4.144	4.181
0.005	0.005	4.124	4.111	4.146	4.183
0.005	0.0025	4.414	4.103	4.138	4.175
0.0025	0.0025	4.140	4.115	4.140	4.177
0.0025	0.00125	4.431	4.111	4.136	4.173
(0.001	0.001	4.172	4.114	4.130)	

From these and other measurements an average value of pK equal to 4.175 was found corresponding to an ionization constant of 6.7×10^{-5} at 25°. At the same temperature, Jones[6] *from conductivity data (not corrected for the* difference between activity and concentration) derived a value of 7.0×10^{-5}, whereas Kilpatrick and Chase[5] in a note mention that according to the same method but corrected for activities a constant of 6.31×10^{-5} is found.

Activity Coefficient of the Benzoate Ions in the Presence of Neutral Salts

Solutions of 0.01 N sodium benzoate containing the indicated concentrations of neutral salt were saturated with benzoic acid at 25.00°. The paH of these solutions was measured at the same temperature with the hydrogen and quinhydrone electrode. In the further calculations only the hydrogen electrode values were used.

The activity coefficient f_B of the benzoate ions can be readily calculated from the relation,

$$K = \frac{[aH^+]\ [cB^-]f_B}{[aHB]}$$

---

[6] Jones: Am. Chem. J., **44**, 159 (1910); **46**, 56 (1912).

TABLE II

Activity Coefficient f_B of the Benzoate Ion in Salt Solutions

Ionic strength of added salt		paH H_2 electr.	paH quinh. electr.	pcB^-	$-\log f_B$	f_B
.09	KCl	3.622	3.642	1.990	.142	.72
.25	,,	3.601	3.627	1.989	.164	.69
.50	,,	3.627	3.654	1.990	.137	.73
1.00	,,	3.652	3.698	1.990	.112	.77
.09	NaCl	3.601	3.625	1.989	.164	.69
.25	,,	3.559	3.583	1.988	.207	.62
.50	,,	3.524	3.561	1.987	.243	.57
.09	LiCl	3.546	3.567	1.988	.220	.60
.25	,,	3.502	3.532	1.987	.265	.54
.50	,,	3.420	3.461	1.984	.350	.45
.05	KNO_3	3.664	3.656	1.990	.120	.76
.09	,,	3.639	3.644	1.990	.125	.75
.25	,,	3.610	3.650	1.989	.155	.70
.50	,,	3.586	3.650	1.989	.179	.66
1.00	,,	3.568	3.689	1.988	.198	.63
.05	$NaNO_3$	3.610	3.617	1.989	.155	.70
.09	,,	3.598	3.622	1.989	.167	.68
.25	,,	3.549	3.590	1.988	.217	.61
.50	,,	3.541	3.603	1.988	.225	.60
.05	$LiNO_3$	3.591	3.600	1.989	.174	.67
.09	,,	3.575	3.590	1.988	.191	.64
.25	,,	3.527	3.563	1.987	.240	.58
.50	,,	3.468	3.529	1.985	.301	.50
.09	KBr	3.615	3.650	1.989	.150	.71
.25	,,	3.622	3.649	1.989	.143	.72
.50	,,	3.561	3.661	1.988	.205	.62
.09	KI	3.610	3.639	1.989	.155	.72
.09	K_2SO_4	3.627	3.625	1.988	.139	.73
.50	,,	3.657	3.617	1.990	.107	.78
.09	$BaCl_2$	3.578	3.593	1.989	.187	.65
.50	,,	3.427	3.427	1.984	.343	.45
.091	$CaCl_2$	3.557	3.574	1.988	.209	.62
.506	,,	3.380	3.414	1.982	.392	.41
.091	$SrCl_2$	3.561	3.590	1.988	.205	.62
.508	,,	3.407	3.444	1.983	.364	.43
.09	$Ba(NO_3)_2$	3.554	3.563	1.988	.212	.61
.25	,,	3.497	3.508	1.986	.271	.54
50	,,	3.478	3.507	1.986	.290	.51
.091	$Ca(NO_3)_2$	3.495	3.503	1.986	.273	.53
.253	,,	3.454	3.461	1.985	.315	.48
.507	,,	3.314	3.349	1.980	.460	.35
.12	$Sr(NO_3)_2$	3.576	3.563	1.988	.190	.65
.334	,,	3.466	3.476	1.985	.303	.50
.668	,,	3.422	3.476	1.984	.348	.45
.09	$Mg(NO_3)_2$	3.563	3.541	1.988	.203	.69
.249	,,	3.461	3.469	1.985	.308	.56
.498	,,	3.420	3.451	1.984	.350	.44

in which [aHB] is a constant (0.02637 at 25°, see previous paper[1]) since the solution is saturated with benzoic acid and [cB⁻] the benzoate concentration *(sodium benzoate + dissociated part of the acid)*

$$- \log f_B = - \log K - \log [aHB] - paH - pcB^- = 4.175 - 1.579 - paH - pcB^-$$

pcB⁻ denotes the negative logarithm of the concentration of the benzoate ions. The results are given in Table II.

Discussion

The change of the activity coefficient of the benzoate ion with the ionic strength of the solution can no longer be represented by the simple Debye-Hückel expression, $-\log f = 0.5\sqrt{\mu}$, because the electrolyte content of the solutions is too high. Only in the case of lithium chloride does the influence of the ionic size seem to be negligibly small (in 0.25 N LiCl: $-\log f_B$ found 0.265; calculated 0.255; in 0.5 N LiCl: $-\log f_B$ found 0.350; calculated 0.357). In most other cases the change of the activity coefficient with the ionic strength can be represented by the more complicated expression:

$$-\log f_B = \frac{0.5\sqrt{\mu}}{1 + A\sqrt{\mu}}$$

in which A is a constant for each salt. In Table 3 examples are given of the application of this equation to solutions in potassium and sodium nitrate respectively. In KNO_3, A = 1.266; in $NaNO_3$, A = 0.340.

TABLE III

Calculated and Experimental Figures of $-\log f_B$ in KNO_3 and $NaNO_3$

	KNO_3			$NaNO_3$	
Total μ	$-\log f_B$ exp.	$-\log f_B$ calc.	Total μ	$-\log f_B$ exp.	$-\log f_B$ calc
0.0602	0.120	0.094	0.0602	0.155	0.113
0.1002	0.125	0.113	0.1003	0.167	0.147
0.2602	0.155	0.155	0.2603	0.217	0.217
0.5103	0.179	0.188	0.5103	0.225	0.287
0.010	0.198	0.221			

In most other cases the values of A have not been calculated, since the number of measurements and the concentration range were too small.

A weak point in the measurement of individual ion activities is that uncertainties are introduced on account of the liquid junction potential. E. A. Guggenheim[7] even states that the electric potential difference between two points in different media never can be measured and has not yet been defined in terms of physical realities. It is gratifying, therefore, that in one instance at least, it is possible to check the reliability of our results with those in which no uncertainty is involved. Kilpatrick and Chase[5] derived the mean activity

---

[7] E. A. Guggenheim: J. Phys. Chem., 33, 842 (1929).

coefficient of the ions of benzoic acid, $\sqrt{f_H f_B}$, from potentiometric and kinetic measurements in solutions of potassium chloride in presence of some sodium benzoate; no uncertainty caused by the liquid junction potential occurs here. In our work, f_B was experimentally determined, whereas f_H could be calculated in potassium chloride solutions by application of the empirical equation of N. Bjerrum and A. Unmack.[8]

$$-\log f_H = 0.178\sqrt[3]{c} - 0.154\,c - 0.003 \ (25°;\ \text{KCl at } c = 0.001 - 1.5)$$

From the experimental value of f_B and the calculated value of f_H the mean activity coefficient $\sqrt{f_H f_B}$ was calculated. The data are given in Table IV and compared with those Kilpatrick and Chase. A better agreement can hardly be expected, considering the experimental difficulties in our work.

TABLE IV

$\sqrt{f_H f_B}$ in KCl Solutions at 25°

Concentration KCl	K. and B.	$\sqrt{f_H f_B}$ Kilpatrick and Chase Potent.	Kin.
0.09	0.79	0.81	0.805
0.25	0.764	0.80	0.78
0.5	0.80	0.805	0.79
1.00	0.90	0.90	0.93

Considering the figures in Table II, it is evident that the activity coefficient of the benzoate ion passes through a minimum in about 0.25 N potassium chloride. From there on it increases with the ionic strength and seems to become even larger than that of the hydrogen ions. E. Güntelberg and E. Schiödt[9] in their excellent paper, found f_H equal to 1.50 and f_B to 1.93 in 3 N potassium chloride, on the other hand, in the more dilute electrolyte solutions, we find f_B smaller than f_H. In the dilute sodium chloride solutions f_B is smaller than in potassium chloride solutions of corresponding strength. By application of the empirical Bjerrum-Unmack[8] relation in sodium chloride:

$$-\log f_H = 0.161\sqrt[3]{c} - 0.178\,c - 0.003 \ (25°)$$

the following values of $\sqrt{f_H f_B}$ are calculated in sodium chloride solutions: 0.78 in 0.09 N NaCl; 0.74 in 0.25 N NaCl; 0.725 in 0.5 N NaCl. In 3 N NaCl, Güntelberg and Schiödt found a mean activity coefficient of 1.89. From the above, it is evident that the minimum in the activity coefficient of the benzoate ion lies at a higher concentration of sodium chloride than of potassium chloride.

Güntelberg and Schiödt[10] conclude that apparently the benzoate ion can be used for activity studies in which an ion with an extremely high activity coefficient is required. This is true at high salt concentrations; from our

---

[8] N. Bjerrum and A. Unmack: Kgl. Danske Videnskab Selskab, 9, 1 (1929).

[9] E. Güntelberg and E. Schiödt: Z. physik. Chem., 135, 393 (1926).

[10] Ref. 9, p. 442.

study it appears that at relatively small ionic strengths the activity coefficient of the benzoate ion is comparable with that of many other monovalent anions. It seems that in relatively dilute solutions the Debye-Hückel expression accounts for the decrease in activity of the benzoate ion; the effect increases with decreasing ionic size: Li > Na > K. In more concentrated solutions, the Debye-Hückel effect is compensated by the salting-out action, which also decreases in the order, Li > Na > K. Therefore, it is quite possible that at very high salt concentrations, the activity coefficient of the benzoate ions is the largest in lithium, smaller in sodium, and the smallest in potassium solutions, or the reverse of that in dilute solutions. The influence of divalent cations on the activity coefficient of the benzoate ion in relatively dilute solutions is of the same order as that of the lithium ions; the effect seems to decrease in the order, Ca > Sr > Mg > Ba, but the differences are relatively small.

In agreement with results of former studies,[11] it is found that the anion effect in relatively dilute solutions is very small.

Summary

1. The quinhydrone electrode no longer gives reliable results in solutions of sodium benzoate. The hydrogen electrode is useful, if the noble metal is covered with a very thin coat of platinum.

2. The ionization constant of benzoic acid is equal to 6.7×10^{-5} at 25°.

3. The activity coefficient of the benzoate ion in the presence of various electrolytes has been determined. It passes through a minimum at about 0.25 N potassium chloride, at a higher concentration of sodium chloride and still higher concentration of lithium chloride. The cation effect may reverse at high ionic strengths. There is a pronounced cation effect, but a slight anion effect.

Minneapolis, Minnesota.

---

[11] I. M. Kolthoff and W. Bosch: Rec. Trav. chim., **47**, 558, 819, 826, 861, 873 (1928); **48**, 37 (1929).

THE MEAN AND INDIVIDUAL ION ACTIVITY COEFFICIENTS OF SILVER BENZOATE IN SALT SOLUTIONS*

BY I. M. KOLTHOFF AND W. BOSCH[1]

The mean activity coefficient, f, of the silver and benzoate ions in silver benzoate has been calculated from solubility measurements of silver benzoate in water and in neutral salt solutions.

$$f = \sqrt{f_{Ag} f_B} = S_o/S$$

in which S_o represents the solubility of silver benzoate at an ionic strength of zero and S the same in the salt solution. The solubility of silver benzoate in water at 25° is of the order of 0.01 N. In such a solution, the simple Debye and Hückel expression,

$$-\log f_{Ag} = -\log f_B = 0.5\sqrt{\mu}$$

was applied to derive the value of S_o. In addition, the activity of the silver ions in all solutions was determined directly by means of the silver electrode. From these figures and S_o the activity coefficient of the benzoate ion could be calculated:

$$[a\ Ag^+]\ [a\ B^-] = S_o^2$$

The values of f_B could be compared with those found with the hydrogen electrode[2] in the same electrolyte solutions of corresponding ionic strength.

From the measurements of the activity of the silver ions in the saturated solution in water, it appeared that the activity coefficient is about 10% lower than that calculated with the simple Debye and Hückel expression. From this deviation it was concluded that silver benzoate no longer behaves as an ideal strong electrolyte and that part of it in solution is present in the undissociated form. Inner complex formation does not account for the difference as could be concluded from solubility measurements in silver nitrate and sodium benzoate. The activity coefficient of the benzoate ion as calculated from the thermodynamic solubility product $[a\ Ag^+]\ [a\ B^-]$ and the experimental value of $[a\ Ag^+]$ within the experimental error was found to be equal to that computed from measurements with the hydrogen electrode in similar solutions (preceding paper).

Materials used: (Comp. previous paper[2]).

Silver benzoate: Forty grams of pure sodium benzoate were dissolved in distilled water, the solution boiled and slowly added to a boiling solution of 45 grams of C.P. silver nitrate in 500 cc. water. After standing over night,

---

[*] Contribution of the School of Chemistry, University of Minnesota.

[1] Comp. Note 1; J. Phys. Chem., **36**, 1685 (1932).

[2] I. M. Kolthoff and W. Bosch: J. Phys. Chem., **36**, 1695 (1932)

the precipitate was collected by suction and washed five times after mixing with the wash water. Finally, the silver benzoate was washed with absolute alcohol and dried at 120° to constant weight.

Tests: Five grams of the preparation were dissolved in boiling water, the silver precipitated with hydrochloric acid and the filtrate evaporated and gently ignited. No residue was obtained, indicating that the salt did not contain inorganic impurities. Moreover, the silver content was determined gravimetrically: 47.05 and 47.00% Ag (calc. 47.13%).

Silver nitrate: Although labelled as C.P. and "maximum impurities less than 0.022%," the product appeared to contain more impurities besides 0.15% water. The salt was melted in a silica dish, kept at the melting point for about 15 minutes and poured upon a porcelain plate. The crust was powdered and dissolved in water, leaving a black residue. After recrystallization, the crystals were heated to the melting point in order to remove water. The purity was tested by potentiometric titrations with pure potassium chloride.

Solubility of Silver Benzoate in Water and in Salt Solutions

In all cases the solutions with the solid body were rotated for at least three days in a thermostat at 25.00° ± 0.01° before the samples were analyzed. This time of shaking was adequate to secure a saturated solution; after rotating for 25 consecutive days the same figures were found. The silver content of the samples was determined by potentiometric titration with pure potassium thiocyanate as a reagent. The latter was standardized potentiometrically against pure silver nitrate which had been checked again against potassium chloride. As an average of 12 independent analyses (different bottles) a solubility of silver benzoate in water equal to 0.01162 ± 0.00002 moles per liter was found at 25°. Assuming that in this solution, the simple Debye and Hückel relation holds, it is found:

$$-\log f_{Ag} = -\log f_B = 0.5\sqrt{0.01162} = 0.054 \text{ or } f = 0.883$$

and, $$S_o = 0.01162 \times 0.883 = 0.01026$$

The results are given in Table I. In the last column $-\log f$ has been calculated for potassium and calcium nitrate solutions by means of the Debye-Hückel expression:

$$-\log f = \frac{0.5\sqrt{\mu}}{1 + A\sqrt{\mu}}$$

In potassium nitrate, A is found to be equal to 1.182, in calcium nitrate to 0.551. E. Larsson and B. Adell[3] at 18° found in potassium nitrate up to a concentration of 3 N the following relation:

$$-\log f = \frac{0.5\sqrt{\mu}}{1 + 1.42\sqrt{\mu}} - 0.005$$

F. H. McDougall[4] calculated from solubility measurements of silver acetate

---

[3] E. Larsson and B. Adell: Z. anorg. allgem. Chem., 196, 354 (1931).

[4] F. H. McDougall: J. Am. Chem. Soc., 53, 1392 (1930).

in potassium nitrate solutions up to an ionic strength of one, a value of A between 1.408 and 1.479.

TABLE I

Mean Activity Coefficient f of Silver and Benzoate Ions of Silver Benzoate in Salt Solutions at 25°

Ionic strength and added salt	Solubility silver benzoate	Total Ionic strength	−log f	f	−log f. calc. Debye-Hückel
Water	.01162	0.01162	.054	.88	
S°	.01026				
.05 N KNO_3	.01298 N	.0630	.1021	.79	0.097
.09 " "	.01369 "	.01040	.1253	.75	0.1253
.10 " "	.01366 "	.1137	.1243	.75	0.121
.25 " "	.01483 "	.2648	.1600	.69	0.160
.50 " "	.01590 "	.5159	.1903	.64	0.194
.50 " $NaNO_3$	.01628 "	.5163	.2005	.63	
.50 " $LiNO_3$	.01648 "	.5165	.2058	.62	
.50 " $Ba(NO_3)_2$	.01697 "	.5170	.2185	.60	
.498 " $Mg(NO_3)_2$	.01759 "	.5156	.2341	.58	
.668 " $Sr(NO_3)_2$	.01784 "	.6858	.2402	.57	
.253 " $Ca(NO_3)_2$	.01633 "	.2693	.2018	.63	0.2018
.507 " " "	.01834 "	.5253	.2553	.56	.2059
1.013 " " "	.02079 "	1.034	.3067	.49	0.326

The results of the solubility measurements in sodium benzoate and silver nitrate solutions respectively are given in Tables VI and VII and will be discussed later.

The Potentiometric Determination of the Silver Ion Activity

From studies reported in the literature,[5] it follows that the readings with the silver electrode depend greatly upon the kind of electrode used and the condition of the solutions; it is hard to obtain reproducible results. In our case it was of primary importance to obtain results reproducible to within at least 0.5 millivolt. A special study of the silver electrode, therefore, had to be made. Carmody[5] states that the following factors are of influence on the potential of the electrode: "cyanide ion adsorbed by the silver plated electrode, time of electrolyzing, light, and concentration of chloride." To this may be added a very important factor: influence of air. After various types of electrodes had been tried, Carmody's plating procedure was finally adopted.

Platinum gauze electrodes of cylindrical shape with a diameter of 0.5 cm., a height of 1 cm., and a mesh of 52 to the inch (wire diameter, 0.01 mm.)

---

[5] Comp. e.g. Randall and Young: J. Am. Chem. Soc., **50**, 990 (1928); W. R. Carmody: **51**, 2901 (1929); Noyes and Ellis: **39**, 2533 (1917); Lewis, Brighton and Sebastian: **39**, 2245 (1917); Brester: Rec. Trav. chim., **46**, 328 (1927); Güntelberg: Z. physik. Chem., **123**, 199 (1926); Brönsted: **50**, 481 (1904); Linhart: J. Am. Chem. Soc., **41**, 1175 (1919); Halla: Z. Elektrochemie, **17**, 179 (1911); Jahn: Z. physik. Chem., **33**, 545 (1900).

after washing were cleaned with boiling nitric acid and ignited to a dull red heat. As plating bath a 1 N solution of potassium silver cyanide prepared by adding 13 grams of potassium cyanide dissolved in 100 cc. water to a solution of 18 grams silver nitrate in 100 cc. water was used. The electroplating was carried out in a black painted H-shaped cell with a current of one milliampere during 18 hours, using a strip of pure silver as anode. After boiling three times with distilled water, the electrodes were anodically covered with a thin layer of silver chloride by electrolyzing them for twenty minutes in one N hydrochloric acid with a current strength of 3.5 milliamperes. Finally, they were washed with very dilute sodium chloride solution and water, and kept in the dark at all times during preparation and measurements.

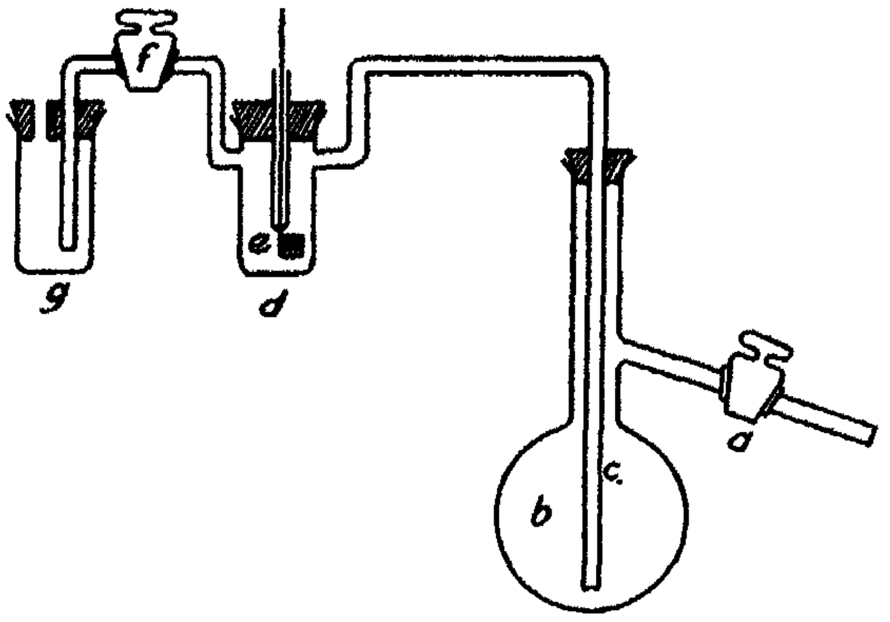


FIG. 1

Although this type of electrode gave better results by far than any of the other types tried, they still were not quite satisfactory, especially, not in very dilute silver nitrate solutions. In all solutions containing air, irregular fluctuations were observed with time. For example, the following readings were made in 0.1 N silver nitrate, using the quinhydrone electrode in 0.01 N hydrochloric acid and 0.09 N potassium chloride as a reference electrode: E.M.F. after 1/2 hour 0.1542 V; after 1 hour 0.1542; 2 hours 0.1549; 3 hours 0.1551; 12 hours 0.1571. With other electrodes, slightly different values were found.

In order to get constant and reproducible results it appeared to be necessary to remove all dissolved gases from the solutions. This was done by evacuation in a similar way as Brester[5] has suggested.

The final design of the apparatus is given in Fig. 1, and resembles that of Brester closely.

The apparatus consists of a vessel, d, in which the silver plated platinum gauze electrode, e, is fixed by means of a one hole rubber stopper. The long tube, c, projects into the distilling flask, b. At the left side is a wide tube which is filled with a glass stopcock of 3 mm. bore, which in turn leads into the vessel, g. This end is closed by means of a piece of rubber tubing and a screw clamp; the distilling flask filled with a suitable amount of the liquid to be measured and the apparatus put together as shown in the illustration with the exception of the vial, g, which is connected later.

After opening of the stopcock, f, suction was applied at the tube, a, by means of an oil vacuum pump. The air was then admitted through the tube, filling the entire apparatus with liquid. This operation was repeated three times, decreasing the pressure each time until the liquid in the vessel started boiling. This was necessary to remove air bubbles adhering to the electrode and to the walls of the vessel as thoroughly as possible. The distilling flask was then removed and the electrode vessel closed at both sides, c, and g, and immersed in the thermostat at 25.00° over night. The next morning the tap, f, was closed and the tubes, c and g, opened. The latter was then connected with the vial, g, which had been filled with a concentrated potassium chloride solution, while the other end, c, was attached to a Kipp apparatus, filled with air. Owing to the pressure it was possible to make a fresh contact in the tube "g" between the silver solution and chloride solution. There was a small turbidity at the exit of this tube, but as it was wide (4 mm. inside diameter), there was no danger of obstruction. The necessary contact with the reference electrode (quinhydrone in standard acid mixture) was made with a 2% agar bridge, saturated with KCl at 25°C (approximately 3.5 N).

The amount of liquid evaporating during the evacuation was negligibly small as was shown by special experiments in which a trap immersed in ether and solid carbon dioxide was placed between the distilling flask and the oil pump. After three successive evacuations, the volume of condensed liquid in the trap was less than one drop, which can be neglected in a total volume of 50 to 70 cc.

With the apparatus described, it was possible to obtain results reproducible within 0.1 to 0.2 milli volt, even in solutions as dilute as 0.001 N silver nitrate. Three electrodes were always placed in the same solution and the readings accepted only if the agreement was within 0.2 to 0.3 milli volt. In the presence of benzoate, it is much more difficult to get constant and reproducible results as will be mentioned later. It is peculiar that the benzoate ion exerts an unfavorable influence upon the silver electrode as well as the hydrogen electrode.

The Normal Potential of the Silver Electrode

The potential of the silver electrode was measured in silver nitrate solutions using the quinhydrone electrode in 0.01 N hydrochloric acid and 0.09 N potassium chloride as a reference electrode. The values of the E.M.F. reported in Table II give the average of at least three determinations which agreed with 0.2 milli volt. The normal potential against the above electrode was calculated by means of the equation:

$$E_o = E + 0.0591 \log \frac{1}{[c\ Ag^+]f_{Ag}}$$

in which E is the E.M.F. measured, $[c\ Ag^+]$ the silver nitrate concentration and f_{Ag} the activity coefficient of the silver ions. The latter value was found by application of the simple Debye and Hückel expression:

$$-\log f_{Ag} = 0.5\sqrt{[c\ Ag^+]}$$

TABLE II

The Normal Potential of the Silver Electrode at 25°

Conc. $AgNO_3$ moles p. l	E.M.F. in Volts	$-\log f_{Ag}$ calculated	f_{Ag} calculated	E_0
0.0504	0.1443	(0.1123)	(0.77)	(0.2276)
0.0402	0.1386	0.1002	0.79	0.2270
0.0202	0.1223	0.071	0.85	0.2267
0.0101	0.1056	0.050	0.89	0.2268
0.0050	0.0891	0.035	0.92	0.2272
0.0030	0.0752	0.027	0.94	0.2268
0.0020	0.0658	0.022	0.95	0.2266
0.0010	0.0480	0.016	0.96	0.2263
0.000			Average	0.2269

From the constancy of E_0 it follows that this simple expression can be applied in the case of silver nitrate up to concentrations of 0.05 N; at higher concentrations the calculated value is smaller than the experimental as could be expected.

The average value of E_0 is 0.2269 ± 0.0002 volts at 25°, or the normal potential of the silver electrode against the normal hydrogen electrode E_{0H} = 0.8030 ± 0.0002 volt. It seems to the authors that this value is more accurate than any of the others reported in the literature.

In Table III the activities of the silver ions in 0.01 N silver nitrate in the presence of various neutral salts as determined with the silver electrode are reported. Similar measurements have been made in silver benzoate solutions instead of silver nitrate (comp. Table IV), and it was interesting to compare the results.

TABLE III

f_{Ag} in 0.01 N Silver Nitrate in the Presence of Neutral Salts

Salt added	Ionic strength salt p. l	E.M.F. in volts	a_{Ag}	f_{Ag}	$-\log f_{Ag}$
KNO_3	.05	.0998	.00706	.70	.155
"	.10	.0982	.00664	.66	.182
"	.25	.0954	.00596	.59	.228
"	.50	.0941	.00566	.56	.252
$NaNO_3$	.50	.0975	.00647	.64	.193
$LiNO_3$	.50	.0992	.00690	.68	.166
$Ba(NO_3)_2$	.50	.0980	.00659	.65	.185
$Ca(NO_3)_2$	.507	.0986	.00675	.67	.175
$Sr(NO_3)_2$	.668	.0987	.00678	.67	.173
$Mg(NO_3)_2$	.498	.0992	.00690	.68	.166

The good reproducibility of all readings gave confidence in the use of the silver electrode for measurements of f_{Ag} in silver benzoate solutions. However, in a saturated solution of silver benzoate in water it was found that the reproducibility was much less than in silver nitrate solutions. Addition of neutral salts had a beneficial effect.

In the saturated solution in water values of E were measured between 0.1068 and 0.1082 volt, the average of seven measurements being 0.1073 ± 0.0005 volt. The total concentration of the silver ions in the saturated solution at 25° is 0.01162 equivalents per liter, whereas from the potentiometric measurement a silver ion activity of 0.009462 is found. Therefore, in the saturated solution f_{Ag} is equal to $\frac{0.009462}{0.01162} = 0.813$, whereas by application of the simple Debye and Hückel expression (comp. Table I) a value of 0.883 was calculated. The difference is much larger than can be accounted for by the experimental error and the conclusion is drawn *that silver benzoate in a saturated solution in water no longer behaves as an ideal strong electrolyte.* This conclusion is supported by the following work.

In Table IV the results are given of the measurements of the silver ion activity in saturated solutions of silver benzoate in the presence of neutral salts. The indicated amounts of salt were added to the water and the solutions saturated with silver benzoate.

TABLE IV

Influence of Salts upon the Activity of the Silver Ions in a Saturated Solution of Silver Benzoate

Salt added	Ionic strength salt p. l	E.M.F.	a_{Ag}	[c $Ag^{\cdot}$]	f_{Ag}	$-\log f_{Ag}$
Water		.1073	.00946	0.01162	.81	.090
KNO_3	.05	.1052	.00873	.01298	.67	.172
,,	.10	.1048	.00859	.01366	.63	.201
,,	.25	.1039	.00830	.01483	.56	.252
,,	.50	.1047	.00815	.01590	.54	.269
$NaNO_3$	.50	.1077	.00962	.01628	.59	.228
$LiNO_3$	.50	.1097	.01040	.01648	.63	.200
$Ba(NO_3)_2$	.50	.1100	.01052	.01697	.62	.208
$Mg(NO_3)_2$	.498	.1110	.01094	.01759	.62	.206
$Sr(NO_3)_2$	.668	.1114	.01112	.01784	.62	.206
$Ca(NO_3)_2$	.253	.1098	.01045	.01633	.64	.194
,,	.507	.1115	.01114	.01834	.61	.216
,,	1.013	.1136	.01211	.02079	.58	.234

In all cases the activity coefficient of the silver ions in silver benzoate solutions is smaller than the same in silver nitrate solutions of corresponding strength (comp. Tables III and IV), which could be expected if the silver benzoate were not completely ionized. From the mean activity coefficient, $f = \sqrt{f_{Ag}f_B}$ as reported in Table I and the values of f_{Ag} as given in Table IV, f_B can be calculated.

However, in the derivation of f (Table I), it has been assumed that silver benzoate in its saturated solution behaves as an ideal strong electrolyte and that $f_{Ag} = f_B = 0.883$. Actually, f_{Ag} is equal to 0.813 and in such a dilute solution a similar value can be accepted for f_B. Therefore, S_0 of silver benzoate is not equal to 0.01162×0.883, but to $0.01162 \times 0.813 = 0.00945$, moreover, all values of f should be multiplied by $0.813/0.883 = 0.920$, and all values of $-\log f$ should be increased by 0.036. In the calculation of f_B this correction has been applied to $-\log f$ in Table I: $-\log f_B = -2 \log f + \log f_{Ag}$. The results are given in Table V.

$2 \log f$ is taken from Table I, but corrected for the above difference; $-\log f_{Ag}$ is taken from Table IV. $-\log f_B$ as given in the fifth column is calculated with the aid of the above equation. In the sixth column values of $-\log f_B$ as found in solutions of sodium benzoate, benzoic acid and neutral salts[6] of similar composition and ionic strength are reported. Finally, the last column gives the difference between the two values of $-\log f_B$ which have been determined in an entirely different way. Considering all the experimental difficulties the agreement between the two columns may be considered as excellent and it supports the conclusion that silver benzoate in its saturated solution is not completely ionized.

TABLE V

$-\log f_B$ derived from Measurements with the Silver Electrode and the Hydrogen Electrode Respectively

Salt added	Ionic strength salt added p. l	$-2 \log f$ (Table I, corrected)	$-\log f_{Ag}$ (Table IV)	$-\log f_B$ from f and f_{Ag}	$-\log f_B$ from H_2 electrode	$\Delta(\log f_B)$
KNO_3	0.05	0.276	0.172	0.104	0.120	−0.016
"	0.25	0.392	0.252	0.140	0.155	−0.015
"	0.5	0.453	0.269	0.184	0.179	+0.005
$NaNO_3$	0.5	0.473	0.228	0.245	0.225	+0.02
$LiNO_2$	0.5	0.484	0.200	0.284	0.301	−0.017
$Ba(NO_3)_2$	0.5	0.509	0.208	0.301	0.290	+0.011
$Mg(NO_3)_2$	0.498	0.540	0.206	0.334	0.350	−0.016
$Sr(NO_3)_2$	0.668	0.552	0.206	0.346	0.348	−0.002
$Ca(NO_3)_2$	0.253	0.476	0.194	0.282	0.315	−0.033

This is also in harmony with results of conductivity measurements. It was found that at 25° the conductivity coefficient $\alpha = \Lambda_c/\Lambda_\infty$ in 0.01 N silver benzoate is equal to 0.875, in 0.01 N sodium benzoate to 0.919, whereas in potassium chloride of the same concentration it is equal to 0.947. Anyhow, the results of this study show that one has to be careful in considering even uni-valent salts of organic acids as ideal strong electrolytes.

---

[6] Comp. I. M. Kolthoff and W. Bosch; J. Phys. Chem., 36, 1695 (1932).

Finally, in Tables VI and VII the solubility of silver benzoate in silver nitrate and sodium benzoate solutions respectively, has been given. Moreover, [a Ag^+] has been determined with the silver electrode and f and f_B calculated:

$$f = \sqrt{\frac{S_o^2}{[c\ Ag^+]\ [cB^-]}}$$

$$f_B = \frac{S_o^2}{[a\ Ag^+]\ [cB^-]}$$

assuming that S_o is equal to 0.00945.

By comparing the figures of f in the two tables, it is evident that the mean activity coefficient of the silver benzoate is the same at the same excess of silver nitrate and sodium benzoate respectively. The individual activity coefficients of the silver and benzoate ions, however, are quite different. The values of f_{Ag} in the presence of an excess of silver nitrate (Table VI) agree closely with those in silver nitrate at corresponding ionic strength (see Table II). It appears then that the activity coefficient of the benzoate ions in the presence of an excess of silver nitrate is extremely small; the values are even lower than calculated on the basis of the simple Debye-Hückel expression.

In the presence of an excess of sodium benzoate extremely low values of f_{Ag} are measured and abnormally high values of f_B are calculated (of the order of 1). Since the potentiometric measurements in the presence of an excess of benzoate are extremely difficult and not quite reproducible the values of f_{Ag} and f_B do not seem to be quite reliable. More work is required before definite conclusions can be drawn and the figures of f_{Ag} and f_B are omitted in Table VII.

From all experimental data given in this paper, however, it is evident that silver benzoate does not behave as an ideal strong electrolyte.

TABLE VI

Solubility of Silver Benzoate in Silver Nitrate Solutions and Values of f, f_{Ag} and f_B at 25°

Conc. silver nitrate moles p. l.	Conc. silver benzoate moles p. l.	f	E.M.F. in Volts	[c Ag^+]	[a Ag^+]	[c B^-]	f_{Ag}	f_B
0.00	0.01162	0.813	0.1073	0.01162	0.0095	0.116	(0.81)	(0.81)
0.01	.00786	.798	.1128	.01786	.0148	.0079	.83	.77
0.02	.00576	.777	.1272	.02576	.0206	.0058	.80	.75
0.03	.00447	.760	.1346	.03447	.0274	.0045	.79	.73
0.04	.00392	.721	.1412	.04392	.0355	.0039	.81	.64
0.05	.00328	.716	.1456	.05328	.0421	.0038	.79	.65
0.10	.00248	.593	.1605	.1025	.0753	.0025	.75	.48

TABLE VII

Solubility of Silver Benzoate in Sodium Benzoate Solutions and Values of f at 25°

Conc. sodium benzoate moles p. l.	Conc. Silver benzoate moles p. l.	f	[c Ag⁺]	[c B⁻]
0.00	0.01162	0.813	0.01162	0.1162
0.01	.00816	.777	.00816	.01816
0.02	.00585	.769	.00585	.02585
0.03	.00477	.734	.00477	.03477
0.04	.00396	.717	.00396	.04396
0.05	.00347	.694	.00347	.05347
0.10	.00240	.603	.00240	.1024

Summary

1. The solubility of silver benzoate in water at 25° is 0.01162 + 0.00002 moles per liter. *The salt does not behave as an ideal strong electrolyte and is not completely ionized in its saturated solution.* It is calculated that $[a\ Ag^+] \times [a\ B^-] = 8.9 \times 10^{-5}$ at 25°.

2. The mean activity coefficients and the individual ion activity coefficients of silver benzoate have been determined in various salt solutions. The computed values of the activity coefficient of the benzoate ion correspond with those derived from measurements with the hydrogen electrode in the system benzoic acid-sodium benzoate-neutral salt, only on the assumption that silver benzoate is not completely ionized in its saturated solution.

3. A special study has been made of the silver electrode. The normal potential of the silver electrode as measured against quinhydrone in 0.01 N hydrochloric acid and 0.09 N potassium chloride as reference electrode is 0.2269 ± 0.0002 volt, or $E_{0H} = 0.8030 \pm 0.0002$ volt at 25°.

4. The activity coefficient of silver ions in 0.01 N silver nitrate in the presence of neutral salts has been determined.

PERHALIDE EQUILIBRIUM IN NON-AQUEOUS SOLUTIONS

BY ERNEST A. DANCASTER

The increased solubility of the halogens in water brought about by the presence of halide acids or salts has long been the subject of much speculation and experimental work, the most fruitful method of investigation being by means of the application of the Distribution Law of Nernst. This method was first used for the purpose by Roloff[1] but Jakowkin[2] was the first to make a systematic study of the equilibrium involved, and the view usually accepted at the present time, that the halogen dissolved in a dilute aqueous solution of a metallic halide is present chiefly in the form of tri-halide is based mainly upon his work, and that of his successors. This investigator assumed that the thermal dissociation of the tri-iodide takes place according to the equilibrium

$$MI.I_2 \rightleftarrows MI + I_2.$$

and further assumed that both the iodide atoms of a bivalent halide are equally active in combining with the dissolved iodine. The corresponding equilibrium constant is given by the expression

$$K = \frac{\{na - (b - x)\}x}{b - x},$$

where n is the valence of the metal under consideration, a is the original concentration of the halide, b is the concentration of the free halogen in the aqueous layer as determined by titration, and x is the concentration of the free uncombined halogen, all concentrations being given in gramme molecules per litre. Jakowkin's investigations have been confirmed and extended by Bray and Mackay,[3] Fedotieff[4] and others. Herz and Kurzer[5] studied the case of barium iodide and iodine, keeping the concentration of the iodide constant, while they varied that of the iodine. They, however, assumed that one only of the two iodine atoms of the barium iodide combined with iodine, according to the equilibrium

$$BaI_4 \rightleftarrows BaI_2 + I_2,$$

the corresponding equilibrium constant being given by the expression

$$K = \frac{\{a - (b - x)\}x}{b - x},$$

employing the same equation, Herz and Bulla[6] investigated the iodides of calcium, strontium and barium. Although the values of K calculated from this equation, exhibit a fair degree of constancy it has been shown by Van

---

[1] Z. physik. Chem., **13**, 341 (1894).
[2] Z. physik. Chem., **13**, 539 (1894); **18**, 585 (1895); **20**, 19 (1896).
[3] J. Am. Chem. Soc., **32**, 1207 (1910).
[4] Z. anorg. Chem., **69**, 122 (1910).
[5] Z. Electrochemie, **16**, 869 (1910).
[6] Z. anorg. Chem., **71**, 25 (1911).

Name and Brown[1] that a much greater constancy is obtained when Jakowkin's equation is used. These investigators, therefore, conclude that the latter is the correct one, a conclusion that has been confirmed by Pearce and Eversole.[2] Van Name and Brown have also shown that the constant, calculated by Jakowkin, holds not only for the halides of the bivalent metals, but also for the trivalent metal lanthanum. These investigators made a distinct advance by showing that the bromides and iodides of mercury and cadmium behave abnormally, while all the other halides which they examined, or which had been previously examined, gave a normal value for the dissociation constant. They also calculated the percentage of complex molecules and ions, on the assumption that these do not combine with the halogen. Although Jakowkin has studied the dissociation of a few perhalogen compounds of the type $XClBr_2$, $XClI_2$ and $XBrI_2$, very little work had been done on the perhalogen compounds containing two different halogens, until Priyadaranjan Rây and Pulin Vihari Sarkar[3] investigated the formation and dissociation of the perhalogen acids $HClBr_2$, $HClI_2$ and $HBrI_2$ in aqueous solution, and Dancaster[4] studied the chloro-perbromide equilibria, and found that the chloro-perbromides of mercury and cadmium exhibited abnormalities to those shown by the perbromides and periodides of these metals, and showed that Jakowkin's constant held for the trivalent metal aluminium. None of the halides examined, except those of mercury and cadmium, showed any abnormality. Pierce and Eversole[5] investigated the distribution of iodine between carbon tetrachloride and aqueous solutions of barium iodide at 25°C. The concentrations were determined on the basis of molecules per 1000 grammes of solvent, with the purpose of eliminating the effects due to variations in the amount of solvent. These investigators found that the distribution ratio of iodine between water and carbon tetrachloride is independent of the concentration of the iodine for the range of concentrations used. This result is at variance with that found by Jakowkin, and as all the work done by means of the distribution method of determining the dissociation constants of the perhalides in aqueous solution has been based upon Jakowkin's figures, Pearce and Eversole's results are of importance, and should be either confirmed or refuted. From the results obtained Pearce and Eversole conclude that the tri-iodide is the only periodide present in dilute solutions unsaturated with iodine, whilst a mixture of the tri-iodide and penta-iodide is present in solutions saturated with iodine. Dawson and his co-workers[6] investigated the existence of periodides in nitrobenzene, and other nitro-organic aromatic compounds, and inferred from the results obtained that periodides as high as the enneaiodide, KI_9, are probably present in the solutions. Jones[7] investigated the existence of hydrogen perbromide in acetic acid and aqueous-acetic acid solutions at 15°C. Most of the investigations have been carried

---

[1] Am. J. Sci., (iv), 44, 1051 (1917).
[2] J. Phys. Chem., 28, 245 (1924).
[3] J. Chem. Soc., 121, 1449 (1922).
[4] J. Chem. Soc., 125, 2038 (1924).
[5] Loc. cit.
[6] J. Chem. Soc., 79, 238 (1901); 81, 524 (1902); 85, 79 (1904); 93, 1308 (1908).
[7] J. Chem. Soc., 99, 403 (1911).

out at 25°C., and there are very few figures available for the dissociation constant at other temperatures. Also, with the exception of the work of Dawson and his co-workers and of Jones, the investigations have been limited to aqueous solutions.

The objects of the present investigation were (1) to develop a method for the determination of the thermal dissociation of perhalides in non-aqueous solutions, (2) to ascertain whether the halides of mercury and cadmium in such solutions showed corresponding abnormalities to those shown in aqueous solution, (3) to extend the number of halides investigated so as to include those which cannot be employed in aqueous solution, (4) to ascertain whether or not any of these halides exhibit any abnormalities such as those shown by mercury and cadmium, and (5) to carry out investigations in aqueous and non-aqueous solutions at various temperatures in order to ascertain whether or not the dissociation constant varied with the temperature, and to compare the values of K obtained in aqueous and non-aqueous solutions. The work, of course, necessitated the determination of the distribution of bromine between the organic solvent and air at the temperature employed, and of the distribution ratio of bromine between water and carbon tetrachloride at temperatures other than 25°C. Jakowkin's values were taken for the distribution of bromine between water and carbon tetrachloride at 25°C.

Experimental.—The materials employed were the purest obtainable, and were usually of A. R. quality. The bromides of tin and aluminium were prepared from bromine and the respective metals. All materials were submitted to further purification. A. R. acetic acid gave very erratic results, owing to reaction with the bromine, but after purification by means of the method of Orton and Bradfield[1] the purified acid was not appreciably affected by bromine, and the results obtained were consistent.

The method employed for the determination of the dissociation constant in an organic liquid was a modification of that employed by Jakowkin for the determination of the constant in aqueous solution, in which the distribution of a halogen between an organic solvent, or a solution of a halide in the organic solvent, and the atmosphere above the liquid is determined, instead of the distribution of the halogen between water, or an aqueous solution of a halide, and an organic liquid. It was necessary that the organic liquid chosen for this purpose should be a fairly good solvent for the halides used, and a very good solvent for bromine, and that this liquid should not be attacked by bromine at the temperature of the experiments. Glacial acetic acid was found to satisfy these conditions better than any other organic liquid tried, and this acid was, therefore, used throughout the investigation, although the solubility of some of the halides was found to be very small. For this reason sodium chloride and aluminium chloride could be investigated in very dilute solution only, and cadmium chloride could not be used because it was found to be practically insoluble in acetic acid. It was found possible to obtain solutions of from 0.02 to 0.1 gramme molecule per litre with all the other halides employed, and the chlorides of tin and antimony, and the bro-

---

[1] J. Chem. Soc., 125, 960 (1924).

mide of tin, were found to be very soluble. Titanium chloride could not be employed because it was found to decompose acetic acid with explosive violence as soon as the two liquids were brought into contact. The halides investigated were the chlorides of lithium, sodium, potassium, mercury, iron, aluminium, tin and antimony, and the bromides of sodium, potassium, mercury, cadmium, aluminium and tin. At the time this method was developed the author was unaware that it had been previously employed, but has since discovered that the same method, differing only in details, was used by Jones[1] for the determination of solubility coefficients.

The method employed for the determination of the dissociation constant in aqueous solution was the usual one, in which the aqueous solution and the solution of halogen in an organic solvent are shaken up in a stoppered bottle, and left in the thermostat to settle out. The amount of bromine in each layer is then determined by titration with sodium thiosulphate.

The determination was carried out as follows. A solution of bromine in acetic acid, or in a solution of a halide in acetic acid, was placed in a wash bottle fitted with a ground-glass stopper, through which passed the inlet and outlet tubes, and the flask was left in the thermostat until the contents had attained the required temperature. 10 c.c. of the solution were then withdrawn by means of a pipette, run into an excess of potassium iodide solution, largely diluted with water, and the liberated iodine titrated with N/20 sodium thiosulphate. An aqueous solution of potassium iodide was placed in a second wash bottle, and the two wash bottles were joined up to the rest of the apparatus, consisting of a tower containing calcium chloride and soda lime, an air chamber, an aspirator provided with a thermometer to register the temperature of the interior, and a manometer. The air chamber and the first wash bottle were kept within the thermostat. About 2 litres of air were slowly drawn through the apparatus. This air was dried and freed from carbon dioxide while passing through the tower, and brought to the temperature of the thermostat in the air chamber. The purified and heated air then bubbled through the solution in the first wash bottle, and the bromine laden air passed through the potassium iodide solution, liberating an equivalent amount of iodine which remained in solution in the second wash bottle. At the end of the experiment a second 10 c.c. of the solution was withdrawn from the first wash bottle and titrated. The first and second titrations gave the initial and final bromine concentrations, and the mean of these two results was taken as the average bromine content of the solution during the experiment. The liberated iodine was also titrated in order to ascertain the amount of bromine removed, and the concentration of bromine in the atmosphere in contact with the solution was calculated from the volume of air passed through the apparatus, after applying corrections for temperature and pressure, and also for the vapour of water in the aspirator, the vapour pressure of acetic acid in the first wash bottle, and the volume of bromine in the atmosphere in contact with the solution.

The distribution coefficient of bromine between acetic acid and the atmosphere in contact with the solution was determined at 15°C, 20°, 25°,

---

[1] Loc. cit.

30° and 40°. This atmosphere, of course, consists of a mixture of air, acetic acid vapour and bromine vapour in equilibrium with the liquid, but it will, in this paper be described simply as air. The results are shown in Table I, where B gives the concentration of the bromine in acetic acid, and G gives the concentration of the bromine in air. In both cases the concentrations are given in gramme molecules per litre.

TABLE I

The Distribution of Bromine between Acetic Acid and Air

	B	G	Ratio
At 40°	0.39274	0.001422	276.2
	0.26092	0.0009312	280.2
	0.23134	0.0008295	278.9
	0.15791	0.0005640	280.0
	0.12658	0.0004583	276.2
	0.12077	0.0004333	278.7
	0.10969	0.0003982	275.5
	0.10331	0.0003930	277.0
	0.09808	0.0003537	277.3
	0.08414	0.0003049	275.8
	0.06863	0.0002469	278.0
	0.04696	0.0001706	275.3
		Average	277.4
At 30°	0.29630	0.0007056	419.9
	0.23382	0.0005577	419.2
	0.21410	0.0005102	419.6
	0.17931	0.0004269	420.0
	0.16350	0.0003922	416.9
	0.14762	0.0003518	419.6
	0.13659	0.0003284	415.9
	0.12125	0.0002894	418.9
	0.11390	0.0002713	419.8
	0.09804	0.0002334	420.0
	0.07906	0.0001885	419.4
	0.05506	0.0001311	420.0
	0.04926	0.0001182	416.7
	0.04017	0.00009589	418.9
		Average	419.1
At 25°	0.89242	0.001707	522.8
	0.64175	0.001237	518.9
	0.42800	0.0008228	520.2
	0.22809	0.0004400	518.4
	0.18107	0.0003498	517.6
	0.15354	0.0002951	520.3
	0.14911	0.0002880	517.7
	0.13846	0.0002673	518.0

TABLE I (continued)

The Distribution of Bromine between Acetic Acid and Air

	B	G	Ratio
	0.12538	0.0002414	519.4
	0.12303	0.0002369	519.3
	0.11643	0.0002242	519.3
	0.10795	0.0002065	522.8
At 25°	0.10360	0.0002000	518.0
	0.09470	0.0001830	517.3
	0.09005	0.0001745	516.0
	0.08544	0.0001645	519.4
	0.08161	0.0001575	518.2
	0.06865	0.0001324	518.5
	0.04272	0.00008228	519.2
		Average	519.0
At 20°	0.58243	0.0009129	638.0
	0.28653	0.0004466	641.6
	0.22421	0.0003485	643.3
	0.17573	0.0002754	638.0
	0.13388	0.0002088	641.1
	0.11255	0.0001760	639.2
	0.10235	0.0001599	640.1
	0.09453	0.0001484	637.0
	0.08639	0.0001347	641.3
	0.07937	0.0001240	640.1
	0.07158	0.0001118	640.2
	0.05893	0.00009225	638.8
	0.04605	0.00007210	638.7
		Average	639.8
At 15°	0.59393	0.0007480	794.0
	0.35998	0.0004554	790.5
	0.19186	0.0002422	792.1
	0.13791	0.0001741	792.1
	0.12326	0.0001560	790.1
	0.10970	0.0001384	792.6
	0.10465	0.0001318	794.0
	0.09215	0.0001166	790.3
	0.08846	0.0001117	791.9
	0.07766	0.00009787	793.5
	0.05806	0.00007314	793.8
	0.04712	0.00005945	792.6
		Average	792.3

It is evident that this ratio is constant at any given temperature for all concentrations of bromine within the range of the experiments. The solubility of bromine in acetic acid therefore follows Henry's law. This ratio is, therefore, a measure of the partial vapour pressure of bromine at different temperatures, and the temperature variation over the range in which the latent heat of vaporization is constant should be given by

$$\text{Log}_{10}\text{R} = \frac{Q}{4.6} \cdot \frac{1 + C}{T}.$$

It was found that between 15° and 40°C,

$$\text{Log}_{10}\text{R} = \frac{1650}{T} - 2.828.$$

The values of R obtained by experiment agree fairly well with those calculated from this equation, as shown below.

Temperature °A	R (observed)	R (calculated)
288	792	796
293	640	636
298	519	513
303	419	415
313	277	278

The agreement between the values of R obtained by experiment and those obtained by calculation is fairly satisfactory. The latent heat of bromine in acetic acid solution, obtained from the above values, is 48 calories, a value which is not far from that of liquid bromine (45.6 calories).

In order to ascertain the effect due to the presence of an indifferent salt, i.e. one that does not combine with bromine to form a perhalogen compound, solutions of sodium acetate, disodium hydrogen phosphate and potassium acetate in acetic acid were employed in place of the pure acid. The sulphates and nitrates of sodium and potassium were also tried, but proved to be too insoluble in acetic acid to be of any value. The results obtained are given in Table II, where A is the concentration of the salt, B is the concentration of the bromine in the salt solution, and G is the concentration of the bromine in air. All concentrations are given in gramme molecules per litre.

It is evident from the figures given in Table II that the dissolved salt has no appreciable effect upon the distribution coefficient. The ratios given in Table I can, therefore, be used for the calculation of the dissociation constants of the perhalides examined.

The distribution of bromine between solutions of lithium chloride in acetic acid and air at 25°C was now determined. The concentration of the lithium chloride was varied from 0.09367 to 0.04152 gramme molecules per litre and the concentration of the bromine in the solution from 0.12354 to 0.08685 gramme molecules per litre. Although the perhalide formed in

TABLE II

The Distribution of Bromine between a Solution of a Salt in Acetic Acid and Air at 25°

A	B	G	Ratio
Sodium acetate			
0.97760	0.16462	0.0003191	515.9
—	0.15938	0.0003070	518.6
0.60128	0.17242	0.0003310	520.9
—	0.16803	0.0003246	517.7
0.48830	0.16786	0.0003234	519.2
—	0.16349	0.0003160	517.2
		Average 518.2	
Disodium hydrogen phosphate			
0.23550	0.10309	0.0001987	518.8
—	0.09991	0.0001925	519.0
—	0.09662	0.0001861	519.1
		Average 519.0	
Potassium acetate			
0.80212	0.11147	0.0002143	520.1
—	0.10684	0.0002061	518.4
0.51255	0.20694	0.0003990	518.7
—	0.20258	0.0003919	516.9
0.12814	0.15094	0.0002906	519.4
—	0.14700	0.0002836	518.3
		Average 518.6	

dilute aqueous solution is the tri-halide, it does not follow that this will also be the case in acetic acid solution. Therefore, four dissociation constants were calculated, according to the equilibrium

$$LiCl + mBr_2 \rightleftarrows LiCl.Br_{2m}, \ (m = 1, 2, 3, 4).$$

The corresponding equilibrium constant is given by

$$K = \frac{\left\{na - \frac{b - x}{m}\right\} x^m}{\frac{b - x}{m}}.$$

where the concentration of the free bromine (x) is found by multiplying the observed concentration in air by the distribution coefficient. The results are shown in Table III.

TABLE III

The Dissociation of Lithium Chloro-Perbromides at 25°

B	G	X	K_1	K_2	K_3	K_4
a = 0.09367 M – LiCl						
0.11163	0.0001706	0.08854	0.2707	0.05579	0.00775	0.000936
0.10870	0.0001662	0.08626	0.2661	0.05468	0.00740	0.000869
0.10585	0.0001613	0.08371	0.2705	0.05510	0.00721	0.000822
		Average	0.2691	0.05519	0.00745	0.000876
a = 0.07862 M – LiCl						
0.09072	0.0001416	0.07348	0.2616	0.04395	0.00503	0.000503
0.08879	0.0001393	0.07230	0.2681	0.04359	0.00502	0.000496
0.08685	0.0001361	0.07064	0.2720	0.04344	0.00478	0.000460
		Average	0.2672	0.04366	0.00494	0.000486
a = 0.05968 M – LiCl						
0.11188	0.0001850	0.09602	0.2653	0.06017	0.00910	0.00120
0.10983	0.0001813	0.09409	0.2625	0.05828	0.00864	0.00111
0.10732	0.0001776	0.09217	0.2709	0.05839	0.00847	0.00106
		Average	0.2662	0.05895	0.00874	0.00112
a = 0.04152 M – LiCl						
0.12354	0.0002146	0.11138	0.2689	0.08020	0.01278	0.00195
0.12056	0.0002091	0.10852	0.2657	0.06945	0.01196	0.00177
0.11749	0.0002040	0.10588	0.2672	0.06902	0.01154	0.00167
		Average	0.2673	0.07289	0.01209	0.00180

The values of K_2, K_3 and K_4 increase rapidly with increase in the concentration of the halogen, and as the concentration of the lithium chloride decreases these values fall to a minimum at a concentration of 0.07862 gramme molecules per litre, and then rise with further decrease in the concentration. On the other hand, the value of K_1 remains fairly constant, and is evidently unaffected by alterations in the concentration of either the bromine or the halide, within the limits of the experimental conditions. It is, therefore, obvious that the principal perhalide formed is the trihalide, $LiClBr_2$, and it was not considered necessary to calculate the values of K other than K_1 in the case of the remaining chloro-perbromides examined. In order to save space the remaining data for the chloro-perbromides are summarised in Table IV. The values quoted for K_1 are the mean of usually three experiments, and the variation in K_1 is shown in the last column.

TABLE IV

The Dissociation of Chloro-Perbromides at 25°

Substance	A molality	B molality	K_1	Range
$NaClBr_2$	0.10050	0.1393 – 0.1456	0.262	0.261 – 0.263
"	0.00948	0.1193 – 0.1262	0.260	0.258 – 0.261
$KClBr_2$	0.02640	0.1302 – 0.1364	0.263	0.261 – 0.2675
"	0.02255	0.1411 – 0.1496	0.262	0.257 – 0.266
$AlCl_3Br_6$	0.01225	0.1317 – 0.1383	0.267	0.265 – 0.269
"	0.01008	0.1000 – 0.1071	0.271	0.264 – 0.276
$HgCl_2Br_4$	0.03794	0.14995 – 0.1584	3.4465	3.368 – 3.5475
"	0.01897	0.18785 – 0.1959	2.994	2.972 – 3.008
$FeCl_3Br_6$	0.02676	0.1675 – 0.1782	1.422	1.422 – 1.423
"	0.02674	0.1553 – 0.1625	1.419	1.411 – 1.424
"	0.01531	0.0812 – 0.0852	1.056	1.052 – 1.059
"	0.01482	0.0664 – 0.0708	1.022	0.994 – 1.0665
$SnCl_4Br_8$	0.05078	0.1824 – 0.1866	3.0835	3.070 – 3.097
"	0.02734	0.1557 – 0.1612	2.391	2.386 – 2.405
"	0.01102	0.1118 – 0.11705	1.749	1.692 – 1.777
$SbCl_5Br_{10}$	0.05120	0.1121 – 0.1177	3.159	3.138 – 3.190
"	0.02550	0.1060 – 0.1117	2.408	2.3945 – 2.417

It is evident that the chlorides of sodium, potassium and aluminium behave "normally," i.e. they give a value of the dissociation constant K which agrees with that given by lithium chloride, at any rate at the concentrations examined, which were the greatest that could be obtained owing to the low solubility of these chlorides in acetic acid. On the other hand, the chlorides of mercury, iron, tin and antimony all give values that are considerably higher than those given by the "normal" halides. The values of K given by ferric chloride are distinctly lower than those of the other abnormally behaving halides examined, though they are still considerably higher than the normal value. In each case the value of K increases with increase of concentration of the halide.

The distribution of bromine between solutions of potassium bromide in acetic acid and air at 25° was next determined. The concentration of the potassium bromide was varied from 0.04199 to 0.00840 gramme molecules per litre, and that of the bromine from 0.22371 to 0.08573 gramme molecules per litre. As in the case of lithium chloride, four dissociation constants were calculated, corresponding to

$$KBr + mBr_2 \rightleftarrows KBr_{2m+1}, \quad (m = 1, 2, 3, 4).$$

The results are given in Table V.

Table V

The Dissociation of Potassium Perbromides at 25°

B	G	X	K_1	K_2	K_3	K_4
a = 0.04199 M − KBr.						
0.11294	0.0001160	0.06020	−0.0119	0.00220	0.000307	0.0000291
0.11122	0.0001148	0.05958	−0.0111	0.00221	0.000305	0.0000284
0.09829	0.00009921	0.05149	−0.00529	0.00211	0.000231	0.0000182
0.09709	0.0001008	0.05232	−0.00325	0.00239	0.000260	0.0000206
0.09592	0.00009720	0.05045	−0.00386	0.00215	0.000227	0.0000174
		Average	−0.00708	0.00221	0.000266	0.0000227
a = 0.04170 M − KBr.						
0.22371	0.0002854	0.14813	−0.00664	0.00227	0.00213	0.000575
0.22000	0.0002790	0.14480	−0.00645	0.00228	0.00201	0.000540
0.21439	0.0002688	0.13951	−0.00618	0.00221	0.00182	0.000491
		Average	−0.00642	0.00225	0.00199	0.000535
a = 0.02359 M − KBr.						
0.09101	0.0001183	0.06140	−0.0125	0.00224	0.000322	0.0000311
0.08835	0.0001147	0.05953	−0.0108	0.00226	0.000307	0.0000285
0.08573	0.0001111	0.05766	−0.00912	0.00226	0.000291	0.0000261
		Average	−0.0108	0.00225	0.000307	0.0000286
a = 0.02100 M − KBr.						
0.15769	0.0002340	0.12145	−0.0511	0.00234	0.00132	0.000287
0.15495	0.0002284	0.11854	−0.0502	0.00216	0.00122	0.000258
0.15223	0.0002245	0.11652	−0.0480	0.00238	0.00121	0.000249
0.11320	0.0001568	0.08138	−0.0277	0.00212	0.000528	0.0000718
0.11112	0.0001540	0.07993	−0.0262	0.00221	0.000521	0.0000691
0.10873	0.0001476	0.07661	−0.0267	0.00181	0.000436	0.0000556
		Average	−0.0383	0.00217	0.000872	0.000165
a = 0.00840 M − KBr.						
0.15307	0.0002658	0.13795	−0.0613	0.00211	0.00175	0.000443
0.14902	0.0002582	0.13400	−0.0586	0.00210	0.00159	0.000386
		Average	−0.0599	0.00211	0.00167	0.000415

It is obvious that in the case of potassium bromide the values of K_1, K_3 and K_4 vary greatly. The values of K_1 are all negative, and decrease rapidly with increase of bromine concentration, whilst the values of K_3 and K_4 are positive, and increase under these circumstances. The variations in the concentration of the halide also appear to have an effect upon these values, but, as shown below, if the concentration of the bromine is kept constant, an increase in the concentration of the halide causes a corresponding increase in the value of K_1 and a decrease in the values of K_3 and K_4.

Concentration of Halide	Concentration of Br in solution	K_1	K_3	K_4
0.00840	0.15307	−0.0613	0.00175	0.000443
0.02100	0.15495	−0.0502	0.00122	0.000258
0.02100	0.11112	−0.0262	0.000521	0.0000691
0.04199	0.11122	−0.0111	0.000305	0.0000284

The value of K_2 is not appreciably affected by variations in the concentration of either the halide or the bromine, and remains fairly constant. It therefore appears that in the case of potassium bromide it is the pentabromide that is the principal product in solutions moderately dilute with respect to bromine, and not the trihalide, as in the case of the chloro-perbromides. The values of K_1, K_2 and K_3 were calculated in the case of all the other bromides examined. The bromides of sodium and aluminium were found to behave in the same manner as potassium bromide, the value of K_2 remaining unaffected by variations in the concentrations of either the halide or the bromine, whilst the values of K_1 and K_3 vary considerably, and in the same manner as in the case of the potassium salt. These halides are, therefore, "normal" salts. The bromides of cadmium, mercury and tin give abnormal values for K_1, K_2 and K_3. The data for the perbromides are summarised in Table VI. In order to save space the values of K_1 and K_3 are not shown, and the values quoted for K_2 are the mean of usually three experiments. The variation in K_2 is shown in the last column.

TABLE VI

The Dissociation of Perbromides at 25°

Substance	A molality	B molality	K_2	Range
$NaBr_3$	0.02419	0.1905 — 0.1994	0.00226	0.00215 — 0.00233
”	0.00964	0.1478 — 0.15395	0.00228	0.00224 — 0.00234
$AlBr_9$	0.03271	0.1735 — 0.1759	0.00226	0.00226 — 0.00227
”	0.01478	0.1658 — 0.1710	0.00225	0.00223 — 0.00228
”	0.00773	0.1548 — 0.1602	0.00223	0.00219 — 0.00228
$CdBr_6$	0.02977	0.1306 — 0.1376	0.257	0.241 — 0.265
”	0.01488	0.1707 — 0.1788	0.1775	0.172 — 0.184
$HgBr_6$	0.038705	0.17075 — 0.1770	1.747	1.696 — 1.7915
”	0.038705	0.07875 — 0.0805	1.689	1.640 — 1.748
”	0.03413	0.1676 — 0.1762	1.561	1.5515 — 1.567
”	0.01935	0.0916 — 0.0962	1.280	1.2555 — 1.307
”	0.017065	0.1528 — 0.1567	1.194	1.187 — 1.201
$SnBr_{12}$	0.11558	0.1151 — 0.1211	0.437	0.433 — 0.441
”	0.04973	0.1229 — 0.1288	0.310	0.295 — 0.319
”	0.024865	0.1088 — 0.1148	0.200	0.193 — 0.206
”	0.01243	0.1376 — 0.1415	0.152	0.145 — 0.159

The dissociation constants of lithium chloro-perbromides and potassium perbromides in acetic acid solutions at various temperatures were now determined, the temperatures chosen being 40°, 30°, 20° and 15°. In each case four dissociation constants were calculated, corresponding to the four constants already calculated at 25°, the results obtained were similar to those found with these two compounds at the latter temperature. The data for lithium chloro-perbromide are summarised in Table VII, and those for potassium perbromide in Table VIII. The values of K_1 in the former case and of K_2 in the latter case are the mean of usually four experiments, The values of K_2, K_3 and K_4 for lithium chloro-perbromide and of K_1, K_3 and K_4 for potassium perbromide have been omitted.

Table VII

The Dissociation of Lithium Chloro-Perbromide at Different Temperatures

Temperature	A molality	B molality	K_1
40°	0.06581	0.09285 — 0.1065	0.266
30°	0.04396	0.0762 — 0.0832	0.268
20°	0.09367	0.1713 — 0.1856	0.268
20°	0.07545	0.1820 — 0.1885	0.266
15°	0.05540	0.1239 — 0.1289	0.268

Table VIII

The Dissociation of Potassium Perbromide at Different Temperatures

Temperature	A molality	B molality	K_2
40°	0.03299	0.1067 — 0.11775	0.00218
30°	0.02250	0.1167 — 0.1259	0.00216
20°	0.02090	0.1614 — 0.1696	0.00227
15°	0.02492	0.1328 — 0.1345	0.00223

It is evident from these results that the dissociation constant does not vary with the temperature within the range of the experiments, and that over the whole range of temperatures considered the chloro-perbromides exist principally as the tri-halides, whilst the perbromides exist mainly as pentahalides.

In order to compare the results obtained in acetic acid with those obtained in water, the dissociation constants of lithium chloro-perbromide and potassium perbromide in aqueous solution were now determined. As already stated, this determination was carried out by the method of Jakowkin. Determinations were made at 40°, 30°, 25°, 20° and 15°, but as satisfactory results had already been obtained with potassium perbromide at 25° it was not thought necessary to carry out any further experiments at this temperature with the latter compound. Before the values of K could be calculated it was necessary to determine the distribution ratios of bromine between water and carbon tetrachloride at these temperatures, at any rate for a range of concentrations somewhat exceeding the limits of those employed in the determination of the dissociation constants. These distribution ratios are given in Table IX. The ratio at 25° was not determined, Jakowkin's figures being used instead. The data for lithium chloro-perbromide and potassium perbromide are summarised in Tables X and XI, the values quoted for K_1 being the mean of usually four experiments.

TABLE IX

The Distribution of Bromine between Water and Carbon Tetrachloride at Different Temperatures

	B	G	Ratio
At 40°	0.02088	0.67767	32.46
	0.01929	0.60117	31.16
	0.01602	0.50610	31.60
	0.01302	0.39840	30.61
	0.01120	0.34221	30.55
	0.01001	0.30066	30.05
	0.007601	0.22656	29.81
	0.006229	0.18650	29.94
	0.005820	0.17240	29.62
	0.004245	0.12278	28.92
	0.003455	0.10124	29.30
	0.002152	0.06287	29.22
	0.001920	0.05569	29.00
	0.001208	0.03514	29.15
	0.001060	0.03079	29.04
At 30°	0.02959	0.99282	33.56
	0.02385	0.75958	31.84
	0.02154	0.65194	30.27
	0.01972	0.60064	30.45
	0.01533	0.44849	29.26
	0.01313	0.38200	29.10
	0.01205	0.35117	29.15
	0.009427	0.27345	29.00
	0.007730	0.22070	28.55
	0.007251	0.20962	28.91
	0.005912	0.16860	28.52
	0.004533	0.12773	28.18
	0.003528	0.09826	27.85
	0.002626	0.07301	27.00
	0.002065	0.05786	28.02

Table IX (Continued)

The Distribution of Bromine between Water and Carbon Tetrachloride at Different Temperatures

	B	G	Ratio
At 20°	0.02535	0.77206	30.45
	0.02320	0.68118	29.36
	0.01865	0.52807	28.32
	0.01301	0.35849	27.55
	0.008125	0.21687	26.69
	0.007845	0.20653	26.33
	0.006504	0.17344	26.67
	0.005258	0.13826	26.29
	0.005291	0.13766	26.02
	0.004202	0.11015	26.21
	0.003236	0.08486	26.22
At 15°	0.03580	1.12675	31.47
	0.03131	0.95247	30.42
	0.03018	0.81538	28.80
	0.02336	0.66542	28.49
	0.02196	0.60013	27.33
	0.02040	0.55512	27.21
	0.01922	0.51684	26.89
	0.01762	0.47580	27.00
	0.01595	0.44815	27.27
	0.01521	0.40880	26.88
	0.01219	0.32756	26.87
	0.01096	0.28768	26.26
	0.009911	0.26089	26.32

Table X

The Dissociation of $LiClBr_2$ in Aqueous Solution at Different Temperatures

Temperature	A molality	B molality	K_1
40°	0.05458	0.003144 — 0.01053	0.7455
30°	0.06043	0.006391 — 0.01120	0.747
25°	0.10254	0.005280 — 0.01302	0.747
20°	0.08849	0.009785 — 0.02783	0.745
15°	0.09358	0.01124 — 0.02279	0.742
15°	0.08978	0.007046 — 0.01081	0.745

Table XI

The Dissociation of KBr_3 in Aqueous Solution at Different Temperatures

Temperature	A molality	B molality	K_1
40°	0.05001	0.005819 — 0.01909	0.06325
30°	0.04712	0.01030 — 0.02104	0.0632
20°	0.02036	0.003980 — 0.01213	0.0628
15°	0.06704	0.007610 — 0.02935	0.0630

Discussion of Results

The method of determining the dissociation constants of perhalides in non-aqueous solutions used in this research has been found to give satisfactory results. It is, therefore, a practical method, and can be used in other cases where it is desired to investigate complex molecules and ions in non-aqueous solutions by means of the distribution method. The method is, of course, limited to those substances which are sufficiently soluble in the liquid chosen, and also in air.

The results obtained for the distribution of bromine between water and carbon tetrachloride at different temperatures show that in each case the ratio increases as the concentration of the halogen is increased, and, therefore, agree with those obtained by Jakowkin at 25°. The curves obtained at the various temperatures are approximately parallel at the comparatively low concentrations investigated; thus indicating that at these concentrations the increase in the distribution ratio of bromine is approximately constant at all temperatures between 15° and 40°. The distribution of bromine between acetic acid and air does not show this increase, but remains constant with increase in the concentration of the bromine.

The values obtained for the dissociation constant of perhalides in acetic acid solution show that in the case of the chloro-perbromides the principal halide existing in the solution is the trihalide, as it is in the case of these compounds in aqueous solution. The results obtained with the perbromides, however, indicate that these compounds exist in acetic acid solution principally as pentabromides, whilst in aqueous solution, under similar conditions, they exist mainly as tribromides. Although the dissociation of periodides in acetic acid solution could not be determined by the method employed because of the low solubility of iodine in air, it appears probably that they, too, would be found to exist as penta- or higher perhalides in this solvent. The results obtained by Dawson and his co-workers[1] are not inconsistent with the view that in some organic solvents the perhalides tend to form compounds richer in halogen as we pass up the series from the chloro-perbromides to the periodides.

Where the same halides have been investigated in both aqueous and acetic acid solutions it has been found that those which give normal values of the dissociation constant in the one case also give normal values in the other, and those which give abnormal values in aqueous solution also give abnormal values in acetic acid. It is, therefore, probable that the other "normal" halides investigated in aqueous solution, but not in acetic acid, would also behave normally in this respect in the latter solvent; and that because aluminium perbromide has been found to give a normal value in acetic acid, it would also be found to give a normal value in aqueous solution. When the values of the dissociation constants obtained with the "normal" halides in aqueous and acetic acid solutions are compared, it is found that those ob-

---

[1] Loc. cit.

tained in the latter case are much smaller than those obtained in the former. Table XII shows the mean values of K_1 obtained with the chloro-perbromides at 25° in aqueous and acetic acid solutions.

TABLE XII

Mean Values of K_1 obtained with Chloro-Perbromides in Aqueous and Acetic Acid Solutions at 25°

Salt	K_1 (aqueous)	K_1 (acetic acid)
$LiClBr_2$	0.75	0.267
$KClBr_2$	0.73 (Jakowkin)	0.263
$AlCl_3Br_6$	0.72	0.269

This difference in the value of K_1 indicates a smaller degree of dissociation of the perhalides in acetic acid than takes place in aqueous solution. In both aqueous and acetic acid solution the value of K given by the "normal" perhalides is found to be constant at temperatures ranging from 15° to 40°. Jakowkin[1] found the value of K at 36.5° for KBr_3 to be 0.069, whilst the value at 25° for the same compound was only 0.063, and, therefore, concluded that the dissociation constant of the perhalides increases with increase of temperature. This is a result which might be expected, but it may be pointed out that the value of K at the higher temperature was not determined with anything approaching the accuracy of that at 25°, and the differences between individual values obtained at the latter temperature are sometimes as great as that found between the values obtained at the two temperatures.

The dissociation constants of certain halides were found to have a much greater value than that given by "normal" compounds, whether the chloro-perbromides or the perbromides of the metals in question were chosen for investigation. The compounds of cadmium, mercury, iron, tin and antimony all showed this abnormal behaviour, which corresponds closely with that shown by the chloro-perbromides, perbromides and periodides of cadmium and mercury in aqueous solution. As in the case of the "normal" perhalides, the chloro-perbromides of these abnormally behaving metals evidently exist in acetic acid solution mainly as the trihalides, whilst the corresponding perbromides exist as the pentahalides. In each case the value of K increases considerably with increase in the concentration of the halide. The mercury salts show the greatest variation from the normal values. The only compounds which have shown this abnormal behaviour in aqueous solution are the perhalides of cadmium and mercury, but it is evident from the results obtained in this investigation that the number of "abnormal" compounds must be extended to ferric, stannic and antimonic perhalides, and it is probable that there are still others. The three new "abnormal" salts could not be examined in aqueous solution because they are not stable in water.

---

[1] Z. physik. Chem. **20**, 19 (1896).

TABLE XIII

The "Active Fraction" of Abnormally Behaving Chlorides in Acetic Acid Solution at 25°

Chloride	$[\Sigma ClBr_2]$	$[Br_2]$	$[\Sigma Cl]$ calculated	$[\Sigma Cl]+[\Sigma ClBr_2]$	"Active fraction" %
Mercuric chloride, $HgCl_2$					
0.03794	0.00318	0.15518	0.00543	0.00861	11.34
	0.00325	0.15072	0.00571	0.00896	11.82
	0.00312	0.14683	0.00563	0.00875	11.53
0.01897	0.00232	0.19358	0.00317	0.00549	14.47
	0.00225	0.18964	0.00314	0.00539	14.21
	0.00221	0.18564	0.00315	0.00536	14.13
Ferric chloride, $FeCl_3$					
0.026760	0.00856	0.16966	0.01337	0.02193	27.32
	0.00836	0.16406	0.01350	0.02186	27.23
	0.00809	0.15944	0.01345	0.02154	27.83
0.026740	0.00783	0.15466	0.01342	0.02125	26.49
	0.00776	0.15113	0.01361	0.02137	26.64
	0.00756	0.14771	0.01356	0.02112	26.33
0.015309	0.00329	0.08190	0.01065	0.01394	30.35
	0.00317	0.07801	0.01077	0.01394	30.35
0.014820	0.00266	0.06814	0.01035	0.01301	29.26
	0.00277	0.06602	0.01112	0.01389	31.24
	0.00265	0.06373	0.01102	0.01367	30.75
Stannic chloride, $SnCl_4$					
0.050782	0.01099	0.17563	0.01659	0.02758	13.58
	0.01067	0.17169	0.01647	0.02714	13.36
0.027342	0.00662	0.15461	0.01135	0.01797	16.43
	0.00656	0.15191	0.01144	0.01800	16.46
	0.00644	0.14926	0.01143	0.01787	16.34
0.011020	0.00266	0.11439	0.00616	0.00882	20.01
	0.00261	0.11184	0.00618	0.00879	19.94
	0.00267	0.10909	0.00649	0.00916	20.78
Antimony chloride, $SbCl_5$					
0.051196	0.00860	0.10909	0.02089	0.02949	11.52
	0.00828	0.10665	0.02058	0.02886	11.27
	0.00818	0.10396	0.02085	0.02903	11.34
0.025502	0.00537	0.10629	0.01339	0.01876	14.71
	0.00528	0.10344	0.01353	0.01881	14.75
	0.00512	0.10090	0.01345	0.01857	14.57

TABLE XIV

The "Active Fraction" of Abnormally Behaving Bromides in Acetic Acid Solution at 25°

Bromide	$[\Sigma Br_3]$	$[Br_2]^2$	$[\Sigma Br]$ calculated	$[\Sigma Br]+[\Sigma Br_3]$	Active fraction %
Cadmium bromide, $CdBr_2$					
0.02977	0.00360	0.021412	0.00038	0.00398	6.68
	0.00343	0.016194	0.00048	0.00391	6.57
	0.00354	0.015259	0.00052	0.00406	6.82
0.01488	0.00407	0.029119	0.00031	0.00438	14.72
	0.00413	0.027755	0.00033	0.00446	14.99
	0.00391	0.026545	0.00033	0.00424	14.25
Mercuric bromide, $HgBr_2$					
0.038705	0.00132	0.030424	0.00010	0.00142	1.83
	0.00125	0.029404	0.00010	0.00135	1.74
	0.00127	0.028296	0.00027	0.00154	1.99
0.038705	0.00030	0.006379	0.00011	0.00041	0.53
	0.00027	0.006117	0.00010	0.00037	0.48
0.034129	0.00131	0.030121	0.00010	0.00141	2.07
	0.00123	0.028716	0.00010	0.00133	1.95
	0.00117	0.027322	0.00010	0.00127	1.86
0.019350	0.00028	0.009149	0.00007	0.00035	0.90
	0.00025	0.008727	0.00006	0.00031	0.80
	0.00025	0.008295	0.00006	0.00031	0.80
0.017065	0.00068	0.024129	0.00006	0.00074	2.17
	0.00063	0.022952	0.00006	0.00069	2.02
Stannic bromide, $SnBr_4$					
0.115578	0.01046	0.010031	0.00235	0.01281	2.77
	0.00960	0.009189	0.00235	0.01195	2.59
0.049730	0.00818	0.012638	0.00146	0.00964	4.85
	0.00741	0.012358	0.00135	0.00876	4.40
	0.00716	0.011788	0.00137	0.00853	4.29
0.024865	0.00529	0.010862	0.00110	0.00639	6.42
	0.00481	0.010453	0.00104	0.00585	5.88
	0.00468	0.009898	0.00106	0.00574	5.77
0.012432	0.00527	0.017142	0.00069	0.00596	11.98
	0.00467	0.016461	0.00064	0.00531	10.68

Van Name and Brown[1] attribute the abnormal behaviour of the salts of cadmium and mercury towards the trihalide equilibrium to the power to unite with the halogen being limited to the normal molecules and ions, and have shown that if we accept this view we can calculate that portion of the total halide concentration which is in the form of simple molecules, which they call the "active fraction." If we make the reasonable assumption that

---

[1] Am. J. Sci., [iv], 44, 105 (1917).

the abnormality shown by these halides in acetic acid solution may be attributed to the same reason as that shown by them in aqueous solution, we can calculate the "active fraction" in this case also. The chloro-perbromides exist in acetic acid solution as the trihalides; the calculation is, therefore, the same as in the case of the salts in aqueous solution, except that Br_2 is obtained by multiplying G by the distribution coefficient of bromine in the former case. The perbromides, however, exist as the pentahalides in acetic acid solution, and must be calculated from the equation,

$$K = \frac{[\Sigma Br]\,[Br_2]^2}{Br_5},$$

where $[\Sigma Br]$ and $[\Sigma Br_5]$ represent the total concentrations of the bromide and pentabromide radicles. Table XIII shows the "active fraction" of the abnormally behaving chloro-perbromides, and Table XIV shows those of the abnormally behaving perbromides.

Owing to the low solubility of cadmium and mercuric halides in acetic acid the results obtained are not so reliable as some of those obtained in aqueous solution. It is, however, obvious that in all the abnormal salts examined the magnitude of the "active fraction" decreases with the concentration of the halogen, and increases as the concentration of the halide is reduced. This result agrees with that found in aqueous solution, and is to be expected. It is also found that where the chloride and bromide of the same metal have been examined, e.g. in the case of mercury and tin, the magnitude of the "active fraction" is much larger in the case of the chloride than it is in that of the bromide. This again agrees with the results found in aqueous solution. In this case it was also found that the "active fraction" was greater in the case of the bromide than in that of the iodide. The magnitude of the "active fraction," therefore, decreases as the atomic weight of the halogen in combination with the metal increases. The value of the "active fraction" in pure solutions of the halides could not be calculated because a sufficient range of concentrations of bromine, expecially of very low concentrations, had not been investigated to enable this value to be obtained.

Summary

A modification of the distribution method of investigating the dissociation of the perhalides, in which the atmosphere in contact with the solvent takes the place of one of the liquids employed in the usual method, has been developed and utilized for the examination of the dissociation of chloro-perbromides and perbromides in glacial acetic acid. It has been found possible by means of this method to extend the investigation to a number of halides which cannot be examined in aqueous solution, e.g. the chlorides of iron, tin and antimony, and the bromide of tin.

It has been found that those halides which give a normal value of K in aqueous solution also give a normal value in acetic acid, but that the magnitude of K is much less in the latter case. It has also been shown that whilst

the chloro-perbromides exist principally as trihalides in both aqueous and acetic acid solution, the perbromides exist mainly as tribromides in aqueous solution, but as pentabromides in acetic acid. The list of "normal" perhalides investigated has been extended to aluminium bromide and lithium chloride, which had not been previously investigated.

The halides of cadmium and mercury, which give abnormal values of K in aqueous solution, also give abnormal values in acetic acid, and in addition to these, the chlorides of iron, tin and antimony, and the bromide of tin were also found to give abnormal values. In every case the value of K is much greater than the normal value, and it increases with the concentration of the halide.

The percentage of simple molecules and ions in acetic acid solutions of the abnormally behaving salts has been calculated by Van Name and Brown's method, and it has been found that this percentage decreases with decrease in the concentration of the halogen, and increases with decrease in the concentration of the halide. The percentage is greater in the case of the chlorides of these metals than in that of the bromides.

The values of K for "normal" halides have been determined in both aqueous and acetic acid solutions, at temperatures ranging from 15° to 40°, and it has been found in both cases that there is no appreciable change in the magnitude of these values over the whole range of temperatures employed.

The author wishes to express his thanks to Dr. G. Senter and Dr. S. Sugden for their valuable advice and guidance throughout the work.

Birkbeck College,
University of London,
London, E.C. 4.

REMARKS CONCERNING THE PHASE RULE

BY PIERRE VAN RYSSELBERGHE

The purpose of this note is to call the attention of physical chemists to a beautifully simple and general formulation of the phase rule obtained by De Donder[1] in 1920. The characteristic feature of this formulation is that it replaces the quantity c of the classical expression

$$v = c + 2 - \varphi \tag{1}$$

(v = variance of the system, φ = number of phases) which is rather vaguely and ambiguously defined as the "number of independent constituents" by the quantity $C - r$ which is the difference between the "total number of constituents of the system" and the "number of distinct chemical reactions" which can take place among the constituents of the system. We write

$$v = C - r + 2 - \varphi \tag{2}$$

We shall: 1) show, following De Donder's method, that this expression of the phase rule is a direct consequence of thermodynamics; 2) illustrate by means of a series of classical examples the superiority of expression (2) over expression (1) and show the straightforward way in which the variance can be determined by means of expression (2) in a system of any degree of complications; 3) show how expression (2) leads to a simple and precise solution of the problem consisting of determining the masses of the constituents in the various phases. It is interesting to mention that the identity

$$c = C - r \tag{3}$$

does not appear in Gibbs' theory.[2]

Bakhuis Roozeboom[3] after a short discussion of the concept of independent constituents, concludes "that the number of (independent) constituents can be either larger or smaller than the number of elements; but that it can never be larger than the number of molecular species and is in many cases smaller."

Expression (3) replaces this qualitative statement by a precise definition.

I. *Proof of the rule* $v = C - r + 2 - \varphi$

The total number of variables of a system of φ phases and C constituents is $C\varphi + 2$: the concentrations of all the constituents in all the phases, pressure and temperature (supposed to be uniform throughout the system).

---

[1] Th. De Donder: "Leçons de Thermodynamique et de Chimie physique," 125-139 (1920).

[2] J. W. Gibbs: Equilibrium of heterogeneous substances, "The Collected Works of J. W. Gibbs," I, pp. 55-100, particularly pp. 96-97.

[3] H. W. Bakhuis Roozeboom: "Die heterogenen Gleichgewichte vom Standpunkte der Phasenlehre," 1, 21 (1901).

We have $(\varphi - 1)$ C necessary conditions between the partial molal free energies of the constituents in the φ phases. For constituent i we have the $(\varphi - 1)$ conditions:

$$\overline{F}_{i1} = \overline{F}_{i2} - - - - = \overline{F}_{i\varphi} \quad (i = 1, 2, - - - C) \tag{4}$$

There are C series of analogous relations.

In each phase the sum of the mol fractions of the C constituents must be equal to 1. Hence we have φ relations of the type

$$\sum_{i=1}^{i=C} x_{ia} = 1 \qquad (a = 1, 2, - - - - \varphi) \tag{5}$$

If r reactions can take place among the C constituents we have r chemical equations of the type

$$\sum_{i=1}^{i=C} n_{i\rho} M_i = 0 \qquad (\rho = 1, 2, - - - r) \tag{6}$$

in which $n_{i\rho}$ is the coefficient of the chemical symbol of constituent i in the reaction ρ ($n_{i\rho}$ may be positive, negative or zero), M_i is the chemical symbol of constituent i; it also represents the molecular mass of this constituent. At equilibrium, the total variation of the free energy of the system must be zero with respect to the occurrence of any of the r reactions. We have then the r conditions:

$$\sum_{i=1}^{i=C} F_i n_{i\rho} M_i = 0 \qquad (\rho = 1, 2, - - - r) \tag{7}$$

We recall that

$$F = \sum_{i=1}^{i=C} F_i \tag{8}$$

and that

$$\overline{F}_{ia} = M_i \frac{\partial F}{\partial m_{ia}} \tag{9}$$

in which m_{ia} is the mass of constituent i present in the phase a. Hence we have $(\varphi - 1)$ C relations of the type (4), φ relations of the type (5) and r relations of the type (7) between the $C\varphi + 2$ variables. The variance is then:

$$v = C\varphi + 2 - (\varphi - 1)C - \varphi - r = C - r + 2 - \varphi \tag{10}$$

For a more complete and detailed thermodynamical theory the reader is referred to De Donder[1]

II. *Examples*

A. *Case of purely physical transformations.*

In this case r = 0 and c = C. The forms (1) and (2) of the phase rule coincide.

---

[1] Loc. cit.

B. *Case of physical and chemical transformations.*

We shall examine successively a number of typical examples.

1. *System $CaCO_3$, CaO, CO_2*

The only reaction taking place under usual conditions is

$$CaCO_3 = CaO + CO_2$$

Hence $C = 3$, $r = 1$ and $c = C - r = 2$.

2. *System Na_2SO_4, H_2O, hydrates of Na_2SO_4.*

Two hydrates are known. Hence two reactions take place:

$$\begin{aligned} Na_2SO_4 + 10H_2O &= Na_2SO_4.10H_2O \\ Na_2SO_4 + 7H_2O &= Na_2SO_4.7H_2O \end{aligned}$$

We have: $C = 4$, $r = 2$, $c = C - r = 2$.

In the same way, we would find $c = 2$ for the system $FeCl_3$, H_2O or any other analogous system.

3. *System $Bi(NO_3)_3$, H_2O.*

Four reactions take place:

$$\begin{aligned} Bi(NO_3)_3 + 2H_2O &= Bi(OH)_2NO_3 + 2HNO_3 \\ 2Bi(NO_3)_3 + 3H_2O &= Bi_2O(NO_3)_2(OH)_2 + 4HNO_3 \\ Bi(NO_3)_3 + 5H_2O &= Bi(NO_2)_3.5H_2O \\ Bi(NO_3)_3 + 1\tfrac{1}{2}\,H_2O &= Bi(NO_3)_3.1\tfrac{1}{2}\,H_2O \end{aligned}$$

Hence: $C = 7$, $r = 4$, $c = C - r = 3$.

4. *System C, CO_2, CO, O_2.*

The following reactions are known to occur

$$\begin{aligned} C + O_2 &= CO_2 \\ C + \tfrac{1}{2}O_2 &= CO \\ CO + \tfrac{1}{2}O_2 &= CO_2 \end{aligned}$$

The first one, however, can be obtained by adding the other two. Two of these three reactions are distinct.

Hence: $C = 4$, $r = 2$, $c = C - r = 2$.

5. *System H_2, O_2, H_2O.*

The only reaction occurring is

$$H_2 + \tfrac{1}{2}O_2 = H_2O$$

Hence $C = 3$, $r = 1$, $c = C - r = 2$.

6. *System Na_2SO_4, $MgSO_4$, H_2O.*

In the case of stable equilibria the following reactions have to be considered:

$$\begin{aligned} Na_2SO_4 + 10H_2O &= Na_2SO_4.10H_2O. \\ MgSO_4 + 7H_2O &= MgSO_4.7H_2O. \\ Na_2SO_4 + MgSO_4 + 4H_2O &= Na_2Mg(SO_4)_2.4H_2O. \end{aligned}$$

Hence: $C = 6$, $r = 3$, $c = C - r = 3$.

In the system carnallite, H_2O we would find:
$C = 9$ (H_2O, KCl, carnallite, $MgCl_2$, 5 hydrates of $MgCl_2$),
$r = 6$, $c = C - r = 3$.
In the system $FeCl_3$, HCl, H_2O we would find[1]
$C = 13$ (H_2O, $FeCl_3$, HCl, 4 hydrates of $FeCl_3$, 3 hydrates of HCl, 3 double hydrates of $FeCl_3$ and HCl), $r = 10$, $c = C - r = 3$.

7. *System Fe, CO, CO_2, C.*
The following reactions have to be considered:

$$
\begin{aligned}
Fe + CO &= FeO + C \\
FeO + CO &= Fe + CO_2 \\
3FeO + CO_2 &= Fe_3O_4 + CO \\
CO_2 + C &= 2CO.
\end{aligned}
$$

The last one can be deduced from a combination of the first two.
Hence $C = 6$, $r = 3$, $c = C - r = 3$.

8. *System Na_2SO_4, KCl, H_2O.*
The following reactions occur:

$$
\begin{aligned}
Na_2SO_4 + 10H_2O &= Na_2SO_4.10H_2O \\
2Na_2SO_4.10H_2O + 3KCl &= K_3Na(SO_4)_2 + 3NaCl + 20H_2O \\
K_3Na(SO_4)_2 + KCl &= 2K_2SO_4 + NaCl.
\end{aligned}
$$

Hence: $C = 7$, $r = 3$, $c = C - r = 4$.

III. *Determination of the masses of the constituents in the various phases of the system.*

De Donder[2] has solved this problem in a direct and unambiguous manner as we shall briefly show. The total number of variables includes now the masses of the φ phases. This total number is then $C\varphi + 2 + \varphi$. The masses of the individual constituents in each phase are deduced from the total mass of the phase and the corresponding mol fractions.

If the total masses of the $C - r$ "independent constituents" are given we have, besides the relations (4), (5) and (7) the $C - r$ conditions:

$$m_i = \sum_{1}^{\varphi} m_{ia} \quad (i = 1, 2, \ldots, C - r) \tag{11}$$

m_i being the total mass of constituent i and m_{ia} the mass of constituent i in the phase a. The variance is given by:

$$v' = C\varphi + 2 + \varphi - (\varphi - 1)C - \varphi - r - (C - r) \tag{12}$$

Or

$$v' = 2. \tag{13}$$

---

[1] See A. Findlay: "The Phase Rule and its Applications."
[2] Loc. cit.

Conclusions

1. In the case of *purely physical transformations* ($r = 0$), in order to determine the masses of all the phases it will be necessary to choose the masses of

2 phases when the system is invariant
1 phase when the system is monovariant

(the other arbitrarily chosen variable being then temperature, for instance). When the system has a variance larger than one, the problem can be entirely solved without knowing beforehand the mass of any of the phases, provided, of course, the total masses of the constituents are known. The arbitrarily chosen variables are then pressure and temperature.

2. In the case of *physical and chemical transformations* we give ourselves the total masses of the $C - r$ "independent constituents." In order to determine the masses of all the constituents in the various phases it will be necessary to choose the masses of two, one or zero phases when the variance ($v = C - r + 2 - \varphi$) is zero, one or larger than one.

We see that the knowledge of the masses of the $C - r$ "independent constituents" is not always sufficient to determine the masses of all the constituents in all the phases.

It is particularly in this respect that the formulation of the phase rule obtained by De Donder and its consequences are valuable. For further details the reader should consult De Donder's book.

Summary

The formulation of the phase rule obtained by De Donder involves a precise definition of the number of "independent constituents" of a heterogeneous system. Its application to systems of any degree of complication is simple and straightforward. It affords an unambiguous solution to the problem consisting of determining the masses of all the constituents in all the phases.

Stanford University,
California.

GRAVITATION CONSIDERED AS NEUTRAL MAGNETISM DUE TO MOTION OF ALL MATTER IN TIME

BY A. P. MATHEWS

The following theory that gravitation is neutral magnetism, set up by motion parallel to the time axis of space-time of all matter in our universe, has at least the merit of novelty, so far as I can find. In addition it enables the computation of the amount of gravitation of two hydrogen atoms, and also of the constant of gravitation, provided a certain velocity of motion in time be assumed. This assumed velocity is of the order of magnitude of the velocity in space of various stars, and is related in a very simple way to the velocity of light in space and also to the velocity in space of the negative end of the tube of force constituting the hydrogen atom. It is in fact equal to the velocity of the negative electron in its orbit in hydrogen of 2.187×10^8 cms/secs multiplied by $2/\sqrt{137.1}$; and 137.1 is the ratio of the velocity of light to 2.187×10^8 cms/secs.

While the proof that gravitation is neutral magnetism thus set up cannot be given until some independent determination of the velocity of movement of matter through space-time, or the ether, parallel with the time axis, at a rate of 3.736×10^7 cms/secs shall have been obtained, yet the simplicity of the idea and the not improbable velocity assumed is certainly in its favor. For the flow of time, i.e., of matter through space-time parallel with the time axis, is undoubted, being perceived both objectively in every time series of events and subjectively directly by consciousness, where it appears as the succession of states of consciousness; and the velocity of 3.736×10^7 cms/secs, or 232 miles per second, is less than the velocity in space recently ascribed by astronomers to distant island universes; that velocity being of the order of 10^9 cms/secs. It is of the order of magnitude of the motion of Betelgeuse, which is about 80 miles per second. There is, therefore, nothing improbable in the assumption as to the rate of motion in time.

All matter, so far as known, is moving in time with an unknown velocity, v_t, and is composed of hydrogen atoms. Most of these hydrogen atoms have been condensed to make more complex atoms. Each hydrogen atom, condensed and uncondensed, is an electrical di-pole, and so may be considered to be a unit of neutral, material electricity. Thus each mass of matter in the universe is a current of neutral electricity. All such currents are flowing in the same direction, in paths parallel to the time axis, and they are abreast in time. Such currents of ordinary electricity are known to attract each other if they be of the same sign. All neutral currents are of the same sign. Such neutral currents are known to attract each other. The attraction may be regarded as neutral magnetism. It is called gravitation.

Since each hydrogen atom consists of two electrons, one positive and one negative, each carrying 4.774×10^{-10} electrostatic units of positive or negative charge, we may regard these electrons as half units of neutral electricity, so that each hydrogen atom is, or carries, 4.774×10^{-10} electrostatic units of neutral, material electricity.

The translational motion of a charge, whether positive or negative, in space-time produces magnetism. The magnetism is polar, or dissymmetrical, if the two ends of the neutral charge or tube of force, the positive and negative charges, move in space at different rates; as, for example, when the negative moves about the positive in a hydrogen atom, or when the negative flows along a wire; but it is non-polar, or symmetrical, or neutral, if the two ends of the tube of force connecting the positive and negative electrons move at the same rate. Movement of a hydrogen atom as a whole in space does not set up ordinary, or polar, magnetism; but it must set up magnetism of some kind, since all motion of a charge, whether positive or negative, is known to set up magnetism. It is the peculiarity of gravitation that it is a neutral force. It is non-polar. It is neither positive nor negative, as is electrostatic force; nor is it north and south, as is ordinary magnetism.

The force of polar magnetism between two poles, north and south, or between two parallel currents of ordinary (positive or negative) electricity, is dependent upon the magnetic polarity of any material substance interposed between the poles or currents. It depends upon the magnetic permeability, μ, of that material. Non-polar, or neutral magnetism, would not, presumably, be at all affected by the interposition of matter; so far, at least, as either the magnetic or electrical polarity of that interposed matter is concerned. Corresponding with this expectation, gravitation is known to be independent both of the magnetic permeability and the specific inductive capacity of any matter interposed between gravitating masses.

Now if each condensed hydrogen atom, making a part of other atoms and carrying 4.774×10^{-10} electrostatic units of neutral electricity, by its motion in space generates neutral magnetism in the same manner and to the same degree as an equal quantity of negative or positive electricity, two hydrogen atoms of neutral charge, e, moving in parallel paths, abreast, and at a velocity of v_s in space, at a distance, d, apart, would act upon each other magnetically (attract) with a force expressed by the formula:

$$\mu e^2/d^2 \times v_s^2 \text{ dynes,} \tag{1}$$

when e is expressed in electromagnetic units; d in centimeters; and v_s, the velocity parallel to a space axis, in cms/secs.

Expressing this in electrostatic units we have:

$$e^2/Kd^2 \times 1^2/c^2 \times v_s^2/1^2 \text{ dynes.} \tag{2}$$

In formula (2) the numeral, one, represents unit velocity; i.e., one centimeter per second.

Two hydrogen atoms moving abreast in parallel paths in space with unit velocity at unit distance and in the same direction should, therefore, if this formula be correct, attract each other with the same magnetic force as two electrons[1] similarly moving, a force of $(4.774 \times 10^{-10})^2/(3 \times 10^{10})^2$ dynes, or $2.28 \times 10^{-19}/(9 \times 10^{20})$, or 2.533×10^{-40} dynes. And if they move in space in parallel paths with a velocity, c, that of light, then such atoms would attract with a force of 2.28×10^{-19} dynes, at unit distance, provided that this formula holds at such extreme velocities.

It hardly seems possible that the gravitational force between two hydrogen atoms due to their parallel motion in space can be as large as this. But on the other hand it is known that the mass of an electron does increase with the velocity of space motion, and directly as $c/\sqrt{(c^2 - v^2)}$; and also by the Newtonian law the gravitational force is a function of the mass. So that it is not improbable that the gravitational force would vary with space velocity as this formula states. If the mass increase with the velocity in the manner supposed by relativity, then formula (2) would need a correction which becomes of material importance only when the velocity comes very close to that of light, since the mass is supposed to become infinite at that velocity. The correction would be of the form $1/(1 - v^2/c^2)$. So that the corrected formula should be:

$$(3) \qquad e^2/Kd^2 \times 1^2/c^2 \times v_s^2/1^2 \times c^2/(c^2 - v_s^2);$$

$$\text{or, } (4) \qquad e^2/Kd^2 \times v_s^2/(c^2 - v_s^2) \text{ dynes.}$$

Whether gravitational attraction does vary with the velocity in space according to this formula, I do not know; but the corresponding formula for the velocity in time appears to give the correct result. Of course movement in space can hardly be the cause of gravitation as we know it since the various masses of matter are moving in all directions in space. But in time they are all moving at the same rate, in the same direction, in parallel paths.

The formula will be changed in one particular if the velocity of motion be not motion in space but motion in time. It is obvious, since a velocity is the ratio of the number of units of space extension traversed by the moving body to the number of units of time endured, that if we increase the component of the velocity parallel with the time axis we accomplish the same result as if we retarded the velocity of motion parallel with the space axis. Any increase in speed of motion parallel with the time axis appears to retard the velocity in space; and any decrease in motion parallel with the time axis appears to accelerate the motion in space; and vice versa, velocity in time appears to increase when velocity in space is diminished. This being so the force must vary inversely with the square of the time velocity, if it vary directly with the square of the space velocity. The mass of a body must be an inverse function of the velocity of its movement in time, if it be a direct function of its velocity in space.

Expressing, now, formula (2) in terms of time velocity, v_t, we have:

$$(5) \qquad e^2/Kd^2 \times 1^2/c^2 \times 1^2/v_t^2 \text{ dynes.}$$

---

[1] Of course the electrostatic force of repulsion between two electrons overbalances this magnetic force; but such repulsion is absent between neutral charges.

Since the polar force of attraction of magnetism, the ordinary form, varies directly as the square of velocity in space it must be inversely as the square of the velocity in time. And if gravitation be neutral magnetism set up by the symmetrical motion in time of the tube of force, which is the atom, then gravitation must follow this same law. If it were corrected for the variation of mass with velocity we would have as the corrected formula:

$$e^2/Kd^2 \times 1^2/c^2 \times 1^2/v_t^2 \times (c^2 - v_t^2)/c^2 \text{ dynes; or,} \tag{6}$$

$$e^2/Kd^2 \times (c^2 - v_t^2)/c^4 v_t^2 \times 1^4 \text{ dynes.} \tag{7}$$

If we suppose that the velocity of the flow of time through matter in our universe, or the velocity of motion of matter parallel to a time axis of space-time, be at the same rate as the velocity of the negative electron moving in space about the positive center in the hydrogen atom, in Bohr's first orbit, or 2.187×10^8 cms/secs, this formula would give for the gravitational attraction of two condensed hydrogen atoms (atomic weight unity) at one centimeter distance $(4.774 \times 10^{-10})^2/(3 \times 10^{10} \times 2.187 \times 10^8)^2$ or 5.295×10^{-57} dynes.

This result is not far from being correct. In fact it is precisely 4/137.1 times the correct figure. For since two one gram masses of matter more complex than hydrogen atoms at unit distance attract gravitationally with the force of 6.670×10^{-8} dynes, according to Heyl's recent careful determination, and there are, in a mass of one gram of material composed of atoms more complex than hydrogen, 6.061×10^{23} condensed hydrogen atoms, each pair of such atoms of hydrogen must attract at unit distance with the force of $6.670 \times 10^{-8}/(6.061 \times 10^{23})^2$ dynes. This is 1.815×10^{-55} dynes. This is 137.1/4 times 5.295×10^{-57} dynes which the formula gives when assuming the motion to be 2.187×10^8 cms/secs.

It is clear from this that gravitation may be regarded as neutral magnetism set up by the translational motion of all matter parallel with the time axis. It is neutral because both ends of the tube of force are moving with the same velocity in time. The positive electron in the atom is moving in time at the same velocity as the negative. From formula (5) we may calculate what that velocity is. It is 3.736×10^7 cms/secs. This gives an exact result. This velocity is $(2.187 \times 10^8)/(\sqrt{137.1}/2)$. And 137.1 is $(3 \times 10^{10})/2.187 \times 10^8)$. It is also 135×1.00776^2.

We may secure further evidence that this is correct. I have shown elsewhere how easily a hydrogen atom may be regarded as a very short light pulse which has been absorbed by the ether, becoming thus protohydrogen, and afterwards partly dissociated to form hydrogen by the absorption of a second pulse having twice the frequency of a Rydberg pulse. The first, or creative, light pulse, of a wave length of about 1.75×10^{-14} cms, is supposed to be moving parallel with the time axis. As long as it moves with the velocity of light it has $hc/2\pi$ erg-centimeters in it. This is the quantity, then, of the pulse before absorption. The gravitational attraction of two pulses thus moving in time with velocity of light will be zero, according to formula (7).

But if the pulses be reduced in velocity by absorption then they will attract each other. And at a distance of L between them, when moving with a velocity, v_t, or 2.187×10^8 cms/secs, the formula:

$$hc/2\pi L^2 \times 1^4/4c^2v_t^2 \text{ dynes} \tag{8}$$

gives, at 1 centimeter for L, the correct force of attraction of 1.815×10^{-55} dynes. Here again 1^4 represents unit velocity to the fourth power.

If, however, we consider the amount of erg-centimeters after absorption, in the atom itself, to be $hv'_s/2\pi$, where v'_s is the velocity of the negative electron in space, or 2.187×10^8 cms/secs, then the formula $hv'_s/2\pi L^2 \times 1^4/c^2v_t^2$ gives the correct value of 1.815×10^{-55} dynes for the attraction of the two atoms at unit distance, when v_t, the velocity in time, is 3.736×10^7 cms/secs, the value already found; h is 6.547×10^{-27} erg-secs, and c is 3×10^{10} cms/secs; L is of course unity. This is the same formula as (5) since $hv'_s/2\pi$ is precisely equal to e^2/K.

The gravitational attraction of two one-gram masses at a distance, d, apart, where the neutral charge, e, on each hydrogen atom is 4.774×10^{-10} e.s.u. will be:

$$(6.061 \times 10^{23})^2 \times e^2/Kd^2 \times 1^4/c^2v_t^2 \text{ dynes.} \tag{9}$$

And for any two masses of n and n′ grams respectively it will be:

$$nn' \, (6.061 \times 10^{23})^2 \times e^2/Kd^2 \times 1^4/c^2v_t^2 \text{ dynes.} \tag{10}$$

This is the Newtonian law of gravitation; since $(6.061 \times 10^{23})^2 \times e^2/K \times 1^4/c^2v_t^2$ is the numerical value of the gravitational constant, k.

If it be corrected, as in formula (7) for velocities approaching the velocity of light, it would be, more correctly,:

$$nn' \, (6.061 \times 10^{23})^2 \times e^2/Kd^2 \times 1^4(c^2 - v_t^2)/c^4v_t^2 \text{ dynes.} \tag{11}$$

The velocity is of course the velocity in time rather than in space.

Since formula (7) gives the gravitational attraction of two condensed hydrogen atoms in other terms than $MM'k/d^2$, we may easily find the value of the gravitational constant, k, of the Newtonian law. If $m_{H'}$ is the mass of a condensed hydrogen atom and equal to $1.663 \times 10^{-24}/1.00776$ grams, the value of k will be:

$$\begin{aligned} k &= e^2/Km^2_{H'} \times 1^4/c^2v_t^2 \text{ dynes}^{-1} \text{ velocity}^4 \\ &= (4.774 \times 10^{-10})^2 \times 1.00776^2/(1.663 \times 10^{-24} \times 3 \times 10^{10} \\ &\qquad \times 3.736 \times 10^7)^2 \\ &= 6.670 \times 10^{-7} \text{ dynes}^{-1} \text{ vel}^4 = 6.670 \times 10^{-8} \, (L^3)/(MT^2) \end{aligned} \tag{12}$$

We may conclude from this examination of the problem that gravitation may very well be a non-polar, or neutral, magnetic force, set up by the equal motion of both poles of the electric tubes of force constituting all matter. The motion is parallel with the time axis, so that all masses of matter constitute parallel currents of neutral electricity; and the velocity of such movement of matter in our universe is at the rate of 3.736×10^7 cms/secs. This velocity may not be the same in other universes. If it vary from this figure the mass of the hydrogen atom and all other atoms would vary also somewhat and presumably the spectral lines of such atoms would be shifted slightly from their position as known to us.

Since motion in space seems to have the opposite effect to motion in time, producing energy in place of inertia, it may very well be that all matter repels other matter gravitationally in time, just as it appears to attract it in space. Accordingly all matter would appear to tend to distribute itself uniformly in time; while it tends to aggregate in space. So far as we know at present, matter is distributed, on the whole, uniformly in time, there being neither increase nor decrease in the total quantity of matter as time progresses.

University of Cincinnati.

ON THE HISTORY AND ANALYTICAL EXPRESSION OF THE FIRST AND SECOND LAWS OF THERMODYNAMICS, AND THE RÔLE OF THE DIFFERENTIALS, dW AND dQ

BY GEORGE TUNELL

The fundamental physical facts on which the science of thermodynamics rests were established long ago. According to Gibbs thermodynamics as a science was brought into existence by Clausius. Gibbs[1] has summarized this part of the history of the subject in the following notable paragraphs:

"The fundamental questions concerning the relation of heat to mechanical effect, which had been raised by Rumford, Carnot, and others, to meet with little response, were now[2] everywhere pressing to the front.

" 'For more than twelve years,' said Regnault in 1853, 'I have been engaged in collecting the materials for the solution of this question:—Given a certain quantity of heat, what is, theoretically, the amount of mechanical effect which can be obtained by applying the heat to evaporation, or the expansion of elastic fluids, in the various circumstances which can be realised in practice?' The twenty-first volume of the Memoirs of the Academy of Paris, describing the first part of the magnificent series of researches which the liberality of the French government enabled him to carry out for the solution of this question, was published in 1847. In the same year appeared Helmholtz's celebrated memoir, 'Ueber die Erhaltung der Kraft.' For some years Joule had been making those experiments which were to associate his name with one of the fundamental laws of thermodynamics and one of the principal constants of nature. In 1849 he made that determination of the mechanical equivalent of heat by the stirring of water which for nearly thirty years remained the unquestioned standard. In 1848 and 1849 Sir William Thomson was engaged in developing the consequences of Carnot's theory of the motive power of heat, while Professor James Thomson in demonstrating the effect of pressure on the freezing point of water by a Carnot's cycle, showed the flexibility and the fruitfulness of a mode of demonstration which was to become canonical in thermodynamics. Meantime Rankine was attacking the problem in his own way, with one of those marvellous creations of the imagination of which it is so difficult to estimate the precise value.

---

[1] "The Collected Works of J. Willard Gibbs," 2, part 2, pp. 261, 262 (1928); or Proc. Am. Acad., New Series, 16, 458, 459 (1889).

The history of the first and second laws has been stated by Lord Kelvin in different words but with very similar conclusions. Lord Kelvin's statement is given as an Appendix to this paper.

[2] In the eighteen-forties. (G.T.)

"Such was the state of the question when Clausius published his first memoir on thermodynamics: 'Ueber die bewegende Kraft der Wärme, und die Gesetze, welche sich daraus für die Wärmelehre selbst ableiten lassen.'[3]

"This memoir marks an epoch in the history of physics. If we say, in the words used by Maxwell some years ago, that thermodynamics is 'a science with secure foundations, clear definitions, and distinct boundaries,' and ask when those foundations were laid, those definitions fixed, and those boundaries traced, there can be but one answer. Certainly not before the publication of that memoir. The materials indeed existed for such a science, as Clausius showed by constructing it from such materials, substantially, as had for years been the common property of physicists. But truth and error were in a confusing state of mixture. Neither in France, nor in Germany, nor in Great Britain, can we find the answer to the question quoted from Regnault. The case was worse than this, for wrong answers were confidently urged by the highest authorities. That question was completely answered, on its theoretical side, in the memoir of Clausius, and the science of thermodynamics came into existence. And as Maxwell said in 1878, so it might have been said at any time since the publication of that memoir, that the foundations of the science were secure, its definitions clear, and its boundaries distinct."

Unfortunately in the formulations of the fundamental principles given in the current text-books full use is not made of the symbols, forms, and theorems in the theory of functions of real variables best adapted to the problems at issue. These symbols and forms are essentially those of Clausius, and it is the purpose of this paper to point out this close relationship.

Clausius used several mathematical theorems the proofs of which he did not introduce into his texts. No proofs of these theorems will be given in this paper but the theorems will be stated and the reader will be referred to clear and rigorous proofs in the literature of the theory of functions of real variables.

The first law of thermodynamics was stated by Clausius[4] as follows:

"Die ganze mechanische Wärmetheorie beruht auf zwei Hauptsätzen. . . . Um den ersten Satz analytisch auszudrücken, denken wir uns irgend einen Körper, welcher seinen Zustand ändert, und betrachten die Wärmemenge, welche ihm während dieser Zustandsänderung mitgetheilt werden muss. Bezeichnen wir diese Wärmemenge mit Q, wobei eine vom Körper abgegebene Wärmemenge als aufgenommene negative Wärmemenge gerechnet werden soll, so gilt für das einer unendlich kleinen Zustandsänderung entsprechende Element dQ der aufgenommenen Wärme folgende Gleichung:

$$dQ = dU + AdW. \qquad \text{(I.)}$$

---

[3] Read in the Berlin Academy, February 18, 1850, and published in the March and April numbers of Poggendorff's "Annalen."

[4] "Abhandlungen über die mechanische Wärmetheorie," Zweite Abtheilung, Abhandlung IX (1867).

The quotations in German may be skipped without disruption of the consecutive development of the subject matter although it is believed that the statements of Clausius are of no inconsiderable interest to the student of thermodynamics.

Hierin bedeutet U die Grösse, welche ich zuerst in meiner Abhandlung von 1850 in die Wärmelehre eingeführt und als die Summe der hinzugekommenen freien Wärme und der zu innerer Arbeit verbrauchten Wärme definirt habe. W. Thomson hat für diese Grösse später den Namen *Energie* des Körpers vorgeschlagen, welcher Benennungsweise ich mich, als einer sehr zweckmässig gewählten, angeschlossen habe, wobei ich aber doch glaube, dass man sich vorbehalten kann, in solchen Fällen, wo die beiden in U enthaltenen Bestandtheile einzeln angedeutet werden müssen, auch den Ausdruck *Wärme- und Werkinhalt* zu gebrauchen, welcher meine ursprüngliche Definition in etwas vereinfachter Form wiedergibt. W bedeutet die während der Zustandsänderung des Körpers gethane äussere Arbeit, und A das Wärmeäquivalent für die Einheit der Arbeit oder kürzer *das calorische Aequivalent der Arbeit.* Hiernach ist AW die nach Wärmemaasse gemessene äussere Arbeit oder, gemäss einer kürzlich von mir vorgeschlagenen bequemeren Benennungsweise, das äussere *Werk.*

"Wenn man der Kürze wegen das äussere Werk durch einen einfachen Buchstaben bezeichnet, indem man setzt:

$$AW = w,$$

so kann man die vorige Gleichung folgendermaassen schreiben:

$$dQ = dU + dw." \qquad \text{(Ia.)}$$

Clausius continued farther on:

"[Eine Grösse], welche sich auf den ersten Hauptsatz bezieht, ist die schon im Anfange dieser Abhandlung besprochene, in Gleichung (Ia.) enthaltene Grösse U, welche den Wärme- und Werkinhalt oder die Energie des Körpers darstellt. Zur Bestimmung dieser Grösse ist die Gleichung (Ia.) anzuwenden, welche wir so schreiben können:

$$dU = dQ - dw, \qquad (57)$$

oder, wenn wir sie uns integrirt denken:

$$U = U_0 + Q - w. \qquad (58)$$

Hierin stellt U_0 den Werth der Energie für einen willkürlich gewählten Anfangszustand des Körpers dar, und Q und w bedeuten die Wärmemenge, welche man dem Körper mittheilen muss, und das äussere Werk, welches gethan wird, während der Körper auf irgend eine Weise aus jenem Anfangszustande in den gegenwärtigen Zustand übergeht. . . ."

From the preceding paragraphs Clausius obtained an important conclusion, his equation (5), by the following reasoning:

"Wenn die Grössen x und y den Zustand des Körpers bestimmen, so muss die Grösse U, die Energie des Körpers, welche nur von dem augenblicklich stattfindenden Zustande des Körpers abhängt, sich durch eine Function dieser beiden Veränderlichen darstellen lassen.

"Anders verhält es sich mit den Grössen w and Q. Die Differentialcoëfficienten dieser Grössen, welche wir folgendermaassen bezeichnen wollen:

$$(1)\qquad \frac{dw}{dx} = m\,;\ \frac{dw}{dy} = n$$

$$(2)\qquad \frac{dQ}{dx} = M\,;\ \frac{dQ}{dy} = N,$$

sind bestimmte Functionen von x und y. Wenn nämlich festgesetzt wird, dass die Veränderliche x in x + dx übergehen soll, während y unverändert bleibt, und dass diese Zustandsänderung des Körpers in umkehrbarer Weise geschehen soll, so handelt es sich um einen vollkommen bestimmten Vorgang, und es muss daher auch das dabei gethane äussere Werk ein bestimmtes sein, woraus weiter folgt, dass der Bruch dw/dx ebenfalls einen bestimmten Werth haben muss. Ebenso verhält es sich, wenn festgesetzt wird, dass y in y + dy übergehen soll, während x constant bleibt. Wenn hiernach die Differentialcoëfficienten des äusseren Werkes w bestimmte Functionen von x und y sind, so muss zufolge der Gleichung (Ia.) auch von den Differentialcoëfficienten der vom Körper aufgenommenen Wärme Q dasselbe gelten, dass auch sie bestimmte Functionen von x und y sind.

"Bilden wir nun aber für dw und dQ ihre Ausdrücke in dx und dy, indem wir unter Vernachlässigung der Gleider, welche in Bezug auf dx und dy von höherer Ordung sind, schreiben:

$$(3)\qquad dw = mdx + ndy$$

$$(4)\qquad dQ = Mdx + Ndy,$$

so erhalten wir dadurch zwei vollständige Differentialgleichungen, welche sich nicht integriren lassen, so lange die Veränderlichen x und y von einander unabhängig sind, indem die Grössen m, n und M, N der Bedingungsgleichung der Integrabilität, nämlich:

$$\frac{dm}{dy} = \frac{dn}{dx} \text{ resp. } \frac{dM}{dy} = \frac{dN}{dx},$$

nicht genügen. Die Grössen w und Q gehören also zu denjenigen, ... deren Eigenthümlichkeit darin besteht, dass zwar ihre Differentialcoëfficienten bestimmte Functionen der beiden unabhängigen Veränderlichen sind, dass *sie selbst aber nicht durch solche Functionen dargestellt werden können sondern sich erst dann bestimmen lassen, wenn noch eine weitere Beziehung zwischen den Veränderlichen gegeben und dadurch der Weg der Veränderungen vorgeschrieben ist.*"[5] (Italics in the last sentence by the author of this paper.)

"Kehren wir nun zur Gleichung (Ia.) zurück und setzen darin für dw und dQ die Ausdrücke (3) und (4) und zerlegen ebenso dU in seine beiden auf dx und dy bezüglichen Theile, so lautet die Gleichung:

$$Mdx + Ndy = \left(\frac{dU}{dx} + m\right)dx + \left(\frac{dU}{dy} + n\right)dy.$$

---

[5] The importance of this sentence makes it worth while to offer the following translation: The quantities w and Q belong to those quantities. . . . the peculiarity of which is that, while their differential coefficients are definite functions of the two independent variables (x and y), the quantities themselves cannot be represented by such functions and can only then be determined when a further relation is given between the variables and the path of the changes is thereby prescribed.

Da diese Gleichung für alle beliebigen Werthe von dx und dy gültig sein muss, so zerfällt sie in folgende zwei:

$$M = \frac{dU}{dx} + m$$

$$N = \frac{dU}{dy} + n.$$

Differentiiren wir die erste dieser Gleichungen nach y und die zweite nach x, so erhalten wir

$$\frac{dM}{dy} = \frac{d^2U}{dxdy} + \frac{dm}{dy}$$

$$\frac{dN}{dx} = \frac{d^2U}{dydx} + \frac{dn}{dx}.$$

Nun ist auf U der für jede Function von zwei unabhängigen Veränderlichen geltende Satz anzuwenden, dass, wenn man sie nach den beiden Veränderlichen differentiirt, die Ordnung der Differentiationen gleichgültig ist, so dass man setzen kann:

$$\frac{d^2U}{dxdy} = \frac{d^2U}{dydx}.$$

Wenn man unter Berücksichtigung dieser letzten Gleichung die zweite der beiden vorigen Gleichungen von der ersten abzieht, so kommt:

$$(5) \qquad \frac{dM}{dy} - \frac{dN}{dx} = \frac{dm}{dy} - \frac{dn}{dx}."$$

The attempt will next be made to prove that the essentials of Clausius's analytical expressions of the first law are in accord with the theory of functions of real variables; Planck's objection to Clausius's use of dQ and its designation as a differential is based on an argument that will be proved erroneous.

The simplest system discussed in thermodynamics consists of a fixed quantity, for example one gram or one mol, of one gaseous phase containing only one component, throughout which the temperature and pressure are uniform. For such a system there exists a characteristic relation that may be expressed as follows:

$$(1) \qquad \Phi(p,v,t) = 0,$$[6]

where p denotes the pressure; v, the volume; and t, the temperature of the gas on the scale of the constant volume hydrogen thermometer, which has been adopted as standard by the International Bureau of Weights and Measures (at Sèvres, France). On the centigrade scale of this thermometer the temperature of melting ice is taken as 0° and that of the vapor of distilled

---

[6] The present discussion applies to systems such as steam, a satisfactory representation of which is not given by a simple, highly specialized equation of state such as the perfect gas law or van der Waals's equation.

water boiling under normal atmospheric pressure as 100°, the hydrogen being under a pressure of one meter of mercury when the temperature is 0°.

The characteristic equation of the gas is in general such that by means of it any one of the variables can be represented as a function of the other two.

For reversible processes (continuous series of equilibrium states)[7] the work done by the system (work of the path),[8] W, is defined by the equation

$$W = \int_{(t_0,p_0)}^{(t,p)} p\,dv = \int_{(t_0,p_0)}^{(t,p)} p\left(\frac{\partial v}{\partial t}\right)_p dt + p\left(\frac{\partial v}{\partial p}\right)_t dp, \tag{2}$$

where W is measured in mechanical units. The heat received (heat of the path), Q, is defined by the equation

$$Q = \int_{(t_0,p_0)}^{(t,p)} c_p dt + l_p dp, \tag{3}$$

where c_p and l_p denote some functions of t and p, and Q is measured in thermal units. These definitions correspond to the facts stated by Clausius that the work done and the heat received each depends on all of the intermediate states as well as the initial and final states; the integrals in (2) and (3) are line integrals that depend on the particular choice of the path of integration. As Clausius says, the quantities W and Q can only be determined when an additional relation between the variables that determine the state of the system is given and the path of the changes is thereby fixed.

The justification for the introduction of heat as a physical quantity in thermodynamics (as contrasted with the justification for the definition utilized in kinetic theory) is well stated by Preston[9] as follows:

"In order to account for the sensation experienced in presence of a hot body an active agent is postulated, and the name given to this agent is heat. A hot body is regarded as a source of heat just as a luminous body is regarded as a source of light. In the same way, when two bodies at different temperatures are placed in contact, the temperature of the warmer falls while that of the other rises. To account for this we say that *heat* passes from one to the other, that the warmer loses heat and the colder gains it. In this sense heat is regarded as something which may be added to or taken away from matter;

---

[7] "On dit qu'une transformation est opérée par voie réversible quand elle est constituée par une succession d'états d'equilibre. Une transformation ne peut donc se produire réelement par voie rigoureusement réversible; elle est la limite de deux séries de transformations *réalisables et s'effectuant en sens* inverses." H. Bouasse: "Cours de Thermodynamique," Deuxième édition, Première partie, 70 (1913).

[8] Gibbs says: "Suppose the body to change its state, the points associated with the states through which the body passes will form a line, which we may call the *path* of the body. The conception of a path must include the idea of direction, to express the order in which the body passes through the series of states. With every such change of state there is connected in general a certain amount of work done, W, and of heat received, H, which we may call the *work* and the *heat* of the *path*." "Collected Works," 1, 3 (1928).

[9] "The Theory of Heat." Third Edition, Edited by J. Rogerson Cotter, 19 (1919).

something which can be communicated to matter, and which can be handed on from one piece of matter to another. Heat thus possesses the rank of a *quantity*, and we are led to seek *how much* heat a body gains or loses when its temperature changes. On the other hand, temperature is regarded rather as a quality which varies from one body to another, or from one part to another of the same body, when heat is being communicated to or abstracted from it, or which may vary . . . in consequence of actions taking place within the body itself, or performed on it from without.

"It must, however, be distinctly remembered that what we directly *observe* is temperature and changes of temperature, and when the temperature of a body (free from other actions) rises we *say* it has received heat. The effect observed is the change of temperature, and the postulated cause is addition or subtraction of heat."

The establishment in thermodynamics of the quantitative character of heat is completed by means of calorimetric mixing experiments as explained by Mach;[10] in such experiments it is always found possible to write a "compensation equation" indicating that the heat received (or given up) by the one body in its change of state is equal to the heat given up (or received) by the second body in its simultaneous change of state. This experimental fact is the basis for the introduction of heat as a physical quantity in thermodynamics.

Heat[11] is then analogous to work since work done by one body is always equal to that done on a second body. The double-ended character of a force of course necessitates the conclusion that work is a physical quantity; when the point of application (that is, the point at which the two bodies touch) of the force moves, the work done by the body exerting the force in one direction is equal in magnitude but opposite in sign to that done by the other body.

Now a line integral[12] can be evaluated as an ordinary integral; thus

$$(4)\quad W = \int_{(t_o,p_o)}^{(t,p)} p\left(\frac{\partial v}{\partial t}\right)_p dt + p\left(\frac{\partial v}{\partial p}\right)_t dp = \int_{\sigma_o}^{\sigma} \left[p\left(\frac{\partial v}{\partial t}\right)_p \frac{dt}{d\sigma} + p\left(\frac{\partial v}{\partial p}\right)_t \frac{dp}{d\sigma} \right] d\sigma,$$

---

[10] E. Mach: "Die Principien der Wärmelehre," 4. Aufl., 182-194 (1923).

The writer is indebted to Professor E. C. Kemble for a clear and cogent development of this topic in his lectures in Physics 6a (a course given in Harvard College), and also for calling the writer's attention to the exposition of Mach.

In numerous books on thermodynamics (for example, Goodenough: "Principles of Thermodynamics," Third Edition, 20 (1920)) it is *proved* that the line integral representing the heat received by a system depends on the path. This proof is based, either explicitly or tacitly, on the postulates of kinetic theory. The argument is that the internal energy depends only on the state of the body and that the work done depends on the path; therefore the heat received, which is equal to the increase in internal energy less the work done, must depend on the path. At the present time it is unnecessary to base the principles of thermodynamics on the postulates of kinetic theory and, for most purposes, it is probably undesirable. The experimental facts of calorimetry discussed by Mach suffice to establish the analytical characterization of heat as a line integral that depends on the path without reference to the postulates of kinetic theory, and this statement is one of the indispensable foundation blocks of the science of empirical thermodynamics.

[11] The developments in this paper are in accord with P. W. Bridgman's illuminating discussion, in terms of experimental operations, of the significance of the quantities, temperature, heat, and energy, in thermodynamics. "The Logic of Modern Physics," 117-131 (1927).

[12] For the definition of the line integral see W. F. Osgood: "Lehrbuch der Funktionentheorie," 5. Aufl., 1, 134-137 (1928).

where σ denotes the parameter that determines the particular series of states through which the system passes, and the path or curve is represented in parametric form by the equations:

$$t = \varphi(\sigma),\ p = \psi(\sigma).\text{[13]} \tag{5) (6}$$

The line integrals in the definitions of work and heat are functions of the upper limit of integration, σ, and may be differentiated with respect to σ.[14] Thus

$$\frac{dW}{d\sigma} = p\left(\frac{\partial v}{\partial t}\right)_p \frac{dt}{d\sigma} + p\left(\frac{\partial v}{\partial p}\right)_t \frac{dp}{d\sigma}, \tag{7}$$

and

$$\frac{dQ}{d\sigma} = c_p \frac{dt}{d\sigma} + l_p \frac{dp}{d\sigma}. \tag{8}$$

Multiplying each of these equations by $d\sigma$, one obtains the results,

$$dW = p\left(\frac{\partial v}{\partial t}\right)_p dt + p\left(\frac{\partial v}{\partial p}\right)_t dp, \tag{9}$$

and

$$dQ = c_p dt + l_p dp, \tag{10}$$

where σ is the independent variable of the functions W and Q and thus $d\sigma = \Delta\sigma$ is the independent (principal) infinitesimal (W and Q are not functions of the independent variables t and p and thus dt and dp are not independent infinitesimals in these equations). The conclusion follows that dQ is just as truly a differential as dv: dv is the differential of a function of two independent variables while dQ is the differential of a function of a single independent variable.

The following statement of Planck concerning dQ has led to much confusion in the literature of thermodynamics, since it is seriously in error and since it has been restated in several text-books. Planck[15] writes:

---

[13] If the path be represented by the equation

$$p = f(t),$$

instead of in the parametric form given in the text, then W and Q can be evaluated by the equations,

$$W = \int_{t_0}^{t} p\left(\frac{\partial v}{\partial t}\right)_p dt + p\left(\frac{\partial v}{\partial p}\right)_t \frac{dp}{dt} dt,$$

and

$$Q = \int_{t_0}^{t} c_p(t, f(t))\, dt + l_p(t, f(t)) \frac{dp}{dt} dt.$$

These two integrals obviously cannot be used to express the work and heat of a straight-line path parallel to the p-axis (change of pressure at constant temperature) and thus these two integrals have a serious disadvantage in comparison with the integrals given in the text. The integrals in the text apply to straight-line paths in all directions as well as to curved paths.

[14] W. F. Osgood: "Advanced Calculus," 215, 216 (1925); E. Goursat: "A Course in Mathematical Analysis," *translated* by E. R. Hedrick, 1, 154 (1904).

[15] "Vorlesungen über Thermodynamik," 7. Aufl., 55, 56 (1922).

"Nach Clausius' Vorgang wird dieser Ausdruck gewöhnlich, um seine unendliche Kleinheit anzudeuten, mit dQ bezeichnet. Dies hat jedoch nicht selten zu dem Missverständnis Anlass gegeben, als ob die zugeleitete Wärme das Differential einer bestimmten endlichen Grösse Q wäre. Der hierdurch nahe gelegte Trugschluss sei durch folgende kleine Rechnung illustriert. Wählt man T und V als unabhängige Variable, so ist

$$dQ = dU + pdV = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] dV.$$

Andrerseits ist:

$$dQ = \left(\frac{\partial Q}{\partial T}\right)_V dT + \left(\frac{\partial Q}{\partial V}\right)_T dV.$$

Folglich, da dT und dV voneinander unabhängig sind:

$$\frac{\partial Q}{\partial T} = \frac{\partial U}{\partial T} \text{ und } \frac{\partial Q}{\partial V} = \frac{\partial U}{\partial V} + p$$

und daraus durch Differentiation der ersten Gleichung nach V, der zweiten nach T:

$$\frac{\partial^2 Q}{\partial T \partial V} = \frac{\partial^2 U}{\partial T \partial V} = \frac{\partial^2 U}{\partial T \partial V} + \frac{\partial p}{\partial T},$$

also $\partial p/\partial T = 0$, was sicher unrichtig ist."

It has been proved in this paper that dQ is the differential of a function, Q, of the parameter, σ, that determines the series of states through which the system passes, and that the rigorous definition of a differential is satisfied by dQ.[16] The first part of Planck's statement is therefore erroneous. Moreover in the equation

$$dQ = c_p dt + l_p dp$$

dt and dp are not independent infinitesimals; likewise in the equation

$$dQ = c_v dt + l_v dv$$

dt and dv are not independent infinitesimals, and therefore it does not follow from the latter equation that

$$\frac{\partial^2 U}{\partial t \partial v} = \frac{\partial^2 U}{\partial t \partial v} + \frac{\partial p}{\partial t}.$$

---

[16] The same definition of the differential is given in the following works:

W. F. Osgood: "Introduction to the Calculus," 91-93 (1922); "Lehrbuch der Funktionentheorie," 5. Aufl., 1, 236 (1928);

E. Goursat: "A Course in Mathematical Analysis," translated by E. R. Hedrick, 1, 19, 20 (1904);

James Pierpont: "The Theory of Functions of Real Variables," 1, 244 (1905);

E. B. Wilson: "Advanced Calculus," 64 (1912);

F. S. Woods: "Advanced Calculus," 28 (1926);

Cf. also the statement by E. L. Mickelson in his review of D. Humphrey's "Advanced Mathematics for Students of Engineering and Physics" that: "alterations in two or three objectionable statements, of which the most important is the statement that the differential of f(x) is the *actual* change when x is increased by dx, would contribute accuracy well within the student's powers of appreciation." American Mathematical Monthly, 38, 454 (1931).

In the special cases of straight-line paths parallel to the coordinate axes the reductions of equations (7) and (8) are as follows.

I. Let the path be a straight line in the t,p-plane parallel to the t-axis:

(11) (12) $t = \sigma,\ p = K$, K, a constant greater than zero.

Then

$$(13)\qquad \frac{dW}{d\sigma} = \frac{dW}{dt} = p\left(\frac{\partial v}{\partial t}\right)_p,$$

and

$$(14)\qquad \frac{dQ}{d\sigma} = \frac{dQ}{dt} = c_p.$$

On account of the relation expressed by equation (14), c_p is called the heat capacity at constant pressure.

II. Let the path be a straight line in the t,p-plane parallel to the p-axis:

(15) (16) $p = \sigma,\ t = K'$, K', a constant.

Then

$$(17)\qquad \frac{dW}{d\sigma} = \frac{dW}{dp} = p\left(\frac{\partial v}{\partial p}\right)_t,$$

and

$$(18)\qquad \frac{dQ}{d\sigma} = \frac{dQ}{dp} = l_p.$$

On account of the relation expressed by equation (18), l_p is called the latent heat of change of pressure at constant temperature.

The derivatives

$$\frac{dW}{dt}, \frac{dW}{dp}, \frac{dQ}{dt}, \text{and} \frac{dQ}{dp}$$

are thus total derivatives, as Professor Kemble[17] has rightly pointed out. Therefore one should not write for them

$$\left(\frac{\partial W}{\partial t}\right)_p, \text{etc.,}$$

since this notation in mathematics has only one meaning, namely, the partial derivative of a function, W, of the independent variables, t and p, taken with respect to t holding p fast; W and Q are not functions of the independent variables t and p.

Clausius's analytical expression of the first law by means of his equation (58) can be rendered more explicit for reversible processes in the system under consideration by the following equation:

$$(19)\quad U(t,p) - U(t_o,p_o) = \int_{(t_o,p_o)}^{(t,p)} \left(Jc_p - p\left(\frac{\partial v}{\partial t}\right)_p\right) dt + \left(Jl_p - p\left(\frac{\partial v}{\partial p}\right)_t\right) dp,$$

which is also written in the more familiar but less explicit form:

---

[17] Lectures in Physics 6a.

$$(20)\qquad U(t,p) - U(t_0,p_0) = \int_{(t_0,p_0)}^{(t,p)} JdQ - dW,$$

the integrals in each of the equations (19) and (20) being extended over any path connecting the points, (t_0,p_0) and (t,p); Q denotes the heat received (heat of the path); W, the work done (work of the path); $J = 1/A$, a constant, the mechanical equivalent of heat; and U, the internal energy per gram measured in mechanical units. The physical hypothesis (experimental fact) embodied in each of the equations, (19) and (20), may be stated in words as follows: The value of the integral in each of the equations, (19) and (20), is independent of the choice of the path of integration, that is, it depends only on the limits of integration, and the integral may therefore be used to define a function, the internal energy per gram, of the independent variables, t and p. Equation (20) may be brought readily into the form (19) by means of (2) and (3).

From (19) it follows directly that

$$(21)\qquad \left(\frac{\partial U}{\partial t}\right)_p = Jc_p - p\left(\frac{\partial v}{\partial t}\right)_p,$$

and

$$(22)\qquad \left(\frac{\partial U}{\partial p}\right)_t = Jl_p - p\left(\frac{\partial v}{\partial p}\right)_t.$$

Two clear and rigorous proofs of this theorem are given by Osgood.[18]

Substituting the values of $(\partial U/\partial t)_p$ and $(\partial U/\partial p)_t$ just obtained in the equation of the total differential of $U(t,p)$,

$$(23)\qquad dU = \left(\frac{\partial U}{\partial t}\right)_p dt + \left(\frac{\partial U}{\partial p}\right)_t dp,$$

one obtains

$$(24)\qquad dU = \left(Jc_p - p\left(\frac{\partial v}{\partial t}\right)_p\right)dt + \left(Jl_p - p\left(\frac{\partial v}{\partial p}\right)_t\right)dp,$$

where t and p are the independent variables of the function U and thus $dt = \Delta t$ and $dp = \Delta p$ are the independent (principal) infinitesimals.

A necessary and sufficient condition for

$$(19)\qquad U(t,p) - U(t_0,p_0) = \int_{(t_0,p_0)}^{(t,p)} \left(Jc_p - p\left(\frac{\partial v}{\partial t}\right)_p\right)dt + \left(Jl_p - p\left(\frac{\partial v}{\partial p}\right)_t\right)dp$$

is

$$(25)\qquad \left[\frac{\partial\left(Jc_p - p\left(\frac{\partial v}{\partial t}\right)_p\right)}{\partial p}\right]_t = \left[\frac{\partial\left(Jl_p - p\left(\frac{\partial v}{\partial p}\right)_t\right)}{\partial t}\right]_p.$$

---

[18] W. F. Osgood: "Lehrbuch der Funktionentheorie," 5. Aufl., 1, 138-150 (1928).

Two clear and rigorous proofs of this theorem are given by Osgood.[19] Both of these proofs are invaluable in thermodynamics; the first has connections with geometry that render it easily remembered; the second admits immediate extension to systems with more than two independently variable properties and is carried through purely arithmetically (without presupposition of geometric axioms) although it is also interpreted geometrically for ease of comprehension and memory. Equation (25) becomes identical with Clausius's equation (5) if his variable properties y and x that determine the state of the system be identified with t and p. As Clausius[20] pointed out, his equation (5) forms an analytical expression of the first law for reversible changes in a system the state of which is determined by two independent variables, y and x. Thus equation (25) constitutes an analytical expression of the first law for reversible processes in the system considered in this paper.[21]

---

[19] W. F. Osgood: "Lehrbuch der Funktionentheorie," 5. Aufl., 1, 138-150 (1928).

[20] Op. cit., p. 9.

[21] Lord Kelvin wrote the analogous equation with t and v as the independent variables as the analytical expression of the "first fundamental proposition" or first law of thermodynamics. His statement follows: "Observing that J is an absolute constant, we may put the result into the form

$$\frac{dp}{dt} = J\left(\frac{dM}{dt} - \frac{dN}{dv}\right).$$

This equation expresses, in a perfectly comprehensive manner, the application of the first fundamental proposition to the thermal and mechanical circumstances of any substance whatever, under uniform pressure in all directions, when subjected to any possible variations of temperature, volume, and pressure." Trans. Roy. Soc. Edinburgh, **20**, 270 (1851). In the notation of this essay Lord Kelvin's equation would be written:

$$\left(\frac{\partial p}{\partial t}\right)_v = J\left[\left(\frac{\partial l_v}{\partial t}\right)_v - \left(\frac{\partial c_v}{\partial v}\right)_t\right],$$

where l_v denotes the latent heat of change of volume at constant temperature and c_v, the heat capacity at constant volume.

Lippmann has made a similar statement as follows:

"Expression générale du principe de l'équivalence.—En général, dU sera fonction de deux variables indépendantes x et y, de sorte que l'on pourra poser

$$dU = Pdx + Qdy$$

et le principe de l'équivalence sera exprimé par la condition

$$\frac{dP}{dy} = \frac{dQ}{dx}."$$

In the preceding paragraph Lippmann denotes a function of x and y (not the heat received or given up) by Q. He continues farther on:

"Applications du principe de l'équivalence.—I. Soit un kilogramme d'un corps quelconque dont on fait varier le volume et la température en lui faisant parcourir un cycle fermé. Formons l'expression EdQ − dT. On a

$$dQ = cdt + ldv$$

c étant la chaleur spécifique à volume constant, l la chaleur latente de dilatation du corps (quantité de chaleur absorbée par le corps pour que son volume varie d'une quantité égale à l'unité, à température constante);

de plus $\quad dT = pdv,$

donc $\quad dU = E\,(cdt + ldv) - pdv$

$$dU = E\,cdt + (El - p)dv.$$

"La condition d'intégrabilité est

$$\frac{d(Ec)}{dv} = \frac{d(El - p)}{dt}$$

$$\text{ou}\quad E\frac{dc}{dv} = E\frac{dl}{dt} - \frac{dp}{dt},\quad \text{ou}\quad \frac{dp}{dt} = E\left(\frac{dl}{dt} - \frac{dc}{dv}\right).$$

"Cette équation est la traduction du principe de l'équivalence."

Cours de Thermodynamique, Professé à la Sorbonne, par M. Lippmann, Rédigé par MM. E. Mathias et A. Renault, pp. 44, 45 (1889). In the paragraph following the heading "Applications du principe de l'équivalence" Lippmann denotes the heat received by Q and the work done by T.

Equation (20), like (2) and (3), may be differentiated with respect to the parameter σ: thus

$$\frac{dU}{d\sigma} = J\frac{dQ}{d\sigma} - \frac{dW}{d\sigma}. \tag{26}$$

Multiplying through by $d\sigma$ one obtains

$$dU = JdQ - dW, \tag{27}$$

where σ is the independent variable of the functions Q, W, and U and thus $d\sigma = \triangle\sigma$ is the independent (principal) infinitesimal. In this equation U is a function of t and p, but t and p are themselves functions of σ so that U is also a function of σ; in this equation dt and dp are not independent infinitesimals. This equation is given by Clausius as one mathematical statement of the first law. According to Rivett[22] it is the best mathematical statement of the first law, and it is the only analytical expression given by Page.[23] Equation (27) is, however, only a necessary condition and is not a sufficient condition to establish the truth of the first law, since it would still be true even if U were not a function of t and p but merely equal to the difference, JQ minus W, and, like Q and W, dependent on the choice of the path. Therefore the other forms of Clausius (or the more explicit equivalents of his equations (58) and (5), the present author's (19) and (25)) should be used and not the differential equation (27); the differential equation (27) cannot properly be called an expression of the first law.[24]

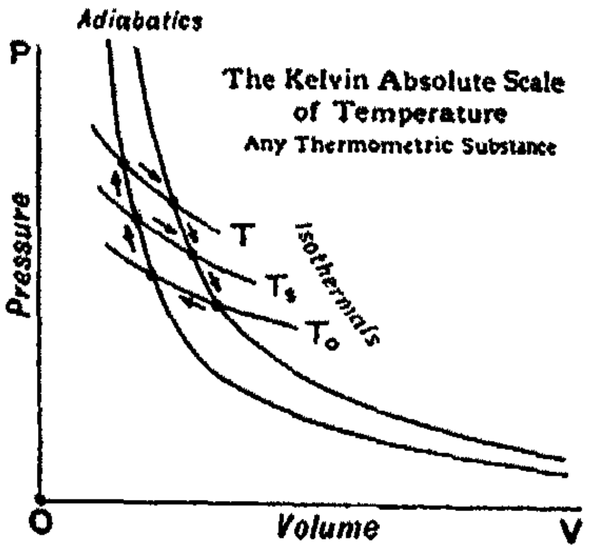


FIG. 1

The second law of thermodynamics was explained by Clausius[25] as follows:

"Um den zweiten Hauptsatz auf die einfachste Art analytisch auszudrücken, wollen wir annehmen, die Veränderungen, welche der Körper erleidet, bilden einen *Kreisprocess*, durch welchen der Körper schliesslich wieder in seinen Anfangszustand zurückkommt. Unter dQ sei wieder ein Element der aufgenommenen Wärme verstanden, und T bedeute die vom

---

[22] A. C. D. Rivett: "The Phase Rule and the Study of Heterogeneous Equilibria," 173 (1923).

[23] Leigh Page: "Introduction to Theoretical Physics," 250 (1928).

[24] In a derivation of the equation of the curve in which a chain hangs between two supports, the catenary curve, Osgood writes: "We use the notation D_x [Osgood here uses Cauchy's notation, D_xy, for the derivative of y with respect to x] for the derivative advisedly; for, the formulation of the physical problem . . . . leads to *derivatives*, NOT to *differentials*. The latter are introduced later for purely *analytical* reasons. Thus the derivative expresses the thought of physics; the differential is the tool of mathematics." "Advanced Calculus," 319 (1925).

[25] Op. cit., Abhandlung IX.

absoluten Nullpunkte an gezählte Temperatur, welche der Körper in dem Momente hat, wo er dieses Wärmeelement aufnimmt, oder, falls der Körper in seinen verschiedenen Theilen verschiedene Temperaturen hat, die Temperatur des Theiles, welcher das Wärmeelement dQ aufnimmt. Wenn man dann das Wärmeelement durch die dazugehörige absolute Temperatur dividirt, und den dadurch entstehenden Differentialausdruck für den ganzen Kreisprocess integrirt, so gilt für das so gebildete Integral die Beziehung:

$$\text{(II.)} \qquad \int \frac{dQ}{T} \leqq 0,$$

worin das Gleichheitszeichen in solchen Fällen anzuwenden ist, wo alle Veränderungen, aus denen der Kreisprocess besteht, *in umkehrbarer Weise* vor sich gehen, während in solchen Fällen, wo die Veränderungen *in nicht umkehrbarer Weise* geschehen, das Zeichen < gilt. . . .

"Man erhält also für alle umkehrbaren Kreisprocesse die Gleichung:

$$\text{(IIa.)} \qquad \int \frac{dQ}{T} = 0."$$

Clausius continued farther on:

"Die andere hier in Betracht kommende Grösse, welche sich auf den zweiten Hauptsatz bezieht, ist in der Gleichung (IIa.) enthalten. Wenn nämlich, wie die Gleichung (IIa.) aussagt, das Integral $\int dQ/T$ jedesmal gleich Null wird, so oft der Körper, dessen Veränderungen von irgend einem Anfangszustande beginnen, nach Durchlaufung beliebiger anderer Zustände wieder in den Anfangszustand zurückgelangt, so muss der unter dem Integralzeichen stehende Ausdruck dQ/T das vollständige Differential einer Grösse sein, welche nur vom augenblicklich stattfindenden Zustande des Körpers und nicht von dem Wege, auf welchem er in denselben gelangt ist, abhängt. Bezeichnen wir diese Grösse mit S, so können wir setzen:

$$(59) \qquad dS = \frac{dQ}{T},$$

oder, wenn wir uns diese Gleichung für irgend einem umkehrbaren Vorgang, durch welchen der Körper aus dem gewählten Anfangszustande in seinen gegenwärtigen Zustand gelangen kann, integrirt denken, und dabei den Werth, welchen die Grösse S im Anfangszustande hat, mit S_0 bezeichnen:

$$(60) \qquad S = S_0 + \int \frac{dQ}{T}.$$

Diese Gleichung ist in ganz analoger Weise zur Bestimmung von S anzuwenden, wie die Gleichung (58) zur Bestimmung von U. . . ."

Clausius obtained an important conclusion, analogous to that obtained in respect to the first law, by the following reasoning:

"In ähnlicher Weise wollen wir nun auch die Gleichung (IIa.) behandeln. Setzen wir in derselben für dQ seinen Werth aus (4) ein, so lautet sie:

$$\int \left(\frac{M}{T} dx + \frac{N}{T} dy \right) = 0.$$

Wenn das hier an der linken Seite stehende Integral jedesmal, so oft x und y wieder zu ihren ursprünglichen Werthen gelangen, Null werden soll, so muss der unter dem Integralzeichen stehende Ausdruck das vollständige Differential einer Function von x und y sein, und es muss daher die oben besprochene Bedingungsgleichung der Integrabilität erfüllt sein, welche für diesen Fall folgendermaassen lautet:

$$\frac{d}{dy}\left(\frac{M}{T}\right) = \frac{d}{dx}\left(\frac{N}{T}\right).$$

Führt man hierin die Differentiationen aus, indem man bedenkt, dass die Temperatur T des Körpers ebenfalls als Function von x und y zu betrachten ist, so kommt:

$$\frac{1}{T}\cdot\frac{dM}{dy} - \frac{M}{T^2}\cdot\frac{dT}{dy} = \frac{1}{T}\cdot\frac{dN}{dx} - \frac{N}{T^2}\cdot\frac{dT}{dx},$$

oder anders geordnet:

$$\frac{dM}{dy} - \frac{dN}{dx} = \frac{1}{T}\left(M\frac{dT}{dy} - N\frac{dT}{dx}\right).\text{"} \tag{6}$$

A more explicit form of the analytical expression of the second law given by Clausius in his equation (60) is the following equation for reversible processes in one-component systems consisting of one gaseous phase of unit mass:

$$S(t,p) - S(t_o,p_o) = \int_{(t_o,p_o)}^{(t,p)} \frac{c_p}{T}\,dt + \frac{l_p}{T}\,dp, \tag{28}$$

which is also written in the more familiar but less explicit form:

$$S(t,p) - S(t_o,p_o) = \int_{(t_o,p_o)}^{(t,p)} \frac{dQ}{T}, \tag{29}$$

the integrals in each of the equations (28) and (29) being extended over any path connecting the points (t_o,p_o) and (t,p); T denotes some function of t alone the same for all systems, $T = \omega(t)$; and S denotes the entropy per gram measured in thermal units. The physical hypothesis (experimental fact) embodied in each of the equations, (28) and (29), may be stated in words as follows: The value of each of the integrals in equations (28) and (29) is independent of the choice of the path of integration, that is, it depends only on the limits of integration, and the integral may therefore be used to define a function, the entropy per gram, of the independent variables, t and p. Equation (29) may be brought readily into the form (28) by means of (3).

From (28) it follows directly[26] that

$$\left(\frac{\partial S}{\partial t}\right)_p = \frac{c_p}{T}, \tag{30}$$

and

$$\left(\frac{\partial S}{\partial p}\right)_t = \frac{l_p}{T}. \tag{31}$$

Substituting the values of $(\partial S/\partial t)_p$ and $(\partial S/\partial p)_t$ in the equation of the total differential of $S(t,p)$,

$$dS = \left(\frac{\partial S}{\partial t}\right)_p dt + \left(\frac{\partial S}{\partial p}\right)_t dp, \tag{32}$$

one obtains

$$dS = \frac{c_p}{T}\, dt + \frac{l_p}{T}\, dp, \tag{33}$$

where t and p are the independent variables of the function S and thus $dt = \Delta t$ and $dp = \Delta p$ are the independent (principal) infinitesimals.

A necessary and sufficient condition[27] for

$$S(t,p) - S(t_o,p_o) = \int_{(t_o,p_o)}^{(t,p)} \frac{c_p}{T}\, dt + \frac{l_p}{T}\, dp, \tag{28}$$

is

$$\left[\frac{\partial\left(\frac{c_p}{T}\right)}{\partial p}\right]_t = \left[\frac{\partial\left(\frac{l_p}{T}\right)}{\partial t}\right]_p.^{28} \tag{34}$$

If the indicated differentiation be carried out and the result be multiplied by T,

$$\frac{\partial l_p}{\partial t} - \frac{\partial c_p}{\partial p} = \frac{l_p}{T}\frac{dT}{dt}, \tag{35}$$

and if Clausius's y and x be identified with t and p, his equation (6) is obtained. As Clausius[29] pointed out, his equation (6) forms an analytical expression of the second law for reversible processes in a system the state of which is determined by two independent variables, y and x. Thus equation

---

[26] Cf. footnote (18).

[27] Cf. footnote (19).

[28] The importance of equations (25) and (34) lies in the fact that from them all of the thermodynamic relations for this system summarized in P. W. Bridgman's "Condensed Collection of Thermodynamic Formulas" (1925) are obtained by direct mathematical methods.

[29] Op. cit., p. 9.

(34) constitutes an analytical expression of the second law for reversible processes in the system considered in this paper.[30]

Equation (29), like (2), (3), and (20), may be differentiated with respect to the parameter σ.
Thus

$$\frac{dS}{d\sigma} = \frac{1}{T}\frac{dQ}{d\sigma}. \tag{36}$$

Multiplying through by $d\sigma$ one obtains

$$dS = \frac{dQ}{T}, \tag{37}$$

where σ is the independent variable of the functions Q, T, and S and thus $d\sigma = \Delta\sigma$ is the independent (principal) infinitesimal. In this equation T is a function of t, but t is itself a function of σ so that T is also a function of σ; similarly S is a function of t and p, but t and p are themselves functions of σ so that S is also a function of σ; in this equation dt and dp are not independent infinitesimals. This equation is a necessary condition but is not a sufficient condition to establish the truth of the second law; and therefore it cannot properly be called an expression of the second law.

The function $T = \omega(t)$ was used by Lord Kelvin to define a new temperature scale, the absolute thermodynamic scale, which does not depend on the properties of any particular substance. Lord Kelvin's later characterization[31] of the absolute thermodynamic temperature scale is as follows:

"In a communication to the Cambridge Philosophical Society of June, 1848, it was pointed out that any system of thermometry, founded either on equal additions of heat, or equal expansions, or equal augmentations of

---

[30] Lippmann has written similarly:

"Pour chercher l'expression analytique de θ, ne fixons pas x et y. Supposons simplement que l'une des deux variables, x, soit une fonction de la température seulement, et varie dans le même sens que la température. Par exemple, x sera donné par un thermomètre à liquide quelconque, inconnu, d'une forme bizarre, irrégulier, astreint à la seule condition que son indication x croisse avec la température. On a alors:

$$dQ = Pdx + Rdy.$$

"P et R seront d'ailleurs des fonctions qui pourront être connues expérimentalement à chaque instant. Alors:

$$dS = \frac{dQ}{\theta} = \frac{P}{\theta}dx + \frac{R}{\theta}dy.$$

"La condition d'intégrabilité qui exprime le principe de Carnot est que:

$$\frac{d\left(\frac{P}{\theta}\right)}{dy} = \frac{d\left(\frac{R}{\theta}\right)}{dx},$$

d'où, en remarquant que θ n'est fonction que de la seule variable x, et que y est indépendant de x,

$$\frac{1}{\theta}\frac{dP}{dy} = \frac{1}{\theta}\frac{dR}{dx} - \frac{R}{\theta^2}\frac{d\theta}{dx}."$$

(Op. cit., pp. 79, 80.) Lippmann here denotes the absolute temperature by θ.

[31] Mathematical and Physical Papers by Sir William Thomson, **1**, 393, 394 (1882), or J. P. Joule and W. Thomson: On the Thermal Effects of Fluids in Motion, Part II, Phil. Trans., **144**, 350-352 (1854).

pressure, must depend on the particular thermometric substance chosen, since the specific heats, the expansions, and the elasticities of substances vary, and, so far as we know, not proportionally with absolute rigour for any two substances. . . . It appears then that the standard of practical thermometry consists essentially in the reference to a certain numerically expressible quality of a particular substance. In the communication alluded to, the question, 'Is there any principle on which an absolute thermometric scale can be founded?' was answered by showing that Carnot's function[32] (derivable from the properties of any substance whatever, but the same for all bodies at the same temperature), or any arbitrary function of Carnot's function, may be defined as temperature, and is therefore the foundation of an absolute system of thermometry. . . . and we may define temperature simply as the reciprocal of Carnot's function. When we take into account what has been proved regarding the mechanical action of heat, and consider what is meant by Carnot's function, we see that the following explicit definition may be substituted:—

"*If any substance whatever, subjected to a perfectly reversible cycle of operations, takes in heat only in a locality kept at a uniform temperature, and emits heat only in another locality kept at a uniform temperature, the temperatures of these localities are proportional to the quantities of heat taken in or emitted at them in a complete cycle of the operations.*

"To fix on a unit or degree for the numerical measurement of temperature, we may either call some definite temperature, such as that of melting ice, unity, or any number we please; or we may choose two definite temperatures, such as that of melting ice and that of saturated vapour of water under the pressure 29.9218 inches of mercury in the latitude of 45°, and call the difference of these temperatures any number we please, 100 for instance. . . . it becomes a question, what is the temperature of melting ice, if the difference between it and the standard boiling-point be called 100°?"

Lord Kelvin's definition of the absolute thermodynamic temperature scale is related to equation (29) as follows. For a Carnot cycle of operations of a reversible thermodynamic engine (a closed cycle consisting of two isothermal and two adiabatic transformations), with any working fluid, equation (29) takes the form

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0, \tag{38}$$

where T_1 denotes the absolute temperature of the upper isotherm of the Carnot cycle (temperature of the heat reservoir); T_2, the absolute temperature

---

[32] Carnot's function, η, is the amount of work done per unit of heat received by a Carnot engine operating in cycles between a heat source and a heat sink that differ in temperature by one degree absolute. It may be proved easily from equations (20) and (29) of this paper that

$$\frac{\eta}{J} = \frac{Q' + Q''}{Q'} = \frac{W}{JQ'} = \frac{T' - T''}{T'} = \frac{1}{T'},$$

where Q' denotes the heat absorbed (a positive quantity) by the working fluid of the Carnot engine at the temperature T'; Q'', the heat absorbed (a negative quantity) at the temperature T''; W, the work done; T', the absolute temperature of the heat source; and T'', the absolute temperature of the heat sink. In regard to the definition of Carnot's function cf. Mathematical and Physical Papers by Sir William Thompson **1**, *224*, *225*, 391, 397.

of the lower isotherm (temperature of the heat sink); Q_1, the heat absorbed (a positive quantity) at the temperature T_1; and Q_2, the heat absorbed (a negative quantity) at the temperature T_2. Thus for the segments of three isotherms at the arbitrary temperature T, and the fixed temperatures T_0 and T_s, one has

$$\frac{Q}{T} = \frac{Q_s}{T_s} = -\frac{Q_0}{T_0} \tag{39}$$

provided all three segments of isotherms connect the same pair of adiabatics (as illustrated in Fig. 1). The temperature T_0 is that of ice melting under the pressure of one atmosphere and T_s that of saturated vapor of water boiling under the pressure of one atmosphere. In the case discussed T is assumed to be greater than T_0. Now let both sides of the equation

$$\frac{Q_s}{T_s} = -\frac{Q_0}{T_0} \tag{40}$$

be multiplied by $T_s\, T_0$; the result is

$$Q_s\, T_0 = -\, Q_0\, T_s. \tag{41}$$

To each side of this equation let $Q_0\, T_0$ be added

$$Q_s\, T_0 + Q_0\, T_0 = -\, Q_0\, T_s + Q_0\, T_0; \tag{42}$$

thus

$$T_0\, (Q_s + Q_0) = -\, Q_0\, (T_s - T_0), \tag{43}$$

and hence

$$-\frac{T_0}{Q_0} = \frac{T_s - T_0}{Q_s + Q_0}. \tag{44}$$

From (39) one has

$$\frac{T}{Q} = -\frac{T_0}{Q_0}. \tag{45}$$

Therefore

$$\frac{T}{Q} = \frac{T_s - T_0}{Q_s + Q_0}. \tag{46}$$

The difference $T_s - T_0$ is defined as 100°.

Hence finally

$$T = \frac{100\, Q}{Q_s + Q_0}, \tag{47}$$

where Q, Q_s, and Q_0 denote heat absorbed and Q and Q_s are thus positive quantities and Q_0 a negative quantity in the case discussed. This equation determines the absolute temperature in terms of heat quantities; and the heat quantities can be measured, in theory, by means of a hydrogen thermometer and calorimeter. In practice this method of evaluating the absolute temperature is replaced by one founded on the Joule-Thomson coefficient (porous plug effect). The equation required in the latter method is derived in the following paragraphs.

The evaluation of the absolute temperature by the determination of the Joule-Thomson coefficient (porous plug effect), together with data for the heat capacity and specific volume of the thermometric substance, is accomplished by means of equations (25) and (35). From (25) one has

$$(48) \qquad J\left(\frac{\partial l_p}{\partial t}\right)_p = J\left(\frac{\partial c_p}{\partial p}\right)_t - \left(\frac{\partial v}{\partial t}\right)_p.$$

From (48) is subtracted (35) multiplied by J

$$J\left(\frac{\partial l_p}{\partial t}\right)_p - J\frac{l_p}{T}\frac{dT}{dt} = J\left(\frac{\partial c_p}{\partial p}\right)_t;$$

thus

$$(49) \qquad \frac{1}{T}\frac{dT}{dt} = -\frac{\left(\frac{\partial v}{\partial t}\right)_p}{Jl_p}.$$

The Joule-Thomson coefficient, μ, is defined by the equation

$$(50) \qquad \mu = \left(\frac{\partial t}{\partial p}\right)_\chi,$$

where χ denotes Gibbs's chi function or the total heat (also called heat content, enthalpy, enkaumy). The function χ is defined by the equation

$$(51) \qquad \chi = U + pv,$$

and is thus a function of the temperature and pressure:

$$(52) \qquad \chi = U(t,p) + p\,v(t,p) = \Gamma(t,p).$$

It is of course assumed in the definition of the Joule-Thomson coefficient, μ, that the equation

$$\chi = U + pv$$

can be solved for t in terms of p and χ : $t = \Psi(p,\chi)$. Then one has

$(52) \quad \chi = \Gamma(t,p)$ $\left\{\text{Independent variables of the 1st class, } (t,p);\right.$

$(53)\ (54) \quad p = p,\ t = \Psi(p,\chi)$ $\left\{\text{Independent variables of the 2nd class, } (p,\chi).\right.$

To these equations the theorem for change of variables in partial differentiation is applied and thereby the result obtained:

$$(55) \qquad \left(\frac{\partial \chi}{\partial p}\right)_\chi = \left(\frac{\partial \chi}{\partial t}\right)_p \left(\frac{\partial t}{\partial p}\right)_\chi + \left(\frac{\partial \chi}{\partial p}\right)_t \left(\frac{\partial p}{\partial p}\right)_\chi,$$ [33]

or

$$(56) \qquad 0 = \left(\frac{\partial \chi}{\partial t}\right)_p \left(\frac{\partial t}{\partial p}\right)_\chi + \left(\frac{\partial \chi}{\partial p}\right)_t.$$

---

[33] Cf. W. F. Osgood: "Advanced Calculus," Chapter V, Section 14, "A Question of Notation" and Exercise 3, p. 141. Section 14 was written with particular reference to problems of thermodynamics such as the one here at issue and is the clearest statement of the solution of this problem known to the present writer.

From the equation of definition of χ and equations (21), (22), and (56), it follows that

$$(57) \qquad \left(\frac{\partial t}{\partial p}\right)_x = -\frac{\left(\frac{\partial x}{\partial p}\right)_t}{\left(\frac{\partial x}{\partial t}\right)_p} = -\frac{J\,l_p + v}{Jc_p}.$$

Hence

$$(58) \qquad J\,l_p = -\,Jc_p\left(\frac{\partial t}{\partial p}\right)_x - v.$$

Substituting this value of l_p in equation (49) one obtains

$$(59) \qquad \frac{d \log_e T}{dt} = \frac{\left(\frac{\partial v}{\partial t}\right)_p}{v + Jc_p\left(\frac{\partial t}{\partial p}\right)_x}.$$

Integrating this equation one obtains

$$(60) \qquad \log_e \frac{T}{T_o} = \int_{(t_o,p_o)}^{(t,p)} \frac{\left(\frac{\partial v}{\partial t}\right)_p}{v + J\,c_p\left(\frac{\partial t}{\partial p}\right)_x}\,dt.$$

The integrand is a function of the temperature, t, alone, and does not vary with the pressure, p; the integral may therefore be evaluated along the path in the t,p-plane followed by the thermometric substance in the constant volume hydrogen thermometer. Let the value of e raised to the power the integral between $t_o = 0°C.$ and $t_s = 100°C.$ be denoted by G:

$$(61) \qquad \frac{T_s}{T_o} = G = e^{\int_{(t_o,p_o)}^{(t_s,p)} \frac{\left(\frac{\partial v}{\partial t}\right)_p}{v + Jc_p\left(\frac{\partial t}{\partial p}\right)_x}dt}.$$

Since, by definition

$$(62) \qquad T_s - T_o = 100,$$

therefore

$$(63) \qquad T_o = \frac{100}{G - 1}.$$

Hence finally

$$(64) \qquad T = \omega(t) = \frac{100}{G - 1}\,e^{\int_{(t_o,p_o)}^{(t,p)} \frac{\left(\frac{\partial v}{\partial t}\right)_p}{v + Jc_p\left(\frac{\partial t}{\partial p}\right)_x}dt}.$$

The integrand and the constant, G, can be determined experimentally. To evaluate the constant, G, that is, the value of e raised to the power the integral in equation (61) between the fixed limits, t_o and t_s, the integrand must be determined experimentally between t_o and t_s. To evaluate $T = \omega(t)$ if t lies above t_s, the integrand in equation (64) must be determined experimentally in the interval (t_s,t) in addition to the interval (t_o,t_s). Similarly to evaluate $T = \omega(t)$ if t lies below t_o, the integrand in equation (64) must be determined experimentally in the interval (t,t_o) in addition to the interval (t_o,t_s).[34]

Numerous investigations of one-component systems of one phase are recorded in the literature and it is not necessary to discuss such a system in detail in this paper. Especially notable is the recent work on the one-component system, H_2O, which is important in applications of thermodynamics in many fields, from power generation to geochemistry. N. F. Osborne[35] has stated that: "The most formidable problem in the preparation of a thermodynamic table or chart for a given substance is to obtain data adequate as to kind, range, and accuracy." The data for the system, H_2O, to which Osborne has contributed so much himself, are based on numerous and consistent measurements that have been improved and greatly extended since 1921. Thus J. H. Keenan[36] has written: "the demand for steam data at still higher pressures and temperatures [than 1200 lb. per sq. in. and 800 deg. Fahr.] has been steadily growing. The additional experimental data recently obtained at the Massachusetts Institute of Technology and at the Bureau of Standards have made possible the development of a complete set of steam tables and diagrams to 3500 lb. per sq. in. and 1000 deg. Fahr. A year ago the Turbine Engineering Department of the General Electric Company undertook this development. The necessary data and many valuable suggestions were obtained from those engaged in the Steam Research Program, and the successful completion of the work is in no small degree due to their cooperation.

"Sources of data. The Harvard Joule-Thomson-effect experiments which extended to 565 lb. per sq. in. and 657 deg. Fahr. had been carefully studied and reformulated by Dr. Davis during 1926 and 1927, and the new formulation was used in this development. It differed only slightly from the older formulation that was used in the work of 1925, but it embodied certain concepts which guided extrapolation.

"The Knoblauch specific-heat measurements extending to 420 lb. per sq. in. were used as in the work of 1925 to supplement the Harvard data.

"In 1927 Dr. Keyes and Dr. Smith at the Massachusetts Institute of Technology completed a set of experimental determinations of the specific volume of superheated steam between 1350 lb. per sq. in. and 3850 lb. per sq. in., and between saturation and 752 deg. Fahr. They constitute the basis of the development between 1000 lb. per sq. in. and 3500 lb. per sq. in.

---

[34] For numerical data and bibliography see Arthur L. Day and R. B. Sosman: Realisation of Absolute Scale of Temperature, "A Dictionary of Applied Physics," Edited by Sir Richard Glazebrook, 1, 836-871 (1922).

[35] Trans. Am. Soc. Mech. Engineers, Fuels and Steam Power, 52, 221 (1930).

[36] Mechanical Engineering, 51, 109, 114 (1929).

"The same experimenters had determined the pressure-temperature relationship at saturation up to the critical point. These data, which agree closely with the Reichsanstalt experiments, were used in this development.

"The Bureau of Standards contributed two very important pieces of data: (1) The mechanical equivalent of heat reported by Dr. Osborne in December, 1927, namely, 1 mean B.t.u. = 778.57 ft-lb. . . . (2) The total heat of saturated water between 32 deg. Fahr. and 482 deg. Fahr. (0.09 lb. per sq. in. and 577 lb. per sq. in.), communicated privately with the permission of the Director of the Bureau. Other experimenters contributed minor parts at various stages of the work, but the development was primarily dependent on those mentioned. . . .

"It is hoped that in the interim [before the goal of an international table is attained] this steam table . . . . will fill the need for a tabulation of the properties of steam covering the critical region and offering both thermodynamic consistency and faithfulness to reliable experimental data.

"It has served to bring to light the remarkable agreement between the experimental results of the three parts of the A. S. M. E. program, and between these results and other high-grade experimental data. It has shown the agreement between work done both by continuous-flow and static methods."

Keenan[37] has subsequently made a comparison of his table and Mollier chart with more recent experimental data. Concerning this comparison he writes as follows:

"The steam table and chart presented . . . . were based on all the experimental data available in April, 1928. Since that time the experimental progress includes a complete experimental check of the Keyes-Smith data which verifies the original values within a few hundredths of 1 per cent; an extension of the Bureau of Standards liquid total heats from 600 lb. per sq. in. to 800 lb. per sq. in.; the Masaryk total-heat measurements; and, most notably, an extension of the Knoblauch specific heats from 420 lb. per sq. in. to 1750 lb. per sq. in. In days like these, steam tables must be well founded to stand the test of the next six months' work. . . .

"The Knoblauch measurements almost completely cover a large range of pressures where the properties of steam could be determined six months ago only by extrapolation of existing experimental data. The new tables represent such an extrapolation, and it is very interesting to compare specific heats computed from them with these new measurements from Germany. The agreement is so good as to justify confidence in these tables even through the range not covered by experiment at the time they were computed. It indicates a fundamental agreement between experimental results obtained at Munich by one method with those obtained at M. I. T. and Harvard by entirely different methods. . . . The evidence at hand shows a general con-

---

[37] Mechanical Engineering, **51**, 129 (1929).

vergence on a well-defined grid of data that will ultimately constitute the international standard."[38]

In concluding this paper one may pause briefly at the part of the boundary of thermodynamics where Clausius labored to construct lines of communication into the adjoining region of atomistics, to consider the fact that Clausius and most investigators since his time have not been content with the evaluation of the relations of thermodynamics and the measurement of thermodynamic quantities, but in addition have correlated thermodynamics with atomistics in various ways. For this purpose the well-known explanations of temperature and heat in terms of atomic properties have been developed. Thus H. A. Bumstead[39] has written:

"[In his earliest publications Gibbs] had been concerned with the development of the consequences of the laws of thermodynamics which are accepted as given by experience; in this empirical form of the science, heat and mechanical energy are regarded as two distinct entities, mutually convertible of course with certain limitations, but essentially different in many important ways. In accordance with the strong tendency toward unification of causes, there have been many attempts to bring these two things under the same category; to show, in fact, that heat is nothing more than the purely mechanical energy of the minute particles of which all sensible matter is supposed to be made up, and that the extra-dynamical laws of heat are consequences of the immense number of independent mechanical systems in any body,—a number so great that, to human observation, only certain averages and most probable effects are perceptible."

The last work of Gibbs is his elaboration of these problems, entitled "Elementary Principles in Statistical Mechanics developed with especial reference to the Rational Foundation of Thermodynamics." However, according to Bumstead, "Gibbs has not sought to give a mechanical explanation of heat, but has limited his task to demonstrating that such an explanation is possible."[40]

These correlations are undoubtedly of very great importance and value, as are, in general, attempts to connect the various fields of science. The fundamental principles of thermodynamics may still be taken as empirical results of experience, however, since sufficient experimental data are available to establish them without reference to the laws of atomistics. And it is probably fortunate in some ways that this is so, because many problems in thermodynamics and its applications in power generation, geochemistry, and other fields, are therefore capable of solution where adequate atomistic data

---

[38] Among the further developments with this system are the "Skeleton Steam Tables" prepared at the International Steam-Table Conference of physicists and engineers from America, Great Britain, Germany, and Czechoslovakia, held in London during July, 1929. In these Tables are given mean values of the properties of saturated and superheated steam, with a plus or minus tolerance attached to each value, which, with the tolerances of the agreed magnitudes, were unanimously accepted by the delegates. Mechanical Engineering, 52, 120-122 (1930).

[39] "The Collected Works of J. Willard Gibbs," 1, 23, 25 (1928), or Am. J. Sci., (4) 16, 197, 199 (1903).

[40] *Footnote on page 1768.*

are lacking. Thus temperature as that which is measured by means of the gas thermometer and thermocouple, heat as that which is measured in the calorimeter, and thermodynamics as the science of heat and work, still serve as powerful artillery in several advancing sectors of science and technology.

Acknowledgment

The author wishes to thank Professor E. C. Kemble of the Department of Physics of Harvard University and Dr. George W. Morey of the Geophysical Laboratory for their kindness in making several valuable suggestions that have been incorporated in this paper.

Appendix

Statement by Lord Kelvin of the history of the first and second laws of thermodynamics.

(Extracts from Lord Kelvin's paper entitled "On the Dynamical Theory of Heat.")[41]

"3. The recent discoveries made by Mayer and Joule, of the generation of heat through the friction of fluids in motion, and by the magneto-electric excitation of galvanic currents, would either of them be sufficient to demonstrate the immateriality of heat; and would so afford, if required, a perfect confirmation of Sir Humphry Davy's views.

"4. Considering it as thus established, that heat is not a substance, but a dynamical form of mechanical effect, we perceive that there must be an equivalence between mechanical work and heat, as between cause and effect. The first published statement of this principle appears to be in Mayer's *Bemerkungen über die Kräfte der unbelebten Natur*, which contains some

---

[40] In this connection it seems worth while to quote the following from Gibbs's "Elementary Principles in Statistical Mechanics" ("The Collected Works of J. Willard Gibbs," 2, part 1, 165, 166, 167):

"If we wish to find in rational mechanics an *a priori* foundation for the principles of thermodynamics, we must seek mechanical definitions of temperature and entropy. . . .

"At least, we have to show by *a priori* reasoning that for such systems as the material bodies which nature presents to us, these relations hold with such approximation that they are sensibly true for human faculties of observation. This indeed is all that is really necessary to establish the science of thermodynamics on an *a priori* basis. Yet we will naturally desire to find the exact expression of those principles of which the laws of thermodynamics are the approximate expression. A very little study of the statistical properties of conservative systems of a finite number of degrees of freedom is sufficient to make it appear, more or less distinctly, that the general laws of thermodynamics are the limit toward which the exact laws of such systems approximate, when their number of degrees of freedom is indefinitely increased. . . .

"The enunciation and proof of these exact laws, for systems of any finite number of degrees of freedom, has been a principal object of the preceding discussion. But it should be distinctly stated that, if the results obtained when the numbers of degrees of freedom are enormous coincide sensibly with the general laws of thermodynamics, however interesting and significant this coincidence may be, we are still far from having explained the phenomena of nature with respect to these laws. For, as compared with the case of nature, the systems which we have considered are of an ideal simplicity. . . .

"The ideal case of systems of a finite number of degrees of freedom remains as a subject which is certainly not devoid of a theoretical interest, and which may serve to point the way to the solution of the far more difficult problems presented to us by nature."

[41] Trans. Roy. Soc. Edinburgh, 20, 261-267 (1851), or "Mathematical and Physical Papers," 1, 174-181 (1882).

correct views regarding the mutual convertibility of heat and mechanical effect, along with a false analogy between the approach of a weight to the earth and a diminution of the volume of a continuous substance, on which an attempt is founded to find numerically the mechanical equivalent of a given quantity of heat. In a paper published about fourteen months later, 'On the Calorific Effects of Magneto-Electricity and the Mechanical Value of Heat,' Mr. Joule, of Manchester, expresses very distinctly the consequences regarding the mutual convertibility of heat and mechanical effect which follow from the fact, that heat is not a substance but a state of motion; and investigates on unquestionable principles the 'absolute numerical relations,' according to which heat is connected with mechanical power; verifying experimentally, that whenever heat is generated from purely mechanical action, and no other effect produced, whether it be by means of the friction of fluids or by the magneto-electric excitation of galvanic currents, the same quantity is generated by the same amount of work spent; and determining the actual amount of work, in foot-pounds, required to generate a unit of heat, which he calls 'the mechanical equivalent of heat.' . . .

"9. The whole theory of the motive power of heat is founded on the two following propositions, due respectively to Joule, and to Carnot and Clausius.

"Prop. I. (Joule).—When equal quantities of mechanical effect are produced by any means whatever from purely thermal sources, or lost in purely thermal effects, equal quantities of heat are put out of existence or are generated.

"Prop. II. (Carnot and Clausius).—If an engine be such that, when it is worked backwards, the physical and mechanical agencies in every part of its motions are all reversed, it produces as much mechanical effect as can be produced by any thermo-dynamic engine, with the same temperatures of source and refrigerator, from a given quantity of heat. . . .

"12. The demonstration of the second proposition is founded on the following axiom:—

It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.

"13. To demonstrate the second proposition, let A and B be two thermodynamic engines, of which B satisfies the conditions expressed in the enunciation; and let, if possible, A derive more work from a given quantity of heat than B, when their sources and refrigerators are at the same temperatures, respectively. Then on account of the condition of complete *reversibility* in all its operations which it fulfils, B may be worked backwards, and made to restore any quantity of heat to its source, by the expenditure of the amount of work which, by its forward action, it would derive from the same quantity of heat. If, therefore, B be worked backwards, and made to restore to the source of A (which we may suppose to be adjustable to the engine B) as much heat as has been drawn from it during a certain period of the working of A, a smaller amount of work will be spent thus than was gained by the working of A. Hence, if such a series of operations of A forwards and of B backwards be continued, either alternately or simultaneously, there will result a continued production of work without any continued abstraction of heat from the source; and, by Prop. I., it follows that there must be more heat abstracted from the refrigerator by the working of B backwards than is deposited in it by A. Now it is obvious that A might be made to spend part of its work in working B backwards, and the whole might be made self-acting. Also, there being no heat either taken from or given to the source on the whole, all the surrounding bodies and space except the refrigerator might, without interfering with any of the conditions which have been assumed, be made of the same temperature as the source, whatever that may be. We should thus have a self-acting machine, capable of drawing heat constantly from a body surrounded by others at a higher temperature, and converting it into mechanical effect. But this is contrary to the axiom, and therefore we conclude that the hypothesis that A derives more mechanical effect from the same quantity of heat drawn from the source than B is false. Hence no engine whatever, with source and refrigerator at the same temperatures, can get more work from a given quantity of heat introduced than any engine which satisfies the condition of reversibility, which was to be proved.

"14. This proposition was first enunciated by Carnot, being the expression of his criterion of a perfect thermo-dynamic engine. He proved it by demonstrating that a negation of it would require the admission that there might be a self-acting machine constructed which would produce mechanical effect indefinitely, without any source either in heat or the consumption of materials, or any other physical agency; but this demonstration involves, fundamentally, the assumption that, in 'a complete cycle of operations,' the medium parts with exactly the same quantity of heat as it receives. A very strong expression of doubt regarding the truth of this assumption, as a universal principle, is given by Carnot himself; and that it is false, where mechanical work is, on the whole, either gained or spent in the operations, may (as I have tried to show above) be considered to be perfectly certain. It must then be admitted that Carnot's original demonstration utterly fails, but we cannot infer that the proposition concluded is false. The truth of the conclusion appeared to me, indeed, so probable that I took it in connexion with Joule's principle, on account of which Carnot's demonstration of it fails, as the foundation of an investigation of the motive power of heat in air-engines or steam-engines through finite ranges of temperature, and obtained about a year ago results, of which the substance is given in the second part of the paper at present communicated to the Royal Society. It was not until the commencement of the present year that I found the demonstration given above, by which the truth of the proposition is established upon an axiom (§ 12) which I think will be generally admitted. It is with no wish to claim priority that I make these statements, as the merit of first establishing the proposition upon correct principles is entirely due to Clausius, who published his demonstration of it in the month of May last year, in the second part of his paper on the motive power of heat. I may be allowed to add, that I have given the demonstration exactly as it occurred to me before I knew that Clausius had either enunciated or demonstrated the proposition. The following is the axiom on which Clausius' demonstration is founded:—

"*It is impossible for a self-acting machine, unaided by any external agency, to convey heat from one body to another at a higher temperature.*

"It is easily shown, that, although this and the axiom I have used are different in form, either is a consequence of the other. The reasoning in each demonstration is strictly analogous to that which Carnot originally gave."

Geophysical Laboratory,
Carnegie Institution of Washington,
March, 1932.

THE PYROLYSIS OF METALLIC ARSENITES

BY EUGENE RAY RUSHTON

Introduction

Simon[1] found that, when heated, calcium pyro-arsenite, $(CaO)_2.As_2O_3$, and calcium meta-arsenite, $CaO.As_2O_3$, gave elemental arsenic and calcium arsenate, part of the arsenite having been oxidized and part reduced. Magnesium arsenite was found to react similarly; but the reaction apparently did not take place to the same extent as with calcium arsenite. When lead oxide was treated with the vapor of arsenious oxide, the mass melted and the lead arsenite, thus formed, was not changed by further heating under the conditions of his experiment. Ferric arsenite was found to give off the vapor of arsenious oxide, leaving a magnetic residue probably magnetite. This could not, of course, be the whole story as such a reaction would not balance. Copper arsenite, when heated, gave arsenious oxide, copper arsenate, and a residue insoluble in nitric acid containing copper and arsenic. Silver arsenite gave arsenious oxide, silver arsenate, and metallic silver free from arsenic.

According to Brame,[2] heating powdered baryta with arsenious oxide causes the formation of barium arsenate and metallic arsenic. Similar results were obtained with potassium and sodium hydroxides; but were less marked.

Tammann[3] determined the heating curves of equimolecular mixtures of arsenious oxide with various metallic oxides. With calcium oxide about fifty percent of the oxides combined to form arsenite when heated to 300°. At 465° some arsenious oxide vaporized and at 468° a rapid exothermal reaction took place with the separation of elemental arsenic. The results for 300° are not equilibrium data. Calcium oxide, arsenious oxide, and a compound of the two can only coexist as three solid phases in equilibrium at a single temperature, the inversion point and there is no reason to suppose that there is any such temperature, though this is not theoretically impossible.

No metallic arsenic was formed when magnesium oxide was heated in a similar manner with an equimolecular quantity of arsenious oxide. The meta-arsenite, when heated further, lost some of its arsenious oxide. Zinc oxide combined with the arsenious oxide to form the meta-arsenite, from which arsenious oxide vaporized when heated higher. With nickel oxide apparently the ortho-arsenite was formed, leaving two-thirds of the arsenious oxide uncombined. With copper oxide the arsenious oxide reacted at 410° to form cuprous arsenate.

---

[1] Pogg. Ann., **40**, 417 (1837).

[2] Compt. rend., **92**, 188 (1881).

[3] Z. anorg. allgem. Chem., **149**, 84 (1925).

Tammann's experiments show that only calcium arsenite reacts to form metallic arsenic and that even calcium arsenite shows some tendency to dissociate into its constituent oxides. According to Simon, magnesium arsenite also decomposes to give some metallic arsenic, while Tammann did not get this result. The difference may be due to a difference in the compositions of the arsenites. Tammann's mixture probably contained more arsenious oxide than the substance with which Simon was working and may therefore have permitted a more ready vaporization of arsenious oxide. On the other hand the difference may have been in the rate of heating. Calcium arsenite apparently reacts to form calcium arsenate and metallic arsenic at a temperature only slightly above the temperature of thermal dissociation. With magnesium arsenite there is probably a greater difference between the initial temperature of thermal dissociation and that of oxidation-reduction. Tammann may not have heated his magnesium arsenite to the temperature at which the arsenious oxide is decomposed. This latter explanation cannot be true if equilibrium conditions were maintained; and it presupposes that arsenious oxide decomposes, an assumption for which there is no satisfactory evidence.

The tendency of arsenious oxide in combination to undergo oxidation-reduction seems to be greater the more basic the oxide with which it is combined. This may be due to the initial temperature of the reaction being lower for the arsenites of the more basic elements, or to a more rapid reaction at a given temperature. On the other hand it may be due to the presumably greater thermal stability of the arsenates of the more basic metals, since the decomposition of the arsenate formed would tend to reverse the reaction.

Arsenates are, in general, known to be more stable towards heat than the corresponding arsenites. Simon found calcium arsenate to be unchanged at red heat. Mitscherlich[1] found that sodium and potassium arsenates did not decompose until above 1100° when heated in a stream of nitrogen. Calcium arsenate was found to decompose at bright red heat with the liberation of oxygen and arsenious oxide. Other arsenates (not specified) were found to decompose at dull red heat. Herbst[2] found that potassium meta-arsenate $K_2O.As_2O_5$, could be heated for hours over the Bunsen burner without decomposing. This apparent contradiction may be due to the tendency of the oxygen of the air to reverse the decomposition of the arsenate into arsenious oxide and oxygen. From the data available it is not possible to determine whether or not the stability of the resulting arsenate has any effect on the oxidation-reduction reaction.

The presence of bases in solution is known to accelerate the oxidation of dissolved arsenious oxide by air.[3] On the other hand, arsenates are more easily reduced by potassium iodide in acid solution. The first is merely another illustration of the well-known fact that reducing agents are stronger in alkaline than in acid solutions. Other instances of the same type are alkaline pyrogallol and all the photographic developers. The other is due to the

---

[1] Ann. Chim. Phys., (6) 27, 22 (1892).

[2] Inaugural Diss. Berne University (1894).

[3] Cf. Berthelot: Bull., 28, 496 (1877).

fact, which we could not have predicted, that the oxidizing potential of hydriodic acid is increased more by acids than the reducing potential of arsenious oxide is decreased thereby.

There is no indication in the literature that arsenious oxide shows any tendency to undergo oxidation-reduction when heated alone. Hautefeuille[1] states that arsenious acid, when heated with hydrogen gives arsenic acid—and presumably metallic arsenic, since he states that sulphurous acid gives sulphuric acid and sulphur. Damm and Krafft[2] found that antimonous oxide, when heated to 1050° in an evacuated tube, decomposed completely according to the equation

$$4\ Sb_4O_6 = 3\ Sb_4O_8 + 4\ Sb.$$

However, Biltz[3] determined the vapor density of arsenious oxide up to 1800° and did not report any decomposition, only depolymerization according to the equation

$$As_4O_6 = 2\ As_2O_3.$$

It appears therefore that the oxidation-reduction of arsenious oxide is brought by the basic oxide and is not simply catalyzed by it.

According to Wanklyn[4] arsenious oxide decomposes in the presence of strongly basic substances according to the equation

$$5\ As_2O_3 = 3\ As_2O_5 + As_4;$$

but he gives no experimental evidence to prove this. Sulphites have been found by Foerster and Kubel[5] and by Zawidski[6] to decompose according to the equation.

$$4\ M_2SO_3 = 3\ M_2\ SO_4 = M_2S.$$

This equation is reversible, probably because both of the reaction products are solid.

There is the possibility that arsenides are formed when arsenites decompose. However, arsenic is more electro-positive than sulphur and would therefore have less tendency to combine with the metal. Soubeiran[7] stated that when basic oxides and elemental arsenic are heated together, arsenites and arsenides are formed; but he gave no conclusive evidence of the presence of the metallic arsenides. Moser and Marian[8] found that the arsenates of sodium, barium, and strontium could be freed completely of their arsenic by heating with ammonium chloride; but that the arsenates of calcium and magnesium were much more difficult to decompose in this way. They attempted to explain this as due to the formation of an arsenide.

---

[1] Bull., (2) 7, 206 (1867).
[2] Ber., 40, 4774 (1907).
[3] Z. physik. Chem., 19, 419 (1896).
[4] "Arsenic," 21 (1901).
[5] Z. anorg. allgem. Chem., 139, 261 (1924).
[6] Roczniki Chem., 52, 488 (1925).
[7] Ann. Chim. Phys., (2) 43, 407 (1830).
[8] Ber., 59B, 1335 (1926).

Arsenides of the alkaline earth metals and of lithium have been prepared by Lebeau[1] heating the arsenates with carbon in the electric furnace. He found that these substances, when heated in the air, give the arsenates. They liberate arsine when placed in cold water. These arsenides are apparently not volatile at the temperature of the electric furnace and so there would be no volatile products if all the arsenic formed arsenide. There is no conclusive evidence that there is not some arsenide formed.

Amat[2] found that acid phosphites are difficult to dehydrate without oxidizing or decomposing. When sodium acid phosphite was heated at 150°-160° the following reaction took place:

$$2\ NaH_2PO_3 = Na_2H_2P_2O_5 + H_2O.$$

When the acid pyrophosphite, thus formed, was heated to 200°, it began to decompose and the decomposition was found to be complete at dull red heat according to the equation

$$5\ Na_2H_2P_2O_5 = 2\ PH_3 + 2\ H_2 + Na_4P_2O_7 + 6\ NaPO_3.$$

In the case of the barium salt and similar substances, Amat found that the odor of phosphine became noticeable when the residue was placed in water or in acid, from which he concluded that a little metallic phosphide is formed, as the phosphides of the alkalies and alkaline earths are known to be hydrolyzed by water. No data appear to be available on the thermal decomposition of anhydrous phosphites; but they would probably form elemental phosphorus.

Thénard[3] found that, when phosphorus and lime are heated together, a large amount of the phosphorus reacts with the lime, the residue consisting of calcium phosphate and phosphide, apparently $Ca_2P_2O_7$ and Ca_2P. He found that the phosphide reacted with water to give the liquid phosphine $(PH_2)_n$. From the similarity between arsenic and phosphorus, it seems quite probable that Soubeiran obtained some arsenide when he heated elemental arsenic with basic oxides. The presence of any appreciable amount of arsenide of the formula M_3As would be immediately evident if the residue were placed in water, due to the liberation of arsine; but arsenides containing a smaller proportion of metal might well yield a solid hydride of arsenic containing less hydrogen than arsenic and having no appreciable odor. Such hydrides contain only about one percent of hydrogen and consequently not much error would be introduced if they were considered to be pure arsenic.

Bloxam[4] observed the liberation of a small amount of arsine when arsenious oxide in excess was heated with an alkali. When the alkali was in excess, pure hydrogen was liberated and the arsenious oxide was oxidized to arsenate by the oxygen of the water. Since Regnault[5] found that there is practically no formation of hydrogen when elemental arsenic is heated to redness in contact with water vapor, the reaction must be due to the presence of the base.

---

[1] Bull., (3) **21**, 769 (1899).

[2] Ann. Chim. Phys., (6) **24**, 324 (1891).

[3] Ann. Chim. Phys., (3) **14**, 5 (1845).

[4] J. Chem. Soc., **15**, 281 (1862).

[5] Ann. Chim. Phys., (2) **62**, 364 (1836).

If any of the arsenic hydrides should be formed during the pyrolysis of an arsenite they would be decomposed quickly into arsenic and hydrogen, and the decomposition would be made visible by the arsenic deposited. On the other hand the evolution of hydrogen would not be so obvious and the presence of arsenate would not be apparent without some analytical test. Complete dehydration of the arsenites employed in these experiments is therefore important.

Arsenic and its Oxides

Before beginning the study of the oxidation-reduction of arsenious oxide when combined with a metallic, a study of the properties of arsenic and its oxides was made.

Elemental arsenic is known to exist in three allotropic forms. These were designated by Petersen[1] as: alpha, steel gray, rhombohedral arsenic, formed when the vapor is condensed above 360°; beta, black-gray, amorphous arsenic, formed when the vapor is condensed below 360° [probably not amorphous according to present-day ideas]; gamma, brown, amorphous arsenic, formed by reduction in aqueous solution, greyish-yellow amorphous arsenic, very instable at room temperature. Petersen measured the heats of oxidation of these forms and found alpha arsenic to be the most stable and gamma arsenic the least stable.

Taschtschencko[2] determined the transition temperatures of these modifications by a calorimetric method. The heat evolved on cooling was plotted against the temperatures to which the substance to determine the breaks in the curve. He found that the beta modification can be converted into the alpha modification by sufficiently prolonged heating at 210°.

The vapor density of arsenic was investigated by Biltz and Meyer[3] and by Preuner and Brockmöller.[4] The latter pair found that As_4 is dissociated slightly into As_2 at 600° and that As_2 is dissociated slightly at 1200°. The alpha modification was found to have a vapor pressure of 6 mm. at 400°.

When heated in air, arsenic is oxidized chiefly to arsenious oxide, although Bloch[5] found that some pentoxide is formed direct. By subliming arsenic in a tube closed at one end Regters[6] obtained a yellowish-brown condensate which he believed to be a suboxide. The existence of this oxide has not been proved definitely.

Arsenious oxide and arsenic pentoxide are well known. Several compounds ranging in compositions between these two have been reported; but their existence has not been established satisfactorily. However, Herbst[7] states that a residue of the composition As_2O_4, the tetroxide, is obtained when the pentoxide is heated. The existence of such an oxide might be inferred from the analogy with antimony. No salts of the tetroxide are known.

---

[1] Z. physik. Chem., 8, 607 (1891).

[2] J. Chem. Soc., 121, 977 (1922).

[3] Z. physik. Chem., 77, 673 (1911).

[4] Z. physik. Chem., 78, 129 (1877).

[5] Compt. rend., 149, 775 (1909).

[6] Z. anorg. Chem., 4, 401 (1893).

[7] Inaugural Diss. Berne University (1894).

Arsenious oxide condenses in the form of octahedra at temperatures below 250°. At 275° the crystals tend to sinter, and above 315° the condensate is vitreous and transparent. Monoclinic crystals are known to exist; but they are not formed from the vapor under ordinary conditions. Arsenic pentoxide was found by Szarvasy and Messinger[1] to decompose at dull red heat. Auger[2] found that the compound could not be melted without decomposing appreciably. He states that the substance is stable at 400° and decomposes at a dull red heat. Whether or not it can exist in the vapor phase does not appear to have been determined.

General Theory

While the data in regard to the pyrolysis of metallic arsenites appear to be hopelessly contradictory, the general theory is really quite simple. The products depend primarily on two factors: *the strength of the base with reference to arsenious oxide; and the reducibility of the base.* If the base is not readily reducible and if the dissociation pressure of the arsenite is relatively high, arsenious oxide will sublime off and the base will be left behind. This case will be exactly similar to calcium carbonate. So far as one can judge, the bases falling in this class are the oxides of aluminium, magnesium, zinc, and lead. If the base is not readily reducible and if the dissociation pressure is relatively low, there will be oxidation to arsenate and reduction to metallic arsenic, which may or may not be accompanied by the vaporization of some arsenious oxide. The oxides of sodium, potassium, calcium, and barium fall in this class. If the base is readily reducible and if the dissociation pressure is relatively low, the base will be reduced and some arsenate will be formed. Depending on the absolute value of the dissociation pressure and the degree of reducibility of the base, one may get vaporization of the excess arsenious oxide or oxidation-reduction to arsenate and metallic arsenic. If the metallic arsenic can react with the reduced base, one may get an arsenide or an arsenic-containing product. The oxides belonging in this class include ferric oxide, cupric oxide, and silver oxide. The ferric oxide tends to go to magnetite, the cupric oxide to cuprous oxide, and the silver oxide to metallic silver.

Preparation of Metallic Arsenites

An extensive summary of the preparation of arsenites prior to 1895 is given by Stavenhagen.[3] Since then, the preparation of the arsenites of the heavy metals has been studied by Reichard.[4] Phase-rule studies of the aqueous systems, K_2O,Na_2O, Li_2O with arsenious oxide were made by Schreinemakers and DeBaat;[5] the systems, BaO, CaO, MgO, and PbO with aqueous arsenious oxide, were studied by Story and Anderson;[6] and the systems, MgO, ZnO,

---

[1] Ber., 30, 1344 (1897).

[2] Compt. rend., 134, 1060 (1902).

[3] J. prakt. Chem., (2) 51, 18 (1895).

[4] Ber., 30, 1913 (1897); 31, 2163 (1898); Chem. Ztg., 26, 1141 (1902).

[5] Chem. Weekblad, 14, 262 (1917).

[6] J. Am. Chem. Soc., 46, 535 (1924).

CuO, FeO, and Fe_2O_3 with aqueous arsenious oxide, were studied by Rutenber.[1] The adsorption of arsenious oxide by precipitated ferric oxide and by alumina has been studied by Sen.[2]

In some of these systems, equilibrium is attained only after a long time and it has, therefore, been difficult to determine whether or not stoichiometric compounds exist. It also seems probable that some of the arsenites, thus formed, adsorb arsenious oxide very strongly from solution, so that the product contains an excess of arsenious oxide. The compounds reported vary widely in composition, probably because of these experimental difficulties.

Three normal acids of arsenious oxide are possible: the ortho, H_3AsO_3; the pyro, $H_4As_2O_5$; and the meta, $HAsO_2$. The corresponding arsenites have been reported as well as many others. Story and Anderson seem to regard the arsenites containing less than arsenious oxide than the meta-arsenite as basic meta-arsenites. From their composition these may be regarded either as basic salts or as hydrated normal salts. Thus $Ca(OH)AsO_2$ has the same composition as $Ca_2As_2O_5.H_2O$, and $Na_3(OH)_2AsO_2$ has the same composition as $Na_2AsO_3.H_2O$. On the other hand, Rutenber concluded that ortho-arsenites are formed with cupric, zinc, and ferrous oxides. He did not discover any pyro-arsenites.

The following general methods have been used by me in the preparation of arsenites:—

1. Reaction of arsenious oxide with the metallic oxide or hydroxide (synthesis).
2. Reaction of a soluble arsenite with a soluble salt of the metal to form an insoluble arsenite (metathesis).

The first of these methods should produce a purer product, as no foreign substance except water is introduced. It was used, therefore, whenever possible. However, previous investigators have only succeeded in a few instances in producing pure compounds by this method, probably due to the slow rate of reaction. There is also danger of partial oxidation of the arsenious oxide at the boiling temperature.

Precipitation methods (metathesis) were found to give arsenites of definite composition only in a few cases and these were so soluble that frequently the precipitates could not be washed without considerable loss. The method generally used was to wash with cold water until one cc. of the wash-water showed a constant titre with standard iodine solution. This was taken to indicate that the excess arsenious oxide had been removed and that the residue should presumably consist of pure arsenite. This conclusion was not always justifiable. In some instances the discrepancy could be explained as due to hydrolysis, and in other cases as due to very strong adsorption of arsenious oxide by the arsenite.

Kahlbaum's arsenious oxide (ph.G.) was tested by the method of Chapin[3] and found to contain appreciable quantities of sulphide but no antimony or

---

[1] Cornell Thesis (1929).

[2] J. Phys. Chem., 31, 419 (1927).

[3] J. Ind. Eng. Chem., 10, 522 (1918).

heavy metals. It also left a very small non-volatile residue at red heat. When heated in a lipless beaker covered with a watch-glass on an electrically-heated hot plate, a red sublimate appeared at first, presumably the disulphide, As_2S_2. When this was removed and a clean watch-glass substituted, colorless octahedral crystals were obtained, which gave no test for sulphide or for antimony, and which left no residue when resublimed by the same method or when heated to a red heat. It was therefore considered to be sufficiently pure for use in the preparation of arsenites.

On evaporating down solutions of alkaline arsenites, a crystalline residue was obtained only with potassium and lithium; the sodium arsenite could not be made to crystallize. The lithium salt was very close to the meta-arsenite in composition; but the potassium salt could not be dehydrated completely without decomposition, so that it may have been a hydrated meta-arsenite. On adding alcohol to the solutions, they became cloudy; but the arsenite formed would not settle and could not be filtered.

When cold, aqueous, arsenious oxide solutions were added to solutions of the hydroxides of the alkaline earths; in cold water, no precipitates were obtained with barium and strontium hydroxides. With lime water in excess, a precipitate was obtained containing three percent more arsenious oxide than the ortho-arsenite. When the arsenious oxide was in excess, the meta-arsenite of calcium was obtained. With barium hydroxide, precipitates were obtained only from the hot concentrated solutions. When the hydroxide was in excess, the precipitate contained four percent more arsenious oxide than the ortho-arsenite; when the arsenious oxide was in excess, the precipitate contained about five percent more arsenious oxide than the meta-arsenite.

On prolonged contact with aqueous arsenious oxide, strontium hydroxide gave a substance that was intermediate in composition between the meta-arsenite and the pyro-arsenite and contained some water. It could not be dehydrated completely without decomposition. The arsenious oxide content could not be increased by allowing to stand for five months. Stavenhagen did not succeed in preparing a strontium arsenite of definite composition.

In contact with aqueous arsenious oxide, magnesium oxide was found to give a substance slightly in excess of the amount required for the ortho-arsenite. This did not increase on standing two months longer. Story and Anderson, and Rutenber found no arsenite of magnesium.

Zinc oxide formed the ortho-arsenite from aqueous arsenious oxide in a few days and the meta-arsenite was formed after three weeks of contact. These compounds were obtained by Rutenber and appear to be about the most easily prepared arsenites known.

The substance obtained on prolonged contact of precipitated lead oxide with aqueous arsenious oxide was found to contain only forty-one percent arsenious oxide, whereas the meta-arsenite was obtained by Story and Anderson and requires forty-seven percent. As in the case of the strontia, the lead oxide apparently refused to take up any more arsenious oxide.

When precipitated alumina was dried at 140°, it was found to retain about twenty percent of water. When the undried gelatinous substance was placed in aqueous arsenious oxide and dried at 140°, it was found to contain about forty percent alumina, forty percent arsenious oxide, and twenty percent water. On the dry basis this is equivalent to fifty percent arsenious oxide. The ortho-arsenite requires sixty-six percent.

It was difficult to determine the amount of arsenious oxide taken up by ferric oxide; but the loss of weight on heating to redness indicates that ferric ortho-arsenite was formed.

Heating Arsenites in Air

Simon[1] heated calcium pyro-arsenite, $(CaO)_2.As_2O_3$, and calcium meta-arsenite, $CaO.As_2O_3$, in the air and found that the loss of weight was always less than that calculated on the assumption that four atoms of elemental arsenic are formed and driven off for every three molecules of arsenious oxide oxidized to the pentoxide and combined with the calcium oxide, as illustrated by the equations:—

(1) $5\ As_2O_3 = As_4 + 3\ As_2O_5$

(2) $5\ Ca_2As_2O_5 = 10\ CaO + 5\ As_2O_3 = As_4 + 10\ CaO + 3\ As_2O_5$

(3) $5\ CaAs_2O_4 = 5\ CaO + 5\ As_2O_3 = As_4 + 5\ CaO + 3\ As_2O_5$

This means that some oxidation is caused by the air. Since the ratio $3\ As_2O_5/5\ As_2O_3 = 0.6970$, a higher ratio means an oxidation by air, while a lower ratio means the volatilization of some As_2O_3 or the decomposition of some As_2O_5.

Various arsenites were heated to constant weight in porcelain crucibles over a Bunsen burner and the arsenious oxide in the residue determined by titration with iodine. In most cases, the amount of arsenious oxide was

TABLE I

A	B	C	D	E	F
CaO	77.9	1:1	76.3	56.8	2.62:1
CaO	77.9	1:1	76.3	61.2	2.30:1
CaO	77.9	1:1	76.3	58.8	2.45:1
CaO	60.0	2.33:1	81.8	91.50	2.98:1
CaO	60.0	2.33:1	81.9	89.42	3.31:1
SrO	56.45	1.48:1	83.2	67.74	3.88:1
SrO	56.45	1.48:1	83.2	66.92	4. 0:1
BaO	63.37	0.745:1	81.1	51.21	4.56:1
BaO	69.37	0.745:1	86.1	49.34	4.10:1
Na_2O	89.35	0.376:1	72.8	33.26	1.77:1
Na_2O	89.35	0.376:1	72.8	29.72	2.18:1
MgO	77.13	1.43:1	76.6	28.23	24. 3:1
PbO	37.70	1.45:1	86.6	77.39	4.26:1
ZnO	44.77	3:1	86.2	93.48	4.10:1

A = basic oxide; B = percent As_2O_3; C = mol ratio basic oxide to As_2O_3; D = percentage residue calculated on assumption that reaction proceeds normally; E = percentage residue found; F = mol ratio basic oxide to As_2O_5.

---

[1] Pogg. Ann., 40, 417 (1837).

negligible and was not considered in the calculations. If all of the arsenious oxide should volatilize, the weight of the residue should be equal to the weight of the basic oxide in the original sample and the percentage weight of the residue would be equal to the percentage of basic oxide. In most cases the residue weighed considerably more than the pure basic oxide would, indicating that appreciable amounts of arsenite had formed. This was confirmed by a qualitative test with potassium iodide on a solution of the residue in hydrochloric acid.

The experimental data are given in Table I.

From these data it is possible to draw the following conclusions:—

(1) Calcium meta-arsenite does not react according to equation (3) at the temperature reached when heating with a Bunsen burner. It loses more weight and the residue contains more lime than predicted by this equation. It is probable that Simon did not heat to so high a temperature or for so long a time; he apparently did not determine whether the reaction had gone to completion.

(2) A substance containing somewhat less arsenious oxide than calcium pyro-arsenite loses less weight than calculated from equation (1) and the residue approximates the composition of calcium ortho-arsenate, containing much more arsenic pentoxide than is predicted by equation (2). This undoubtedly means oxidation by the air.

(3) Strontium arsenite, of a composition between those of the pyro-and meta-arsenites, left a residue much smaller than calculated, although strontium oxide might be expected to be more reactive than calcium oxide, as it is more basic. This arsenite was found to contain some combined water, probably combined with the strontia as hydroxide, and this may have interfered with the reaction.

(4) Barium arsenite containing more arsenious oxide than the meta-arsenite was found to leave a residue smaller than that calculated and this difference is much less than the corresponding difference for the calcium meta-arsenite. However, this salt apparently contains a small amount of combined water also and Stavenhagen[1] regards it as an acid salt.

(5) Sodium arsenite containing a large excess of arsenious oxide over the meta-arsenite left residues approximating the composition of sodium pyro-arsenate. This indicates that sodium oxide is much more reactive than barium oxide, although this difference may be due to the fact that sodium arsenite melted before much arsenious oxide vaporized from it. The liquid may have held more arsenious oxide in solution until it reacted.

(6) Magnesium oxide was found to retain much less arsenic pentoxide than any of the substances investigated, differing very markedly from calcium oxide in this respect. Apparently it is much less basic.

(7) Arsenite of lead, between the meta and pyro in composition lost much less weight than the magnesium compound of closely corresponding composition, and much less than might be expected from the position of this element in the periodic table. The fact that the substance melted may account for this.

---

[1] J. prakt. Chem., (2) 51, 17 (1895).

(8) Zinc ortho-arsenite left more residue than calculated, showing that some oxidation by air took place. This was due to some extent to the large proportion of zinc oxide in the compound; but it appears to be the most active element studied, next to calcium, and it is much more active than might be expected from its weakly basic, in fact amphoteric, nature.

Going back to the behavior of calcium meta-arsenite when heated in air, there are two ways of accounting for the relatively small amount of residue. One is that some arsenious oxide vaporizes off. The other and more probable one is that calcium meta-arsenate may be instable at a bright red heat and may decompose into calcium ortho-arsenate or into a mixture of calcium ortho-arsenate and pyro-arsenate. The data in the literature are contradictory.

Bloxam[1] prepared calcium meta-arsenate by dissolving calcium carbonate and arsenious oxide in nitric acid, evaporating to dryness and igniting the residue. This indicates that the compound is stable at a bright red heat. However, Mitscherlich[2] heated an arsenate of calcium, probably the pyro-arsenate, in a porcelain tube in a stream of nitrogen and found it to be almost completely decomposed at a bright red heat.

To determine whether or not the meta- and pyro-arsenates can be formed from calcium oxide and arsenious oxide in presence of air, at bright red heat, the amount of arsenic pentoxide taken by a given amount of calcium oxide was determined.

Chemically pure calcium oxide was heated to constant weight in a porcelain boat in a silica combustion tube heated by means of Bunsen burners. A boat containing arsenious oxide was then placed in the tube and the vaporized arsenious oxide drawn over the calcium oxide by means of a stream of air. This was done fourteen times and the boat containing calcium oxide was weighed after each addition of arsenious oxide. The data are given in Table II.

TABLE II

Increase in Weight of Calcium Oxide when reacting with Arsenious Oxide and Oxygen. Weight of CaO = 1.9386 g.

No.	Gain in Weight	Percent Gain	No.	Gain in Weight	Percent Gain
1	2.4166 g	131.0	8	0.0604 g.	3.3
2	0.2214	12.0	9	0.0210	1.2
3	0.0956	5.2	10	0.0192	1.0
4	0.0206	1.1	11	0.0032	0.2
5	0.0508	2.8	12	0.0108	0.6
6	0.0263	1.4	13	0.0284	1.5
7	0.0317	1.7	14	0.0030	0.2

The final weight of the product was 4.8824 g. The percentage calcium oxide was 37.6. Since there was very little arsenious oxide in the product, the percentage of arsenic pentoxide was very close to 62.4. After the first run the

---

[1] Chem. News, 54, 193 (1886).

[2] Ann. Chim. Phys., (6) 27, 22 (1892).

percentage of arsenic pentoxide was 56.7 which is not much below the theoretical value of 57.9 for calcium ortho-arsenate. It seems probable that the reaction takes place rapidly to form the ortho-arsenate, after which the final equilibrium is approached much more slowly. The final product seems to be an equimolecular mixture of the ortho- and pyro-arsenates.

When there is an excess of lime the residue is greater than the theoretical. This phenomenon occurred only with calcium and zinc oxides. The great activity of calcium oxide, and possibly also that of zinc oxide, might perhaps be explained by an experiment done by H. B. Baker.[1] Silica tubes containing a mixture of hydrogen and nitrous oxide dried to such an extent that the moisture was only a few milligrams to a million liters, were heated in a resistance furnace in pairs. One tube contained lime and the other powdered Jena glass. When the combining temperature was reached, the rate of union in the lime tube was five times that in the tube containing the powdered glass. After fifteen minutes heating, when a large amount of water had been formed from the reaction, the reaction velocities became the same. Baker regards this as due to the calcium oxide causing gaseous ionization, which accelerates the reaction by furnishing nuclei for the condensation of the water vapor. He found radio-active substances to have a much greater effect than calcium oxide.

Heating Arsenites in an Inert Atmosphere

In order to provide a method of heating sealed glass tubes uniformly and without danger from flying glass in case of explosion, electric furnaces were constructed as follows:—

A section of 1¼" iron pipe about 8" long and threaded at both ends was fitted with an asbestos collar at each end and the pipe surface in between was covered with alundum cement to a thickness of about ¼". No. 20 gauge chromel wire was then threaded through a small hole in the asbestos and wound spirally on the surface of the alundum cement. The wire was then covered with a second layer of alundum cement, and this was covered with asbestos cement to a thickness of several inches. One end of the pipe was then closed with a pipe-cap and this was also covered with a thick layer of asbestos cement. The other end was provided with a cap with a hole about ½" in diameter drilled at one side for the insertion of a thermometer or thermocouple. The furnace was placed in a vertical position with the removable cap uppermost. The bottom of the pipe was filled with asbestos fibre to prevent the loss of heat through the lower end and to prevent breakage of the sealed tubes by striking the bottom.

The furnaces were connected to alternating current outlets through lamp banks. When tungsten lamps were used, the daily variation in temperature was much less than with carbon lamps. This is probably due to the negative temperature coefficient of resistance of carbon, which would permit less current to flow through the filament when the temperature is decreased by a decrease in the power, and more when there is an increase.

---

[1] J. Chem. Soc., 1928, 1054.

Since the carbon filament lamps caused a greater variation in the temperature than tungsten lamps when connected in series with the furnace, it seemed probable that they would decrease in variation if connected in parallel, since they would by-pass more current as their temperature increased, and less when it decreased. It was found that when six carbon lamps of 120 watts were connected across the terminals of a furnace that had previously shown a maximum temperature variation of 22°, it showed a temperature variation of only 13° over a much greater length of time. Another furnace that had varied as much as 17° formerly, when connected to two 120-watt carbon lamps in a similar manner, varied only 11°. These experiments are not regarded as conclusive; but they give promise of a method of regulating temperatures without the use of the elaborate equipment required by other methods.[1]

To determine if air can be displaced from a tube filled with nitrogen, the following experiment was performed:—

Two pyrex tubes were sealed off and rounded at one end. Some bright copper wire was placed in the bottom of each, and the tubes were then drawn out to form a narrow constriction three or four inches from the closed end. Nitrogen from a small cylinder was passed into one of these through a small pyrex tube inserted through the constriction and held in place by means of an asbestos plug. The nitrogen was allowed to flow for several minutes, the tube was then withdrawn beyond the constriction and the copper wire sealed off with the nitrogen still flowing at the point of sealing. The other tube was sealed off with the air which it contained.

Both tubes were heated in the furnaces previously described for about twelve hours at 270°-300°. The copper sealed off in nitrogen remained completely unchanged, whereas that sealed off in air had turned completely black. This was taken as evidence that atmospheric oxygen can be displaced by this method, although, of course, adsorbed air on the surface of fine powders may not be so easily displaced. The method dispenses with the vacuum pump and makes stronger seals possible.

The method of displacing the air in the tube as outlined above, was used for the study of the thermal decomposition of arsenites in the absence of oxygen. To insure the complete absence of oxygen, the nitrogen was bubbled through a wash-bottle filled with potassium pyrogallate. The substance to be examined and the tube in which it was sealed were dried at about 150° for the purpose of driving off adsorbed air. A higher temperature would cause decomposition or oxidation of some of the substances.

The amount of arsenious oxide in the original sample was determined by titrating with iodine solution standardized against pure arsenious oxide. After sealing off in nitrogen and heating for various lengths of time, the tube was cracked open and the residue in the bottom titrated again. When a sublimate of elemental arsenic or arsenious oxide was formed in the upper end of the tube the amount of this was determined by weighing this part of the tube,

---

[1] See Adams: J. Optical Soc. America, 9, 599 (1924).

heating to drive off the sublimate, and weighing again. The amount of arsenious oxide oxidized was estimated from the difference in the two titrations, and could be compared with the amount of sublimate.

A weighed sample of copper ortho-arsenite, $Cu_3(AsO_3)_2$, prepared by Mr. Rutenber, was sealed in nitrogen by the method described above and heated at 370°-387° for about eight days. At the end of this time the green substance had turned to an orange-red color, and a small amount of vitreous arsenious oxide condensed in the upper part of the tube when it cooled. The tube was cracked open by making a file mark around it and touching this with a white-hot piece of pyrex. The upper portion of the tube was weighed, heated to redness, and weighed again, the weight of arsenious oxide being determined by difference. This was found to be 20.8 percent of the weight of the sample, while the total arsenious oxide in the original sample was 45.33 percent.

The residue, the red substance formed in the bottom of the tube, was found to dissolve readily in hydrochloric acid and in ammonia. When the ammoniacal solution was acidified with acetic acid, potassium iodide produced a white precipitate, showing that a cuprous salt was present. When silver nitrate was added to the acetic acid solution, a brown precipitate of silver arsenate was formed.

A mixture of cupric oxide (Baker's analyzed) and of arsenious oxide (purified by sublimation) containing the two oxides in the same proportions, (54.17 and 45.33 percent) as in copper ortho-arsenite was sealed in nitrogen and heated at 337°-348° for twenty-five days. The residue, after heating, had the same appearance as in the preceding experiment, and there was also formed a vitreous condensate which caused the tube to crack when cooled. The fragments were collected and the arsenious oxide determined by dissolving in sodium hydroxide solution, neutralizing with acid, and titrating with iodine in the presence of an excess of bicarbonate. The percentage of arsenious oxide thus formed was 21.8, very close to the value obtained in the preceding experiment. If we assume, as seems probable, that all of the arsenious oxide that did not react condensed in the upper portion of the tube, something over one-half of the arsenious oxide was oxidized to arsenate. Since there is enough cupric oxide in cupric-ortho arsenite to oxidize three-quarters of the arsenious oxide, and only about fifty-four percent was oxidized, the amount of arsenious oxide oxidized to arsenic pentoxide is only a little over seventy percent of the amount theoretically possible. Consequently some of the cupric arsenite lost arsenious oxide direct without any corresponding reduction of the cupric oxide.

Silver ortho-arsenite was prepared by adding a solution of arsenious oxide in sodium hydroxide to an equivalent quantity of silver nitrate. The yellow precipitate turned black on drying at 150°. The substance was analyzed by dissolving in dilute nitric acid, precipitating, and weighing the silver as silver chloride. The filtrate was neutralized and titrated for arsenious oxide in presence of bicarbonate. The silver oxide came out 77.63 and 77.72 percent and the arsenious oxide 19.82 and 19.72 percent. The low value for arsenious oxide was probably due to partial oxidation by nitric acid while dissolving the samples, because silver ortho-arsenite calls for 77.84 percent silver oxide and 22.16 percent arsenious oxide. In the following experiments it is assumed that the salt contained the theoretical amounts of the two oxides.

A weighed sample was sealed in nitrogen and heated for ten days at 378°-402°. The condensate of vitreous arsenious oxide cracked the tube as it cooled in such a way that the fragments could not be collected. The residue had sintered to a brownish-black lump which was found to contain particles of silver mixed with silver arsenate. The silver arsenate was dissolved in ammonia and the metallic silver collected on a filter paper, ignited and weighed. It was then dissolved in nitric acid and titrated with thiocyanate solution. The silver was thus found to be 98.97 and 96.51 percent pure and to constitute 31.2 and 30.8 percent of the weights of the samples. The silver in solution was precipitated as silver chloride and calculated as 48.96 and 48.84 percent silver oxide. The filtrate was neutralized and titrated with iodine in the presence of bicarbonate. The volume of iodine taken was the same as for a blank on the ammonia used, and therefore no appreciable amount of arsenious oxide was present. The content of arsenic pentoxide was therefore about 20.1 percent, by difference.

Another sample of the silver ortho-arsenite was heated at 206°-218° for fourteen days. A condensate of octahedral arsenious oxide formed in the upper part of the tube as it cooled, and the residue in the bottom of the tube had about the same appearance as in the preceding experiment. The tube was opened by the method used previously and the arsenious oxide in the upper portion determined to be 6.7 percent of the original weight of the sample. The residue was found to contain 34.6 and 35.2 percent metallic silver, 46.5 and 46.9 percent silver oxide, and about 18.4 percent arsenic pentoxide, the last by difference.

The reaction probably takes place essentially according to the equation

$$2\ Ag_2O + As_2O_3 = 4\ Ag + As_2O_5.$$

Since silver ortho-arsenite contains three molecules of silver oxide to one of arsenious oxide, there is enough silver oxide to oxidize all the arsenious oxide, in which case the residue should contain silver oxide and arsenic pentoxide in equivalent amounts. Actually the molecular ratio was 2.43 in the first case and 2.51 in the second case. This means that the composition lies about halfway between the ortho- and the pyro-arsenate, which is substantially what was found with lime. Since the amount of arsenate is less than the calculated amount, some arsenious oxide must have vaporized, as was shown experimentally to be the case.

Another sample of silver ortho-arsenite heated in nitrogen for thirty-six hours at 116°-119° showed no sign of change. The temperature was increased gradually by about ten degrees at a time. A condensate of arsenious oxide appeared at 149°-156°, and the residue appeared to turn slightly brown. The initial temperature of the reaction is therefore about 150°.

Potassium arsenite was prepared by dissolving arsenious oxide in potassium hydroxide solution and evaporating until crystals appeared. The liquid was then decanted off and more water added. This solution was evaporated to dryness and the residue dried at 110°. When heated in a test-tube over the Bunsen burner, the substance turned black, giving off water vapor and the garlic-like odor attributed to metallic arsenic, showing that the substance undergoes oxidation-reduction readily. Qualitative tests showed the presence of some arsenate and carbonate. Titration with iodine gave 56.24 and 56.55 percent arsenious oxide, average 56.4. The formula for the meta-arsenite requires 67.95 percent. This substance may be the meta-arsenate with large amounts of water, arsenate, and carbonate. It was found impossible to dry the substance completely as it turned slightly dark at 150°.

A weighed sample of this substance was heated in nitrogen for sixteen days at 382°-401°. At the end of this time it had turned quite dark; but no condensate appeared on cooling. Samples of the product were dissolved in water, and the black portion, which did not dissolve, was collected on Gooch crucibles and weighed. It was found to be completely volatile when heated to redness, and was apparently elemental arsenic. The losses of weight on heating were 0.37 and 0.26 percent, average 0.32. The solution was neutralized with acid and titrated with iodine in presence of bicarbonate. The percentage of arsenious oxide found was 52.1 and 51.8 percent, average 52.0. This is a decrease of 4.4 percent from the amount originally present.

If we assume that the reaction takes place according to the equation

$$5\ As_2O_3 = As_4 + 3\ As_2O_5,$$

there should have been 1.3 per cent metallic arsenic instead of the 0.32 percent actually found. It is probable that there was oxidation by water vapor. This is the more likely because Bloxam[1] has shown that alkaline arsenites can be oxidized by water vapor.

Barium arsenite was prepared by adding crystals of arsenious oxide purified by sublimation) to baryta water and heating gently. The residue, dried at 140°, was found by titration with iodine to contain 34.9 and 34.5 percent arsenious oxide and to be free from arsenate. The formula for barium ortho-arsenite, $Ba_3(AsO_3)_2$ calls for 30.0 percent arsenious oxide.

A weighted quantity of this substance was heated at 388°-393° for ten days. The residue turned yellowish-brown, and the grey modification of metallic arsenic condensed at the top of the tube when it was removed from the furnace. This condensate was vaporized off and the loss of weight determined. It was 5.5 percent of the original weight. The residue was found to dissolve partially in dilute hydrochloric acid, leaving a brownish residue which was assumed to be metallic arsenic. In both experiments it amounted to 0.85 percent of the original weight of the sample. The filtrate was neutralized and titrated with iodine, showing 14.89 and 16.46 percent of arsenious oxide. The decrease in arsenious oxide is 35.2 − 14.7 = 20.5 percent, while the metallic arsenic is equivalent to 21.0 percent, which is probably identical within the limit of experimental error.

---

[1] J. Chem. Soc., 15, 281 (1862).

Calcium meta-arsenite was prepared by boiling crystals of arsenious oxide with lime water. When dried at 100°, it was found by titration with iodine to contain 77.57 and 77.31 percent arsenious oxide, very close to the 77.93 percent calculated for $Ca(AsO_2)_2$. A weighed quantity was sealed in nitrogen and heated at 354°-357° for 53 hours. When examined at the end of this time, the arsenite had turned brown and a small amount of metallic arsenic had condensed at the top of the tube on cooling. The tube was cracked open, treated as before, and the total metallic arsenic found to be 0.05 percent. The acid filtrated was neutralized and titrated with iodine. The amount of arsenious oxide found was 77.8 and 70.2 percent. Since this is more than we started with, the original sample must have contained water which was lost on heating. The arsenic pentoxide was slightly in excess of the theoretical, showing that there had probably been some oxidation by water vapor. The essential reaction is oxidation-reduction.

Arsenites containing more Arsenious Oxide than the Meta-arsenites

Bloxam[1] found that, when potassium carbonate and sodium carbonate were saturated with arsenious oxide, the residue left on driving off the water contained two molecules of arsenious oxide combined with one molecule of the respective basic oxides. These bi-arsenites, as he called them, are probably formed by the dehydration of the acid meta-arsenites, $KH(AsO_2)_2$ and $NaH(AsO_2)_2$. They can be fused at temperatures at which the vapor pressure of arsenious oxide is high without liberating this anhydride, which indicates that they do not contain free arsenious oxide. However, Bloxam found that, in the presence of moisture, some arsenic is liberated on fusion and some arsenate is formed, even in an atmosphere of carbon dioxide. This suggests that arsenious oxide undergoes some oxidation-reduction when in combination with alkali oxides, even when the relative amount of the basic oxide is relatively small. The following experiments were made to determine to what extent the reaction takes place in such compounds.

A commercial sodium arsenite (J. T. Baker's) was titrated with iodine and found to contain 89.50 and 89.13 percent arsenious oxide, as compared with 70.71 percent for sodium meta-arsenite and 86.5 percent for sodium di-arsenite, $Na_2O.2As_2O_3$. A weighed sample was sealed in nitrogen and heated for six days at 339°-353°. A small, transparent, vitreous condensate was formed on cooling, and there was no discoloration of the residue. Titration of the residue with iodine indicated a decrease of only 0.88 percent arsenious oxide, showing that only a small amount vaporized.

Another sample of the same substance was heated at 362°-387° for 4.5 days. There was no discoloration of the residue, indicating that no elemental arsenic was formed. The weight of the transparent condensate was 0.66 percent of the weight of the original sample. Titration of the residue indicated a loss of 1.34 percent arsenious oxide, so there was probably a small amount of oxidation to arsenate without the formation of metallic arsenic. This may have been due to adsorbed air or to small amounts of moisture.

---

[1] J. Chem. Soc., **15**, 284 (1862).

Barium arsenite, prepared by adding an excess of a solution of arsenious oxide to baryta water, was dried at 140°, and found to contain 63.18 and 63.37 percent arsenious oxide as compared with 56.34 percent for barium meta-arsenite, $Ba(AsO_2)_2$. Bloxam[1] obtained an arsenite containing only slightly less arsenious oxide by precipitating barium chloride with sesqui-arsenite of soda, $2Na_2O.3As_2O_3$, which also contained more arsenious oxide than sodium meta-arsenite. Story and Anderson[2] appear to have prepared a hydrated sesqui-arsenite of barium in their study of the system, $BaO-As_2O_3-H_2O$.

A weighed amount of the substance prepared as described was sealed in nitrogen and heated at 312°-317° for twenty-four hours. A slight, transparent, vitreous condensate appeared. The heating was continued at 316°-323° for four days without any apparent, further change. The temperature was raised to 402°-410° and held there for four days. A small amount of a black condensate appeared when the tube cooled. Apparently a straight thermal dissociation takes place at the lower temperature and oxidation-reduction does not occur until an appreciable amount of the arsenious oxide is driven off.

The amount of arsenious oxide at the top of the tube was only 0.3 percent and the amount of elemental arsenic was so small that it could not be determined. The residue dissolved practically completely in hydrochloric acid and gave only a slight color with potassium iodide, indicating that oxidation-reduction took place only to a negligible extent.

Crystalline strontium hydroxide was allowed to stand in contact with a supersaturated solution of arsenious oxide until there was no further decrease in the titre of the solution. The solid was then collected on a filter and dried at 105°. Titration with iodine gave 73.99 and 71.4 percent arsenious oxide, which indicates that the substance is the sesqui-arsenate, $2SrO.3As_2O_3$, which contains 74.13 percent arsenious oxide.

A weighed quantity of this substance was sealed in nitrogen and heated for five days at 373°-385°. A vitreous, transparent condensate was formed on cooling with a few small crystals of elemental arsenic. The residue had turned dark gray. The arsenious oxide sublimed off was 29 percent of the original weight and the decrease in arsenious oxide as shown by titration was 28.6 percent. The total amount of metallic arsenic was only 0.32 and 0.28 percent. This corresponds to about 0.9 percent arsenious oxide. The residue contained 62.5 and 63.1 percent arsenious oxide, rather less than the 65.63 percent corresponding to the meta-arsenite. Much more arsenious oxide vaporized than was the case with sodium and barium oxides. This may have been due to the presence of some free arsenious oxide in the samples.

To make calcium di-arsenite a saturated solution of arsenious oxide was mixed with lime water and evaporated slowly until a precipitate appeared. This was filtered off and found to contain 89.71 and 89.92 percent arsenious oxide as compared with 87.6 percent in calcium di-arsenite, $CaO(As_2O_3)_2$. Some of this substance was sealed in nitrogen and heated for 18 hours at 350°-360°. The residue turned gray and a transparent, vitreous condensate

---

[1] J. Chem. Soc., **15**, 294 (1862).

[2] J. Am. Chem. Soc., **46**, 535 (1924).

appeared in the top of the tube on cooling. The tube cracked so much that the amount of this condensate could not be determined. Titration of the residue with iodine gave 87.99 and 88.30 percent arsenious oxide. The Gooch-Browning titration showed about 0.2 percent arsenic pentoxide, corresponding to about 0.1 percent metallic arsenic and about 0.3 percent arsenious oxide.

The decrease in arsenious oxide content is 1.67 percent, 0.3 of which can be attributed to oxidation-reduction, leaving 1.3 percent as the arsenious oxide driven off. This is not as great as the difference between the arsenious oxide content of the substance and that of the di-arsenite, showing that the excess above the di-arsenite, as in the sodium compound, was not free to vaporize as arsenious oxide, or at least did not do so in the rather short time of heating.

The results of these experiments are summarized in Table III.

Table III

Basic Oxide	Mol Ratio Basic Oxide to As_2O_3	Decrease in As_2O_3 %	As_2O_3 Condensed %	Metallic Arsenic %	Temperature
Na_2O	0.38	1.34	0.66	None	362°-387°
BaO	0.75		0.30	Trace	402°-410°
SrO	0.67	29.5	28.6	0.23	373°-385°
CaO	0.40	1.7	1.3	0.1	350°-360°

All of the arsenites which contain more arsenious oxide than the meta-arsenite, with the exception of the strontium salt, lose only small quantities of arsenious oxide when heated in closed tubes at temperatures at which this anhydride has an appreciable vapor pressure. The amount of elemental arsenic, due to oxidation-reduction is likewise small.

The thermal stability of these substances indicates that (with the exception of the strontium salt) they are true compounds and not meta-arsenites containing an excess of uncombined arsenious oxide. Di-arsenites may be regarded as analogous to dichromates and tetraborates:—thus sodium di-arsenite, $Na_2O.(As_2O_3)_2$, can be written $Na_2As_4O_7$ or $(NaAsO_2)_2.As_2O_3$, completely analogous to the formula for borax. The existence of these di-arsenites or tetra-arsenites stable toward heat is probably related to the weakly acid character of arsenious anhydride, as boric acid is also very weak, and a strong base may be expected to form stable compounds with an excess of a weak acid.

The data for the calcium and sodium salts indicate that arsenious oxide may be retained in combination even when present in excess of the theoretical amounts for the di-arsenites. This failure of the excess arsenious oxide to vaporize may be due to the slow rate of evaporation of melted arsenious oxide observed by Tammann and Bätz,[1] or to a tendency of arsenious oxide to dissolve in the di-arsenite.

---

[1] Z. anorg. allgem. Chem., **156**, 94 (1926).

The fact that oxidation-reduction took place to so slight an extent in these substances indicates that this reaction is dependent upon the presence of a basic oxide. When the basic oxide is so saturated with the acid anhydride as to lose its basic character, it is to be expected that the reaction will no longer take place. The comparison of the two barium arsenites studied is particularly striking in this connection. The data show that the substance containing about 35.2 percent arsenious oxide undergoes oxidation-reduction at 380°-393° to such an extent that about 58.5 percent of the arsenious oxide present is decomposed, whereas the substance containing 63.5 percent arsenious oxide showed apparently only a small thermal dissociation into its anhydrides and only a trace of metallic arsenic to indicate oxidation-reduction.

Determination of Initial Temperature of Reaction

The substance was sealed off in a glass tube about 10 cm. long, as described previously, in an atmosphere of nitrogen at atmospheric pressure. This means about two atmospheres pressure when heated to around 300°. It was found that Jena glass tubes were quite apt to blow up if handled with crucible tongs when hot, and the tubes were therefore placed in spirals of nichrome wire, by which they were lifted from the furnace without coming in contact with cold metal. To determine the initial temperature of reaction, the tubes, enclosed in the spiral of nichrome wire, were placed in the furnace at about 200°, heated at that temperature for about twenty-four hours, removed from the furnace and examined. They were then allowed to cool to room temperature and were examined again. By this method the presence of a condensing vapor in the tube can be detected. If no change occurred, the temperature was raised about ten degrees and the experiment repeated until a change could be detected.

A commercial sample of potassium arsenite (Vernier and Hobein) dried at 150° was found to contain 57.05 and 57.57 percent arsenious oxide with appreciable quantities of arsenite, water, and carbon dioxide. The formula for the meta-arsenite requires 67.75 percent arsenious oxide, so this might be meta-arsenite with a large amount of impurities. A sample of this substance was sealed in nitrogen and heated as described. A slight darkening was first noticed at 313°-317° and there was no condensate. When heated to 365°, the substance became only slightly darker, and no vaporization of the arsenic took place, although some water condensed on cooling. The presence of water vapor may interfere with the accurate determination of the initial temperature of reacting with the arsenic formed. The initial temperature of the oxidation-reduction of this substance is placed tentatively at 313°-317°.

Calcium meta-arsenite, prepared by the interaction of calcium oxide with an aqueous solution of arsenious oxide, was found on analysis to contain about 75.74 percent arsenious oxide, as compared with 77.92 percent for calcium meta-arsenite, $Ca(AsO_2)_2$. The lime contained some impurities, which may account for this difference. When sealed in nitrogen and heated as described, it became slightly discolored at 360°, and a very small yellow sublimate appeared. It seems probable that the yellow color is due to some interaction of the arsenic with water vapor. The solid hydrides, $(AsH)_n$ and $(As_2H)_n$ may have this color under certain conditions; but, as they are known to be instable at 200°, the color may be due to the brown suboxide, the existence of which has been disputed. There is a yellow modification of elemental arsenic; but this is known to be very instable at ordinary temperatures.

A commercial sample of zinc ortho-arsenite (Häen) was found by titration with iodine to contain 42.27 and 42.48 percent arsenious oxide, as compared with 44.77 percent in $Zn_3(AsO_2)_2$. The substance gave a positive test for arsenite. It may be ortho-arsenite that has undergone some oxidation. This substance, when sealed in nitrogen, gave a condensate of octahedral crystals (arsenious oxide) when cooled from 510° and a small amount of a black condensate appeared when the temperature reached 549°.

The experiment was repeated, using a zinc arsenite prepared by the reaction of zinc oxide with aqueous arsenious oxide and containing 45.14 and 44.83 percent arsenious oxide, a little above the composition of the ortho-arsenite, and no arsenate. With this substance octahedral crystals appeared at 500°-508° after 24 hours. When heated 24 hours longer at the same temperature, a black condensate appeared, indicating that the oxidation-reduction reaction takes place with time. The heating was continued for 48 hours at the same temperature without changing the nature of these condensates.

The difference in the initial reaction temperatures of these two samples of zinc arsenite indicate that the initial dissociation temperature of the substance into its components is lowered by increasing the arsenious oxide content, and that the initial temperature of the oxidation-reduction reaction is raised by appreciable quantities of arsenate, a product of this reaction.

A substance prepared by the interaction of pure, precipitated alumina with aqueous arsenious oxide, when dried at 150°, was found to contain 31.52 and 31.58 percent arsenious oxide on titration with iodine. However, when samples were heated to redness in porcelain crucibles, they were found to lose between 31 and 46 percent of their weights, and the residues were found still to contain appreciable quantities of the oxides of arsenic. The results of the titrations are probably low due to the adsorption of arsenious oxide by the alumina precipitated by the bicarbonate of soda used. The substance probably contains about fifty percent arsenious oxide. The ortho-arsenite contains 66.0 percent.

When cooled from a temperature of 491°-502°, this substance gave a white condensate of arsenious oxide, followed by an orange-yellow condensate. It therefore appears to undergo thermal dissociation and and the oxidation-reduction simultaneously at this temperature. The temperature was lowered and heating continued for thirteen days at 449°-466° without any apparent change, indicating that neither reaction is reversible at this temperature. The condensates were found to be completely soluble in potassium hydroxide solution (about 3 N), which indicates that the orange-yellow substance is not elemental arsenic and that it may be the suboxide.

Pure, precipitated ferric oxide was allowed to stand in contact with arsenious oxide solution until the supernatant solution showed a constant titre. It was then filtered and dried at 150°. Titration with iodine gave inconstant results, probably due to the adsorption of arsenious oxide by the ferric oxide precipitated by the bicarbonate. The substance was found to dissolve readily and to give a colorless solution when heated with phosphoric acid. When bicarbonate was added to this, the precipitate formed was almost colorless and therefore did not interfere with the end-point. Titration with iodine under these circumstances gave 44.33, 44.39, and 44.30 percent arsenious oxide. When the substance was heated in air, however, a loss of weight was found which corresponded to the composition of ferric ortho-arsenite, $FeAsO_3$, containing 55.35 percent As_2O_3.

Some of this substance, dried at 150°, was found to give a white condensate when cooled from 300°. When heated to 501°-512°, the condensate was much larger and consisted of vitreous arsenious oxide which cracked the tube on cooling. The fact that no metallic arsenic appeared at the higher temperature suggests that oxidation of the arsenious oxide may have occurred together with reduction of the ferric oxide to magnetite. The residue was found, however, to be quite red and not to be attracted by a small horseshoe magnet. Arsenite could not be detected by the usual test with potassium iodide and hydrochloric acid, because ferric chloride itself sets free iodine. The quantity of arsenious oxide condensed could not be determined because the tube broke.

The results are summarized in Table IV which shows that the reaction temperature increases with decreasing basicity. None of these figures, except those for zinc ortho-arsenite are to be regarded as accurate, because of the interference of water vapor with the determination. A method has been developed for heating the tubes during evacuation to eliminate the water, and this has been found successful with arsenites which are stable up to 300°.

TABLE IV

Initial Reaction Temperatures for the Oxidation-Reduction

Potassium arsenite, 57% As_2O_3	313°-317°
Calcium arsenite, 75% As_2O_3	368°
Zinc ortho-arsenite, 45% As_2O_3	500°-508°
Aluminum arsenite, 50% As_2O_3 (?)	491°-502°

Determination of Initial Temperatures of Reaction in Evacuated Tubes

A small furnace for heating the tubes during evacuation was constructed like those previously described except that the iron pipe used as the core was smaller, with its internal diameter only a little larger than the external diameter of the glass tubes used. This furnace was placed in an iron clamp so that it could be tilted at an angle. The current was controlled by means of a lamp-bank, and the temperature was estimated by placing an attached-scale thermometer in the furnace with its stem projecting. The tube containing the sample of arsenite was drawn out so that it could be attached directly to the rubber tube from the vacuum pump, and was constricted very much at one point to facilitate sealing off. The pump was tested by connecting directly to an open-end manometer, and comparing the manometer reading with the barometric pressure. It was found to give a vacuum of less than one millimeter, which was as close as the manometer could be read.

Difficulty was sometimes experienced in finding a temperature at which the water could be driven off without decomposing the arsenite. Substances containing more arsenious oxide than the pyro-arsenite were found to give off arsenious oxide during the evacuation at temperatures lower than the initial temperatures of oxidation-reduction. In the previous experiments attached-scale thermometers were used for temperatures up to 405°. These were checked at the boiling-points of water and naphthalene, and at the freezing-points of potassium dichromate. Two were found that gave 99° at the boiling-point of water, 218° at the boiling-point of naphthalene, and 391° at the freezing-point of potassium dichromate, all measurements taken with about half the scale exposed, as the thermometers were to be used under these conditions. The value for naphthalene was about one degree high and that for dichromate five degrees low, probably due to exposed stem. Since exposed-stem corrections are not applicable to attached-scale thermometers, no corrections were applied. A 570° nitrogen-filled, engraved-scale thermometer was used for higher temperatures and the exposed-stem corrections calculated.

A chromel-alumel thermocouple was also used for temperatures above 400°. This was attached directly to the millivoltmeter without using a cold junction. The room temperature near the furnace was found to be 30°, which corresponds to 1.2 mv. according to the values given in the International Critical Tables, 1, 59. This value was subtracted from the E. M. F. values. The values for the freezing-point of potassium dichromate, lithium chloride, and potassium chloride were then determined and found to check the curve within 2°. The thermocouple was insulated by threading one wire with short sections of small porcelain tubing. It was placed in a Bohemian glass tube which served as a protection tube. The leads were only about one meter in length, so the error due to the resistance of the leads was negligible.

Satisfactory samples of potassium and sodium arsenites could not be obtained by the usual methods, as has been pointed out. An attempt to prepare sodium meta-arsenite by pumping off the necessary amount of arsenious oxide from a sample of the diarsenite at 300°-310° for two hours, resulted in a residue which melted in vacuo at about 400° without darkening and which gave off a small amount of arsenious oxide but no metallic arsenic.

On titrating with iodine it was found to contain 81 percent arsenious oxide, about five percent more than the meta-arsenite.

A substance containing 27.3 percent arsenious oxide prepared from arsenious oxide in ammoniacal solution and lithium chloride, turned brown when heated to about 300°. The residue gave an odor of arsine when placed in cold water, and so the brown color is thought to have been due to the formation of arsenide. Lithium meta-arsenite was sealed off in a Bohemian glass tube after evacuating for one hour at 250°. When heated to 286°-290°, a small condensate of arsenious oxide appeared, and arsenic was observed at 310°-322°. When the tube was heated to 400°, more arsenic appeared but the arsenious oxide did not diminish perceptibly.

A substance containing only slightly more arsenious oxide than barium meta-arsenite was sealed off after evacuation for one hour at about 200°. The substance gave a small condensate of arsenious oxide during evacuation. This was removed from the drawn-off tube after sealing, by dissolving in potassium hydroxide solution. The amount of arsenious oxide seemed to correspond with the excess over that required by the meta-arsenite. When the material in the sealed tube was heated, it darkened at 315°-323°, but no condensate appeared until the temperature was raised to 400°-405°. It seems probable that some arsenic was formed at the lower temperature; but was adsorbed so strongly that it did not appear as vapor. The initial temperature is therefore placed at about 320°. When the tube was heated subsequently at 560°-569°, both arsenious oxide and metallic arsenic condensed, indicating that at higher temperatures both oxidation-reduction and thermal dissociation take place simultaneously. The residue obtained at 579° was almost pure white and gave a very faint odor when placed in cold water, indicating only a very small amount of arsenide.

Calcium meta-arsenate, dried at 140° and sealed in an evacuated tube without further heating, turned brown at 343°-345°, and black when the temperature was raised to 384°-387°. No further change appeared after heating for seven days at 391°-401°. It was thought that water in the sample interfered with the formation of arsenic, but when the tube was evacuated at 200° it lost some arsenious oxide without eliminating all the water, as water condensed when the sample was subsequently heated in vacuo at 308°-311°. It was concluded therefore that metallic arsenic failed to condense because it reacted with the lime to form arsenide, according to the equation

$$As_4 + 3\ CaO = Ca_3As_2 + As_2O_3.$$

To prove this, the residue was examined and found to give a very faint odor of arsine.

It seemed probable that arsenic is the primary product of the reaction and that the formation of arsenide takes place slowly. To prove this, another sample of calcium meta-arsenite was sealed in an evacuated tube and placed in the furnace at 397°-399° for 24 hours. When removed from the furnace, the substance was found to be yellow. On cooling, it became black and a black condensate appeared in the top of the tube. Thus, by rapid heating above the initial temperature of reaction, arsenic was produced, whereas it was not produced by raising the temperature slowly, indicating that a secondary reaction took place. However, the possibility is not excluded completely that this is due to water vapor.

A preparation containing 89.8 percent arsenious oxide, with the remainder presumably calcium oxide, was evacuated for one hour and sealed off. A large amount of arsenious oxide was condensed in the constricted portion of the tube. From a titration of this residue was estimated to contain 67 percent arsenious oxide. When this was heated to 313°-321°, it became grayish in color; but no condensate appeared at this temperature or when the sample was heated at 342°-353° for 24 hours. From the weight of the residue it was calculated that the sample must have contained about 62 percent arsenious oxide before undergoing pyrolysis. This is a little less than that required for the pyro-arsenite, $Ca_2As_2O_5$, and indicates that the arsenite is not stable at 250°, and decomposes to form the pyro-arsenite by thermal dissociation; also that the pyro-arsenite, containing a higher proportion of the basic oxide, undergoes oxidation-reduction at a lower temperature than the meta-arsenite. In line with this is the fact that the substance containing less arsenious oxide than the lithium ortho-arsenite, and being therefore a basic arsenite, darkened at a lower temperature. This confirms the view that the basicity of the metallic oxide affects the initial temperature of oxidation-reduction.

A substance containing magnesia and arsenious oxide, approximately in the proportion required to form magnesium ortho-arsenite was dried at 140° and sealed in vacuo without further heating. A condensate of water appeared at 427°-446°, and a white, solid condensate, apparently arsenious oxide, at 469°-473°. No metallic arsenic appeared, even when the temperature was increased to 540°.

Another sample was pumped off for two hours at 285° before sealing. A slight, yellow condensate appeared at 504°-508°, probably a mixture metallic arsenic with arsenious oxide. It was thought that the white color of the condensate in the first instance and the yellow color in the second were both due to incomplete elimination of water. For this reason, another sample was evacuated at 350° for one hour; this gave a very black condensate when cooled from 500°. No water condensed but a drop appeared when the temperature was raised to 531°-537°, and the condensate became brown instead of black.

Zinc ortho-arsenite, dried at 140° and sealed off without further heating, liberated arsenious oxide when heated to 425°-435°, and a black condensate appeared when the temperature was increased to 520°-525°. When the temperature was increased gradually to 590°-595°, the black portion of the condensate disappeared almost completely, leaving the arsenious oxide. This may mean that the reaction is reversed at this temperature or it may mean that arsenide is formed.

Zinc meta-arsenite was dried at 140° and sealed off after evacuating for one hour without further heating. Arsenious oxide just appeared on cooling from 376°-378°. A black condensate first appeared at 496°-508°.

Lead arsenite, containing 41 percent arsenious oxide and corresponding to no definite formula, gave off arsenious oxide when heated to 289°. This disappeared when the temperature was reduced slightly and reappeared when the temperature was raised again. A grayish condensate, apparently metallic arsenic, appeared at 525°-530°. The residue had melted to a yellowish liquid which became white on cooling. Crystals of arsenious oxide also condensed at this temperature.

A substance containing ferric oxide and arsenious oxide in approximately the proportions to form the ortho salt was sealed in an evacuated tube at room temperature. A white condensate appeared when this was cooled from 282°-286°. The amount of this increased with rising temperature; but the heating was continued to 525° without any metallic arsenic appearing.

A product containing approximately 40 percent each of arsenious oxide and alumina, and 20 percent water was evacuated at 370°. The powder appeared to boil at this temperature due to the rate at which adsorbed gases were driven off. The tube was sealed off after having been evacuated for two hours. This substance gave off arsenious oxide at 385°-396°. Water appeared in the tube on cooling from 441°. Heating to 550° produced no further change.

With another sample of the same material evacuation was started at 250° and increased to 450° during two hours. Some arsenious oxide was driven off during the latter part of this evacuation. Water was evidently eliminated by this treatment, as none appeared on cooling the tube. No metallic arsenic was formed even when the tube was heated to 586°.

The results are summarized in Table IV.

TABLE IV

Approximate Formula	Initial Temperature Oxidation-Reduction	Initial Temperature Thermal Dissociation
4 $Li_2O.As_2O_3$	300° approx.	
$Li_2O.As_2O_3$	318°-320°	286°-290°
$BaO.As_2O_3$	315°-323°	Above 500°
$CaO.As_2O_3$	343°-345°	
2 $CaO.As_2O_3$	313°-321°	
3 $MgO.As_2O_3$	500°	
3 $ZnO.As_2O_3$	520°-525°	425°-435°
$ZnO.As_2O_3$	496°-508°	376°-378°
1.3 $PbO.As_2O_3$	525°-530°	289°
$Fe_2O_3.As_2O_3$		282°-286°
Al_2O_3.50%As_2O_3		385°-386°

The general results of this investigation are as follows:—

1. When a metallic arsenite is heated in an inert atmosphere, there may be thermal dissociation into basic oxide and arsenious oxide; there may be simultaneous oxidation of the arsenious oxide to arsenic oxide and reduction of the arsenious oxide to metallic arsenic which may occur as such or may react further; there may be simultaneous oxidation of arsenious oxide to arsenic pentoxide and reduction of the basic oxide.

2. If the dissociation pressure of the arsenite is high and the basic oxide is not readily reduced, thermal dissociation may be the only reaction which occurs. The oxides of aluminium, magnesium, zinc, and lead belong chiefly in this class.

3. If the dissociation pressure of the arsenious oxide is relatively low and the basic oxide is not readily reducible, the reaction products will be largely arsenic pentoxide and metallic arsenic or a reaction product of arsenic. The oxides of sodium, potassium, and barium belong chiefly in this class. For some reason strontium oxide appears to be more nearly like zinc oxide than like calcium oxide.

4. If the dissociation pressure of the arsenious oxide is relatively low and the basic oxide is readily reducible, the reaction products will be largely arsenic pentoxide and the reduction product of the basic oxide. The oxides of silver and copper belong chiefly in this class, and ferric oxide to a lesser extent.

5. There seems almost always to be some thermal dissociation and this is more marked the larger the content of arsenious oxide. The oxidation-reduction reaction can usually be increased by rapid heating to a high temperature.

6. When metallic arsenites are heated in the air, oxidation by the air may be superposed on the other reactions.

7. No experiments have been made at constant pressure and varying volume beyond a few of the evacuation experiments. It is certain that such a study would give more clear-cut results.

Cornell University.

A STUDY OF GLYCINE ANHYDRIDE

BY IRENE HANNAH SANBORN

Yet another study of glycine anhydride may be of interest—a study undertaken, as it were, in the face of much conflicting evidence, but having as its incentive a theory which is constantly accumulating new supporting facts and correlating many old ones.

Constructive research into the structure of the proteins started with the almost simultaneous pronouncement by F. Hofmeister and E. Fischer of the —CO·NH— linkage as characteristic of proteins. It is not necessary to discuss the well-known peptide theory, or to dwell upon its usefulness. Its relation to the most important criterion in the study of the structure of proteins, namely that furnished by their biological behavior, their reaction with enzymes, is of great import. It is recognized that the breaking down of proteins by chemical means or by peptic and tryptic enzymes has yielded compounds which are of cyclic structure and not straight polypeptide chains. Such cyclic compounds, recognized early in investigations, were 2, 5-dioxopiperazines. These 2, 5-dioxopiperazines are composed of two amino acids, with glycine anhydride in the rôle of their simplest representative.

Although the dioxopiperazines were obtained from proteins comparatively early, no systematic experiments were carried out aiming at their establishment as elementary building stones for the protein structure. The polypeptide theory was too well supported. The possibility, however, of the occurrence of preformed dioxopiperazines was not disregarded by either Fischer[1] or Abderhalden.[2] Fischer states that the simple amide bond does not represent the only possible linkage within the protein molecule, but on the contrary that the occurrence of piperazine rings is rather probable. . . . By intramolecular formation of anhydrides, the numerous hydroxyl groups of hydroxyamino acids can be transformed into ether and ester groups; the variety increasing still more when one considers that the polyamino acids are probable constituents of proteins."

In a comprehensive article by Klarmann,[3] the theories of the cyclic structure of proteins are well discussed and summarized. It is interesting to note that while he considers the pyrrole theory, the dioxopiperazine theory, the experiments of Waldschmidt-Leitz on enzyme separation and subsequent elucidation of protein structure, the synthetic heterocyclic compounds which might possibly occur in proteins, the iso- and allodioxopiperazines, and the ureide theory, he devotes four times as much space to the dioxopiperazine section as to any other. This may or may not be indicative of any particular

---

[1] Ber., 38, 607 (1905); 39, 607 (1906).

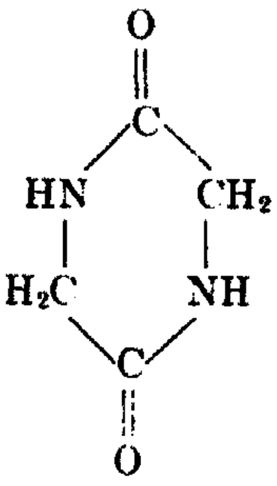
[2] "Lehrbuch physiol. Chemie," 3rd ed., 885 (1915).

[3] Chem. Reviews, 4, 51 (1927).

aptness of this theory. It does mean that the 2, 5-dioxopiperazine structure is one of considerable importance to many who possess an urge to use it in explaining the behavior of proteins.

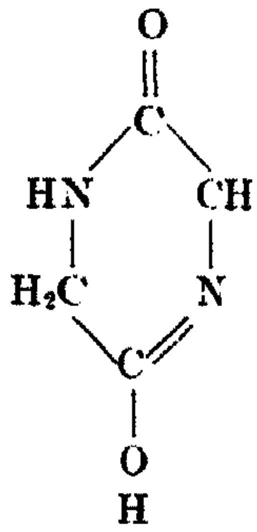
Not only have homologous dioxopiperazines been repeatedly isolated from the degradation of proteins, but they have also been the object of thorough synthetic work. Curtius and Goebel[4] prepared them from esters of amino acids; whereas E. Fischer by a similar method, studied the transformation of dioxopiperazines into dipeptides. The primary occurrence of the dioxopiperazines was questioned by Abderhalden and Funk[5] and later[6] (1923) confirmed by Abderhalden when he first identified a piperazine derivative obtained from a protein. While in some cases, the anhydrides must be present in a preformed state, in other cases the possibility of a secondary formation cannot be ignored. This has been shown clearly by several workers, among them Grave, Marshall, and Eckweiler,[7] Brigl[8] and finally Abderhalden and Komm.[9,10] The latter have listed[10] the possible tautomeric forms of glycine anhydride as follows:

(A)



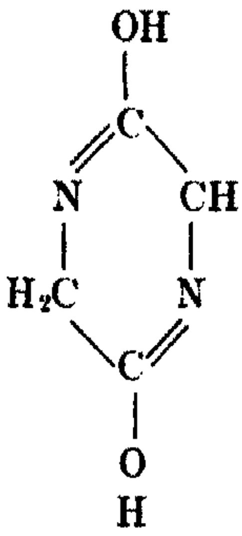
diketo

(B)



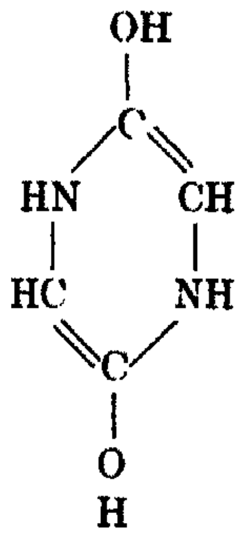
keto-enol

(C)



dienol

(D)



diethylene

They prepared several derivatives of glycine anhydride and proved their structures—among them, N, N′ diacetyl-2, 5-diketopiperazine; dibenzoyl-2, 5-diketopiperazine; N, N′ dibenzyl-2, 5-diketopiperazine and O,O′ dibenzoylether-2, 5-dioxydihydroxypiperazine. They conclude: "The acceptance of an acid amide linkage for the albumin building stone in the protein molecule is supported by certain facts. Polypeptides, so long as they are built up from the amino acids occurring in nature, are hydrolyzed with few exceptions by ferments which are present in the pancreas and intestinal juice. In case of separation, amino acids are formed by the absorption of water.

One thing is certain, i.e., acid amide-like linked amino acids are present in albumin, and if one assumes that piperazines are also present as building

---

[4] Ber., 16, 753 (1883); 17, 953 (1884).

[5] Z. physiol. Chem., 53, 19 (1907).

[6] Z. physiol. Chem., 129, 143 (1923); 132, 238 (1923).

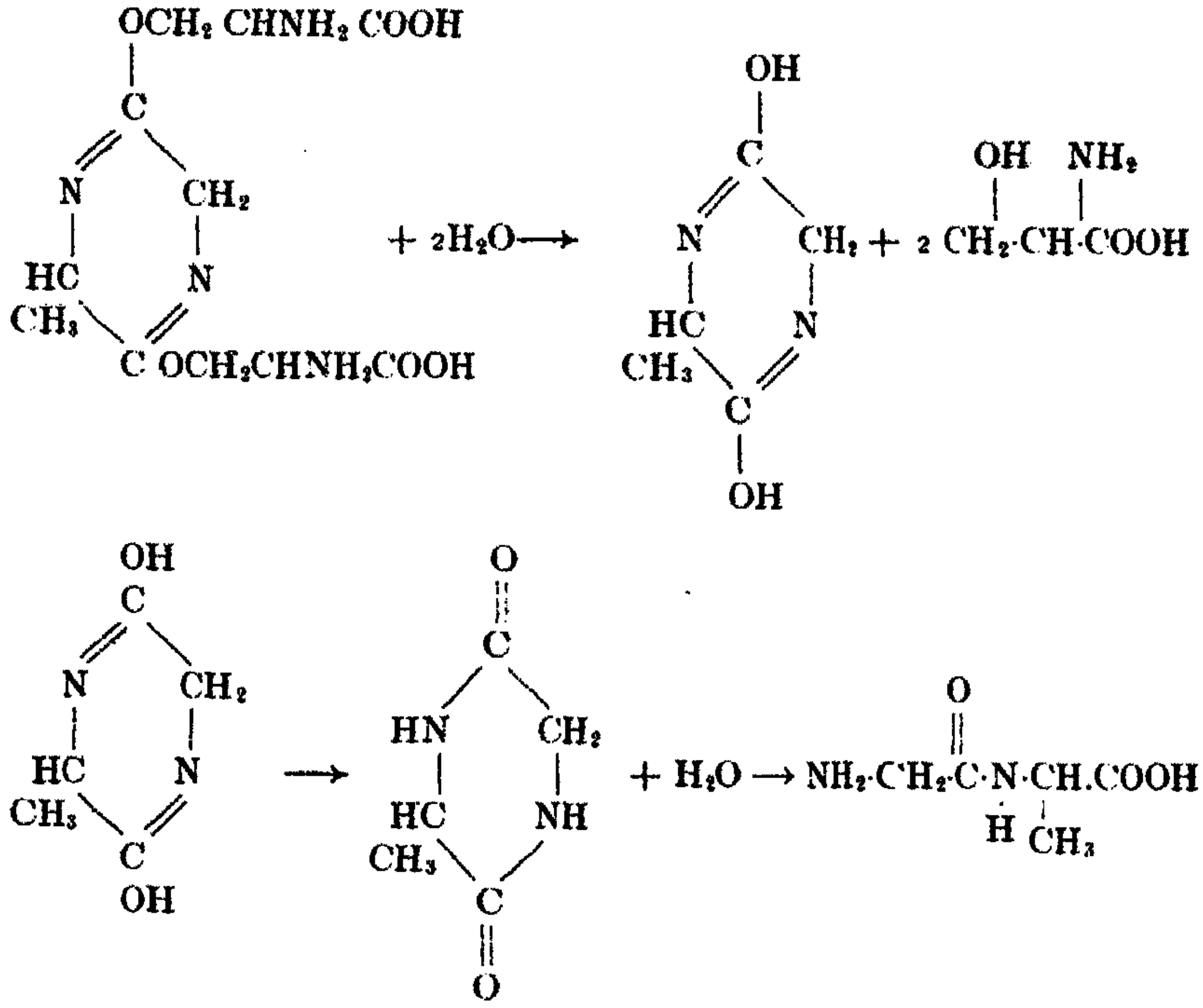
[7] J. Am. Chem. Soc., 39, 112 (1917).

[8] Ber., 56, 1887 (1923).

[9] Z. physiol. Chem., 134, 121 (1924).

[10] Z. physiol. Chem., 139, 188 (1924).

stones,—they should be temporary polypeptides—and dipeptides could appear as follows:



So far it is assumed that a special ferment exists for the building up of the anhydride ring. Every assumption of rings stable toward alkalies and acids, as the piperazine ring, would appear entirely in contradiction with the rapid decomposition of the protein molecule by ferments. It seems then, that the argument of the presence of special ferments would indicate that such ring systems might possibly be in existence. It is not unthinkable that ferments exist which effect the rearrangement, and change one tautomeric form into another whereby in special cases a decomposition of the molecule could be hypothetical.

Any acceptance of a definite structure of the proteins must finally stand in harmony with the facts that the fermentation decomposition as likewise that by acids and alkalies leads to amino acids.

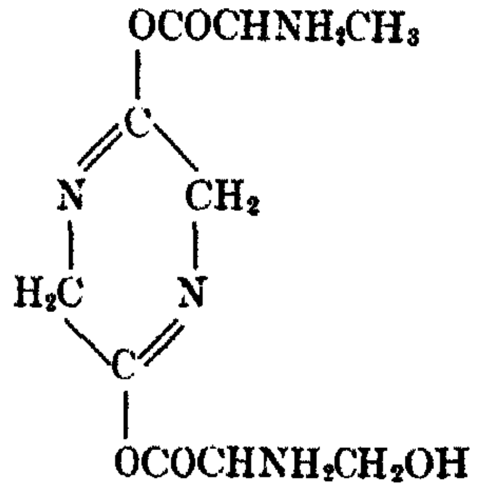
With these requirements the acceptance of anhydrides easily separable by dilute alkalies and dilute acids stands in complete agreement. It is now only the question whether the anhydrides consisting of two amino acids produce 2,5-diketopiperazine, or another form of the same substance.

There is much in favor of the first idea. It is easy to obtain methyl piperazine by reduction from peptized silk. Other piperazines[11] have been isolated

---

[11] Z. physiol. Chem., 129, 143 (1923).

which can originate only from diketopiperazine. There remains the possibility that these are formed secondarily. It is certain that for their origin no dipeptide is to be considered, for among conditions mentioned in the transformation by reduction, no piperazine could be obtained from the polypeptides. Thus, there is probably a tautomeric form. In that case it is possible that the anhydride could occur in relation to amino acids in this form;



It would actually be possible under these conditions i.e. in the case of reduction, that the amino acids coupled with the anhydride are separated by simultaneous rearrangement of the enol into the keto form. There is much to substantiate the keto structure."

Much evidence exists to show that dioxopiperazines occur in a preformed state, having been extracted from proteins which were cleaved by enzymes or by concentrated acids. Salaskin[12] obtained leucine anhydride by the action of gastric juice on oxyhemoglobin and subsequent extraction with ethyl acetate. Glycyl proline anhydride was isolated from the ether extract of the decomposition product obtained from the action of pancreatin on edestin.[13] These are only two of many similar cases.

Some of the dioxopiperazines appear to be resistant to acid. E. Fischer[14] found that leucine anhydride dissolved in concentrated acids without decomposition, although the ring was split upon prolonged heating. The methods used, aiming at the hydrolysis of the proteins, do not exclude the possibility of a secondary formation of anhydrides; hence mainly interesting from the point of view of dipeptide combinations.

Studies of the reduction and oxidation of proteins contributed more substantial results to the conception of a dioxopiperazine structure. Regardless of how dioxopiperazines might combine with each other, or with amino acids and polypeptides, respectively, it is true that a reduction which prevented the splitting of dioxopiperazines produced volatile piperazines which could be driven off by steam distillation and hence identified. Abderhalden and Stix[15] reduced silk peptone with metallic sodium and amyl alcohol. The distillate gave typical piperazine reactions although the yield was small. This

---

[12] Z. physiol. Chem., **32**, 592 (1901); **38**, 573 (1903).

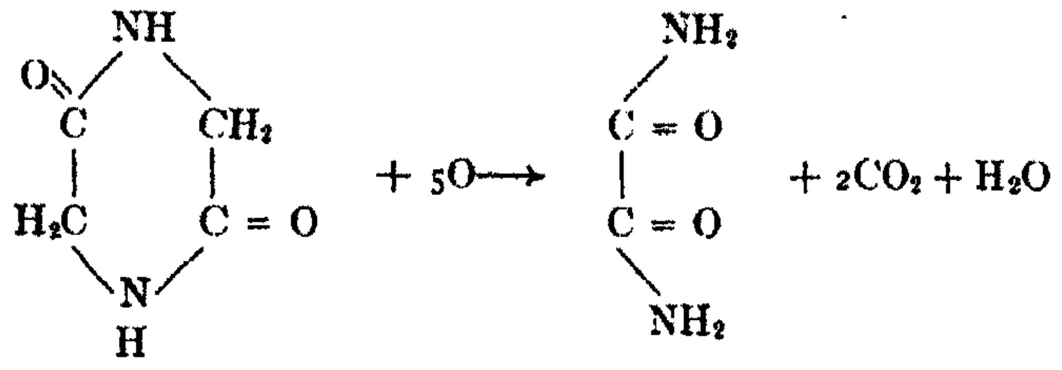
[13] Z. physiol. Chem., **47**, 143 (1906).

[14] Ber., **35**, 1164 (1908).

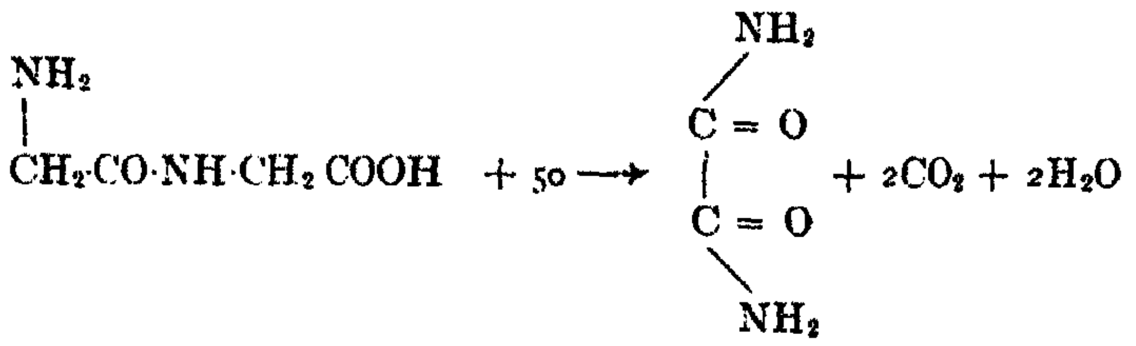
[15] Z. physiol. Chem., **132**, 238 (1925).

did not indicate that the amount of dioxopiperazines in the protein was small, since direct treatment of dioxopiperazine in the same manner also leads to small yields. The dioxopiperazines apparently have low resistances which allow for cleavage in the presence of sodium or sodium alcoholate, whereas only a small portion is reduced. Glycine anhydride and leucyl glycine anhydride were subjected to reduction also and their respective piperazines obtained.[16]

Having contented themselves that the results from reduction pointed toward the probability of the primary occurrence of dioxopiperazine, Abderhalden[17] and his co-workers carried out another series of experiments aiming at the establishment of their presence by oxidation methods. Their results were corroborated by those of Goldschmidt and Steigerwald.[18] All dioxopiperazines yielded oxamide; whereas the dipeptides were decomposed with the exception of glycyl-glycine which also yielded oxamide. With the simplest dioxopiperazine, oxidation takes place thus:



Abderhalden[19] and Komm showed that only polypeptides which contain the glycyl-glycine group would yield oxamide.



The method was used on the proteins with permanganate as the oxidizing agent. Some proteins were difficultly attacked; but oxamide was obtained from blood globulin, egg albumen, gelatin, caseinogen and silk peptone, thus confirming a well-grounded suspicion.

A comparative investigation of the dioxopiperazines, peptides, amino acids, and proteins or their cleavage products included the application of color reactions which would be specific for one class and would not be given by other classes. Color reactions of the proteins have been long and extensively

---

[16] Z. physiol. Chem., **139**, 169 (1924).

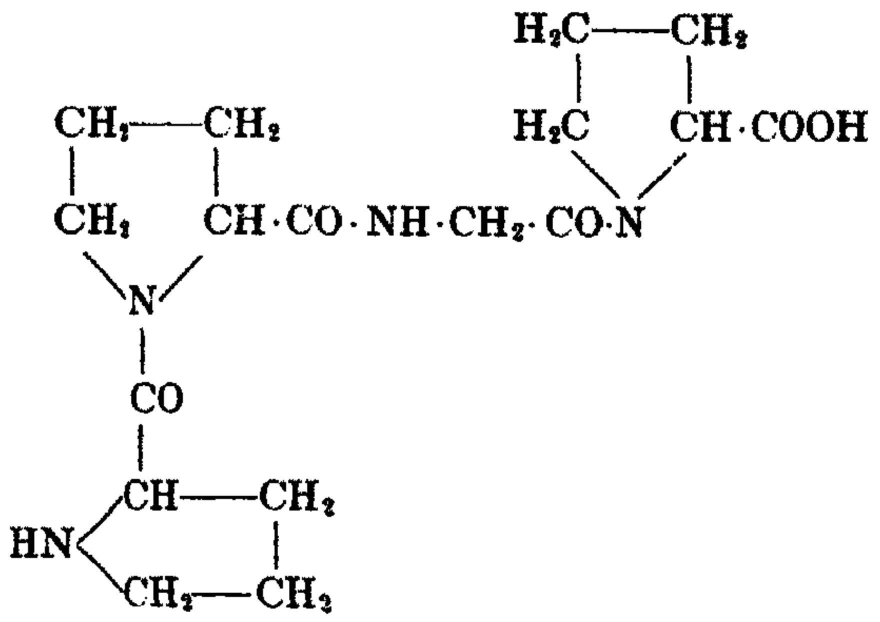
[17] Z. physiol. Chem., **140**, 92 (1924).

[18] Ber., **58**, 1346 (1925).

[19] Z. physiol. Chem., **143**, 128 (1925).

useful as means of distinguishing them. Abderhalden and his co-workers[20] after discarding many reagents which showed color with other substances than the dioxopiperazines hit upon a group of reagents, the aromatic nitro compounds, which gave characteristic reactions with dioxopiperazines. Other substances, among them hydantoins, glucose, and malonic ester, gave positive reactions also, but the likelihood of their occurrence in proteins is highly improbable. Picric acid and sodium carbonate will give a positive reaction with all peptones and most of the proteins; whereas, amino acids, and polypeptides do not. m-dinitrobenzene and 3,5-dinitrobenzoic acid give comparable results to those of the picric acid and sodium carbonate. Although these color reactions are not specific, they do constitute another support for the dioxopiperazine theory.

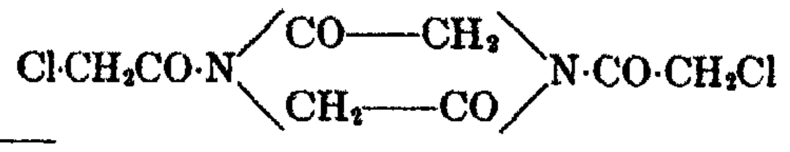
The connection of the dioxopiperazines, which in themselves represent only small complexes, with compounds of high molecular weight, has not been neglected by Abderhalden and his workers. A compound consisting of three molecules of l-proline[21] isolated from a native protein is assigned the tentative formula:



Many compounds of this type could be given as examples[22] to produce an idea as to the assumed nature of combinations of dioxopiperazines and amino acids.

One point, that upon the addition of alkali the amount of —NH_2— nitrogen increases, is of interest as it indicates that the ring is opened on one side by this treatment.

The problem has also been approached synthetically. Abderhalden and Klarmann[23] found that when water is excluded a condensation may take place at a higher temperature with the formation of the corresponding dihalogen acyl-dioxopiperazine.



---

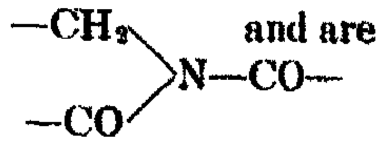
[20] Z. physiol. Chem., **139**, 181 (1924); **140**, 99 (1924).

[21] Z. physiol. Chem., **127**, 281 (1923); **129**, 106 (1923).

[22] Z. physiol. Chem., **131**, 284 (1923); **139**, 169 (1924); **134**, 113 (1924); **136**; 134 (1924).

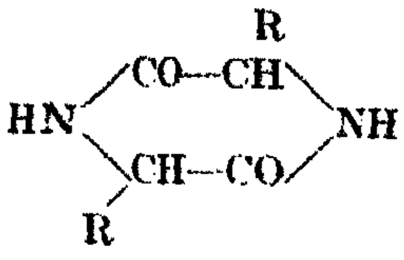
[23] Z. physiol. Chem., **135**, 199 (1924).

At the same time, Bergmann prepared compounds which probably have the structure and are resistant to ammonia.[24]

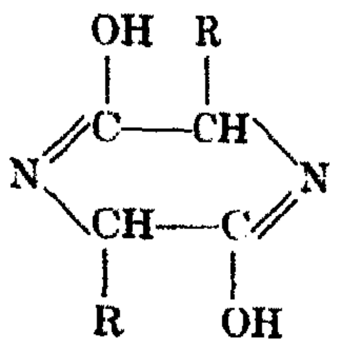


$$\begin{array}{l} -CH_2\diagdown \\ \qquad\; >N-CO- \\ -CO\diagup \end{array}$$

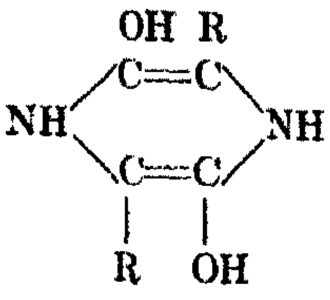
The structural formula of the dioxopiperazine nucleus allows the assumption of the following tautomeric structures:[25]



I.



II.



III.

Compounds possessing a markedly unsaturated character were obtained under certain conditions.[26] When glycine anhydride was heated with glycerol in the presence of tyrosine, a compound was isolated which had the empirical composition of glycine anhydride, but in contrast to it immediately decolorized permanganate, gave a positive xanthoprotein reaction and readily allowed the introduction of methyl groups via diazo methane. Abderhalden and Schwab[26] assume that formula III is the most probable for this compound. In the absence of tyrosine the compound obtained loses its unsaturated nature during the course of purification. The rôle of tyrosine is not quite clear. Rearrangement of the enol form of 2,5-dioxopiperazine into its keto form took place by heating in aqueous solution to 90-100°.[27]

Dioxopiperazines were obtained in the enol form by heating the respective dipeptides with diphenylamine.[28] Several enolic anhydrides, among them, d,l-leucyl-glycine, d,l-leucyl-d,l-valine, were prepared in excellent yields. Glycyl-glycine and glycylalanine behaved differently from the other dipeptides. The first gave a difficultly soluble compound, probably a polymer, with composition of glycine anhydride. The dioxopiperazines in the keto form are not changed into the enol form by heating with glycerol or diphenylamine, but the change is effected by heating with aniline. A proof for the assumed structure (I) is given by preparing the anhydride from alpha-aminoisobutyryl-alpha-aminoisobutyric acid. The anhydride cannot exist in the enol form on account of its particular structure.

---

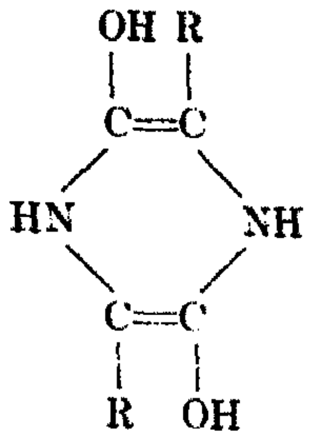
[24] Z. physiol. Chem., 140, 128 (1924); 143, 108 (1925); 146, 247 (1925); 152, 189 (1926).

[25] Z. physiol. Chem., 139, 64 (1924); Naturwissenschaften, 13, 99 (1925).

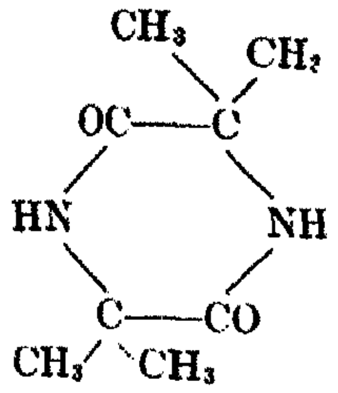
[26] Z. physiol. Chem., 149, 100 (1925).

[27] Z. physiol. Chem,. 152, 90 (1926).

[28] Z. physiol. Chem., 152, 125 (1926).



I.



II.

The product gave all anhydride reactions, but unlike other anhydrides prepared by the same method, did not give the xanthoprotein reaction or decolorize permanganate. Since it was possible to obtain sarcosine anhydride in the unsaturated form,[29] the existence of the —C = C— linkage in enolic dioxopiperazines seems close to establishment.

Methods have been devised to distinguish between these tautomer compounds in a physical way. Abderhalden and Haas have found that several amino acid anhydrides give a characteristic absorption in the ultraviolet, the enol form showing a more pronounced absorption than the keto form. Some proteins also absorb in the ultraviolet. The absorption spectrum of an amino acid depends on the method of its preparation. In one case, the enol-keto rearrangement could be observed spectroscopically in d, l-leucyl-glycine anhydride. The rearrangement was complete after eight hours.[30] Abderhalden continued this particular bit of his work by examinations via polarized light of the copper salts of optically active amino acids and their polypeptides.[31] Moreover his conclusion based upon this and further studies of absorption in the ultraviolet region by polypeptides,[32] is that when treated with alkali, amino acids assume an inner anhydride structure; whereas, in the case of polypeptides where the inner anhydride structure is improbable, no absorption is shown. Such studies were continued[33] and the absorption spectra for several aromatic amino acids and their derivatives were determined, among them, 3,5-diiodotyrosine anhydride.

Shibata[34] and Asahima in their investigations of desmotropy of dioxopiperazines prepared glycine anhydride, alanine anhydride, and sarcosine anhydride by heating the corresponding amino acids in glycerol according to Balbiano[35] and Maillard.[36] None of the compounds showed an absorption spectrum; hence the conclusion that they existed in the keto form only. There would appear to be a disagreement between these observations and those of Abderhalden and Haas.

Other interesting observations, capable of utilization for structural investigations of the dioxopiperazines are: 1) the refractive index of the enol

---

[29] Z. physiol. Chem., 153, 83 (1926).

[30] Z. physiol. Chem., 155, 202 (1926).

[31] Z. physiol. Chem., 164, 37 (1927).

[32] Z. physiol. Chem., 164, 1 (1927).

[33] Z. physiol. Chem., 166, 78 (1927).

form is found to be higher than the keto form;[34] 2) the optical rotation of solutions of dioxopiperazines decreases under the influence of x-rays and ultraviolet rays, while that of the corresponding peptides remains unchanged. The formation of ozone under irradiation may cause oxidation.

Abderhalden[37] and Schwab have evidence that the cleavage of enolic dioxopiperazines leads to unsaturated peptides. Glycyl-glycine prepared from enolic glycine anhydride behaves differently from that obtained from the keto form in that it decolorizes permanganate, gives the xanthoprotein reaction, no anhydride reaction, and dissolves in aqueous sodium hydroxide, giving solutions bright yellow in color. The color disappears upon heating. d,l-leucyl-glycine shows a similar behavior. The two forms of leucyl-glycine behave differently toward alkalies, the saturated form being unchanged while the unsaturated form is split quantitatively.

Anhydride rings such as glycyl-d-alanine, which may undergo cleavage due to action of alkali, are undoubtedly of use in enzymic digestion. Glycine-l-tyrosine anhydride, on the other hand, is rendered more susceptible to alkali cleavage by the action of enzymes. Abderhalden and Schnitzler[38] studied this by the formation of copper salts. Open chain structures with a —COOH group form copper salts immediately; otherwise the anhydride ring must be broken by an alkali before salt formation can occur. The change was detected by changes in rotation using a quartz-mercury lamp.

In the further preparation of diketopiperazines, an unsaturated anhydride from d-l-leucyl glycine anhydride is mentioned[39] although no comments are made concerning its structure. It is resistant to hydrolysis by normal alkalies, adds bromine, gives an intense red picric acid reaction, shows strong absorption in the ultraviolet, and hydrolyzes with dilute sulphuric acid to yield glycine, ammonia, and alpha-keto caproic acid. Another paper[40] indicated other combinations of diketopiperazine with amino acids, i.e. leucyl glycine anhydride with glycine anhydride gives a crystalline substance.

A still later report of Abderhalden and Mahn[41] concerning the action of alkali, acid, and enzymes on proteins, polypeptides and 2,5-diketopiperazines decides that acids and alkalies act in the same manner though at different velocities, their action alone furnishing no insight into the behavior of the diketopiperazine groupings which are probably present in these proteinoids.

According to Karrer,[42] the double bonds are not in the position assumed by Abderhalden and Schwab. Karrer states that the dibenzyl compound is derived from an enolic form for which he suggests the following formula:

---

[34] Bull. Chem. Soc. Japan, **1**, 71 (1926).

[35] Ber., **33**, 2323 (1900); **34**, 1501 (1901).

[36] Compt. rend., **153**, 1078 (1911); Ann. Chim., (9) **1**, 519, 2210 (1914).

[37] Z. physiol. Chem., **154**, 99 (1926).

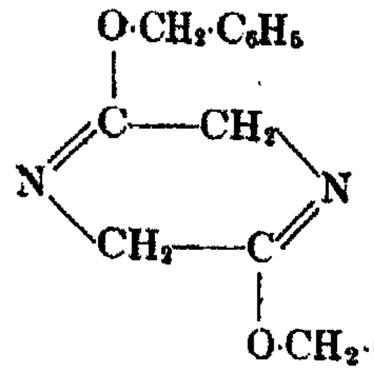
[38] Z. physiol. Chem., **164**, 159 (1927).

[39] Z. physiol. Chem., **163**, 149 (1927).

[40] Z. physiol. Chem., **164**, 274 (1927).

[41] Z. physiol. Chem., **174**, 47 (1928).

[42] Helv. Chim. Acta, **6**, 1108 (1923).



The enolic form, moreover, must possess a higher reactivity, since it was previously found that glycine anhydride must be heated with chloroacetyl chloride in the presence of nitrobenzene to 160° in order to effect substitution; and the dichloroacetyl compound results on heating the dibenzyl dioxopiperazine with chloroacetyl chloride on a water bath.

Maillard[43] in his study of compounds formed from glycine anhydride (2,5 diketopiperazine) states that 2,5 diketopiperazine does not possess a sufficiently basic character to form with acids, salts stable in the presence of water or alcohol. Fischer and Fourneau[44] have shown the same thing to be true. They showed that the "chlorhydrate of glycine anhydride" obtained by Th. Curtius and Fr. Goebel[45] by boiling the anhydride with concentrated hydrochloric acid and recrystallizing from alcohol is none other than the chlorhydrate of glycyl-glycine: $HCl{\cdot}NH_2{\cdot}CH_2{\cdot}CO\text{-}NH{\cdot}CH_2,COOH$. The action of the hot acid has broken down the ring structure of the piperazine. Maillard confirmed this work by repetition. Moreover, being interested in an investigation of crystalline compounds which would permit preparation and differentiation by microscopic observation, he sought to differentiate between the chloroplatinates of cyclo glycyl-glycine, glycyl-glycine, tri glycyl-glycine and glycine anhydride. All his efforts furnished exactly the same substance quite regardless of whether his initial reactant was cyclo glycyl-glycine or glycyl-glycine,—analysis indicating the following formula—$(HCl{\cdot}NH_2{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}COOH)_2\ Pt\ Cl_4{\cdot}2H_2O$. This substance is evidently identical with that described by Th. Curtius and Fr. Goebel to which they attributed the formula $(NH{\cdot}CH_2{\cdot}CO)_4(HCl)_2{\cdot}PtCl_4 + 3H_2O$.

When Maillard tried to prepare the chloroplatinate of 2,5-diketopiperazine, he states that the piperazine ring is opened at once as in the case of the chlorhydrate.

Another sidetrack was investigated by Zelinski and Gavrilov[46] in their work on the anhydride nature of the proteins. They find the proportion of glycine anhydride to vary in proteins, being highest in gelatin and lowest in sturine. Their method is to carry out acid hydrolysis by autoclaving dipeptides and anhydrides. Hydrolysis of aqueous solutions of dipeptides results in the formation of anhydrides which increases with the concentration of the dipeptide solution. Since the synthesis of anhydrides is inhibited by weak

---

[43] Ann. Chim., (9) 1, 542 (1914).

[44] Ber., 34, 2868 (1901).

[45] J. prakt. Chem., (N.F.) 37, 178 (1888).

[46] Biochem. Z., 182, 11 (1927).

acid and suppressed by 1 molar acid, their formation in autoclave hydrolysis appears impossible.

Goldschmidt and co-workers[47] report that upon treating diketopiperazines with hypobromic acid, no decomposition occurs in neutral solution, but only a normal bromination of the ring. Morel and Preceptis[48] find that picric acid hydrolyzes 2,5-diketopiperazine to glycyl-glycine; while Levene and co-workers[49] find the rate of hydrolysis of diketopiperazine much lower when a methyl group is substituted on the α carbon.

Yaichnikov[50] reports the hydrolysis of 2,5-diketopiperazines and dipeptides as monomolecular reactions, and Olander[51] finds the basic dissociation constant of diketopiperazines in 0.01 N NaOH too small to be measured electrometrically, and the acid dissociation constant to be 7×10^{-14}. Stiasny and Scotti,[52] in their study of the acid-alkali binding power of peptides, have run a series of titration curves to determine whether the peptide unions play a part in the acid and alkali binding power of peptides. They used glycine, and its mono, di, and tri homologues in order to have an increasing number of peptide unions along with one $—NH_2$ and one —COOH group. At the same time they ran glycine anhydride. Their results showed glycine to behave like a weak monacidic base and a weak monobasic acid. The addition of hydrochloric acid at first greatly diminished the pH value of its solution and then slowly decreased the pH value of the resulting buffer. After the addition of one equivalent of hydrochloric acid, the curve coincided with that of hydrochloric acid itself. The curve for glycine anhydride indicated that there was no acid binding and only a very slight binding of the alkali.

Another interesting sidelight upon the structure of the enol form of diketopiperazine is found in some work of Richardson, Welch, and Calvert.[53] They found that diketopiperazine did not condense with aromatic aldehydes upon fusion. The Perkin reaction (sodium acetate and acetic anhydride) seemed to be the only method to prepare derivatives of diketopiperazine without acetylation of amino nitrogen. Even so the reaction was not general; aliphatic aldehydes did not form simple 3,6 derivatives, and though generally applicable to the aromatic series, O-hydroxy-subaldehyde gives poor yields. By this reaction condensations of vanillin, cinnamaldehyde, piperonal, salicylaldehyde, tolualdehyde and O-chlorobenzaldehyde with glycine anhydride were effected. Diketopiperazine failed to condense with benzylidene aniline on fusion. Likewise, all attempts to condense diketopiperazine with substituted amidines have been unsuccessful. There would appear to be five possible enol forms:

---

[47] Ann., **456**, 1 (1927), Proteins IV.

[48] Compt. rend., **187**, 236 (1928).

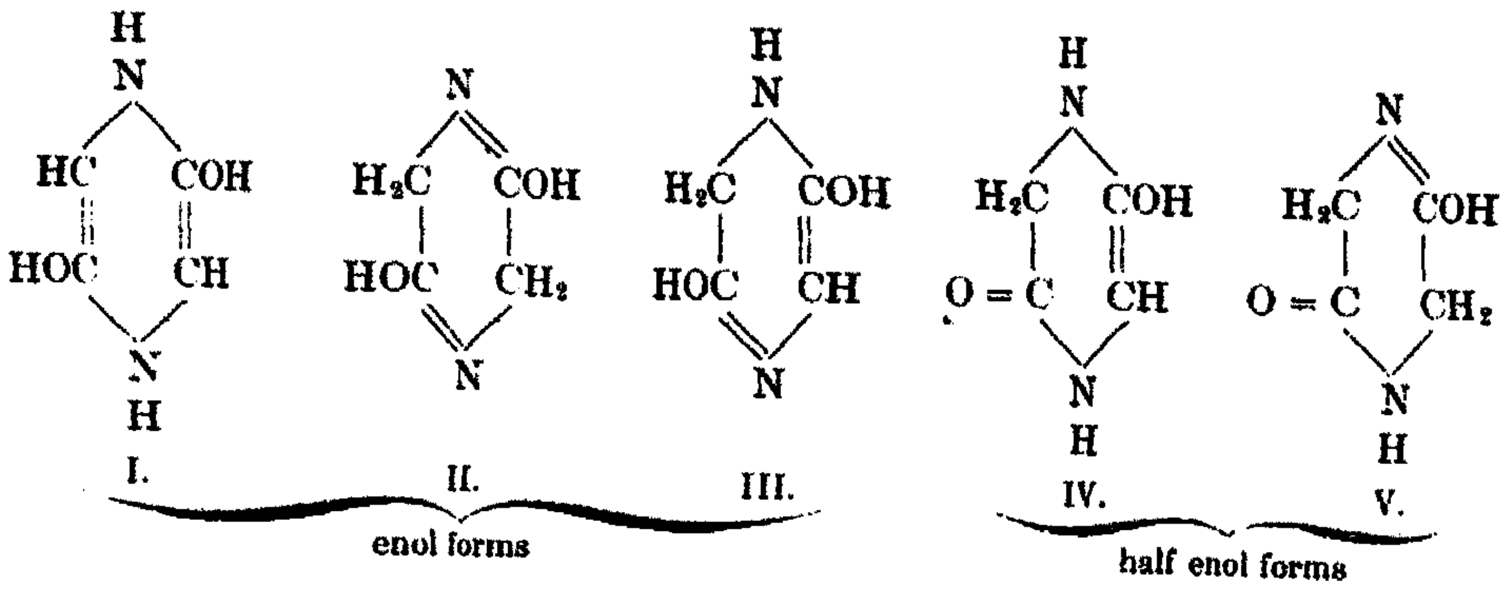
[49] J. Biol. Chem., **81**, 697 (1929).

[50] Biochem. Z., **190**, 114 (1927).

[51] Z. physiol. Chem., **134**, 381 (1928).

[52] Ber., **63B**, 2977 (1930).

[53] J. Am. Chem. Soc., **51**, 3074 (1929).


I. II. III. IV. V.

enol forms

half enol forms

The proof of the presence of hydroxyl groups in the enol form of diketopiperazine is based mainly upon color tests, i.e. positive xanthoproteic and a negative picric acid reaction. Definite confirmation of their presence is that two moles of α naphthyl isocyanate condense easily with one mole of diketopiperazine. Probably there is only one enol form present in appreciable quantity. Concerning the structure of that one we know that there are two hydroxy groups by its behaviour with isocyanate. In order to determine the predominant enol form, a condensation with m-nitrobenzaldehyde was tried.

If compound I—no condensation, therefore no $—CH_2—$ groups.

If compound II—condensation, with two aldehyde groups.

If compound III—condensation with one aldehyde group.

Upon condensation, the product showed a nitrogen content of 14.73%, an amount identical with that obtained from condensation of glycine anhydride and m-nitro benzaldehyde. If enol form (II) had resulted, the condensation product would have 11.70% nitrogen, and if enol form (III), 13.21% nitrogen.

The probable explanation seems to be that during the course of the reaction the isocyanate first hydrolyzed, forming enol-diketopiperazine, which reverted to a more stable keto form and then condensed with the aldehyde. One would expect (II) to condense without hydrolysis, but (I) must hydrolyze before condensing. Analysis showed that nearly complete hydrolysis has taken place, therefore (I) must be the ordinary form of diketopiperazine.

To confirm this, another condensation was made with tolualdehyde. The resulting compound has a nitrogen content of 8.81%, while the condensation product of the diketopiperazine derivative of α naphthyl isocyanate has 8.92%. Hence, the probability of —C = C— is supported, since α naphthyl isocyanate derivative condenses with aldehydes only after hydrolysis.

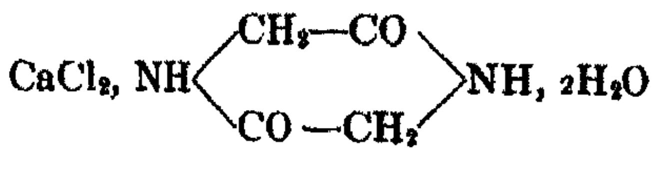
If one is justified in making deductions based upon researches into the polysaccharides, it can be assumed that associations of elementary complexes are present in the proteins. Although only a working hypothesis, the conception has seemed so convincing that the existence of specifically acting disaggregating enzymes was assumed by Oppenheimer.[54] Pepsin was relegated to the rôle of a non-hydrolyzing ferment whose disaggregating mechan-

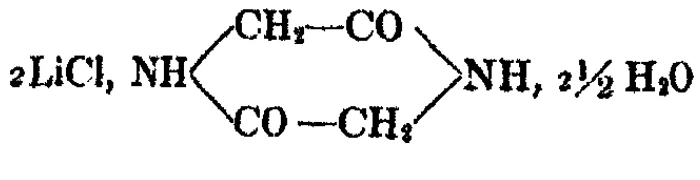
---

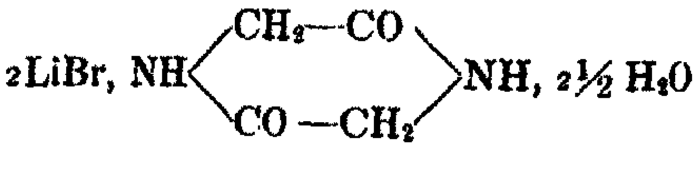
[54] "Die Fermente und ihre Wirkungen," 2, 811, 1208 (1926).

ism was to dissolve the subordinate valences which held together the elementary complexes. Delightful though this theory might be, it could not be corroborated by experiment.

Certain experiments have been adduced in favor of the existence of associated compounds. Pfeiffer and Wittka[55] showed that certain dioxopiperazines, among them glycine anhydride, are capable of forming molecular combinations with various salts, amino acids and organic compounds. The following are described as well-crystallized compounds:







Sarcosine compounds with sodium iodide, potassium bromide, potassium iodide and rubidium bromide were easily obtained, whereas Pfeiffer and Angern[56] found sarcosine anhydride to give molecular compounds with tryptophane, scatole, anthranilic and p-aminobenzoic acids.

Asahina and Tsurumatsu[57] have prepared other molecular compounds with heavy metals. By mixing hot solutions of glycine anhydride with salts of heavy metals, and evaporating to incipient crystallization, the following compounds were obtained in crystalline form: $C_4H_6N_2O_2 \cdot 2HgCl_2$, $C_4H_6N_2O_2$ $UO_2Cl_2 \cdot H_2O$, $C_4H_6N_2O_2$ $UO_2(NO_3)_2$, $C_4H_6N_2O_2$ $CdCl_2$. All of these are insoluble in organic solvents, but soluble in water with separation into their components. There are probably many formulations of these compounds, the metal in each case being linked directly with the nitrogen. There might be a possibility of breaking the double bond in case of the $—C = N—$ linkage, and this linkage might be ruled out since the compounds are soluble in water and later separate. In the case of the $—C = C—$ enol form, there could be simple addition to the nitrogen, which is what one might expect.

The anhydride linkage is referred to again by Speakman and Hirst[58] who claim that in the breaking down of the keratins, the anhydride linkage is broken before the disulphide bond is attacked.

Considering the abundance of interest, evidence, and work which the anhydride linkage excites, any contribution which may further elucidate the structure of its simplest building stone, glycine anhydride, should be of some value.

---

[55] Ber., **48**, 1292, 1306 (1915).

[56] Z. physiol. Chem., **143**, 265 (1925).

[57] Z. physiol. Chem., **186**, 133 (1929).

[58] Nature, **127**, 665 (1931).

A résumé of this work finds much evidence in favor of the diethylene formula for the enol form of glycine anhydride. All of Abderhalden's work, whether that of synthesis or analysis, oxidation or reduction or a study of absorption spectra indicates a preference for the $-C = C-$ configuration. The contributions of Goldschmidt, Richardson, Welch and Calvert are also in agreement. Shibata and Asahina apparently continue to prefer the diketo formula only.

Another point of agreement appears to be that glycine anhydride is incapable of reacting with acids without subsequent hydrolysis to form either glycine or glycyl glycine. The work of Maillard, Moreland and Levene is evidence, quite regardless of the titration curves submitted by Stiasny and Scotti.

Goldschmidt finds, however, that in neutral solution, glycine anhydride is brominated at points of unsaturation by hypobromic acid without decomposition, and Fischer finds the ring structure resistant to concentrated acids unless prolonged heating is used.

The work of Bancroft and Barnett in studying the behavior of protein and protein-like substances with ammonia and hydrogen chloride has done much to show the true nature of these weakly basic and weakly acidic substances. Because glycine anhydride presents a molecule containing two nitrogen atoms in conjunction with either two carbonyl groups for the diketo form or two ethylene groups, or just possibly the $-N = \overset{H}{\dot{C}}-$ configuration, for the enol forms, it seemed desirable to check its behavior with hydrogen chloride. The slightly basic character of the nitrogens would be quite covered if they existed in either the diketo or diethylene configuration in accordance with the deductions made by Bancroft and Barnett. If, however, glycine anhydride showed any inclination to form even an adsorption complex, there would still be the possibility for it to react with a more active acid which might make the most of these very weakly basic tendencies and so form compounds.

With this in mind, glycine anhydride has been studied in relation to hydrogen chloride, perchloric acid, sulphuric acid, and hydrofluoric acid. With the exception of hydrogen chloride, compounds have been prepared in each case. With hydrogen chloride, glycine anhydride forms an adsorption complex—although C. L. A. Schmidt of the University of California[59] may be able to construe even these data to show the formation of a real compound.

The behavior of glycine anhydride with hydrogen chloride was studied by means of a mechanism similar to the one used first by Bancroft and Barnett in their work on Phase Rule Studies on the Proteins.[60]

The apparatus used for these determinations is a modified form of the original, and is described in careful detail by B. C. Belden in his work on Gelatin with Ammonia and Hydrogen Chloride.[61] See Fig. 1. The discussion in that paper[61] regarding the behavior of samples at high and low gas pressures,

---

[59] J. Biol. Chem., 87, 327-335 (1930).

[60] J. Phys. Chem., 34, 449-498, 753-798, 1217-1253, 1930-1946, 2433-2471 (1930).

[61] J. Phys. Chem., 35, 2172 (1931).

impossibility of obtaining equilibrium points quickly, the tendency of apparatus to leakage, are very much to the point in this study with glycine anhydride as well as with gelatin.

Working at a fairly constant temperature (22°-24°C.), varying measured quantities of dry hydrogen chloride are added to a dry weighed sample of glycine anhydride. The apparatus having been carefully calibrated, the amount of gas in the apparatus is readily calculated from an observation of the pressure levels of the manometer. As the glycine anhydride combines with the dry hydrogen chloride the manometer levels change until such a time as an equilibrium point may have been reached. A further addition of dry hydrogen chloride will lead to the establishment of new equilibrium points. The theory of this apparatus operates upon Gibb's Phase Rule, $F+P=C+2$. We have two components, glycine anhydride and hydrogen chloride. If a compound is formed, we shall have three phases, namely, glycine anhydride, glycine anhydride hydrochloride and hydrogen chloride. We have used up our one degree of freedom, the temperature variable, and hence our system is defined. If, however, we are dealing with an adsorption complex, there will be only two phases and the system will have two variables, allowing a change of pressure with concentration of hydrogen chloride while the temperature remains constant.

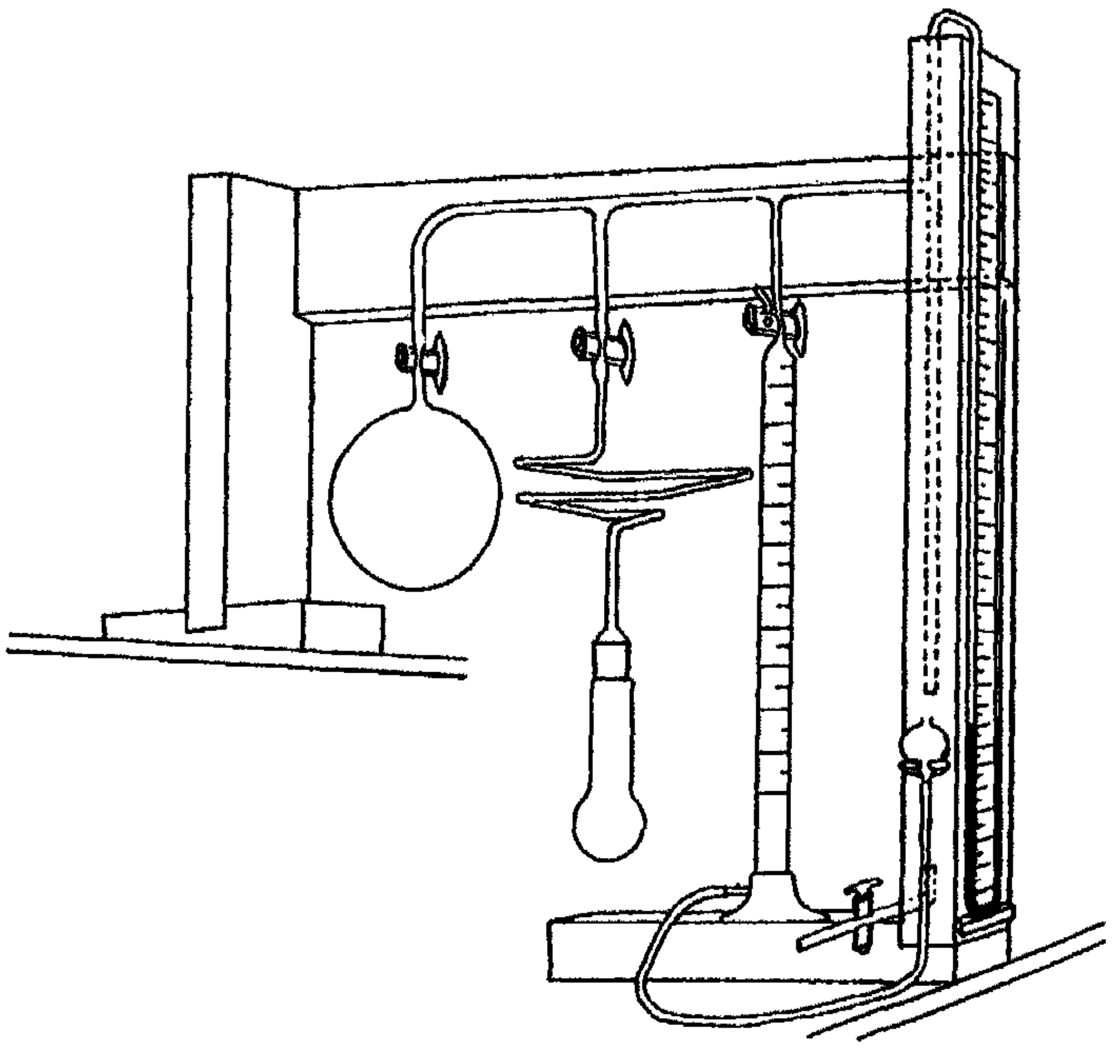


Fig. 1

The glycine anhydride used in the determination is a product of the Eastman Kodak Company. No effort was made to check the purity of the product as similar studies have shown that the presence of moderate amounts of water or other impurities tend to displace curves, although the type of curve obtained is not altered.[62]

The samples used were dried by standing in a desiccator over concentrated sulphuric acid and anhydrous sodium carbonate for at least a week. Sample 4 remained over concentrated sulphuric acid for several months before it was run. It will be noted that the points for this sample are in accord with the other data.

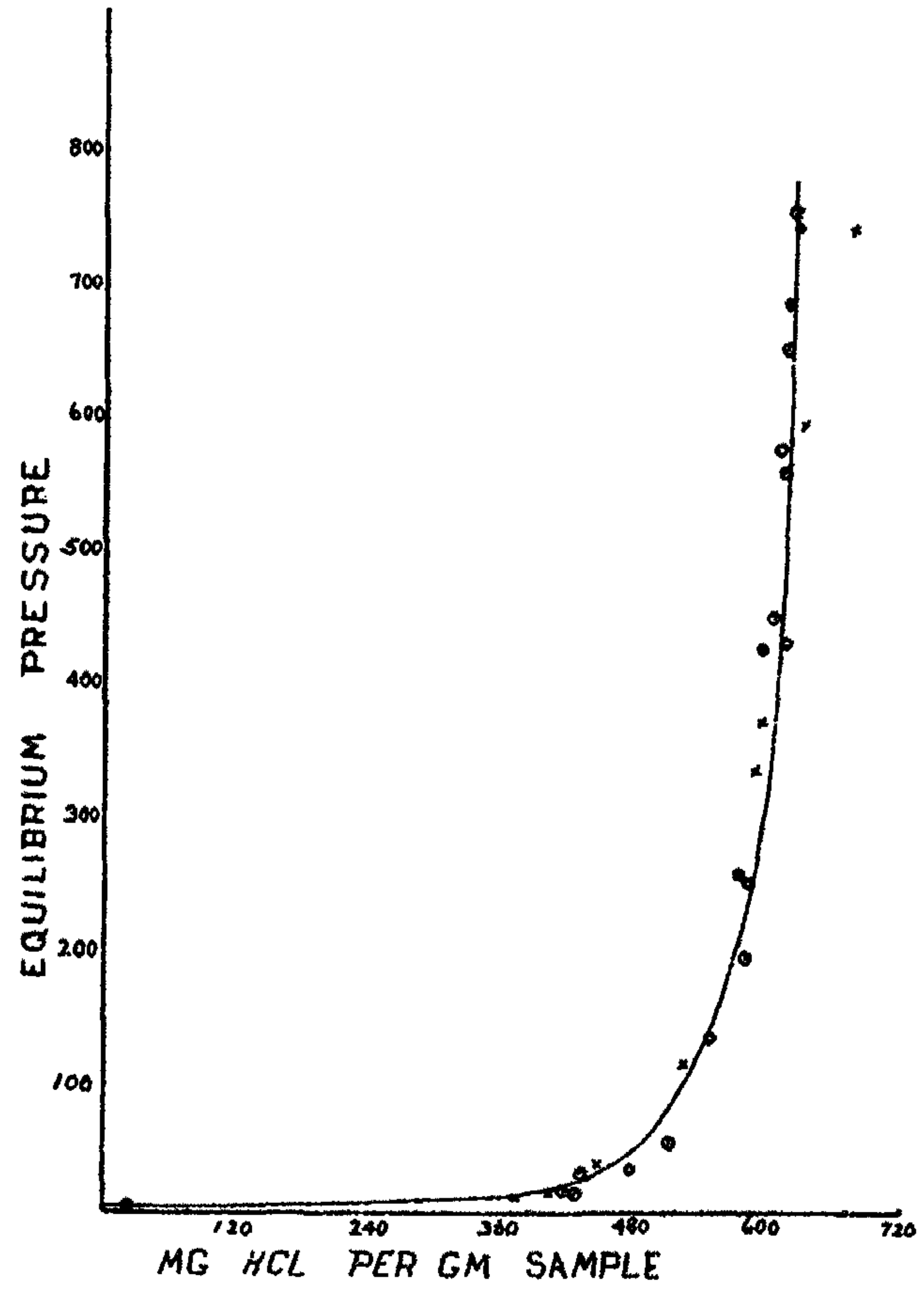


Fig. 2
Glycine Anhydride and Hydrogen Chloride
Sample 1 ● Sample 3 ○
Sample 2 × Sample 4 ⊙

Glycine anhydride, like some other compounds (gelatin and tribromaniline) appears to reach its equilibrium points more quickly when it is under a considerable gas pressure. Points determined from the up-curve of a substance

---

[62] J. Phys. Chem., 34, 491 (1930).

having a high initial adsorption, hence a low gas pressure, are likely to mean little. Months would be required to reach the true equilibrium points by this method. For this reason, a large volume of dry hydrogen chloride was added in each case, and then given volumes withdrawn, allowing the system to reach a new equilibrium point after each withdrawal

At a pressure of 750 mm. dry hydrogen chloride was taken up at a rate of 6 mm. per minute. The reaction flask was shaken, keeping the finely divided solid in motion and preventing any caking. In another case where the reaction flask was agitated only occasionally, the time required to reach an equilibrium point was four hours, with a change in manometer level amounting to 69 mm. or 0.29 mm. per minute. In general, equilibrium points were reached at high gas pressures within 10-15 minutes when the sample was agitated. Each equilibrium point was read only after the manometer had remained constant for several hours.

The data for four typical samples are found in Tables I, II, III, and IV, while the curve obtained by plotting equilibrium points against milligrams hydrogen chloride per gram sample are found to form a curve which can be recognized easily as that of an adsorption isotherm. See Fig. 2. The curve is smooth at junction with lowest pressures. There is, moreover, no reason to expect compound formation at this point. If glycine anhydride, molecular weight 114, combined with two moles of hydrogen chloride the ratio (73:114)

TABLE I

(1) Sample 0.604 gm. Dry

Volume HCl added cc.	Volume HCl removed cc.	Net vol. cc.	P_1 mm.	Volume remaining up cc.	Volume taken up cc.	Wt. HCl taken up mgm.	Wt. HCl taken up per gm. sample mgm.
546		546	736	312	234	384	636
	29	517	679	288	229	376	622
	177	400	420	178	222	364	603
	80	320	253	107	213	349	578

TABLE II

(2) Sample 0.508 gms. Dry

336		336	366	149	187	307	603
179		515	736	302	213	349	687
	76	439	588	240	199	327	642
	119	320	330	135	185	304	597
	108	212	110	47	165	271	532
	53	159	36	14	145	238	467
	22	137	15	7	130	208	408
	16	121	11	4	117	192	378

would be 640 mg. hydrogen chloride per gram glycine anhydride, or if for some reason only one of the nitrogens of glycine anhydride were active and a compound consisting of one mole glycine anhydride to one mole hydrogen chloride were formed, the ratio 36.5:114 would give 320 mg. hydrogen chloride per gram glycine anhydride. Inspection of the curve of Fig. 2 shows that nothing of the sort is indicated.

TABLE III

(3) Sample 0.574 gms. Dry

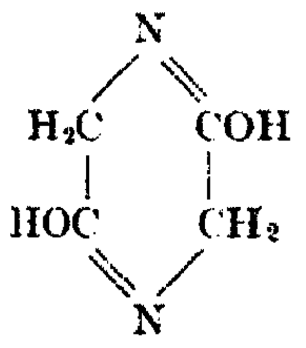
458		458	570	243	215	355	618
	60	398	434	180	218	357	623
	88	310	245	105	205	336	587
	56	254	130	57	197	323	564
	70	184	36	16	168	276	481
	30	154	16	7	147	241	421

TABLE IV

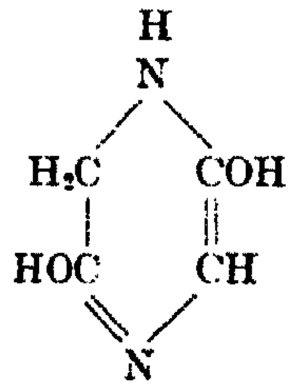
(4) Sample 0.915 gms. Dry

675		675	749	323	352	577	631
	50	625	645	277	348	571	624
	44	581	553	235	346	567	620
	49	532	445	190	342	561	613
	126	406	190	80	326	535	585
	92	314	52	20	294	482	527
	48	266	33	19	247	405	443
	15	251	12	6	245	402	438
	237	14	3.5	1.7	12.3	20.2	22

The diketo formula for glycine anhydride is not in keeping with its behavior with hydrogen chloride. The presence of any methylene groups surely would tend toward activating the glycine anhydride sufficiently to cause compound formation even though the methylene groups are adjacent to the carbonyl. Richardson's[33] enol forms (2) and (3) do not seem applicable, since they possess

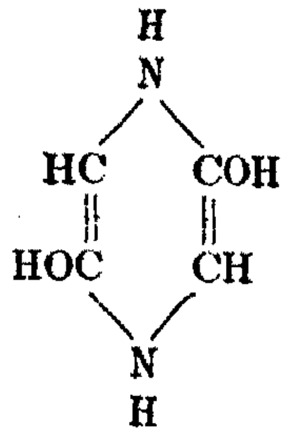


(2)



(3)

active methylene groups. Richardson's enol form (1)



however, contains no active methylene groups and the activity of the imino nitrogens is reduced by the adjacent ethylene linkages, thus giving a possible explanation for the formation of an adsorption complex rather than a true compound.

The basis for such reasoning, it may be recalled, appears in certain of the phase rule conclusions[60], namely that:

(1) Carbonyl groups attached directly to the nitrogen, or an aliphatic ethylene carbon linkage decrease the tendency of the nitrogen to react stoichiometrically with hydrogen chloride. (2) Two keto linkages or one keto and one ethylene linkage will destroy the tendency to add hydrogen chloride unless compensated by the presence of alkyl groups.

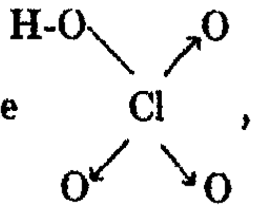
In the diketo form (p. 1803) each nitrogen is attached on the other side to a methylene group and the diketo form would therefore add two hydrogen chlorides. In enol forms (2) and (3) we have not even the partial effect of the keto group and the enol forms would also add two hydrogen chlorides. In Richardson's half enol form (IV) p. 1810, it is possible that the presence of one active methylene group would sufficiently activate the imino nitrogen so that the molecule could combine with one hydrogen chloride. His enol form (1) however, containing two ethylene linkages, and no carbonyl groups could not possibly combine with hydrogen chloride to form a compound. The existence of an adsorption complex is however in keeping with our theory.

Glycine Anhydride Hydrofluoride

The behavior of glycine anhydride with hydrogen chloride having been determined, interest was felt concerning any reaction with hydrofluoric acid. Anhydrous hydrofluoric acid is very soluble in water. At its boiling point, 19.4°C. it has a vapor density H_4F_4 although at 90° it is practically HF. In water solution there is no evidence of any molecule containing more than two fluorine atoms. According to Sidgwick,[63] the highest polymer must contain F-H←F-H with 2-covalent fluorine, but this is evidently unstable. In water, hydrofluoric acid occurs as the single or double molecules HF and H_2F_2 or their ions. It has been shown that while the polymerized form is a strong acid $H(F_2H)$ and is wholly ionized, the true dissociation constant of the simple HF is only 7×10^{-4},

---

[63] "The Electronic Theory of Valency," 270 (1927).

so that the weakness of hydrofluoric acid as compared with the other halogen acids is only partly explained by its polymerization. Sidgwick concludes, "whereas other halogen hydrides are practically completely ionized in H_2O, H_2F_2 is mainly covalent. This is a particularly surprising fact in view of the greater tendency of fluorine to ionization, which is established both practically and theoretically." In the hydrogen compound this is overcome by the unusual strength of its covalent link to hydrogen. The same theory accounts for the peculiar tendency of the fluoride ion to hydrate, i.e. F ion being negative, attaches itself to hydrogen of the water. Moreover, while fluorine itself has an unusually low covalency, it tends to bring out the highest covalences of other atoms with which it combines, i.e. $(F_2H)^{--}$, AsF_5, IF_5, SF_6, SeF_6 and OsF_8. The other halogens offer no analogues. The cause may very well be the small size of the fluorine atom, whereas other halogens readily assume covalency of more than one with greater ease as atomic number increases. Hence the very stable  , perchloric acid.

Preparation of Hydrofluorides

The methods of preparation used can conveniently be classified as follows:

A. Organic Method: Use of 48% hydrofluoric acid solution:

Crystalline glycine anhydride treated with 48% hydrofluoric acid solution (Sterling Chemicals or Baker's Analyzed) until just dissolved, then added in excess, placed in ice bath and the hydrofluoride precipitated with ether; filtered and dried between filter papers.

B. Reaction in Solution: Use of 48% hydrofluoric acid solution:

Crystalline glycine anhydride was treated with excess 48% hydrofluoric acid solution in paraffin-coated evaporators, placed in paraffined vacuum desiccators over stick sodium hydroxide and exhausted to 9 mm. The uncombined hydrofluoric acid was removed during the evacuation, leaving a dry solid in the evaporator. The amount of hydrofluoric acid which combines with glycine anhydride depends upon the length of time which the acid solution and glycine anhydride were in contact before drying in the desiccator.

C. Use of liquid hydrofluoric acid:

Since the boiling point of liquid anhydrous hydrofluoric acid (H_4F_4) is 19.4°C., it should be possible to prepare it as such from a salt working at a sufficiently low temperature; and thence by raising the temperature to bring the gaseous hydrogen fluoride (HF or H_2F_2) into direct contact with the basic substances in whose reaction we have interest.

With this in mind crystalline c.p. potassium acid fluoride was placed in a large platinum dish containing small platinum crucibles. The depths of the crucibles was considerably less than the depth of the platinum dish. The samples of finely divided bases, i.e. glycine anhydride, guanidine carbonate, etc., were placed in the crucibles, and the large platinum dish was surrounded by an ice-concentrated hydrogen chloride freezing mixture at – 15°C. A volume of concentrated sulphuric acid was brought to the same temperature, and gradually added to the KHF_2 surrounding the crucibles. At the low temperature the reaction proceeded slowly with a layer of a thin colorless liquid forming over the surface of the KHF_2. The dish was held at a temperature below 0°C. until a sufficient volume of cold concentrated sulphuric acid had been added to form twice the amount of hydrogen fluoride necessary to form the maximum compound possible between the base and the acid. The dish was then sealed by Pregl's wax with a large watch glass whose surface was protected by a thick coating of the same wax. The temperature of the bath surrounding the platinum dish was gradually raised through successive baths of cracked ice, and cold H_2O, until it had reached room temperature. Evidence of the progress of the reaction was had by noting the escape of hydrogen fluoride through a small vent made in the wax of the seal. From time to time the platinum dish was opened, some of the contents of the crucibles removed, the platinum dish recharged with KHF_2 and the experiment repeated. In this manner it was possible to judge when the maximum hydrofluoride possible with this method had been formed. Quantitative calculations of amounts of KHF_2 and concentrated c.p. sulphuric acid were made on the basis of the following reaction:

$$KHF_2 + H_2SO_4 = H_2F_2 + KHSO_4$$

Upon removing samples from the reaction vessel, they were placed over stick sodium hydroxide in paraffined vacuum desiccators. In the case of each sample note the times during which the sample was held in the reaction chamber, and kept in either evacuated or unevacuated desiccator.

Note: Theoretically it should be possible to use paraffined glassware for this preparation, but because of the tendency of paraffin to crack at low temperatures and to melt at temperatures above 35°C., platinum dishes were used.

Method of Analysis

Samples were weighed into small weighed pyrex beakers, dissolved or suspended in distilled water, and the hydrofluoric acid set free subsequent to hydrolysis, was titrated immediately with standard sodium hydroxide in the presence of phenolphthalein.

This method corresponds for the most part to the conventional volumetric method advocated by Treadwell and Hall.[64] They use platinum dishes coated with beeswax, add an excess of standard sodium hydroxide and titrate the excess of the latter with an acid of known strength.

Six samples from the same preparation of glycine anhydride hydrofluoride were treated in pairs as follows: a) exactly according to Treadwell and Hall method; b) using paraffined beakers and titrating directly with standard sodium hydroxide; c) using uncoated pyrex glass beakers and titrating directly with standard sodium hydroxide.

---

[64] "Analytical Chemistry," Vol. II, 7th Ed., p. 498.

The analyses in all three cases checked. Since the third method of procedure is a ready one and the phenolphthalein end-point is best recognized in glass, it has been used throughout the analyses. The Treadwell-Hall method is undoubtedly very desirable for samples containing a high concentration of hydrofluoric acid, and it does do away with the necessity of immediate titration; whereas the reasons for the success of the simpler method are undoubtedly: first, the fact that the hydrofluoric acid set free is titrated before it has a chance to attack the glass, and secondly, that the samples used are small and hence set free correspondingly small amounts of the hydrofluoric acid. The two factors are easily taken care of by titrating the samples immediately after weighing them.

Phenolphthalein appears to be a suitable indicator for the titration not only from the point of view of pH, but also because of the tendency of hydrofluoric acid to form acid salts by adding onto neutral salts normally set free in titration. This is another example of the tendency of hydrofluoric acid to bring out the maximum covalency of the substances with which it is in contact, i.e. $NaF \cdot HF$ and $BaF \cdot 2HF$. Characteristic reactions according to Winteler:[65]

$$2HF + NaOH \rightarrow NaF \cdot HF + H_2O$$

$$NaF \cdot HF + NaOH \rightarrow 2NaF + H_2O$$

The data presented in Tables V, VI, and VII and in Fig. 3 indicate something more than the formation of an adsorption complex between the glycine anhydride and hydrofluoric acid. The combination with mole portions of hydrofluoric acid rather than some fractional part can not be mere chance. The maximum compound formed by any method used successfully appears to be one corresponding to what one might have predicted from Sidgwick's discussion of hydrofluoric acid, namely that although fluorine itself has a particularly low covalency it tends to bring out the highest covalencies of the atoms with which it combines.

Data for:

Method A—Organic method using 48% hydrofluoric acid solution.

TABLE V

Samples	(1)	(2)
	0.2384	0.1568
cc. NaOH 0.2033 N required for titration	7.94	5.16
equivalence in grams of HF	0.0323	0.0210
% HF in sample	13.5%	13.4%
Mole equivalent to H	0.91	0.90

---

[65] Z. angew. Chem., 1902, 33.

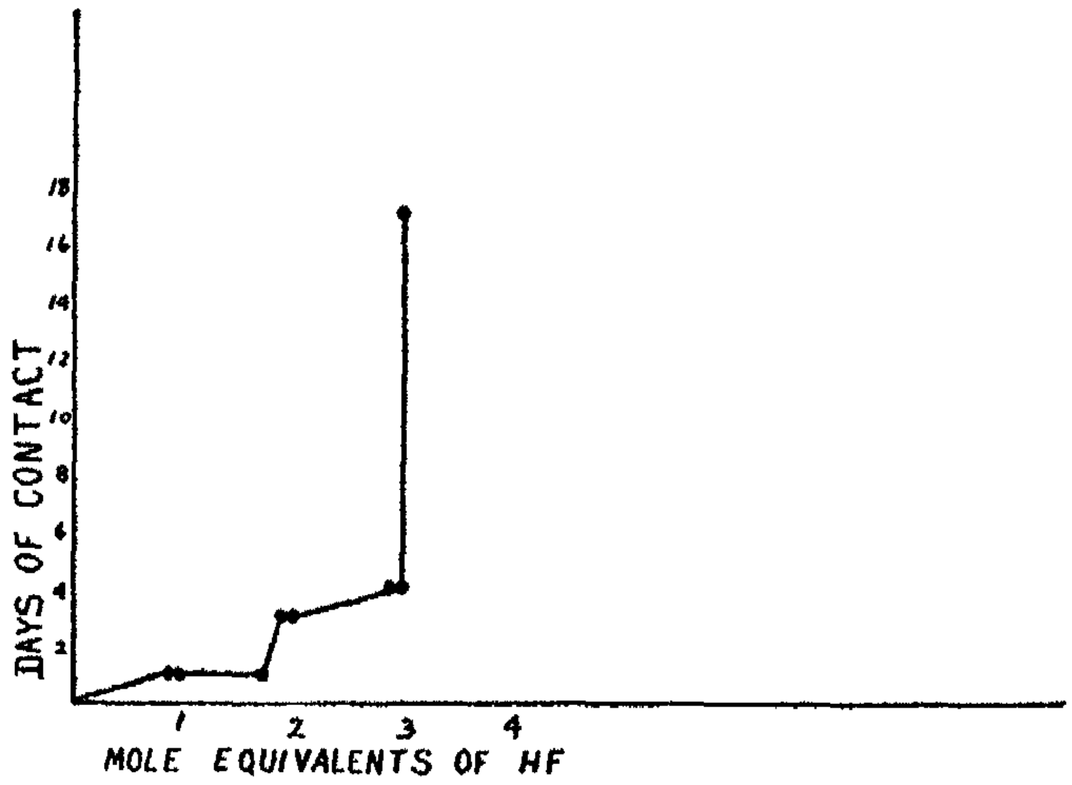


FIG. 3
Glycine Anhydride and Hydrofluoric Acid

TABLE VI

Data for: Method B—Use of 48% hydrofluoric acid solution.

History of samples:

Sample	(1)(2)(3)	(4)(5)	(6)(7)	(8)(9)
Contact time	1 day	3 days	4 days	17 days
Drying time	1 day	1 day	1 day	2 days

Appearance: dry white solid.

	Samples	cc. NaOH 0.1562 N needed for titration	Equivalence in grams of HF	% HF in sample	Mole equivalent to HF
	gm.	cc.	gm.	%	
(1)	0.2802	13.48	0.0421	15.0	1.01
(2)	0.2740	22.44	0.0702	25.6	1.97
(3)	0.3458	14.84	0.0464	13.4	0.90
(4)	0.1806	11.65*	0.0473	26.2	2.00
(5)	0.0776	4.76*	0.0194	25.0	1.92
(6)	0.3120	34.51	0.1180	34.5	3.00
(7)	0.2753	29.22	0.0916	33.2	2.88
(8)	0.1666	14.32*	0.0583	35.0	3.00
(9)	0.2233	18.77*	0.0765	34.2	2.97

* Used NaOH 0.2033N for titration
1 mole equivalent of HF = 14.9%
2 mole equivalent of HF = 26.0%
3 mole equivalent of HF = 34.5%
4 mole equivalent of HF = 41.2%

These data expressed graphically (see Fig. 3) indicate that the maximum combination with HF by this method is in the molecular ratio of 1:3.
Data for: Method C—Use of liquid anhydrous hydrofluoric acid.

Table VII

History: 4 days in reaction chamber.
Samples (1) and (2) held in unevacuated desiccator 2 days.
Samples (3) and (4) held in desiccator evacuated to 4 mm. 2 days.
Appearance: while, dry, friable, with strong odor of HF.

Samples	(1) 0.0997 g.	(2) 0.0781 g.	(3) 0.1423 g.	(4) 0.1422 g.
cc. NaOH 0.1206 N. needed for titration	17.03	12.33	22.99	21.88
Equivalence in grams of HF	0.0411	0.0298	0.0555	0.0530
% HF in sample	41.2	38.2	39.0	40.7

Average percentage of HF in samples: 39.8%
Mole equivalent in HF: 3.86.

These data correspond to the theoretical possibility of a compound between one mole of glycine anhydride and four moles of HF or two moles of H_2F_2, that is, to a maximum combination in the ratio of 114:80 or 41.3%. Furthermore, there appears to be little tendency for the hydrofluoride to decompose under reduced pressure conditions.

The behavior of glycine anhydride with hydrofluoric acid, reacting in simple molecular ratios, indicates that the anhydride must possess a somewhat more basic nature than the work of Stiasny and Scotti[66] would favor.

A consideration of the work done by Hofmann and his co-workers with perchloric acid, in which he obtained well-defined crystalline perchlorates, caused the present experimenter to hope for the formation of a perchlorate of glycine anhydride. In his extensive work, Hofmann[67] has prepared and analyzed, among others, such crystalline compounds as the perchlorates of fluorescein, diazo toluidin, diazonium aniline, pyridine, carbazol, phenanthrene and triphenyl amine. He[68] states in translated form: "Perchloric acid is

---

[66] Ber., 63B, 2977 (1930).

[67] Ber., 39 (3), 3146 (1906); 59 B, 448 (1926); 43 (1), 178, 183 (1910); 42 (2) 2031, 4856 (1909).

[68] Ber., 43 1080 (1910).

a convenient means of studying the basic characteristics of carbon and oxygen substances. Like no other acid, perchloric is able to turn to account the smallest amount of affinity of the chief and secondary valences for the formation of beautiful crystalline compounds. It surpasses in this respect, as we shall show by the examples of triphenylamine and tritolyamine, even picric acid, and is suitable, in most cases even better than that, for the separation of carbinols, ketones and amines from resinous admixtures. In general it is sufficient to treat the solutions in ether, benzene, tetrachlorethane, or carbon tetrachloride with seventy percent perchloric acid in order to obtain completely pure perchlorates. If the above-named liquids will not serve as solvents, one can use the concentrated acid itself as a solvent and filter off the crystals through clay, in which case resinous impurities stay in solution; or one can evaporate the acid in vacuum over phosphorus pentoxide or calcium oxide at ordinary temperatures. One obtains particularly beautiful crystals from an acetic acid solution mixed with perchloric acid when one concentrates this in a vacuum. Against the wide-spread opinion to the contrary, perchloric acid acts at room temperature, even up to 100°C., non-oxidizingly, and the handling of seventy percent perchloric acid is scarcely dangerous."

According to the data obtained with hydrofluoric acid, it should be possible for glycine anhydride to combine with perchloric acid in the ratio of 1:2; thus providing additional evidence for the existence of an enol form. If, however, the ratio proved to be 1:1 something might be said for the existence of glycine anhydride in one of Richardson's[69] half enol forms.

The perchloric acid used for the preparation was approximately 71.5% perchloric acid prepared from the concentrated commercial perchloric acid according to Hofmann's[70] directions by evaporating to 140°, and then distilling. Most of the distillate came over at 200°C, the boiling point of the dihydrate, and this solution, consisting of a mixture of the mono and dihydrate, approximately 71.5% perchloric acid, was used for the reaction.

Since glycine anhydride is insoluble in alcohol, acetic acid, chloroform and carbon tetrachloride as well as other common organic solvents, it was eventually treated in one of two ways; either Method A, by suspending it in absolute alcohol, adding the perchloric acid until solution had occurred, and placing in vacuum desiccator over P_2O_5 until a crystalline mass separated; or Method B, adding the acid directly to the crystalline glycine anhydride in sufficient excess to bring about solution, concentrating somewhat on hot plate; and finally placing in vacuum P_2O_5 desiccator until crystallization has occurred. Either procedure appeared to be successful and analyses from crystals prepared by each method tallied.

Small quantities of reagents were used, usually not more than one gram of glycine anhydride with always an excess of perchloric acid. Three or four

---

[69] J. Am. Chem. Soc., 51, 3074 (1929).

[70] Ber., 42, 4856 (1909).

days in the frequently evacuated desiccator passed before the separated crystals were filtered through sintered glass and dried on clay in a P_2O_5 desiccator.

Samples were weighed and titrated directly with standard sodium hydroxide using phenolphthalein as an indicator. Titration provides a sharp end-point.

It has been a matter of considerable interest to compare the method of procedure used in this work with that of Read and Campbell[71] in an analysis of similar compounds; for instance, diphenyl ethyl amine derivatives such as sulphonates and cyanides. In these cases the authors titrated first to an end-point with standard aqueous sodium hydroxide and then added alcohol or some inert organic solvent in which the salt liberated was soluble, and again titrated to an end-point. The alcohol acting as a solvent for the salt, thus removed any acidity or basicity due to its hydrolysis by decreasing or preventing its dissociation.

This procedure seems totally unnecessary and even somewhat in error if a proper selection of indicator has been made in the first place. Let us suppose for instance, that one is titrating the salt of a weak base and strong acid with sodium hydroxide. An indicator should be selected which will show an end-point somewhere in the 8-10 pH range; in other words, one which is sensitive to a slight excess of base. This end-point will represent the stoichiometrical end-point of the titration. If alcohol is added, assuming our salt to be soluble in it, the salt is removed, the effect of its hydrolysis is no longer felt and the titrated mixture again becomes colorless. More sodium hydroxide must be added to compensate for the removal of the weakly basic salt. This too, is an end-point, at pH 7, the point of true neutralization, but it is not the end-point representing the stoichiometrical relationship in which we are interested.

A microscopic examination of the crystals prepared by each method showed them to be colorless hexagonal prisms, optically anisotropic, with side views of prisms exhibiting parallel extinction. No confusion of these crystals with the fine needles of glycine anhydride would be likely.

The perchlorate melted sharply at 117° at 742 mm. on the Dennis-Shelton melting-point block.

One factor causing some difficulty in an otherwise simple procedure was that the perchlorate of glycine anhydride is an extremely deliquescent substance. First analyses made on samples weighed and titrated at the usual laboratory rate showed varying results; moreover, samples dried only a few days would show a difference in percentage of combined perchloric acid amounting to 7-8%, compared to samples taken from the same preparation and dried for a longer period.

The following data represent two series of analyses made on the same preparations from samples which were dried for different intervals.

---

[71] J. Chem. Soc., 1930, 2377, 2674.

Glycine Anhydride Perchlorate

TABLE VIII

Series I

Days dried before analyzing	13	14	15
Sample	0.2912 g.	0.1314 g.	0.1151 g.
cc. NaOH 0.1012 N required for titration	14.40	7.09	6.53
Equivalence g. $HClO_4$	0.1465	0.0721	0.0664
% $HClO_4$	50.3	55.0	57.7

Preparation was exhausted at this stage.

TABLE IX

Series II

Days dried before analyzing	13	26	27	28
Sample	0.1396	0.2336	0.2400	0.2398
cc. NaOH 0.1012 N required for titration	7.32	14.59	14.89	14.88
Equivalence g. $HClO_4$	0.0745	0.1483	0.1515	0.1515
% $HClO_4$	53.4	63.5	63.2	63.2

By a wiser disposition of the preparation analyzed in Series II the maximum time for drying was settled. It is possible that a month may be a longer time than is necessary for an equilibrium to be reached. No work was done to check that point.

The analyses for four typical samples of the perchlorate of glycine anhydride follows (Table X).

TABLE X

Method of Preparation	A	A	B	B
Drying time (days)	28	28	28	28
Sample	0.2429	0.2367	0.2435	0.2432
cc. NaOH 0.1012N needed for titration	15.10	14.78	15.23	15.29
Equivalence g. $HClO_4$	0.1539	0.1503	0.1550	0.1555
%$HClO_4$	63.4	63.5	63.7	63.8

A consideration of the possibilities of perchlorates which could be formed from glycine anhydride included the following:

		%$HClO^4$
(a) diperchlorate of glycine anhydride—Mol.Wt.	315	63.8
(b) monoperchlorate " " — " "	214.5	46.8
(c) glycine perchlorate " " — " "	175.5	57.3
(d) glycyl glycine perchlorate " — " "	232.5	43.2

The data obtained indicate only one of these, namely the diperchlorate of glycine anhydride.

If one were considering only the perchlorate data, either the diketo or diethylene formula for glycine anhydride would be suitable. Its behavior with hydrogen chloride rules out the keto formula because of the presence of the active methylene groups. The greater activity of perchloric acid, however, would easily account for compound formation with the imino nitrogen of the diethylene formula whereas hydrogen chloride might not be active enough. Such would appear to be the case. The behavior of glycine anhydride with concentrated sulphuric acid and hydrofluoric acid would also appear to be in harmony with the choice of the diethylene formula as the usual enol form.

The procedure used with concentrated sulphuric acid follows:

Glycine anhydride was treated with a large excess of concentrated sulphuric acid in a glass beaker. There was no evidence either of reaction or of solution. The mixture was poured onto a watch glass in a vacuum desiccator over phosphorus pentoxide and evacuated to 11 mm. On the following day, the soft white residue was transferred from the watch glass to a piece of porous plate and returned to the vacuum desiccator over phosphorous pentoxide. Its appearance on the following day was that of a white brittle substance, readily powdered. Upon standing, it combined greedily with moisture in the atmosphere.

Analysis: Samples were weighed rapidly and titrated with standard sodium hydroxide in the presence of phenolphthalein as an indicator.

The data for four typical samples follow representing two different preparations:

TABLE XI

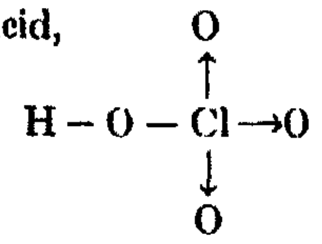
	(1)	(2)
Weight of sample (g.)	0.5741	0.5070
cc. NaOH 0.102 N required for titration	72.88	63.89
Equivalent gms. NaOH	0.2954	0.2585
Equivalent gms. H_2SO_4	0.3620	0.3170
% H_2SO_4 in sample	63.25	62.50

TABLE XII

	(3)	(4)
Weight of sample (g.)	0.1476	0.1568
cc. NaOH 0.2033 N required for titration	9.40	10.08
Equivalent gms. NaOH	0.0765	0.0807
Equivalent gms. H_2SO_4	0.0935	0.0988
% H_2SO_4 in sample	63.35	63.10

If one mole of glycine anhydride combines with one mole of sulphuric acid the molecular ratio would be 114:98, or a compound with 46.2% sulphuric acid; whereas if one postulates a one to two ratio, that is, 114:196, the percentage of sulphuric acid would be 63.25%. The data obtained from the analysis indicate the formation of a disulphate.

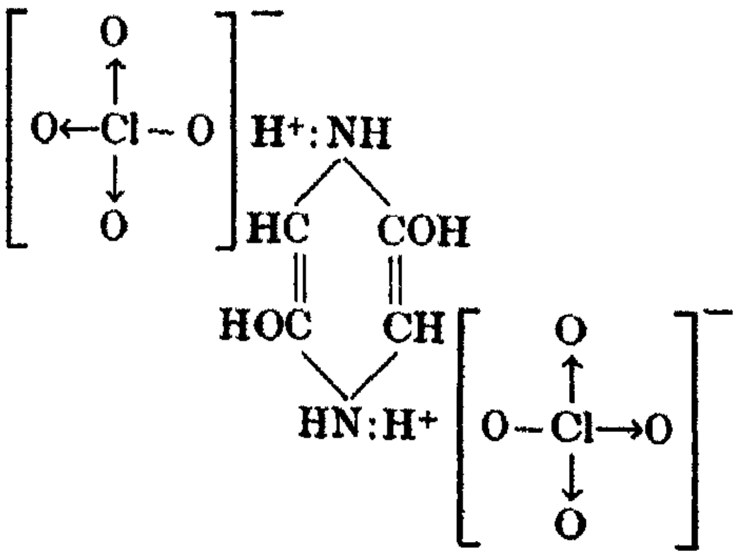
All results obtained serve as additional evidence for the diethylene enol form, a form already in excellent repute. The compounds reported in this paper are in accord with Sidgwick's theory of covalency.[1] Nitrogen has a maximum covalency of four with its fifth, an electrovalence. In the case of combination with perchloric acid,



$$H-O-\underset{\downarrow \atop O}{\overset{O \atop \uparrow}{Cl}}\rightarrow O$$

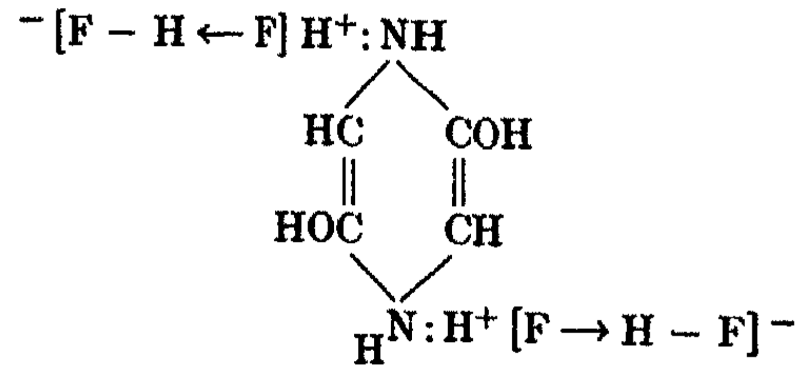
, Sidgwick's

formula, the imino nitrogens of glycine anhydride must share their two unused electrons with the hydrogen of perchloric acid. The configuration of glycine anhydride diperchlorate or better, the perchloric acid derivative of 2,5-dihydroxy diethylene piperazine is probably this:

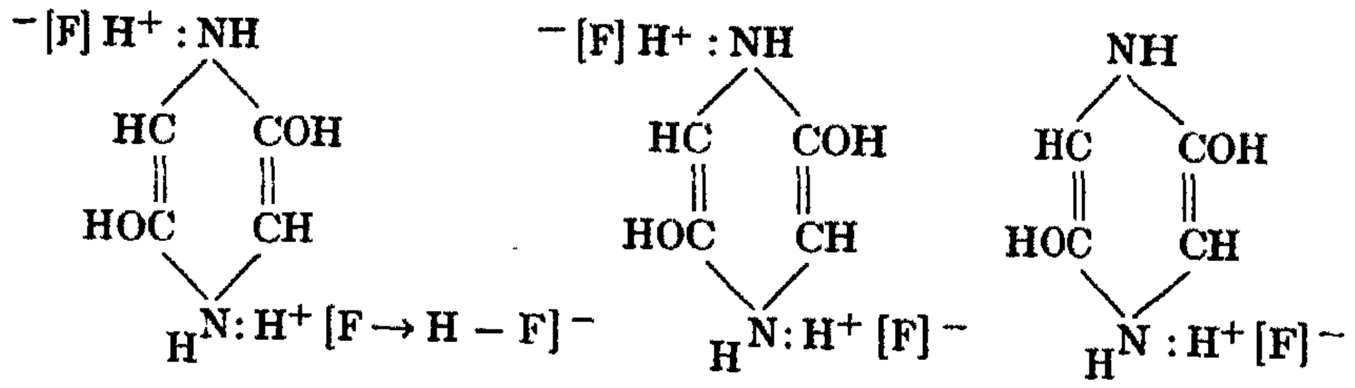


Since the maximum amount of hydrofluoric acid combining with one mole of glycine anhydride is four moles, and since there are only two nitrogens in each molecule of glycine anhydride, hydrofluoric acid must be existing in its polymerized form H_2F_2. This form, mainly covalent, is represented by the formula F – H←F – H←. Its highest compound with glycine anhydride

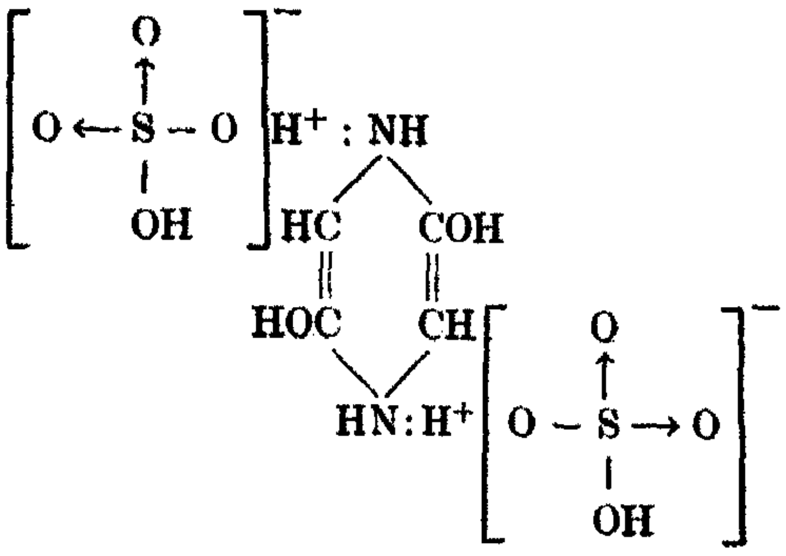
will be:



whereas the lesser combinations would be represented by:



The sulphuric acid derivative could be written in a similar manner, i.e.:



An application of the Phase Rule to the systems discussed in the preparation of the hydrofluoric acid, perchloric acid and sulphuric acid derivatives of glycine anhydride finds all except one to be three-component systems. In the preparation of the hydrofluoride by the use of liquid anhydrous hydrofluoric acid, Method C, we have a two-component system, namely glycine anhydride and hydrofluoric acid, or glycine anhydride hydrofluoride and glycine anhydride, or glycine anhydride hydrofluoride and hydrofluoric acid, existing in two phases, gas and solid. The Phase Rule[72] $F = C + 2 - P$, reading in this case, $F = 2 + 2 - 2$, or $F = 2$, limits the system to two degrees of freedom, a divariant system where the concentration is constant and the temperature may be varied.

In each of the other cases, the addition of an acid solution to glycine anhydride with the subsequent separation of the glycine anhydride derivative from solution, the systems are three component ones, existing in two phases having three variables, temperature, pressure, and concentration.

Summary

The principal points made in this paper are:

1. It would appear from this work that glycine anhydride has a somewhat greater acid-binding power than has been considered probable.

2. Glycine anhydride forms an adsorption complex with hydrogen chloride.

3. Glycine anhydride forms a series of compounds with hydrofluoric acid, the molecular ratio of combination depending upon time of contact and concentration of acid. The maximum compound is that formed by the combination of two moles of polymerized hydrofluoric acid (H_2F_2) with one mole of glycine anhydride.

4. With perchloric acid, a more active acid than hydrogen chloride, a crystalline perchlorate is formed having a composition which indicates the combination of one mole of glycine anhydride with two moles of perchloric acid.

---

[72] Findlay: "The Phase Rule and Its Applications."

5. Similarly with sulphuric acid, glycine anhydride is found to form a disulphate.

6. The compounds and adsorption complex studied in this paper present more evidence for the diethylene configuration of the enol form of glycine anhydride.

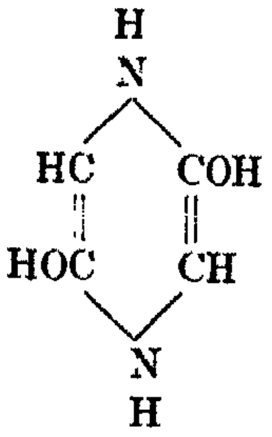
7. The possibility of preparing crystalline compounds with perchloric acid and very weakly basic nitrogen compounds has been indicated. More data concerning the formation of other crystalline perchlorates will appear in an early paper.

8. The ability of hydrofluoric acid to bring out the maximum covalency of the imino nitrogen of glycine anhydride has been used as a hypothesis for the formation of other hydrofluorides. An early report will supply more information.

9. The method of titrating a strong acid set free by the hydrolysis of a salt in the presence of a weakly basic substance using phenolphthalein as an indicator has been utilized throughout the analyses of the perchlorates, hydrofluorides and sulphates.

10. It is probable that the behavior of glycine anhydride may explain in part the behavior of zein which probably contains no $-\overset{H}{\dot{N}}-\overset{O}{\ddot{C}}-$ linkages.

Throughout this paper the name glycine anhydride has been conscientiously used. The experimenter preferred to show no structural preference, until sufficient experimental data had been collected to justify a choice. The evidence submitted here is construed in favor of 2,5-dihydroxy diethylene piperazine.:



Cornell University.

AN ANALYSIS OF THE ADSORPTION PHENOMENA WITH SILICA GEL AT LOW TEMPERATURES

BY WM. D. URRY[1]

(A). The Mercury Diffusion Pump as a Gas Collector

In dealing with very small quantities of gas it is often required to pump these gases from an apparatus of large volume and quantitatively collect them again at atmospheric pressure. Such a process has been described by Peters and Weil.[2] In principle the apparatus here described is similar. The introduction of an automatically operated "Toepler" and burette, however, warrants a description of the apparatus to be applied to the measurement of the adsorption of oxygen, methane, helium and argon on silica gel.

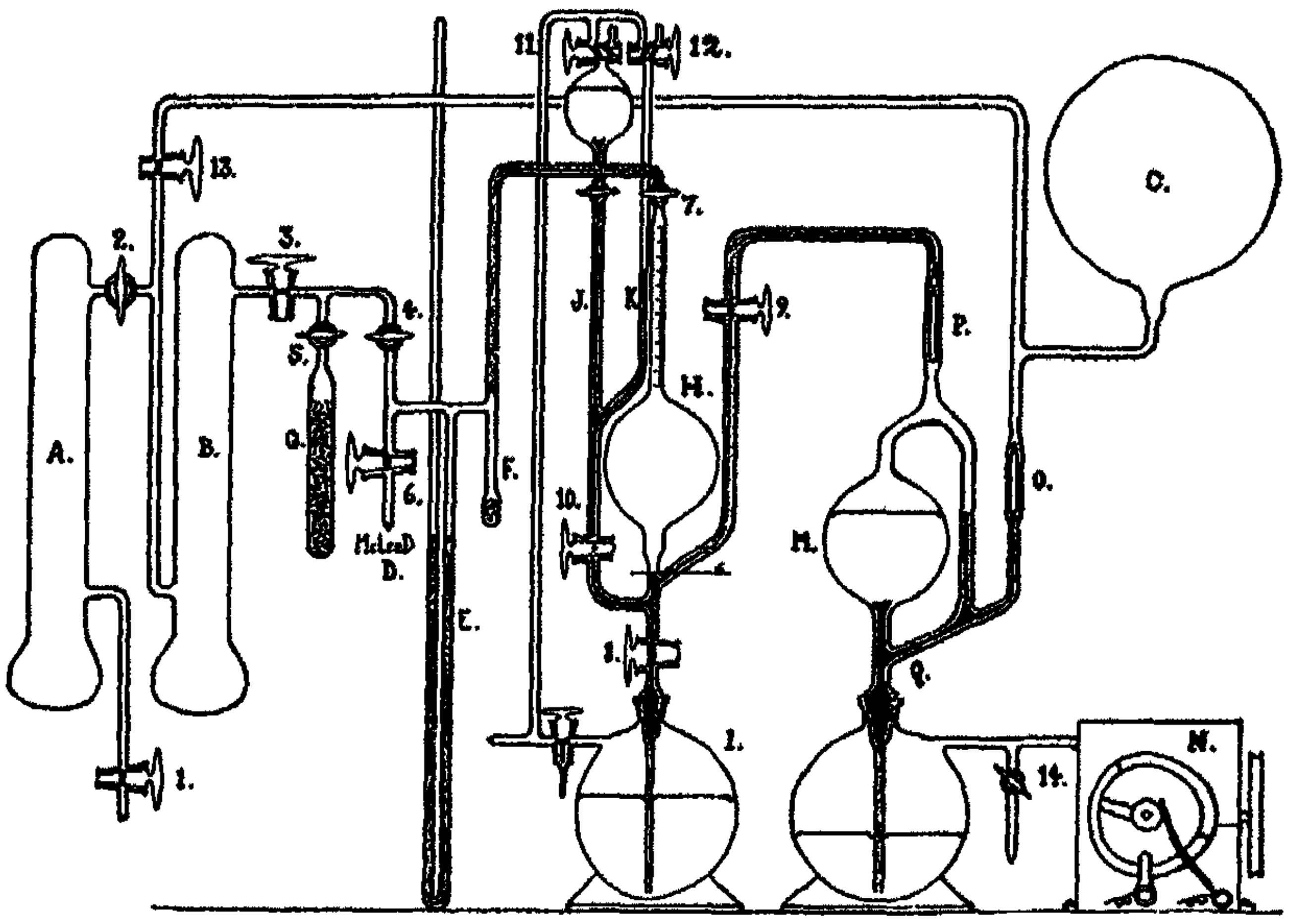


Fig. 1

Fig. 1 represents the apparatus diagrammatically, A and B being two mercury diffusion pumps in series with an oil pump shut off by stopcock 1. Stopcock 2 shuts off the second from the first diffusion pump. Stopcock 3 shuts off the adsorption apparatus which includes G, a charcoal tube for the purification of the gas in use, E, a carefully prepared manometer for pressures down to 3 mms. Hg., D, a McLeod gauge for pressures to 10^{-4} mm. Hg. with an intermediate arm for pressures between 0.1 and 3 mms. Hg. and F, a glass bulb containing 1.00 grm. of silica gel. The adsorption "Dead space" is therefore the volume between the stopcocks 4, 6 and 7 at pressures above 3 mms. and is maintained as

---

[1] Henry E. Johnston scholar at the Johns Hopkins University.

[2] Peters and Weil: Z. physik. Chem., 148 A, 1 (1930).

small as possible by the use of capillary wherever convenient.[1] For lower pressures 6 is opened and the "Dead space" includes the volume of the McLeod. At low pressures the "Dead space" factor is negligible. The low pressure side of the second pump is connected to a store C and also to an automatic Toepler M. By adjusting stopcock 14 to a certain leak and by means of a timing contact on the oil pump N, the mercury in M may be made to rise to the valves O and P and then fall back to some point Q at the rate of about a cycle per 50 seconds. In this process the gas in M is compressed into the capillary joining the Toepler to the burette H, through the capillary stopcock 9. The mercury in H is adjusted by stopcock 8 to a level just shutting off the capillary side-arm from the burette. The pressure increases as the mercury in M rises and the gas bubbles through this mercury into the burette. If H, however, were not of comparatively great volume, after several ccs. had been collected the pressure in H would be great enough to reverse the process when the mercury in M sinks, whereas if H is made large enough, on the mercury in M sinking in the second half of the Toepler cycle, the mercury in the capillary side-arm of H rises only a few millimetres. Supposing H has a volume of 360 ccs. and 12 ccs. of gas at 760 mms. are collected. A pressure of approximately 25 mms. exists in H and the mercury in the capillary will rise about 25 mms. above the level in H.[2] When the gas no longer bubbles through the mercury, the volume of the residual gas in the capillary, of total volume 0.2 cc. is therefore 0.006 cc., a negligible "Dead space" volume of gas. The mercury in the reservoir I can be raised or lowered by a three-way stopcock to the air and a separate vacuum pump. The mercury in J and K, J being an extra mercury reservoir and K the reading arm for the pressure of the gas in H, is manipulated in the same way by stopcocks 11 and 12. Stopcock 10 shuts off J and K whilst the collection is in progress. The burette tube of H is calibrated in 0.05 cc. units.

Modus operandi. The entire apparatus is flushed with electrolytic air free hydrogen and evacuated several times. The gas to be used in the adsorption experiments is adsorbed on G. Stopcock 2 is shut. The mercury is adjusted to the level a in the burette and the Toepler set in motion, stopcock 7 being shut. The gas in G is desorbed at the correct pressure and temperature and is pumped by B into C whence it is toeplered by M into H. For a second fractional desorption, 13 is shut, 2 is opened and the charcoal re-activated, 3 is then shut, 4 and 7 opened and the mercury in H raised to the stopcock 7 and the gas re-adsorbed in G. The desorption is repeated and the gas again collected in H. The silica gel is activated at 300°C for twenty-four hours and the entire apparatus except H again evacuated to 10^{-6} mm. Hg. Stopcocks 2, 4, 5 and 6 are then shut. The mercury in I is run up into H as far as possible and stopcock 8 shut. By adding mercury from J the gas is compressed until the level in H and K is the same. K being open to the atmosphere, the gas in H is under a known pressure—the barometric pressure.[3] The temperature of the burette is read and the volume reading in H. Stopcock 7 is then carefully opened and nearly all the gas run into the adsorption system. A second volume reading gives, by difference, the volume of the gas run into the adsorption system. The pressure in this system is read on E or if below three mms., stopcock 6 is opened and the pressure read by the McLeod D. Thus the first point on the adsorption curve is obtained. Stopcock 3 is opened carefully and a little gas pumped out. Meanwhile the mercury in H has again been lowered and this gas is toeplered into H and the new volume reading taken. The pressure in the adsorption system is measured and a second point obtained and so the process continues until all the gas admitted to the adsorption system is once again in H. The initial and final reading in H must therefore be the same. The greatest difference was less than 0.025 cc. in any run. Thus with such an apparatus it is possible to distribute a few ccs. of a gas throughout a large volume and to quantitatively re-collect exactly the same volume at any required pressure in H.

(B). The Adsorption on Silica Gel

Experiments carried out as described above show that the equilibrium is rapidly established when air is entirely excluded, both in adsorption and desorption runs. The two curves coincide. The same gel was used for all four gases and had a water content of 1.51%. The temperature of the adsorption was controlled by a thermostat consisting of two concentric Dewar flasks. The various constant temperatures were obtained by mixtures as given in the

---

[1] Capillary tubing may not be used to connect the adsorption chamber F on account of the Knudsen pressure effect at the break between the liquid air temperature and room temperature.

[2] The capillary depression and the pressure of the residual gas in the capillary make this value only approximate.

[3] The gas may also be measured under reduced pressure.

International Critical Tables I, or by a pentane bath cooled to the correct temperature by liquid air in a separate compartment. Wherever possible the bath contents were kept stirred. The temperature was controlled to 0.1°C by a copper-constantan thermocouple standardised against a certificated thermocouple.

The preparation of the gases. Oxygen was obtained by electrolysis in an air-free electrolyser.[1] The hydrogen was removed by combustion over palladium black at 300°C as described by Paneth and Peters[1]. The oxygen was adsorbed at 150°A in G and desorbed at 195°A into H. Methane was prepared from purified methyl magnesium bromide and water. The Grignard solution in ether was cooled to 190°A since the apparatus was completely evacuated, and air-free water slowly added. Any ether was frozen out in a trap and as the pressure increased the cooling bath for the Grignard reagent was removed. The methane was adsorbed in G at 90°A and desorbed at 170-180°A. Both argon and helium were obtained from bombs. Both gases were purified by passing through a calcium oven. The helium was left in contact with a charcoal immersed in liquid air whereupon all other gases were adsorbed and the helium pumped off and found to be spectroscopically pure and free from neon. The argon was adsorbed in G at 90°A and desorbed at 175°A and also tested spectroscopically in the capillary of the McLeod using an external electrode.

The cooling effect and the "Dead space" correction.
Let P = the equilibrium pressure in the *system.*
Let V be the total volume of the adsorption system less the volume of the gel. Let V_1 be the volume at the room temperature T_1°A and v the volume at the temperature T_2°A, of the thermostat surrounding F. Then:—

$$\frac{PV}{T_1} = \frac{PV_1}{T_1} + \frac{Pv}{T_2} \text{ and } V_1 = V - \left(v \times \frac{T_1}{T_2}\right) \qquad \text{(I)}$$

If however, F were at the same temperature as the rest of the apparatus we should have:—

$$V'_1 = V - v \qquad \text{(II)}$$

The cooling effect correction is therefore given by the factor V'_1/V_1, and the volume occupying the "Dead space" that is not adsorbed on the gel is given by:—

$$\frac{V'_1}{V_1} \times V \times \frac{P}{760} \times \frac{T_1}{273} \text{ ccs. at N.T.P.} \qquad \text{(III)}$$

V *must* itself be corrected slightly for each reading owing to the movement of the mercury in the manometer E., the arm of which must be previously calibrated.

Each burette reading is reduced to N.T.P. and subtracted from the initial burette reading giving the volume of gas in the adsorption system at N.T.P. By subtraction of the volume given by equation (III), which becomes negligible below 1 mm. Hg. pressure, the volume of gas at N.T.P. *adsorbed on the silica gel* at *the* equilibrium pressure P is obtained. The apparatus was so constructed that V and v could be measured by filling with mercury, withdrawing and weighing.

Table I gives the results on helium, argon, oxygen and methane, "a" being the volume at N.T.P., adsorbed. Fig. 2 shows the log-log isotherms for oxygen which are similar to those for methane, helium and argon. Above 137°A these log-log isotherms are straight lines as given by the Freundlich equation $a = kP^n$, k being the adsorption at 1 mm. pressure. Of particular interest is the fact that a distinct discontinuity occurs, as shown in Figs. 3 and 4, in the curves of n and k against absolute temperature, the latter better to be seen by plotting log k against T.

---

[1] Paneth and Peters: Heliumuntersuchungen. I, Z. physik. Chem., **134**, 353 (1928).

TABLE I

Helium. 89.86°A

P.	Log P.	a.	Log a.
216.0	2.3345	2.06	0.3139
169.5	2.2292	1.70	0.2304
110.0	2.0414	1.10	0.0414
79.5	1.9004	0.80	$\bar{1}$.9031
55.0	1.7404	0.55	$\bar{1}$.7404
28.0	1.4472	0.31	$\bar{1}$.4914

Argon. 194.53°A

P.	Log P.	a.	Log a.
193.0	2.2856	5.00	0.6990
88.5	1.9469	2.39	0.3784
64.5	1.8096	1.76	0.2455
55.5	1.7443	1.52	0.1818
38.0	1.5798	1.07	0.0294
25.0	1.3979	0.65	$\bar{1}$.8129
10.0	1.0000	0.27	$\bar{1}$.4314

Methane. 273.1°A

P.	Log P.	a.	Log a.
227.0	2.3560	3.10	0.4914
133.5	2.1255	1.89	0.2765
99.5	1.9978	1.37	0.1367
75.0	1.8751	1.04	0.0170
48.0	1.6812	0.67	$\bar{1}$.8261

Methane. 92.72°A

P. 10^3	Log P.	a.	Log a.
50.2	$\bar{2}$.7007	12.16	1.0849
2.5	$\bar{3}$.3979	7.58	0.8797
1.45	$\bar{3}$.1614	6.03	0.7803
0.45	$\bar{4}$.6532	3.03	0.4814
51.0	$\bar{2}$.7076	10.77	1.0322
4.0	$\bar{3}$.6021	8.95	0.9518
1.51	$\bar{3}$.1790	6.42	0.8075
50.2	$\bar{2}$.7007	9.60	0.9823
20.0	$\bar{2}$.3010	11.59	1 0641
4.0	$\bar{3}$.6021	9.91	0.9961
5.0	$\bar{3}$.6990	10.27	1.0116
2.05	$\bar{3}$.3118	8.05	0.9058
1.05	$\bar{3}$.0212	4.90	0.6902
0.50	$\bar{4}$.6990	3.32	0.5211

Argon. 255.74°A

P.	Log P.	a.	Log a.
186.5	2.2768	1.87	0.2718
142.5	2.1538	1.46	0.1644
92.0	1.9638	1.00	0.0000
80.0	1.9031	0.82	$\bar{1}$.9138
57.0	1.7559	0.60	$\bar{1}$.7782
38.5	1.5855	0.34	$\bar{1}$.5315
20.0	1.3010	0.22	$\bar{1}$.3424
8.0	0.9031	0.08	$\bar{2}$.9031

Argon. 152.97°A

P.	Log P.	a.	Log a.
46.5	1.6675	7.08	0.8500
35.5	1.5502	5.90	0.7709
28.0	1.4472	4.85	0.6857
18.0	1.2553	3.77	0.5763
14.0	1.1461	2.74	0.4378
8.5	0.9294	1.86	0.2695
4.3	0.6334	1.02	0.0086
1.4	0.1461	0.42	$\bar{1}$.6232

Methane. 194.53°A

P.	Log P.	a.	Log a.
104.5	2.0191	9.60	0.9826
91.0	1.9590	8.34	0.9212
72.5	1.8603	7.11	0.8519
59.5	1.7745	6.13	0.7875
44.5	1.6484	4.93	0.6920
29.5	1.4698	3.53	0.5478
19.5	1.2900	2.44	0.3874
8.8	0.9445	1.16	0.0644
3.0	0.4771	0.51	$\bar{1}$.7076

Methane. 173.94°A

P.	Log P.	a.	Log a.
42.0	1.6232	11,00	1.0414
34.0	1.5315	9.57	0.9809
32.0	1.5052	9.08	0.9580
29.0	1.4624	8.47	0.9279
20.5	1.3118	6.83	0.8344
10.0	1.0000	3.80	0.5798
4.0	0.6021	2.26	0.3541
0.17	$\bar{1}$.2405	0.26	$\bar{1}$.4150

TABLE I (Continued)

Oxygen. 273.1°A

P.	Log P.	a.	Log a.
195.0	2.2900	2.02	0.3045
89.0	1.9494	0.91	$\bar{1}.9600$
34.0	1.5315	0.33	$\bar{1}.5162$
15.0	1.1761	0.18	$\bar{1}.2553$

Oxygen. 219.80°A

P.	Log P.	a.	Log a.
230.0	2.3617	3.81	0.5803
99.0	1.9956	1.68	0.2253
40.0	1.6021	0.66	$\bar{1}.8196$
18.5	1.2672	0.29	$\bar{1}.4594$

Oxygen. 181.37°A

P.	Log P.	a.	Log a.
159.5	2.2028	6.91	0.8396
96.5	1.9845	4.62	0.6647
59.5	1.7745	3.05	0.4840
32.5	1.5119	1.72	0.2345
9.0	0.9542	0.54	$\bar{1}.7324$

Oxygen. 160.68°A

P.	Log P.	a.	Log a.
86.0	1.9345	9.92	0.9967
60.0	1.7782	7.56	0.8785
24.0	1.3802	3.94	0.5951

Oxygen. 137.00°A

P.	Log P.	a.	Log a.
19.0	1.2788	12.51	1.0971
14.0	1.1461	10.89	1.0368
11.0	1.0414	9.11	0.9594
4.25	0.6284	5.22	0.7177
1.8	0.2552	3.25	0.5122

Oxygen. 254.37°A

P.	Log P.	a.	Log a.
260.0	2.4150	3.15	0.4983
145.5	2.1614	1.70	0.2304
79.0	1.8976	0.98	$\bar{1}.9934$
50.0	1.6990	0.61	$\bar{1}.7853$
29.0	1.4624	0.31	$\bar{1}.4914$
13.0	1.1139	0.16	$\bar{1}.2041$

Oxygen. 195.85°A

P.	Log P.	a.	Log a.
147.0	2.1673	3.51	0.5453
147.0	2.1673	3.37	0.5276
128.0	2.1072	3.10	0.4914
122.0	2.0864	3.00	0.4771
98.5	1.9934	2.50	0.3979
88.5	1.9469	2.21	0.3444
70.0	1.8450	1.66	0.2201
57.5	1.7597	1.41	0.1492
49.0	1.6902	1.14	0.0569
25.0	1.3979	0.61	$\bar{1}.7853$
10.0	1.0000	0.25	$\bar{1}.3979$
6.0	0.7782	0.15	$\bar{1}.1761$

Oxygen. 148.41°A

P.	Log P.	a.	Log a.
46.0	1.6628	11.41	1.0574
25.0	1.3989	7.45	0.8723
9.0	0.9542	3.95	0.5964

Oxygen. 92.14°A

P. 10^2.	Log P.	a.	Log a.
1.05	$\bar{2}.0212$	3.47	0.5403
1.90	$\bar{2}.2788$	5.26	0.7209
3.50	$\bar{2}.5440$	7.19	0.8567
7.59	$\bar{2}.8802$	10.54	1.0228
23.5	$\bar{1}.3710$	20.61	1.3141

To definitely establish this break the adsorption of oxygen was measured at as many temperatures between 90°A and 273°A as possible. The temperature at which this discontinuity occurs is on the average 38° above the critical temperature of the gas adsorbed in the case of oxygen, methane and argon. In Fig. 4 the values of k for argon on charcoal from the work of Peters and

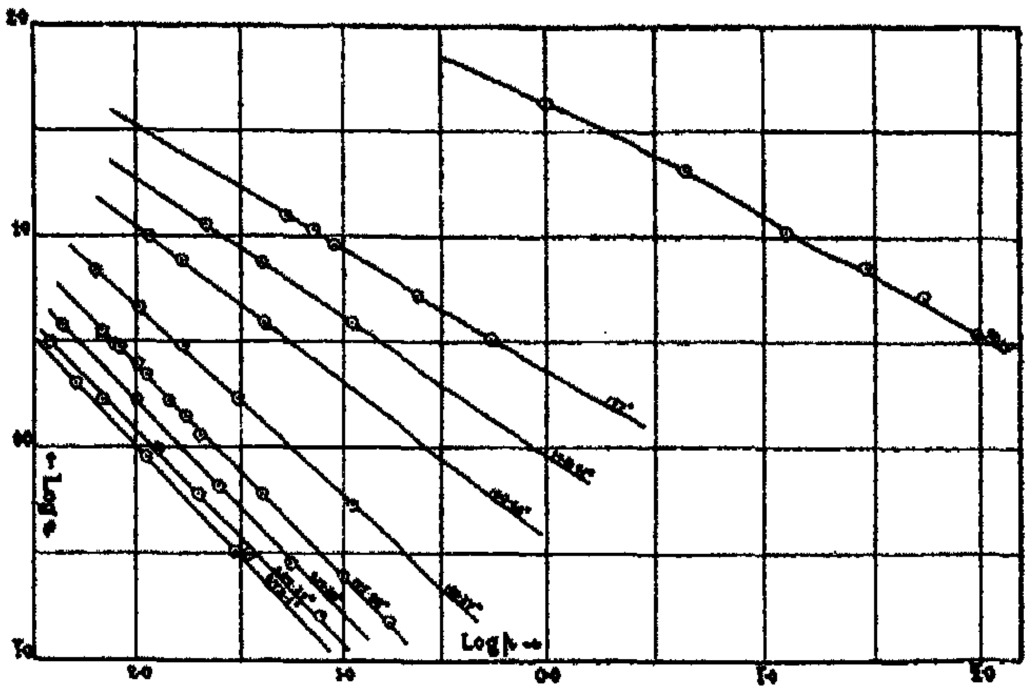


Fig. 2
The log-log adsorption isotherms of oxygen

Weil[1] are also plotted. Above the break n = 1 and a = kP, k varying but little with temperature. Thus above and below the break two very different processes of adsorption must occur. The adsorption on silica gel has been studied comprehensively by Patrick[2] and his collaborators with a view to establishing the theory of capillary condensation. Patrick, Preston and Owens brought forward evidence to show qualitatively that the critical temperature of a gas is raised in the pores of an adsorbent. Since the phenomena described above must be connected with the critical temperature, the theory

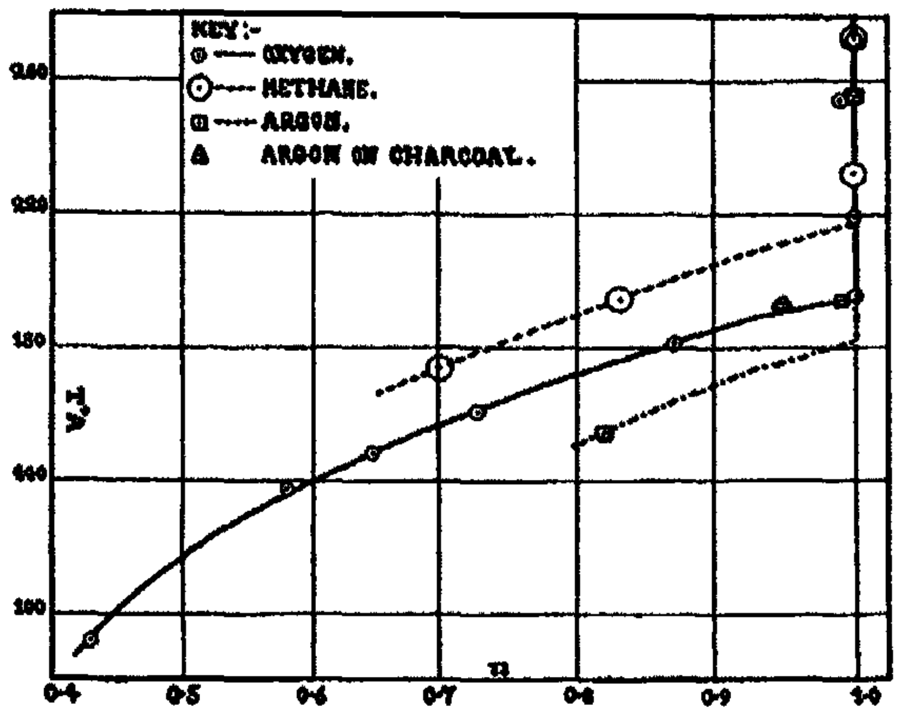


Fig. 3
Variation of n with temperature

---

[1] Peters and Weil: Loc. cit.

[2] Davidheiser and Patrick: J. Am. Chem. Soc., 44, 1 (1922); Patrick and Long: J. Phys. Chem., 29, 336 ; Patrick, Preston and Owens: 421 (1925).

of Patrick will be applied to the results below the discontinuity. Above the true critical temperature capillary condensation cannot be considered as a process in adsorption.

If V is the volume of liquified gas adsorbed per grm. of gel, P the equilibrium pressure as measured and P_o the vapor pressure of the gas adsorbed at the temperature of the adsorption, σ being the surface tension, then the experimental work of Patrick's collaborators has shown that the empirical equation derived from considerations of capillary condensation is verified. Moreover the equation should be independent of temperature and the constants K and m dependent only on the gel in use.

$$V = K\,(P\sigma/P_o)^m \tag{IV}$$

The value of σ for a plane surface is obtained from the equation

$$\sigma\,(M/d_l)^{2/3} = 2.1(T_c - T - 6) \tag{V}$$

where M = the molecular weight of the gas and d_l the density in the liquid state at the temperature T.

The values of d_l and T_c and P_o have been taken from the International Critical Tables and are collected in Table II for convenience.

TABLE II

Temp. °A.	d_l.	P_o Atmos.	Log σ/P_o.
		Oxygen	
92.14	1.130	1.02	1.0959
137.0	0.840	24.0	$\bar{2}$.9403
140.0	0.820	27.8	$\bar{2}$.7354
145.0	0.763	34.6	$\bar{2}$.2172
150.0	0.685	42.2	—
154.28 = Tc.			
		Methane	
173.94	0.305	26.2	$\bar{2}$.8011
191.00 = Tc.	—	—	—
		Argon	
130.0	1.053	20.0	$\bar{1}$.1341
150.66 = Tc.	—	—	—
		Helium	
5.19 = Tc.			

If d_g is the density of the gas at N.T.P. then; $V = ad_g/d_l$ (VI)

For fixed values of V the values of "a" can therefore be calculated at various temperatures and from the log a − log P curves the values of log P and hence of log $\sigma P/P_o$ found.

From equation (IV) it is seen that the plot of log V against log $(\sigma P/P_o)$ should be one and the same straight line independent of temperature and the particular gas adsorbed. Straight lines are obtained which, however, do not coincide for various temperatures although parallel to one another. This was found to be the case with CO_2 and N_2O in the neighbourhood of the critical temperatures by Patrick, Preston and Owens.[1] It has been accounted for by the above authors by a consideration of an increase in the surface tension in

---

[1] Patrick, Preston and Owens: Loc. cit.

capillaries and consequently a raising of the temperature at which $\sigma = 0$, therefore a raising of the critical temperature. Thus they concluded that at 40°C or 9° above Tc for CO_2, capillary condensation takes place.

The relation between σ and the lowering of the vapor pressure in a capillary is given by the Kelvin equation:

$$\mathrm{Ln}\,\frac{P_o}{P} = \frac{2\sigma M}{r d_l R T} \qquad \text{(VII)}$$

r being the radius of the capillary, the other symbols as in equations (IV) and (V). If now σ be known at a temperature far enough removed from the critical temperature not to be effected by capillary considerations, values of r may be obtained by substituting in values of Ln P_o/P corresponding to values of V, and the appropriate values of M, d_l, and T. That r is dependent on V is due to the conical shape of the pores. Now on taking the corresponding value of Ln P_o/P and r as found above, for a given value of V at other temperatures, the value of σ in the capillaries of the adsorbent is computed.

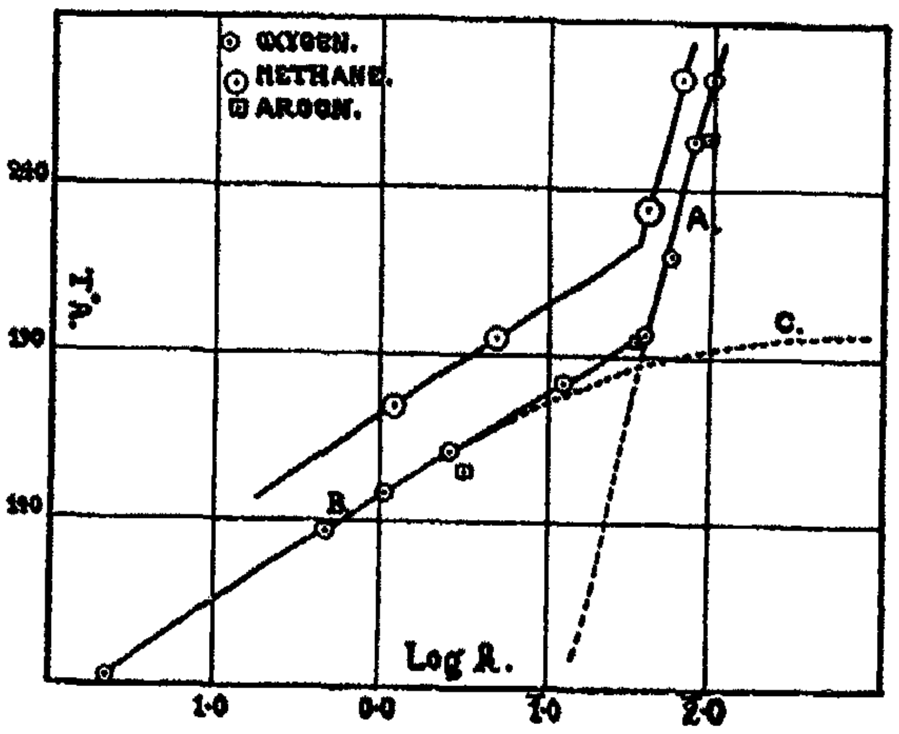


FIG. 4
The variation of log k with temperature

Using the values so computed in deriving log $(\sigma P/P_o)$ Patrick, Preston and Owens[1] found that for CO_2 and N_2O all values of this expression at various temperatures for varying volumes V lay approximately on the same straight line. A similar method of treatment was applied here to the adsorption of oxygen, r being computed from the values of Ln P_o/P at 92.14°A or 2.04° above the boiling point. The surface tension for different values of V at 137°, 140°, 145° and 150°A was then determined from the Kelvin equation. The values of σ required to make the corresponding values of log $(\sigma P/P_o)$ at these various temperatures lie on the straight line of log V against log $(\sigma P/P_o)$ at 92.14°A, where it is assumed σ has still the value of the surface tension in a plane surface, were determined and compared. If the departure from the condition that equation (IV) is independent of temperature, is entirely due to the change in surface tension on altering the surface shape, then corresponding values of σ must be the same on comparison. Such was not the case. One fact

---

[1] Patrick, Preston and Owens: Loc. cit.

TABLE III

T°A	P = 1.0 mm.				P = 5.0 mms.			
	a.	a′.	a_0.	Log a_0	a.	a′.	a_0.	Log a_0
195.85	0.0309	0.0309	0.000	—	0.126	0.118	0.080	$\bar{2}.9031$
181.37	0.0794	0.0282	0.051	$\bar{2}.710$	0.324	0.138	0.186	$\bar{1}.2686$
160.68	0.3802	0.0363	0.344	$\bar{1}.540$	1.202	0.178	1.024	0.0103
148.41	0.9441	0.0427	0.901	$\bar{1}.955$	2.692	0.200	2.492	0.3965
137.00	2.2647	0.0490	2.216	0.346	5.755	0.229	5.526	0.7424
92.14	42.658	0.0831	42.575	—		negligible alteration.		
		P = 10.0 mms.				P = 50.0 mms.		
195.85	0.251	0.229	0.022	$\bar{2}.3424$	1.230	1.135	0.095	$\bar{2}.9777$
181.37	0.603	0.275	0.328	$\bar{1}.5159$	2.512	1.380	1.132	0.5380
160.68	1.995	0.355	1.640	0.2148	6.607	1.738	4.869	0.6874
148.41	4.169	0.407	3.762	0.5754	11.750	2.000	9.750	0.9890
137.00	8.710	0.468	8.242	0.9160	21.880	2.371	19.509	1.2902
92.14		negligible alteration.				negligible alteration.		
		P = 100.0 mms						
195.85	2.455	2.291	0.164	$\bar{1}.2148$				
181.37	4.678	2.754	1.924	0.2842				
160.68	10.965	3.428	7.537	0.8772				
148.41	18.200	3.981	14.219	1.1529				
137.00	31.630	4.519	27.111	1.4331				
92.14		negligible alteration.						

emerges, however, that the surface tension up to 137°A is not very different from that in the plane surface since up to this temperature log V against log $(\sigma P/P_o)$ actually lies on one and the same straight line using values of σ from equation V.

Now although at the lower temperatures capillary condensation may be considered as playing the important rôle it must be presumed that the surface adsorption as exhibited above the discontinuity, Fig. 4 is still a factor. Moreover as we increase the temperature up to the critical temperature the surface adsorption becomes an increasingly important factor and we may no longer take our value of "a" and attempt to apply purely capillary condensation principles. If now we assume that the straight line relation of log k against T above the break may be extrapolated to lower temperatures, then we can within a limited degree of accuracy, determine the volume adsorbed by capillary condensation alone. $a_o = a - a'$; where a_o is the adsorption by capillary condensation and a′ that by surface adsorption as in regions far above the critical temperature. This was done in the following way. Values of log a for five different pressures, read off from the log-log isotherms, were found for all temperatures and these values plotted against the temperature giving a series of five curves similar to that of log k against T in Fig. 4. The straight line A of log a against T above the discontinuity point was extrapolated and for each temperature was read off from B below the discontinuity, the value of log a, and from the extrapolation the corresponding value of log a′, giving a_o. Plotting log a_o against T curve C is obtained. At 92.14°A a′ is negligible and a_o = a, but at 140-150°A, a_o is appreciably less than "a." Table III shows the relative effect of the two factors, surface adsorption and capillary condensation. From the curves C are read off the values of log a_o at the five pressures and the five temperatures as given in Table IV.

TABLE IV

T°A.	Log a_o.				
	P = 1.0	P = 5.0	P = 10.0	P = 50.0	P = 100.0
137.00	0.346	0.742	0.916	1.290	1.433
140.00	0.220	0.650	0.810	1.200	1.350
145.00	0.080	0.515	0.665	1.080	1.240
150.00	$\bar{1}$.890	0.350	0.515	0.950	1.125

Log a_o-log P isotherms are now constructed which are slightly curved towards the P axis. From these isotherms can be read off values of log P for values of log a_o corresponding to given values of log V. (See equation (VI).) In Table V are values of log $(\sigma P/P_o)$ for three values of log V,[1] from the boiling point to a few degrees below the normal critical temperature, using σ for the plane surface from equation (V.) It must be noted that up to 137°A the value of

---

[1] Although the value of d_l and P_o is known at 150°A the value of σ cannot be obtained from equation (V) since in this equation σ is already zero at 148.28°A. The value of σ required to make log $(\sigma P/P_o)$ the same as at the lower temperatures can however be computed.

log $(\sigma P/P_o)$ for a given value of log V is very constant. As before the values of σ required to make log $(\sigma P/P_o)$ at 140°, 145° and 150°A the same as at 92.14 to 137°A were ascertained and compared to the corresponding values derived from the independent Kelvin equation. The agreement was much better than before the surface adsorption was taken into consideration but certain discrepancies remained to be accounted for.

It is of peculiar interest to note that at 137°A where log $(\sigma P/P_o)$ just begins to become too low to lie on one and the same straight line, the density (liquid) curve starts the downward trend (Fig. 5) typical of the approach to the critical temperature and the departure from the equation $d_t = d_o(1 + at)$. The same is true of argon and methane.

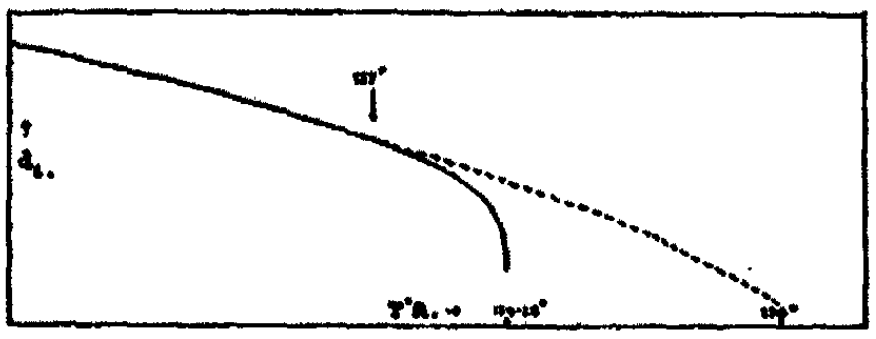


Fig. 5
The density of liquid oxygen

Now if the critical temperature in the pores is considerably higher than in a plane surface this departure from the above equation will occur at a higher temperature. The curve of d_l against temperature below 137°A has therefore been extrapolated up to 150°A and would eventually be of the form shown by the dotted line. Now the term d_l appears in equation (V) for the calculation of σ for a plane surface but the new value of d_l gives a value of σ not appreciably differing from the original. It occurs also in the Kelvin equation but here again the change has only a small influence. It occurs in equation (VI) giving the relation between V and a_o and since for a given value of V we determine a_o and log a_o and read off log P, a very small change in V is very sensitive. Hence, in introducing this correction the greatest effect will be on the value of a_o for each given value of V and hence on the value of log P. Corrected values of a_o were found from the equation $V = a_o d_g/\bar{d}_l$, where $\bar{d}_l$ is the corrected density from the extrapolation. From the log a_o-log P curves the new values of log P were found. Table VI shows the final values of log a_o, log P, and log $(\sigma P/P_o)$ for three values of log V, using σ for the plane surface from equation (V). Below 137°A there is no departure from the ordinary density curve or of the surface tension from the value in the plane surface.

Above 137°A, log $(\sigma P/P_o)$ for a given value of log V begins to fall off. Again in order to ascertain whether this is due entirely to the difference of the surface tension in the plane surface and in the capillaries of the adsorbent, the surface tensions required to make log $(\sigma P/P_o)$ a constant at all temperatures

TABLE V

T°A	Log V = $\bar{3}$.8000			Log V = $\bar{2}$.2000			Log V = 2.6000		
	Log a_0.	Log P.	Log $\sigma P/P_0$	Log a_0.	Log P.	Log $\sigma P/P_0$.	Log a_0.	Log P.	Log $\sigma P/P_0$.
92.14	0.6981	$\bar{2}$.26	$\bar{1}$.3559	1.0981	$\bar{2}$.98	0.0759	1.4981	$\bar{1}$.71	0.8059
137.00	0.5693	0.36	$\bar{1}$.3003	0.9693	1.11	0.0453	1.3693	1.86	0.8003
140.00	0.5588	0.54	$\bar{1}$.2954	0.9588	1.25	$\bar{1}$.9854	1.3588	2.01	0.7454
145.00	0.5275	0.72	$\bar{2}$.9322	0.9275	1.43	$\bar{1}$.6422	1.3275	2.17	0.3872
150.00	0.4807	0.90	—	0.8807	1.58	—	1.2807	2.29	—

TABLE VI

T°A.	Log V = 3.8000			Log V = $\bar{2}$.2000			Log V = $\bar{2}$.6000		
	Log a_0.	Log P.	Log $\sigma P/P_0$.	Log a_0.	Log P.	Log $\sigma P/P_0$.	Log a_0.	Log P.	Log $\sigma P/P_0$.
92.14	0.6981	$\bar{2}$.26	$\bar{1}$.3559	1.0981	$\bar{2}$.98	0.0759	1.4981	$\bar{1}$.71	0.8059
137.00	0.5693	0.36	$\bar{1}$.3003	0.9693	1.11	0.0453	1.3693	1.86	0.8003
140.00	0.5615	0.54	$\bar{1}$.2754	0.9615	1.26	$\bar{1}$.9954	1.3615	2.00	0.7354
145.00	0.5448	0.73	$\bar{2}$.9472	0.9448	1.45	$\bar{1}$.6672	1.3448	2.19	0.4022
150.00	0.5235	0.91	—	0.9235	1.65	—	1.3235	2.36	—

for a given value of log V were found. For a given value of V let $A = \sigma P/P_o$ between 92.14 and 137°A and σ' the required value of the surface tension.

Then:—$\log \sigma' = \log P_o + \log A - \log P$ (VIII)

Table VII shows the very close agreement between σ' and the surface tension as computed from Kelvin's equation in the capillaries of the adsorbent. Moreover, if the values of the surface tension as found above, either σ' or from the equation be plotted against temperature and extrapolated, σ becomes zero about 190-200°A (Fig.6). This is in good agreement with the temperature at which the discontinuity in the $\log a - T$ curve occurs, namely 196°A.

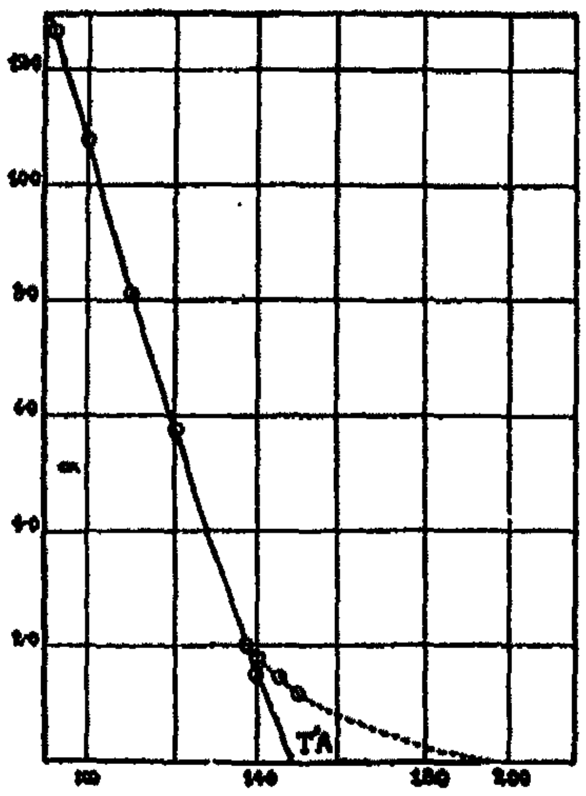


Fig. 6

The surface tension of oxygen

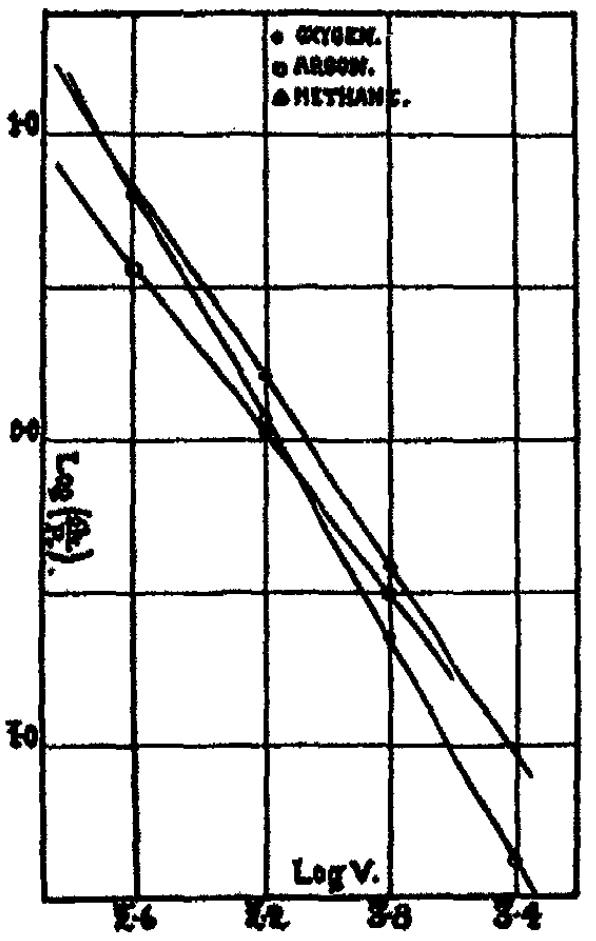


Fig. 7

Thus employing values of σ above 137°A found from the Kelvin equation, all values of $\log(\sigma P/P_o)$ for various values of log V and T fall on one and the same straight line, when capillary forces and their reaction on surface tension and density are taken into account.

Table VII

A comparison of the Surface Tension required to that calculated

Log V	140.0°A		145.0°A		150.0°A	
	σ'	σ	σ'	σ	σ'	σ
$\bar{3}.8000$	1.82	1.82	1.46	1.47	1.18	1.18
$\bar{2}.2000$	1.82	1.84	1.46	1.49	1.13	1.18
$\bar{2}.6000$	1.78	1.82	1.45	1.45	1.18	1.15

That is for the same gel K and m are independent of temperature. How far they are independent of the nature of the adsorbate may be seen from Fig. 7 where the plot of log $(\sigma P/P_0)$ against log V is given for argon at 130°A, far enough below the critical temperature to ensure that σ and d_l are those for a plane surface liquid and at 173.94°A for methane just below the temperature at which the density departs from the normal curve. The adsorption of helium conforms to the foregoing conclusions in that $a = kP$ at 89.86°A or 84.67°A above T_c. Table VIII gives the values of K and m for the three adsorbates on the same silica gel.

TABLE VIII

	K	m
Oxygen	0.0144	0.56
Argon	0.0151	0.74
Methane	0.0114	0.65

It has been brought to the recent notice of the author that P. Kubelka[1] in studying the adsorption on charcoal at 20°C has proceeded in the opposite manner by expressing the volume of the liquid adsorbed as a function of the radius r of the capillaries in the adsorbent using the Kelvin equation. Of particular interest is the fact that he also concludes that capillary condensation takes place at temperatures considerably above the normal critical temperature. His estimated capillary critical temperature for CO_2 (Normal $T_c = 31°C$) of about 190°C, however is far higher than that which may be estimated from the results of Patrick, Preston and Owens, which would be between 60 and 70°C for silica gel, in good accord with the present results. This can be reconciled if the pores in charcoal have an average diameter correspondingly lower than that of the silica gel pores.

Summary

(A). A method of studying phenomena like adsorption, wherein several cubic centimetres of a gas may be distributed throughout a large system in various phases and again quantitatively collected at any required pressure is described.

(B). The adsorption of helium, argon, oxygen and methane between 90°A and 273°A on the same silica gel has been studied.

1). The adsorption of a gas on silica gel takes place in at least two phases. The discontinuity of adsorption phenomena at some definite temperature has been observed. This temperature is probably very close to the critical temperature of the gas in the capillaries of the gel.

2). Above the discontinuity the adsorbed volume is proportional to the pressure and the adsorption may be visualised as an increasing effective adsorption surface or an increase proportional to pressure in the fraction of the effective area occupied by the gas molecules. The temperature coefficient of the adsorption in this region is very small.

3). Below the discontinuity capillary condensation occurs. The adsorption constant n in the Freundlich equation: $a = kP^n$, is no longer unity

---

[1] Kolloid-Z., 55, 2, 129 (1931).

but decreases rapidly with a decrease in temperature. dk/dT or the temperature coefficient of adsorption is much greater than above the break.

4). Below the discontinuity the two phases of adsorption may be quantitatively separated under certain assumptions and the capillary condensation adsorption treated mathematically by Patrick's theory.

5). By the application of the capillary condensation values for oxygen to the Kelvin equation the surface tension becomes zero around 195°A which is close to the temperature at which the adsorption becomes discontinuous and 41° above normal critical temperature.

6). By employing values of the surface tension in the capillaries as found by the Kelvin equation in the equation $V = K(\sigma P/P_o)^m$ and with due consideration to the abnormal temperature coefficient of the density of a liquified gas in the immediate neighbourhood of the critical temperature, it is found that the constants K and m are independent of temperature and do not vary much even for three markedly differing adsorbates. This is required to be the case in the derivation of the above equation for capillary condensation.

7). Capillary condensation occurs at temperatures considerably above the critical temperature of a liquid in a plane surface.

Baltimore, Md.

OCCURRENCE AND ETIOLOGY OF RICKETS

BY N. R. DHAR

Rickets has long been known to be a disease of improper nutrition and caused by faulty feeding. Chronic diarrhœa, which may itself depend on unsatisfactory food, frequently precedes this disease. The fault in the diet, upon which the occurrence of rickets depends, is poorness in animal proteins and fats and excess in carbohydrate, especially starch. Deficiency of good class fats is decidedly more important than deficiency in protein and perhaps some of the harm caused by the excess of carbohydrates is due to their interference with the digestion of fat.

It has been emphasised by the author[1] that vitamins A and D, which are associated with fatty food materials act as promoter and inductor in the oxidation of fats in the body. When vitamins A and D are absent in foods, incomplete oxidation of fats take place and rickets may result.

In publications from the author's laboratories,[2] it has been shown that the oxidation of various substances by air or oxygen can be markedly retarded by the presence of carbohydrates, which in their turn are also oxidized by air in presence of the above substances. Moreover, the oxidation of fats is retarded by the presence of carbohydrates. Consequently when too much of carbohydrate food is given to children, the fatty food material is not properly burnt, especially when vitamins A and D are absent and hence rickets may originate.

In a communication the author[3] has developed a new conception of the formation of bones in the animal body and has shown that normal calcium phosphate existing in the serum in the colloidal state is adsorbed and precipitated by the cartilage. Similarly small amounts of calcium carbonate also exist in the colloidal state in the serum and this is also adsorbed and precipitated by the cartilage and thus normal ossification takes place. It is well known that blood is slightly alkaline. If by any means, there is a slight increase in the $H^{\cdot}$ ion concentration in the blood, the amount of calcium phosphate and carbonate existing in the colloidal state will partly dissolve and hence their concentration will decrease and thus there will be disturbance of bone formation.

It seems likely that in the body there is a definite equilibrium condition as represented by the following scheme

$$3\,Ca^{\cdot\cdot} + 2\,PO_4''' \leftrightarrows Ca_3(PO_4)_2\,(\text{Colloidal}) \leftrightarrows Ca_3(PO_4)_2\ (\text{Solid in bones})$$

If the food lacks either in $Ca^{\cdot\cdot}$ or PO_4''' ions, bone formation cannot take place normally because the proper concentration of calcium phosphate in the

---

[1] N. R. Dhar: Chemie der Zelle und Gewebe, **12**, 217 (1925); **13**, 209 (1926).

[2] C. C. Palit and N. R. Dhar: J. Phys. Chem., **32**, 1663 (1928); **34**, 711 (1930).

[3] N. R. Dhar: Z. anorg. allgem. Chem., **162**, 243 (1927).

colloidal state to be adsorbed by the cartilage is not attained. If the food is rich in phosphorus and lacks calcium, there might be a tendency to form acid phosphate of calcium, which is soluble. It has been emphasised that rickets is very likely due to the incomplete metabolism of fatty food materials. It has also been stated that the metabolism of fat is accelerated either by the presence of vitamins A and D or by the presence of thyroid secretions. Moreover metabolism in general can be accelerated by light, in presence of which food materials can be oxidised in aqueous solutions or suspensions by passing air at the ordinary temperature.[4] Hence rickets can be partially or wholly avoided by sunlight or artificial light. It is well known that the incomplete metabolism of fat leads to acidosis in diabetes and in later stages of starvation. Hence alkalies are found useful in several diseases. Moreover we[5] have shown experimentally that the presence of alkali is associated with greater oxidation of carbohydrates, fats and proteins. Hence addition of alkalies will not only neutralize the acids generated in the incomplete metabolism of food materials but is likely to increase metabolism in the animal body.

In recent years attempts have been made to connect the occurrence of rickets with the alkaline reaction of the feces. But the results obtained in this line are contradictory and inconclusive. Zucker and Matzner[6] working with rats were the first to point out that rickets stools are more alkaline than the normal. These results were confirmed by Jephcott and Bacharach,[7] and for some time the problem appeared to have been well settled. For instance, Morse[8] writes in his Applied Biochemistry, that "one of the characteristics of rickets is the alkalinity of stools as Zucker has shown. Experimentally such stools runs to about pH 7.5 and may be reduced to acidity by different means. . . . One of the primary factors in rickets may be the inability of the intestine to absorb calcium. This may be correlated with the alkaline stools." But Shohl and Bing[9] and Redman,[10] the latter working with rachitic children, have arrived at the conclusion that there is no possible correlation between the incidence of rickets and the alkalinity of the feces. It appears, therefore, that more variables were involved in the fluctuation of the intestinal pH than merely the rachitic or non-rachitic condition of the animal or the infant.

The author is of the opinion that more fruitful and consistent results could be obtained by a study of the pH of the blood of rachitic and non-rachitic children. The pH of the blood of normal human beings is slightly on the alkaline side of neutrality, but this will be changed in rachitic subjects slightly to the acid side. That acidity is detrimental to normal ossification will be clear from the following considerations. It is well known that serum contains more calcium than can remain in the dissolved condition in the form of calcium

---

[4] C. C. Palit and N. R. Dhar: J. Phys. Chem., 32, 1263 (1928).

[5] C. C. Palit and N. R. Dhar: J. Phys. Chem., 29, 799 (1925).

[6] T. F. Zucker and M. J. Matzner: Proc. Soc. Exp. Biol. Med., 21, 186 (1924).

[7] H. Jephcott and Bacharach: Biochem. J., 22, 60 (1928).

[8] H. Morse: "Applied Biochemistry" (1927).

[9] A. T. Shohl and F. C. Bing: J. Biol. Chem., 79, 269 (1928);

[10] T. Redman: Biochem. J., 22, 15 (1928).

phosphate or carbonate by the same volume of water. From the researches of Cushny,[11] Loeb and Steinberger,[12] and of Clark[13] on the amount of dialysable and non-dialysable calcium in serum, it is certain that much of the calcium phosphate and carbonate exists in the colloidal condition, due to the peptising influence of serum albumin and other organic colloids. The author has already pointed out that the following equilibrium exists in the animal body:—

$$\underset{\text{solid in bones}}{Ca_3(PO_4)_2} \leftrightarrows Ca_3(PO_4)_2 \text{ (Colloidal)} \leftrightarrows \underset{\text{in solution.}}{3Ca^{\cdot\cdot} + 2\ PO_4'''}$$

A similar equilibrium may also exist in the case of calcium carbonate. Now this equilibrium is profoundly affected by the *acid base equilibrium of the blood*, i.e. by the pH of the blood. If the medium is acidic more and more of the calcium phosphate in the colloidal condition will dissolve and hence also the calcium phosphate of the bones and the calcium phosphate passes out. Therefore, the total calcium and phosphate content of the serum will decrease with increasing acidity of the blood. Looking from the other side, the greater the acid reaction of the blood, the less will be the tendency of the calcium phosphate to exist in the insoluble condition and hence the less will be the tendency for bone formation. It is, therefore, clear and a slight change in the acid-base equilibrium of the blood greatly affects the bone formation. If rickety blood is more acidic than normal, the total calcium and phosphate content of the serum of rickety children should be below the normal. Hess, Calvin, Wang and Felcher[14] found that in moderate rickets, the phosphorus or calcium or both may be moderately lowered. Karelitz and Shohl[15] observed that in young rats suffering from rickets as the result of a diet lacking in vitamin D, rich in calcium but poor in phosphorus, the retention of calcium is 50% and that of phosphorus 20% of the normal. Telfer[16] found that in rickets there is diminished retention of lime and phosphate, the latter being possibly due to diminished fixation by the calcium. Howland and Kramer,[17] as a result of extensive investigations, have arrived at the conclusion that the calcium and phosphorus content of the blood of rickety children is distinctly lower than the normal. This diminished retention of calcium and phosphorus by the rachitic children points to increased acidity of their blood.

From the equilibrium, $Ca_3(PO_4)_2 \leftrightarrows 3Ca^{\cdot\cdot} + 2\ PO_4'''$, we learn that $[Ca^{\cdot\cdot}]^3 \times [PO_4''']^2$ will be a constant, the so-called solubility product. Unless and until the product of the calcium and phosphate concentrations of the blood exceeds the solubility product, there will be no tendency of calcium phosphate to precipitate and hence no tendency for bone formation. The acid-base equilibrium of the blood greatly influences this. In presence of acids,

---

[11] A. R. Cushny: Compare Annual Reports Chem. Soc., **17**, 161 (1920).

[12] R. F. Loeb and S. Steinberger: J. Gen. Physiol., **6**, 453 (1924).

[13] J. H. Clark: J. Hyg., **3**, 481 (1923).

[14] J. H. Hess, J. K. Calvin, C. C. Wang and A. Felcher: Am. J. Dis. Children, **26**, 271 (1931).

[15] S. Karelitz and A. T. Shohl: J. Biol. Chem., **73**, 655, 665 (1927).

[16] S. V. Telfer: Quart. J. Med., **16**, 63 (1922).

[17] J. Howland and B. Kramer: Am. J. Dis. Children, **22**, 105 (1921).

the solubility product is hardly approached by the existing calcium and phosphate. Holt,[18] Howland and Kramer[19] have shown that the calcium phosphate plays an important part. According to the latter workers, if the quotient,

$$\frac{\text{Milligrams inorganic blood phosphate} \times \text{Milligrams blood calcium}}{\text{100 cc. whole blood}} = 40,$$

or greater than 40, rickets will not develop, if less than 40, rickets will develop. Willis, Sanderson and Paterson[20] have stated that calcium retention is reduced by milk containing HCl or NH_4Cl.

From what has been said above it will be seen that rickets is due to the disturbance of the acid-base equilibrium of the system; the blood of the rickety being slightly more acidic than the normal. Hodgson[21] reported that in her experience in many cases of rickets acidosis developed at the height of the disease. Pritchard[22] stated his belief that the true cause of rickets is probably a relative excess of acid substances produced in the system. Burgess and Osman[23] reported three cases of acute rickets in which they found severe acidosis.

In this connection the following results are interesting:—

The mineral content of average diet is as follows:—

Acid	cc. 0.1 normal	Base	cc. 0.1 Normal
Phosphorus	925	Calcium	365
Chlorine	810	Magnesium	283
Sulphur	813	Potassium	910
		Sodium	850
Total	2548		2368

The child retains base up to one year to the extent of 12 ccs. of decinormal base per kilogram of body weight. 50 out of the 58 parts of the base retained by a child is used up in the making of bone. Slight disturbances in the base retained by the child will, therefore, act adversely on bone formation. It is well known that calcium regulates the acid-base equilibrium in the body. The necessity, therefore of supplying adequate amounts of base-forming substances to a child during growth is evident.

Further evidence in support of the author's contention is obtained from the fact that on exposure of human beings to ultraviolet light their blood becomes more alkaline.

The curative action of ultraviolet light on rickets, therefore, appears to be partly due to its power of changing the reaction of the blood more to the alkaline side.

---

[18] L. E. Holt, Jr.: J. Biol. Chem., **64**, 579 (1925).

[19] J. Howland and B. Kramer: Trans. Am. Pediat. Soc., **34**, 204 (1922).

[20] L. Willis, P. Sanderson, and D. Paterson: Arch. Dis. Childhood, **1**, 245 (1926).

[21] A. Hodgson: Lancet, **1921 II**, 945.

[22] E. Pritchard: Brit. Med. J., **1923 I**, 887.

[23] N. Burgess and A. A. Osman: Lancet, **1914 I**, 281.

It is well known that rickets is caused by the lack of vitamin D in the food taken. But it is not yet clear in what way vitamin D affects bone formation. The author has given out the view that vitamin D is essential for the proper oxidation of fatty substances taken in the animal body. In its absence the fats will be incompletely oxidised with the production of acid substances. Thus the acid base equilibrium of the animal system is disturbed, the pH of the blood is thus changed more to the acid side, and this disturbs normal ossification as explained in the previous pages. The administration of vitamin D or exposure to ultraviolet light leads to complete oxidation of fats, thus diminishing the acid substances in the body and restoring the acid-base equilibrium of the animal body to its original state. Hence normal ossification will set in and rickets is likely to be cured. This appears to be the rational explanation of the curative action of vitamin D or of ultraviolet and light therapy.

The author[24] has also suggested that thyroid administration will prove beneficial in rickets, inasmuch as thyroid secretion acts as an accelerator in the oxidation of fats and brings about the complete oxidation of fatty foods.

Summary

(1) The disturbance of the acid-base equilibrium, resulting in a slight change of the pH of the blood to the acid side, is shown to be the immediate cause of rickets.

(2) A rational explanation for the curative action of vitamin D or of ultraviolet light in rickets is given.

(3) It is suggested that thyroid administration should prove useful in curing rickets.

Chemical Laboratory,
Allahabad University,
Allahabad, India.
August 5, 1931.

---

[24] N. R. Dhar: Chemie der Zelle und Gewebe, 13, 119 (1926).

NOTE ON SODIUM THIOCYANATE

BY C. K. BUMP

In the preparation of very concentrated solutions of sodium thiocyanate, it was found that solutions saturated at about 60°C and cooled to room temperature, were highly supersaturated. When such a metastable solution crystallized out, long needle-shaped crystals were formed which were quite different in appearance from the regular sodium thiocyanate crystals (anhydrous).

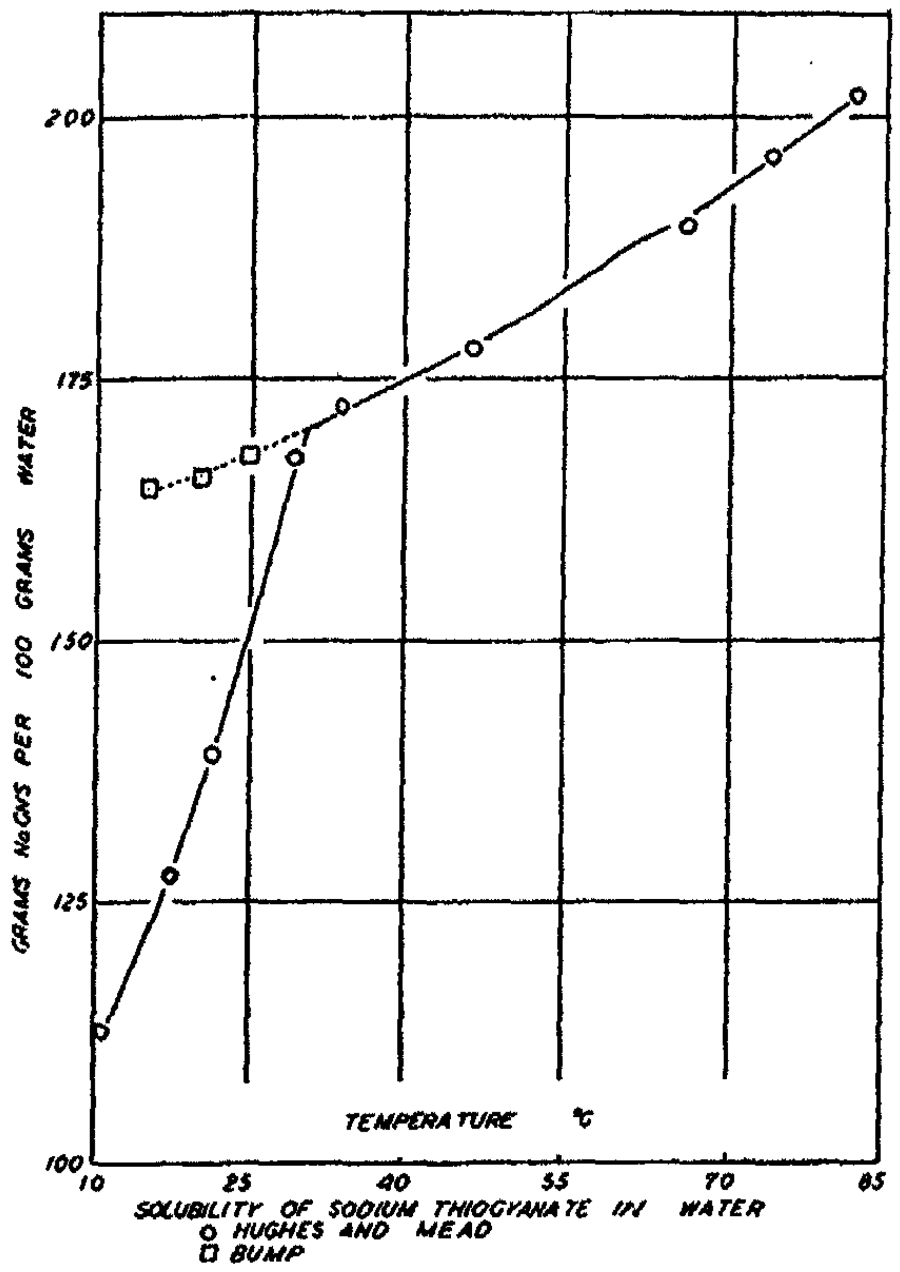


FIG. 1

A consultation of the literature[1] showed that a monohydrate $NaCNS \cdot H_2O$ is known, the melting-point of which is 30°C. The melting point of our crystals was 30°C. Fig. 1 is the solubility curve for the stable form taken from Hughes and Mead[1] with the metastable portion taken from our data.

It was found that on standing in the open the crystals effloresced, while the usual experience is that sodium thiocyanate takes up moisture. The vapor

---

[1] Hughes and Mead: J. Chem. Soc., 1929, 2282-2284.

TABLE I

Solubility of Sodium Thiocyanate in Water

Hughes and Mead		Bump	
Temp °C	gms. NaCNS/100gms. H_2O	Temp °C	gms. NaCNS/100gms H_2O
10.7	112.7	15	164.5
17.3	127.5	20	165.6
21.3	139.3	25	167.8
29.2	167.5		
33.8	172.4		
46.1	178.9		
65.8	189.5		
73.8	196.2		
81.8	202.0		

pressures of stable, saturated solutions were measured and compared with the vapor tension of water in the room. At 17°C and 25°C the vapor pressures of saturated solutions were 5.2 and 7.5 mm Hg, respectively. At 25°C the vapor tension of the water in the air was 4.8 mm Hg. With the given humidity the crystals must effloresce since they have the higher vapor pressure.

Because these measurements were made in a steam-heated room they serve as a check on the statement that artificially heated rooms are exceptionally dry unless some means of humidifying the air is supplied.[2] 4.8 mm Hg corresponded to 20.4% relative humidity, while normal relative humidity varies from 30% to 60%. In England the average humidity is about 75% and rarely goes below 50%.[3]

The vapor pressure of the saturated solution at 25°C being 7.5 mm Hg, the humidity would have to be 32% or better at this temperature for the salt to be deliquescent. Therefore, since this is more liable to be the rule than the exception, sodium thiocyanate is generally noted as deliquescent.

Microscopic examination of the crystals (hydrate) gave the following information:

The crystals are monoclinic showing clinopinacoid faces. The anhydrous form is rhombic.[4]

The optic axial angle, $2V$, is not more than 30°.

There is strong dispersion, the optic axial angle for violet light being greater than for red, $(v > r)$.

α is very near the refractive index of the mother liquor. The refractive index of the mother liquor at 27°C is 1.4954. The refractive index in the other direction is higher than that of the mother liquor, but the solubility of the crystals prevents its determination by immersion methods. The crystals are optically positive.

The axial plane is perpendicular to the plane of symmetry (B_{x_o} to "b").

The extinction angle is about 12° and the angle β is about 78°.

Cornell University.

---

[2] Grierson: "Some Modern Methods of Ventilation," 63 (1917).
[3] Stevenson and Murphy: "Treatise on Hygiene," 1, 48 (1892).
[4] Friend: Text Book of Inorganic Chemistry, 2, 147 (1924).

SUPERSATURATION

BY J. R. PARTINGTON

A recent paper by Professor Kolthoff[1] leads me to draw attention to some former relevant publications to which he makes no reference. In these[2] the relation between the effect of particle size and supersaturation phenomena (not merely solubility, which was then well known) was, so far as I am aware, first quantitatively expressed. Although several refinements and extensions of this theory have since been published, and many more await investigation, the main lines of thermodynamic and kinetic theory of supersaturation were developed, and must necessarily retain priority. When these communications have not simply been ignored (as in the present instance) they have been the object of criticism to some extent based on misunderstanding.[3] It should be pointed out that, although kinetic considerations were introduced when they were appropriate, the main theory is based on thermodynamics, and thus possesses the advantages of this method. Some parts of the theory are capable of extension. Thus, the effect of particle size on solubility as affected by interfacial tension must take account of the possible variation of the latter with very small particles. There seems every reason to suppose that any such variation, about which nothing of importance is even yet known, will introduce no fundamental change in the theory. The possibility of preferential adsorption of ions, not established when the theory was advanced, is very probably of minor significance. The replacement of concentrations by activities is obvious. The introduction of activation energies in considering rates of solution and precipitation would no doubt open fields of possibilities, but is foreign to a theory based on thermodynamic equilibrium states. The hasty assumption by Adam of an amorphous layer on the particles, produced by grinding, is trivial and not relevant, since small particles need not be produced by grinding, and in any case the reversibility of the phenomenon, established by my experiments, makes it entirely superfluous.

The quantitative formulae developed were based on thermodynamics, and neither they nor the experimental results are in contradiction to the second law of thermodynamics, a circumstance which one critic will doubtless appreciate.[4] The experiments were regarded as establishing the fact that the *solution* process was reversible in contact with small particles, although the much greater length of time required to reach equilibrium from the side of

---

[1] J. Phys. Chem., 36, 860 (1932).

[2] J. R. Partington and W. J. Jones: Phil. Mag., 29, 35 (1915); M. Jones and J. R. Partington: J. Chem. Soc., 107, 1019 (1915).

[3] Dundon and Mack: J. Am. Chem. Soc., 45, 2479 (1923); Rideal: "Surface Chemistry," 253 (1930)—no reference to the first paper, giving the general theory; Adams: "Physics and Chemistry of Surfaces."

[4] E. K. Rideal and B. Lewis: J. Am. Chem. Soc., 48, 2553 (1926); Godenstein and Jost: 49, 1416 (1927).

supersaturation was pointed out. The dependence on heat of solution was an important factor made out both in the theory and experiments, the particular solute used being chosen deliberately as one for which the heat of solution changed sign in the temperature range used. The actual calculations in the second paper were legitimately but perhaps unnecessarily harshly, criticised by Dundon and Mack on the ground that the ionisation of the calcium sulphate was neglected. It is very much open to question whether the use of Ostwald's dilution law by these authors is an appreciable improvement; in any case the numerical change resulting is not large, and even if it were, it would leave the general theory quite unaffected. The use of an equation for calculating experimental results which is capable of improvement does not necessarily invalidate experimental or theoretical work, as one critic will no doubt admit.[1] That the particle size was not determined is a legitimate criticism. The work was interrupted by the war, and the second paper was written whilst the present author was in military service. Many experiments had been made on the determination of particle size but, as other workers have no doubt found, this is a tedious and difficult investigation and could not be completed. The powders used were lost during the course of the war.

It is hoped that future students of this work will find it possible to apprehend that its main object is the development of theory of supersaturation, and will consider how far any criticisms of detail they may put forward—and there are many opportunities for such—will affect the general theory as a whole.

East London College,
University of London,
London, England.

---

[1] Mack: J. Am. Chem. Soc., 47, 2468 (1925); Topley: Nature, 118, 802 (1926).

NEW BOOKS

Elektrophorese, Elektroosmose, Elektrodialyse in Flüssigkeiten. *By P. H. Prausnitz and J. Reitstötter. 22 × 15 cm; pp. xii + 307. Dresden and Leipzig: Theodor Steinkopff, 1931. Price: 18.50 marks, bound 20 marks.* This is volume twenty-four of the Wissenschaftliche Forschungsberichte edited by Raphael Ed. Liesegang. The chapters are entitled: general introduction; electrophoresis; electroosmosis; electrodialysis; technical applications with special discussion of the patent literature.

"The dependence of the migration velocity of the colloidal particles of an arsenious sulphide sol on the electrokinetic zeta potential was studied by Freundlich and Rona when a series of complex cobalt salts with univalent to hexavalent cations was added gradually. The electrokinetic potential was deduced from the migration velocities. In accord with Freundlich's adsorption theory the characteristic concentrations for each complex cation were dependent in exactly the same way on the valences of the ions," p. 26.

"According to Keller methylene blue is slightly anodic in water, strongly anodic in alkali, and strongly cathodic in acid, while acid fuchsine seems to go to both poles. Even a ferric oxide sol moves to the anode in alkali. On the other hand, congorubin—an acid dye—goes to the cathode in alcohol," p. 38.

"According to Winslow, Falk and Caulfield the isoelectric point of bacterial suspensions is at about pH = 3.0. They usually move to the anode but go to the cathode between pH 3 and 1. When the solution is more acid than pH = 1.0, the movement ceases. In alkaline solutions they always move to the anode," p. 43.

"It should be mentioned that Coehn has shown the effect of an electrical current on non-ionized crystalloids in true solution. Cane sugar, for instance, moves to the cathode under a potential drop of 220 volts in acid sugar solutions containing 2-20 percent of sugar and under conditions in which the formation of true complex ions of sugar are out of the question," p. 45. Glucose usually goes to the anode, as do starch and insulin, p. 56.

On p. 52 there is an account of Humphry and Jane showing the absence of electrophoresis for dry rubber in dry benzene. In dilute water suspensions mastic moves most rapidly in red light, less rapidly in the dark, and least rapidly in blue light, p. 59.

"Freundlich and his co-workers showed that the electrokinetic zeta potential is not identical with Nernst's thermodynamic epsilon potential. Freundlich and Rona considered the epsilon potential to be the potential difference between the solid phase itself and the free liquid in contact with it, while the zeta potential measures the potential drop between the bound and the free solution," p. 63.

"Michaelis showed that blood charcoal is ampholytoid while sugar charcoal and retort charcoal are acidoid. From solutions of simple salts, charcoal may adsorb both ions in equivalent amounts; but, over and above this adsorption of ions, charcoal alone has the power of adsorbing in considerable quantities indifferent(not surface-active) substances of high molecular weight, including many colloids. Kaolin can only adsorb basic dyes, while the corresponding anion remains in solution. Colloidal hydrous ferric oxide can only adsorb acid dyes. Substances like these two have very little power of adsorbing indifferent or uncharged substances, p. 65. The authors seem not to know about the adsorption of kerosene by ferric oxide.

The experiments of Prausnitz, p. 83, confirm the older experiments by Wiedemann that 500-600 times as much water may be transferred by electrical endosmose as is decomposed electrolytically. On p. 91 is the statement, which is probably not the whole truth, that an ion has more difficulty in passing a membrane the higher its valence is. Local anaesthesia by cocaine can be done better by electroosmosis. There is no damage to the skin when the current densities are less than 1.2 milliamperes per square centimeter, p. 105.

Much of the rest of the book is taken up with a very good account of Count Schwerin's work. The authors have gone over an enormous amount of literature and have presented it fairly well in a non-critical way. Since they incline to Perrin's view that only the relative adsorptions of hydrogen and hydroxyl ions count, they are rather puzzled by some of the changes in the charges on diaphragms. On p. 260 they call attention in a grieved way to the fact that the isoelectric points of the proteins vary with the nature of the electrolytes.

Wilder D. Bancroft.

A Course in Quantitative Analysis. *By J. Samuel Guy and Augusta Skeen. 21 × 15 cm; pp. ix + 242. Boston: Ginn and Company, 1932. Price: $2.20.* This book is written as a text for an elementary course in Quantitative Analysis and not as a reference book. The experiments are designed to familiarize the student with a number of quantitative chemical manipulations and to aid him in gaining what may be termed the quantitative conception.

The book includes (1) A brief outline of some chemical theories; (2) General directions; (3) Preparations of solutions; (4) Determination of the relationship of the prepared solutions; (5) Standardization of prepared solutions; (6) Analyses involving the use of the prepared standard solutions; (7) Representative types of simple gravimetric procedures; (8) Optional experiments in gravimetric procedures; (9) Discussion of the theory involved in the hydrogen ion concentration determination and (10) Determination of hydrogen ion concentration by colorimetric method.

The authors believe "that it is well to begin the study of quantitative analysis with volumetric procedures. These yield more progress with a given amount of work, they are less exacting in their demands on the student, they are less open to serious error, and, all in all, better adapted to a beginner in the subject." The experimental directions for the determinations are clearly and well written and the authors have fulfilled their idea of giving "detailed instruction and information for each determination so that the student may develop maximum dependence upon the text and require minimum assistance from the instructor." However, the course as outlined where each student requires eleven one-liter bottles and where he must prepare such solutions as ammonium molybdate etc., would be rather wasteful of apparatus and chemicals with large classes.

There are a few errors in the directions that should be corrected such as in the titration of oxalic acid with potassium permanganate; on p. 56 the authors say, "warm to about 60°C.," while on p. 84 in the standardization of potassium permanganate against sodium oxalate, the authors say, "warm to boiling." Also the reviewer objects to the direction given on p. 18 that in draining a pipette, "to force the liquid completely out, it is sometimes necessary to close the upper end of the pipette with the thumb and gently surround the bulb with the other hand (temperature thus aiding the removal)."

M. L. Nichols

Colloids. *By Ernest S. Hedges. 14 × 22 cm; pp. viii + 272. London: Edward Arnold & Co., 1931. Price: 12 shillings, 6 pence.* Students who wish to learn something of colloids in as short a time as possible will be well advised to obtain this volume. The research worker in physical chemistry will also find it stimulating reading and if he is not already a specialist in this branch of research the references that are included in the text of the book will serve as a valuable guide to the original literature. The first eight chapters are devoted to a consideration of the general properties and methods of preparation of colloidal solutions. A number of experimental details are given which are sufficient to enable the student to use the book as a guide to practical work in the laboratory. The only criticism that can be brought against this section of the book is that too little is demanded from the reader. His previous knowledge is assumed to be negligible and these chapters occupy a considerable amount of space some of which might have been better utilized for the subjects considered in the later part of the book. A chapter on adsorption serves as an introduction to the second part of the book. The following subjects are dealt with here in considerable detail: the properties of hydrophobic and hydrophilic colloids, emulsions, gels, colloids and chemical reactivity and some applications of colloid principles. Forty-six pages are devoted to a consideration of gels and their properties. This is justified by the general interest of these materials and their especial importance to the biologist, who should find this book very valuable. The treatment of the applications of colloid principles must necessarily be unsatisfactory in the limited space that is available. The following examples are dealt with in a very brief manner: smokes and fumes, clays and soils, colloidal graphite, dyestuffs, leather, rubber, milk, wool, sewage disposal, photography. Although there are many other applications that are not even mentioned, the treatment of the above examples does emphasise how important the study of colloids is industrially and it is certain that this will become increasingly apparent as time goes on.

R. H. Purcell