The Absence of Fatty Acids Associated with Potato Starch

BY LEO LEHRMAN AND ELVIN KABAT

In the course of some work on potato starch[1] it was necessary to know the amount of fatty acid, if any, associated with the starch. Though 0.04% "fat by hydrolysis," has been reported in this starch,[2] Taylor and other workers in this field now believe that it is fat free.

To establish this point definitely we extracted a 50-g. sample of potato starch with petroleum ether for several hours and found 0.02% extraneous extractable material. Then we hydrolyzed[3] 2000 g. of the starch and found approximately 0.02% "fat by hydrolysis."

Thus potato starch does not contain fatty acids associated with it and is the best whole starch to use as carbohydrate.

---

[1] The authors wish to thank Stein Hall & Co., Inc., N. Y. C., for their kindness in supplying this material.

[2] Taylor and Nelson, THIS JOURNAL, **42,** 1726 (1920).

[3] Lehrman, *ibid.*, **51,** 2185 (1929).

CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF THE
COLLEGE OF THE CITY OF NEW YORK
NEW YORK CITY

RECEIVED OCTOBER 29, 1932
PUBLISHED FEBRUARY 9, 1933

COMMUNICATIONS TO THE EDITOR

AN EQUATION RELATING DENSITY AND CONCENTRATION

Sir:

Redlich and Rosenfeld [*Z. physik. Chem.*, **A155,** 65 (1931)] have shown on the basis of the Debye–Hückel theory that the partial molal volume of an electrolyte in dilute aqueous solution is proportional to the square root of the normality. This gives a theoretical basis for Masson's empirical rule [*Phil. Mag.*, (7) **8,** 218 (1929)] connecting the apparent solution volume of a salt with its concentration in the solution.

$$\phi = \phi_0 + K\sqrt{N}$$

The relation between the concentration and density of a salt solution and the apparent solution volume of the salt can be shown to be

$$\phi = \frac{\text{Eq. Wt}}{D_{\text{H}_2\text{O}}}\text{salt} - \frac{1000}{D_{\text{H}_2\text{O}}}\left[\frac{D_{\text{soln.}} - D_{\text{H}_2\text{O}}}{N}\right]$$

By combining these two equations one obtains for the equation relating the density and normality of a solution of a strong electrolyte in water

$$D = D_0 + c_1N + c_2N^{3/2}$$

where c_1 and c_2 are constants, and D_0 is the density of pure water.

This equation was found to hold within the limits of experimental error for solutions of the alkali (without lithium) and alkaline earth halides to a concentration at least as high as 10 *N;* and for sulfuric acid to a concentration of about 25 *N* (75 wt. %) where there was a point of inflection. The constants c_1 and c_2 were found to be additive.

DEPARTMENT OF CHEMISTRY
HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS
WILLIAM C. ROOT

RECEIVED DECEMBER 6, 1932 PUBLISHED FEBRUARY 9, 1933

THE SPECIFIC SURFACE AND THE ADSORBENT PROPERTIES OF LEAD SULFATE

Sir:

1. In agreement with the results of F. Paneth and W. Vorwerk [*Z. physik. Chem.*, **101,** 445, 480 (1922)], it was found that the specific surface of lead sulfate was the same in suspensions in water as in the presence of an excess of lead nitrate. P. and V. derived an equation from which may be inferred that in the suspension of lead sulfate in water about 40% of the surface of the solid was covered with adsorbed lead ions, whereas the surface was covered with a monatomic layer of lead ions in a solution of 0.005 molar lead nitrate. We determined also the specific surface of lead sulfate in dilute solutions of sodium sulfate and found the same value as before. This constancy of the specific surface indicates that lead sulfate adsorbs neither lead ions from dilute lead nitrate solutions nor sulfate from dilute sodium sulfate solutions. This conclusion was supported by the determination of the adsorption of the two salts according to chemical methods. Considering that we worked with coarsely crystalline precipitates of lead sulfate (of the same size as those of P. and V.) it is quite possible that an adsorption takes place at the corners and the edges. If the latter would have been completely covered with adsorbed lead or sulfate ions, the adsorption would amount to less than 0.1% of the total surface of the coarse crystals, which is beyond detection by the experimental methods used.

2. The adsorption of the sodium salt of Ponceau 4R by lead sulfate was determined under various conditions. It was found that only dye ions were adsorbed, no sodium ions being removed from the solution. This means that we are dealing here with an exchange adsorption, sulfate ions being replaced by ponceau ions in the surface. Experiments are being carried out in this Laboratory with various ionic precipitates showing that the exchange adsorption occurs quite generally.

A detailed account of all the work will soon be presented for publication.

SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA
I. M. KOLTHOFF
CHARLES ROSENBLUM

RECEIVED DECEMBER 6, 1932 PUBLISHED FEBRUARY 9, 1933

MODIFICATION OF THE DUMAS TECHNIQUE FOR SUBSTANCES DIFFICULT TO BURN

Sir:

When a large number of nitrogen determinations by the Dumas method is to be made it is common practice to abandon the classical method, which requires emptying and refilling the combustion tube for each determination, and instead to proceed as in the determination of carbon and hydrogen, weighing the substance into a combustion boat, covering it with fine copper oxide and inserting it into the posterior end of the filled tube. This method has obvious advantages that do not need comment here. However, in the case of substances that are difficult to burn this modification may lead to low results because of incomplete combustion. In the work on the lupine alkaloids being conducted in this Laboratory it was found that some of these substances could not be analyzed in this way on account of the fact that they yielded non-volatile split products that were deposited on the walls of the tube out of contact with copper oxide and were not thoroughly oxidized.

A method for overcoming this difficulty while preserving the advantages of the general method has been developed and is here described for the benefit of those who may encounter similar difficulties. In principle the new technique involves mixing the weighed substance with a large excess of copper oxide and packing this into a metal tube which is then inserted into the combustion tube in the location ordinarily used for the combustion boat. We are using a copper tube 15 cm. long and 1.27 cm. external and 1 cm. internal diameter. The tube is ignited, cooled and filled as follows.

The forward end of this tube, which we refer to as a cartridge, is loosely plugged with a centimeter long roll of copper gauze. Upon this is poured with the aid of a solid funnel about two centimeters of previously ignited fine copper oxide,[1] then the substance mixed with copper oxide enough to form a layer of ten to twelve centimeters is poured in, the mortar is rinsed with fine copper oxide and the rinsing added to the cartridge until it is filled. It may now be inserted in the combustion tube, backed in the usual manner with a roll of oxidized copper gauze and the combustion carried out according to the classical technique.

At the conclusion of the analysis the cold cartridge may be emptied of its spent charge and if it is handled with tongs will be ready for a new charge without reignition.

Somewhat high results may be expected from the use of such a cartridge because the air adsorbed on the fine copper oxide cannot be displaced completely by the carbon dioxide stream. Blank runs, however, indicate that the error due to this factor is no greater than that encountered in the ordinary technique. The excess air due to the cartridge amounts, on the

---

[1] Copper oxide is usually sufficient, but the cartridge may be filled with lead chromate or with mixtures of catalytic oxides when desirable.

average, to 0.2 cc. The results obtained by this method have been satisfactory as the following table will indicate.

Substance	% N without cartridge	% N with cartridge	Calcd.
Sparteine mercuric chloride	2.01	4.83	4.86
Alkaloid A from *Lupinus caudatus*	5.90 6.17 9.62 9.73	10.03 10.13	10.02
Alkaloid from *Lupinus cruckshanksii*	6.97 9.60	10.34 10.23	
Alkaloid from *Lupinus palmeri*	9.54 9.31	9.97 10.07	
Alkaloid from *Lupinus andersoni*	6.61 6.51	10.47	

BUREAU OF ANIMAL INDUSTRY
WASHINGTON, D. C.
JAMES FITTON COUCH

RECEIVED DECEMBER 23, 1932 PUBLISHED FEBRUARY 9, 1933

CONCERNING THE EXISTENCE OF THE SO-CALLED HEATS OF TRANSFER (Q^* VALUES) IN PELTIER HEATS

Sir:

To explain the Ludwig-Soret effect, Eastman [THIS JOURNAL, **48,** 1482 (1926)] introduced the concept of the heat of transfer (Q^*) [the heat of transfer of a mole of component A is designated as $\overline{Q}_A$ by Eastman], a latent heat which appears at some point in a homogeneous solution when a mole of dissolved component is transferred from this point to another place in the solution. The same quantity occurs in a discussion of electrolytic thermal forces. Wagner [*Ann. Physik,* (5) **3,** 629 (1929)] and later Lange and co-workers [Lange and Mischtschenko, *Z. physik. Chem.,* **A149,** 1 (1930)] extended these considerations to the electrolytic Peltier heats. According to them

$$_{\text{metal/solution}}\pi_i = T({}_{\text{metal}}\overline{S}_i - {}_{\text{solution}}\overline{S}_i) - z_iQ^*_\theta - n_CQ^*_C + n_AQ^*_A \qquad (1)$$

(π_i is the Peltier heat given up at the anode by a mole of the potential determining ion i of valence z_i, n_C and n_A are transference numbers and Q^*_C and Q^*_A are molar heats of transfer of cation and anion).

To date the following evidence for the existence of these novel heat effects (Q^*) could be advanced: (1) Eastman [THIS JOURNAL, **50,** 292 (1928)] found a certain agreement between the Q^* values determined from Ludwig-Soret coefficients and estimated from suitable thermo-electric measurements.

(2) Thermo-electric forces between differently oriented single crystals of the same metal can only be explained by Q^* values depending on direction [Wagner, *loc. cit.*] if one does not wish to postulate a directional dependence of $\overline{S}$.

(3) Measurements of the Ludwig-Soret effect and of thermoelectric forces on solid salts and mixed crystals have been explained by use of heats of transfer [Reinhold, *Z. physik. Chem.,* **B11,** 321 (1931)].

All these proofs rest on measurements made on non-isothermal systems, which, because of unavoidable irreversible heat conductivity, can only be treated thermodynamically under limited conditions [*cf.* Boltzmann, *Sitzungsber. Akad. Wiss. Wien, Math. Naturw. Klasse,* **96,** 1285 (1887)].

It therefore seemed desirable to test the assumption of heats of transfer by means of electrolytic Peltier heats which can be measured *isothermally* [Lange and Monheim, *Z. physik. Chem.,* **A150,** 186 (1930)].

Peltier heats, measured with a sensitive differential calorimeter [Lange and Robinson, *Chem. Rev.,* **9,** 89 (1931)] of the system Ag/AgNO$_3$ confirmed more exactly than previously the validity of the Thomson relationship between Peltier heat (π) and thermo-electric force (ϵ)

$$\pi/T = \epsilon$$

for electrolyte systems, so that objections raised against the non-isothermal foundations mentioned above have been weakened [Lange and Hesse, *Z. Elektrochem.,* **38,** 428 (1932)].

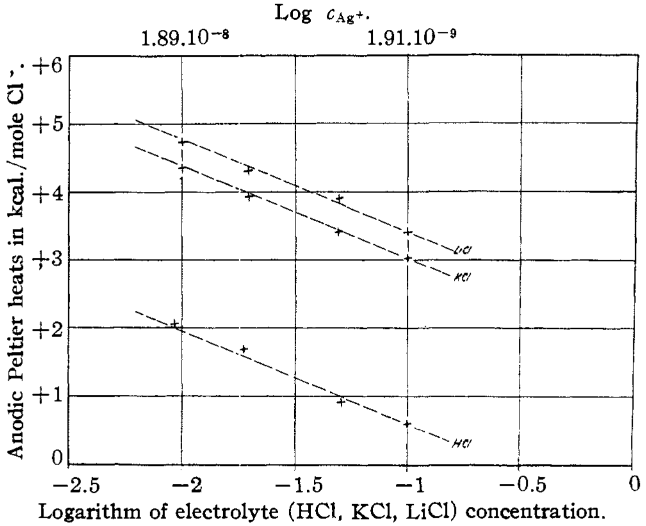

Fig. 1.—Electrolytic Peltier heats of the system Ag/AgCl/HCl (KCl, LiCl).

Peltier heats were also measured at 25° for the system Ag/AgCl/Cl$^-$ in the presence of different cations (K$^+$, H$^+$, Li$^+$).

According to equation (1) it follows for equal Cl$^-$ concentration that

$$\begin{aligned} {}_{\mathrm{AgCl/KCl}}\pi_{\mathrm{Cl}^-} - {}_{\mathrm{AgCl/HCl}}\pi_{\mathrm{Cl}^-} &= T({}_{\mathrm{HCl}}\bar{S}_{\mathrm{Cl}^-} - {}_{\mathrm{KCl}}\bar{S}_{\mathrm{Cl}^-}) \\ &+ ({}_{\mathrm{HCl}}n_{\mathrm{H}^+}Q^*{}_{\mathrm{H}^+} - {}_{\mathrm{KCl}}n_{\mathrm{K}^+}Q^*{}_{\mathrm{K}^+} + {}_{\mathrm{KCl}}n_{\mathrm{Cl}^-}Q^*{}_{\mathrm{Cl}^-} - {}_{\mathrm{HCl}}n_{\mathrm{Cl}^-}Q^*{}_{\mathrm{Cl}^-}) \end{aligned}$$

A more exact discussion shows that the first term on the right is practically zero for the small concentrations of the investigation. Therefore without consideration of the Q^* terms the electrolytic Peltier heats should be equal within the limits of experimental error for the different electrolytes.

As a matter of fact there are appreciable differences (almost 3 kcal.) even in 0.01 *M* solutions as the figure shows.

The existence of and therewith the necessity for considering these Q^* terms which Eastman introduced is thus established. It is also evident that the differences of partial molar entropies can not be determined by employing Peltier heats and thermo-electric forces alone [*cf.*, on the contrary, Bruzs, *Z. physik. Chem.*, **A161,** 83 (1932)].

A more detailed presentation of this material will be published shortly in a German journal.

PHYSICAL CHEMISTRY LABORATORY
OF THE UNIVERSITY
ERLANGEN, GERMANY
E. LANGE
TH. HESSE

RECEIVED JANUARY 6, 1933 PUBLISHED FEBRUARY 9, 1933

THE THERMAL INTERCONVERSION OF MIXED BENZOINS

Sir:

Julian and Passler [THIS JOURNAL, **54,** 4756 (1932)] record another case of the transformation of the mixed benzoin not formed by the cyanide condensation (anisbenzoin) into the isomer formed by the cyanide method (benzanisoin). The reverse transformation, which is the object of our work, has not hitherto been recorded. The present writers have found that pure benzanisoin (cyanide condensation), after heating for three hours at 125–130° and fractionation from cold dilute alcohol, gives appreciable amounts of anisbenzoin, m. p. 89°, identical with Asahina and Terasaka's compound. Evidently, above the melting point, an equilibrium lying far over to the side of benzanisoin exists. The amount of pure anisbenzoin isolated, after heating, from 20 g. of benzanisoin was 0.10 g. but considerably more was present.

EXPERIMENTAL RESEARCH LABORATORIES
BURROUGHS WELLCOME AND CO.
TUCKAHOE, N. Y.
JOHANNES S. BUCK
WALTER S. IDE

RECEIVED JANUARY 9, 1933 PUBLISHED FEBRUARY 9, 1933

THE NEUTRON, THE ATOMIC NUCLEUS AND MASS DEFECTS

Sir:

Two general theories of the constitution of atomic nuclei have been proposed: (1) that the nucleus is built up largely from α-particles (Harkins and Wilson[1]) and (2) that the Harkins–Masson[2] nuclear formula $(p_2e)_z(pe)_I$ (a), $(np)_zn_I$ (b) or $(\alpha/2)_zn_I$ (c), represents the constitution of any nucleus

---

[1] (a) Harkins and Wilson, *Proc. Nat. Acad. Sci.*, **1,** 276 (1915); (b) THIS JOURNAL, **37,** 1368, 1383 (1915).

[2] (a) Harkins, THIS JOURNAL, **42,** 1956 (1920); *Phil. Mag.*, **42,** 305 (1921). See also Ref. 1(b) and Durrant, THIS JOURNAL, **39,** 621–7 (1917). (b) Masson, *Phil. Mag.*

(Heisenberg.[3] See also the earlier paper of Iwenko[4]). Here p represents a neutron; e, an electron; n, a neutron; α, an α-particle, and z and I, the atomic and isotopic numbers. Form (b) of the formula expresses the Heisenberg theory best, though he does not deny the existence of α-particles in the nucleus. Obviously the total number of neutrons is

$$N = Z + I$$

in which Z gives the number of neutrons combined with protons, and I the number of "extra" neutrons.

The energy of binding of (a) a proton and electron to give a neutron is one million electron volts, of (b) a neutron and proton to give H^2 is also one, while that of two H^2 atoms to give one helium atom is 23 million electron volts (Table I). The values for (a) and (b) are uncertain, but the sum is $1.91 \cdot 10^6$.

Thus the pairing of the neutrons and extra protons in the helium nucleus involves a binding energy twelve times as great as the sum of the binding energies of (1) a proton and an electron, and (2) of a neutron and a proton.

Thus if a neutron enters into an α-particle it is subjected to such ex-

TABLE I

BINDING ENERGY OF ATOMS IN 10^6 ELECTRON VOLTS

$$\left.\begin{array}{lll} p + e \longrightarrow n_2 & 1.\,(?) & \\ n + p \longrightarrow H^2 & & 1.\,(?) \end{array}\right\} \text{Sum} = 1.91$$

$$2p + e \longrightarrow H^2 \quad 1.91$$

	Proton		Neutron		H^2	
	Odd	Even	Odd	Even	Odd	Even
$2H^2 \longrightarrow He$						23.2
$He + H^2 \longrightarrow Li^6$					3.42	
$Li^6 + n \longrightarrow Li^7$			6.2			
$Li^7 + H \longrightarrow 2He$		14.0				
$B^{10} + n \longrightarrow B^{11}$			6.3			
$B^{10} + H^2 \longrightarrow C^{12}$						21.0
$B^{11} + H \longrightarrow C^{12}$		14.1				
$C^{12} + n \longrightarrow C^{13}$			5.7			
$C^{12} + H^2 \longrightarrow N^{14}$					8.5	
$C^{13} + H \longrightarrow N^{14}$		(4.0)[a]				
$N^{14} + H^2 \longrightarrow O^{16}$						20.0
$O^{16} + n \longrightarrow O^{17}$			3.2			
$O^{16} + 2H^2 \longrightarrow Ne^{20}$					(12.4 av.)	
$F^{19} + H' \longrightarrow Ne^{20}$		6.8				
$Ne^{20} + 2n \longrightarrow Ne^{22}$				(4.2 av.)		
$Ne^{22} + H \longrightarrow Na^{23}$	9.3					
$A^{36} + 4n \longrightarrow A^{40}$				(7.4 av.)		

[a] This value is not directly comparable with the others in this column, since it relates to the formation of a nucleus which does not contain a whole number of α-groups.

---

(3) Heisenberg, *Z. Physik*, **77**, 1 (1932); **78**, 156 (1932).

(4) Iwenko, *Nature*, **129**, 798 (1932).

tremely powerful forces of polarization that if it does not entirely lose its individuality it becomes very different from a neutron not thus combined.

Table I also gives the approximate binding energy for the union of any atom listed in column 1 with a proton, neutron, or H^2 nucleus. Column 6 shows that the binding energy for the union of an $\alpha/2$ group is much larger (value about 20 million volts) if the final number of such groups in the nucleus is even, than if this number is odd (from 3 to 9 million volts). If the final number is even, then the last p_2e group presumably forms an α-particle with the odd p_2e group already present. Relatively high values are also found for the completion of an α-particle, by a proton (column 3, about 14 million volts for Li^7 and B^{11}, though only 6.8 for F^{19}). No data are available for the calculation of the binding energy for a single neutron in any case in which the final nucleus presumably consists of α-particles alone.

TABLE II

MASS DEFECT OR BINDING ENERGY PER α-PARTICLE

	$m' = \frac{-\Delta m}{N_\alpha} \times 10^4$	$\frac{-\Delta m'}{N_\alpha} \times 10^4$
C^{12}	10	12
O^{16}	22	0
Ne^{20}	22	
...	..	
A^{36}	48	3
A^{40}	51	4
Cr^{52}	62	−0.3
Zn^{64}	61	−0.5
Kr^{80}	59	−1.0
Sn^{112}	51	−2.6
Xe	43	

Table II is of interest since it shows that the mass defect per α-particle rises rapidly with the number of α-particles contrary to the assumption of Gamow's formula,[5] up to mass 52 (assumed number of α-particles = 13) and then decreases slowly with the mass number. There is no apparent discontinuity in the values where, between A^{36} and A^{40} according to theory (1) the first pair of cementing or "free" electrons enters, or theory (2) the first set of "free" neutrons (4 in number) come into the nucleus.

In a later paper the two theories will be compared on the basis of the above and other relations. In this connection, the mass numbers for magnesium, silicon, sulfur and calcium are badly needed, but are not at present available.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS

WILLIAM D. HARKINS

RECEIVED JANUARY 14, 1933 PUBLISHED FEBRUARY 9, 1933

---

[5] Gamow, "Constitution of Atomic Nuclei and Radioactivity," Oxford, 1931.

THE ATOMIC WEIGHT OF CESIUM

Sir:

Some years ago about four kilograms of cesium nitrate was extracted from pollucite and fractionally crystallized in the hope of concentrating an alkali element of higher atomic weight [Baxter, THIS JOURNAL, **37,** 286 (1915)]. This hope was not realized. A part of the fourth and fifth less soluble fractions of the last (18th) series of this crystallization which together amounted to 1200 g. have been further purified by three crystallizations as perchlorate, and, after conversion to chloride and fusion, by three crystallizations as chloride, all in platinum. The product was tested spectrographically in an arc formed by pure copper electrodes and was found to be wholly free from rubidium and potassium so far as could be seen. Analysis was then carried out by fusing the chloride in a weighed platinum boat in a quartz bottling apparatus and then comparing the salt with silver nephelometrically. In Analyses 1 and 2 the fusion atmosphere was nitrogen, in Analyses 3 and 4 the fusion atmosphere was hydrogen containing a small proportion of hydrogen chloride, while in Analysis 5 it was hydrogen only. The close agreement of the results seems to indicate that cesium chloride shows no tendency to become basic under these conditions nor to retain hydrogen chloride.

THE ATOMIC WEIGHT OF CESIUM

Analysis	CsCl in vacuum, g.	Ag in vacuum, g.	Ratio CsCl:Ag	Atomic wt. of cesium
1	8.96291	5.74296	1.56068	132.91
2	9.60983	6.15751	1.56067	132.91
3	9.70288	6.21686	1.56074	132.92
4	9.53125	6.10708	1.56069	132.91
5	7.52304	4.82025	1.56072	132.91
			Average 1.56070	132.91

The atomic weight found in our experiments is about 0.1 unit higher than that found by Richards and Archibald [*Proc. Am. Acad. Arts Sci.*, **38,** 443 (1903)] and Richards and Françon [THIS JOURNAL, **50,** 2162 (1928)], a difference which we can explain only by suggesting that the material used by these experimenters may not have been wholly free from rubidium and potassium, only 0.2% of even the former of which would be necessary to explain the discrepancy.

It is interesting that Aston [*Proc. Roy. Soc.*, (London) **A134,** 571 (1932); *Phil. Mag.*, **42,** 436 (1921)] and Bainbridge [*J. Franklin Inst.*, **212,** 317 (1931)] agree that cesium is a simple element and that Aston calculates from measurements of its packing fraction (-5×10^{-4}) an atomic weight of 132.917, using the conversion factor, 1.000125. With the factor 1.00022, cesium becomes 132.904. Our result therefore appears to remove the chief discrepancy between atomic weights determined by physicochemical methods and those obtained from mass-spectrographic data.

We expect to continue work on this problem.

COOLIDGE MEMORIAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASSACHUSETTS
G. P. BAXTER
J. S. THOMAS

RECEIVED JANUARY 18, 1933 PUBLISHED FEBRUARY 9, 1933

THE HABER–WILLSTÄTTER CHAIN MECHANISM OF ORGANIC AND ENZYMATIC PROCESSES

Sir:

Haber and Willstätter [*Ber.*, **64,** 2844 (1931)] have proposed chain mechanisms for a number of organic and enzymotic processes of which we may cite the oxidation of alcohol as typical. Their reaction scheme is

$$\mathrm{CH_3CH_3OH + Enzyme = CH_3\overset{/}{C}H(OH) + Mono\ desoxy\text{-}enzyme + H^{\cdot}} \qquad \text{(a)}$$

$$\mathrm{CH_3\overset{/}{C}HOH + CH_3CH_2OH + O_2 = 2CH_3CHO + H_2O + OH} \qquad \text{(b)}$$

$$\mathrm{OH + CH_3CH_2OH = CH_3\overset{/}{C}HOH + H_2O} \qquad \text{(c)}$$

A similar chain can be set up for aldehyde oxidation. We have attempted to verify such a mechanism, starting the chain of processes at stage (c) by decomposing hydrogen peroxide photochemically in mixtures of alcohol and oxygen suitably agitated. We find that the photo-decomposition of peroxide markedly sensitizes the interaction of alcohol and oxygen. The oxidation process is a chain reaction, sensitive to inhibitors but the chain length is short. It is much shorter than the assumed chain length ($\sim 10^5$) in the communication of Haber and Willstätter. Dilute aqueous aldehyde solutions behave similarly and the chain length is somewhat longer. The detailed results will be communicated immediately.

DEPARTMENT OF CHEMISTRY
PRINCETON UNIVERSITY
PRINCETON, N. J.
HUGH S. TAYLOR
AUSTIN J. GOULD

RECEIVED JANUARY 20, 1933 PUBLISHED FEBRUARY 9, 1933

ORIENTATION IN THE FURAN NUCLEUS

Sir:

The introduction of an aldehydic group into 3-methylfuran, by means of hydrogen cyanide and hydrogen chloride, results in the formation of 3-methyl-2-furfural [Reichstein, Zschokke and Goerg, *Helv. Chim. Acta*, **14,** 1277 (1931)]. The nitro-β-methylfuran obtained from 3-methylfuran by the action of fuming nitric acid in acetic anhydride has been shown to be 3-methyl-2-nitrofuran [Rinkes, *Rec. trav. chim.*, **49,** 1125 (1930)] by comparison with an authentic specimen kindly provided by Dr. I. J. Rinkes.

The 3-methylfuran was synthesized by the following sequence of reactions: 3-furoic acid ⟶ 3-furoyl chloride ⟶ 3-furaldehyde ⟶ 3-furaldehyde-hydrazone ⟶ 3-methylfuran. It readily forms a chloromercuri compound (3-methyl-2-furylmercuric chloride) which melts at 142°, and such mercurials are recommended as satisfactory derivatives for the characterization of many furan compounds, including those with an α-carboxylic group [*Rec. trav. chim.*, **51,** 1054 (1931), and **52** (March) (1933)].

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA

HENRY GILMAN
ROBERT R. BURTNER

RECEIVED JANUARY 23, 1933 PUBLISHED FEBRUARY 9, 1933

THE EFFECT OF WATER ON THE PHOTOSYNTHESIS OF HYDROGEN CHLORIDE

Sir:

In the last few months several papers have questioned the necessity of having water vapor present in order to bring about the photochemical union of hydrogen and chlorine in visible light [Rodebush and Klingelhoefer, THIS JOURNAL **55,** 130 (1933); Kimball and Eyring, *ibid.*, **54,** 3876 (1932); Allmand and Craggs, *Nature*, **130,** 927 (1932)]. Coehn and Jung [*Z. physik. Chem.*, **110,** 705 (1924)] reported several years ago that the reaction would not proceed if the water vapor pressure was reduced below 10^{-7} mm., and the maximum rate was not attained unless the water vapor exceeded 10^{-5} mm. In order to test this observation it is obvious that great care must be taken to prevent the accidental entry of sufficient water to cause the reaction to go. The most certain method is to carry out the experiments with the entire reaction vessel at such a temperature that the equilibrium value for the water vapor pressure is within the desired limits. We have performed such experiments at various temperatures between 145 and 200°K. and we find no evidence of the falling off in the rate such as reported by Coehn and Jung. If we had confirmed their results, there should have been a marked decrease in the rate between 160 and 177°K. In a recent note Baker [*Nature*, **131,** 27 (1933)] claims to have demonstrated the effect of water on this reaction as a lecture experiment. As he used phosphorus pentoxide to dry his gases the results he observed must have been due to inhibitors introduced by this reagent. We feel that our results show definitely that water vapor has no effect on the rate of photosynthesis of hydrogen chloride.

In our experiments the reaction vessel was a Pyrex glass bulb placed in a lead block provided with a Pyrex window. This ensemble was suspended in a Dewar vessel and cooled by means of liquid air and a cold air blast. Resistance thermometers wound on the reaction vessel and the lead block permitted accurate measurements of the temperature. In the temperature range covered, liquid or solid chlorine was present in the reaction vessel and therefore the rate could be followed by observing the pressure change.

At the present time we are investigating the rate law over the temperature range mentioned above. Preliminary results indicate that the dependence on the light absorbed changes from the first power to the square root as the temperature is lowered.

CHEMISTRY DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA
G. K. ROLLEFSON
J. C. POTTS

RECEIVED JANUARY 24, 1933 PUBLISHED FEBRUARY 9, 1933

NEW BOOKS

Hundert Jahre Liebigs Annalen der Chemie. (One Hundred Years of Liebig's Annalen der Chemie.) By RICHARD WILLSTÄTTER. Verlag Chemie, G. m. b. H., Corneliusstrasse 3, Berlin W 10, Germany, 1932. 12 pp. 14 × 22 cm.

The appearance during December, 1932, of the 500th volume of Liebig's *Annalen der Chemie* is a significant event in the life history of our science. This periodical, founded by Liebig just one hundred years ago, has had in the past as editors a succession of the great organic chemists of Germany—Wöhler, Kopp, Hofmann, Kekulé, Erlenmeyer, Volhard, Fittig, Von Baeyer, Wallach, Fischer, Graebe and Zincke. Today its editorial board consists of Willstätter, Wieland, Windaus and H. Fischer—every one of them a Nobel Prize laureate. In the pages of the *Annalen* are to be found a large proportion of the great classics of organic chemistry. Its five hundred volumes constitute substantially a history of the development of that science.

What other scientific journal has so inspiring a past and so brilliant a present!

ARTHUR B. LAMB

An Introduction to Chemistry. By FRANK B. KENRICK, Professor of Chemistry in the University of Toronto. The University of Toronto Press, Toronto, Canada, 1932. viii + 434 pp. 33 figs. 15 × 23 cm. Price, $3.00.

Not since Ostwald's attempt, a quarter of a century ago, to account for the fundamental laws of chemistry without the use of the atomic theory, has appeared a more interesting and consistent development of the principles of the science from actual laboratory observations than in "An Introduction to Chemistry" by Professor Kenrick. It is difficult to believe that in these days elementary students will "struggle" (to use the author's own word) with the labored and involved presentation of the subject, which is necessary when all terms and conceptions which are not rigidly defined by experiment are abandoned. It is equally difficult to believe that teachers will consider that a student can afford the time to master, for example, one hundred and forty-five difficult pages, in order to get the distinction between mechanical mixtures, solutions and pure substances. In short, to quote directly from the preface, "This will not be found to be a 'teachable' book; a teachable book must be a learnable book, and that is a most danger-