Summary

The distribution of monochloro- and dichloro-acetic acids between aqueous sulfate solutions and normal dibutyl ether has been measured.

The "activity coefficient" as measured by the ratio of the molality in pure water to that in a salt solution at a constant activity is determined by the salting-out effect of the sulfate on the undissociated part of a weak acid, and the amount of formation of hydrosulfate ion.

At constant ionic strength the "activity coefficient" is lower the greater the dissociation constant of the weak acid.

The "activity coefficient" is lowered to a greater extent by potassium sulfate than by magnesium sulfate.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE ROYAL VETERINARY AND AGRICULTURAL COLLEGE]

THE EFFECT OF SHAKING ON THE EVOLUTION OF GASES FROM SUPERSATURATED SOLUTIONS AND ITS IMPORTANCE FOR THE MEASUREMENT OF THE VELOCITY OF CERTAIN CHEMICAL REACTIONS

BY KAI JULIUS PEDERSEN

RECEIVED APRIL 13, 1927 PUBLISHED NOVEMBER 5, 1927

Introduction

During the examination of the rate of decomposition of nitro-acetic acid in aqueous solution

$$NO_2CH_2COOH \longrightarrow NO_2CH_3 + CO_2$$

by means of an apparatus described by J. N. Brönsted[1,2] in which the pressure of the gas is measured during the reaction, it was found necessary to examine whether the gas was evolved sufficiently quickly to prevent a supersaturation effect. In order to get a quick evolution of the carbon dioxide the reaction flask was shaken horizontally. It was found that the supersaturation is very much less at a certain rate of shaking than with slower or quicker shaking. When the rate of shaking is not kept very constant, the supersaturation may, even when it is only small, as a consequence of this variability, cause a considerable error. The author thinks that this examination of the influence of the supersaturation may have some interest for other investigators who study the velocity of chemical reactions by measurement of the rate of gas evolution. Part 1 of this paper is an examination of the velocity of the evolution of carbon dioxide from supersaturated solution and its dependence upon the length and number per minute of the horizontal shakings of the reaction vessel. Part

---

[1] Brönsted and King, THIS JOURNAL, **47**, 2523 (1925).

[2] Brönsted and Duus, *Z. phyiks. Chem.*, **117**, 299 (1925).

2 is a mathematical treatment of the influence of supersaturation on the measurement of the velocity of a unimolecular reaction.

Part 1

The experiments were made at 18° in the Brönsted apparatus. The volume of the spherical part of the flask was 210 cc. Usually 100 cc. of solution was used; in one series of experiments only 60 cc. In each experiment 0.08–0.10 g. of sodium bicarbonate (about 0.001 mole) was weighed roughly in a little platinum bucket which was suspended at the top inside the apparatus so that it could be dropped into the solution after evacuation of the apparatus. The solution was usually 0.1 *M* hydrochloric acid; in some experiments a buffer solution: 0.06 *M* acetic acid + 0.04 *M* sodium acetate (*P*H about 4.5).

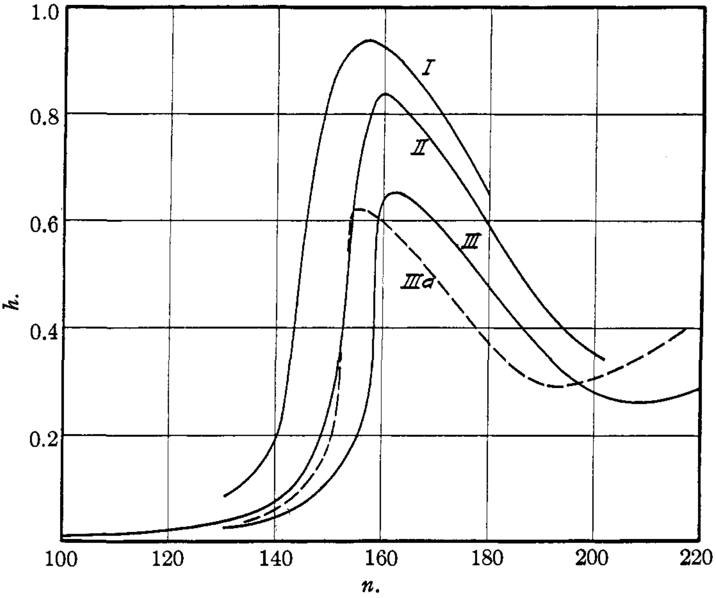

Fig. 1.—The velocity of the evolution of carbon dioxide from supersaturated solution.

In all the experiments (about 100) the rate of evolution of carbon dioxide followed the unimolecular law. Although the reaction in most cases was very quick, the agreement with the formula for the unimolecular reaction

$$ht = \text{constant} - \log P \qquad (1)$$

(h being the velocity constant; t, the time in minutes; $P = p_\infty - p$, the difference between the pressure p_∞ above the solution after the reaction has finished and the pressure p at the time t) was very good; h was computed graphically by plotting log P against t. As seen from (1) it is not necessary to know the exact weight of the sodium bicarbonate nor the time when it is dissolved. The shaking was stopped before the bucket was dropped and the reaction flask was kept quiet for some minutes until the first vigorous evolution of carbon dioxide had ceased, after which the pressure remained almost constant. Then the shaker was started and the rate of evolution from the supersaturated solution determined.

The finite velocity of the reaction in the aqueous phase, $H_2CO_3 \longrightarrow H_2O + CO_2$ (dissolved), was found to be without importance even in the quickest experiments with acetate buffer solutions. This is in agreement with the measurements of C. Faurholt,[3] who has determined the velocity of the above reaction. At $P_H = 5$ he finds at 18° the velocity constant $k = 9$ (min.$^{-1}$, decad. logs) for the unimolecular reaction. In 0.1 M hydrochloric acid the reaction is practically instantaneous. Thus the velocity of the formation of dissolved carbon dioxide from the bicarbonate is, even at $P_H = 5$, ten times greater than the greatest velocity found for the evolution of gaseous carbon dioxide from the solution.

The evolution of carbon dioxide from its supersaturated solution is a limited reaction consisting of two opposing reactions: CO_2 (dissolved) $\rightleftarrows CO_2$ (gas). As is well known, the constant h which has been measured is really the sum of the constants for the velocities of the two opposing reactions.

The experimental results are given in Fig. 1 and in Tables I–VI; h is the velocity constant (min.$^{-1}$, decad. logs), t is the time in minutes, n is the number of horizontal movements forwards and backwards of the reaction flask and l is the length in mm. of the single movement.

In Table I an experiment is given in full to give an idea of the accuracy of the measurements; $t = 0$ is the time when the shaker is started some time after the bicarbonate has been dissolved.

Table I

Evolution of Carbon Dioxide from Supersaturated Solution

Solution: 60 cc. of 0.1 M HCl. $n = 160$. $l = 7$ mm.

t, min.	p(cm. Hg)	P	log P	log P_0 − log P	h
0			0.074[a]	0.000	..
1/4	7.02	0.86	.934-1	.140	(0.56)
1/2	7.28	.60	.778-1	.296	.59
3/4	7.46	.42	.623-1	.451	.60
1	7.58	.30	.477-1	.597	.60
1 1/4	7.66	.22	.342-1	.732	.59
1 1/2	7.72	.16	.204-1	.870	.58
1 3/4	7.78	.10	.000-1	1.074	.61
∞	7.88	.00		Mean value: h = 0.60	

[a] Extrapolated.

In Fig. 1 the curves represent the following series of experiments, Curve I: 100 cc. of solution, $l = 18$ mm. (Table II); Curve II: 100 cc. of solution,

---

[3] Faurholt, *J. chim. phys.*, **21**, 430 (1924).

l = 12 mm. (Tables III–IV); Curve III: 100 cc. of solution, l = 7 mm. (Table V); Curve IIIa: 60 cc. of solution, l = 7 mm. (Table VI).

Table II

Solution: 100 cc. 0.1 M HCl. l = 18 mm.

n	h	n	h
133	0.096	157	0.94
144	.43	161	.91
150	.84	166	.88
156	.93	178	.68

Table III

Solution: 100 cc. 0.1 M HCl. l = 12 mm.

n	h	n	h
100	0.0095	156	0.70
119	.021	158	.81
134	.052	162	.84
139	.060	163	.81
149	.22	166	.77
152	.37		

Table IV

Solution: 100 cc. 0.06 M acetic acid + 0.04 M sodium acetate. l = 12 mm.

n	h	n	h	n	h
113	0.016	155	0.62	172	0.72
130	.046	160	.86	177	.62
140	.077	160	.85	185	.52
148	.35	160	.81	191	.425
154	.62	164	.82	201	.35

Table V

Solution: 100 cc. 0.1 M HCl. l = 7 mm.

n	h	n	h	n	h
133	0.028	161	0.64	187	0.36
142	.040	161	.67	196	.27
147	.096	162	.64	198	.29
152	.13	166	.64	207	.26
154	.13	170	.59	209	.27
157	.25	177	.54	217	.275
159	.40	180	.49	224	.31
159	.50				

Table VI

Solution: 60 cc. 0.1 M HCl. l = 7 mm.

n	h	n	h	n	h
135	0.037	163	0.56	181	0.36
146	.103	165	.51	192	.285
151.5	.21	165	.53	201	.32
154	.61	166	.55	213	.37
160	.60	172	.48		

When n is about 160, h has a maximum. It falls quickly when n is increased or diminished, especially rapidly when n is diminished. In Curve

III it falls to half its value when n is diminished from 159 to 158 per minute. At greater values of n, h will pass through a minimum, as seen in the figure. The shape of the curves is similar to that of an ordinary curve of resonance. The maxima can be explained as due to resonance. When n has about that value corresponding with the maximum of h, the solution reaches the neck of the flask and falls down again. When it is shaken more quickly, it does not reach so far before it is stopped in its movement. It behaves like a pendulum, which prefers a certain number of oscillations per minute. If it is pushed at other intervals than its own time of oscillation it does not move so well.

Part 2

Let us consider the reactions (I) $A \longrightarrow B + C$ (dissolved), velocity constant k (decad. logs) or k_n (natural logs), $k = k_n \log e$; (II) C (dissolved) $\rightleftarrows$ C (gas), velocity constant h (decad. logs) or h_n (natural logs), h is the sum of the velocity constants for the two opposing reactions.

Let p denote the observed pressure of C (gas) at the time t. π is the pressure we would have obtained if there were no supersaturation. $\pi - p = \delta$ is a measure for the supersaturation. The subscripts 0 or ∞ denote that the pressures correspond with $t = 0$ or $t = \infty$. We put $P = p_\infty - p$ and $P_0 = p_\infty - p_0$.

We have the following two differential equations

$$-\frac{d(P - \delta)}{dt} = k_n\,(P - \delta) \qquad (2)$$

and

$$\frac{dp}{dt} = h_n\delta \qquad (3)$$

They express, respectively, that Reaction (I) would give the unimolecular constant k_n in the experiment if there were no supersaturation, and that reaction (II) approaches the equilibrium as if it were a unimolecular complete reaction with the constant h_n. (2) and (3) are the exact mathematical expressions for the velocities of Reactions (I) and (II); (3) can also be written

$$-\frac{dP}{dt} = h_n\delta \qquad (4)$$

By integration of (2) we have

$$P - \delta = (P_0 - \delta_0)\,e^{-k_n t} \qquad (5)$$

which, together with (4), gives

$$\frac{dP}{dt} + h_nP = h_n\,(P_0 - \delta_0)\,e^{-k_n t} \qquad (6)$$

By integration we obtain

$$P = (P_0 - \delta_0)\cdot\left[\frac{h_n}{h_n - k_n}\,e^{-k_n t} - \left(\frac{k_n}{h_n - k_n} - \frac{\delta_0}{P_0 - \delta_0}\right)e^{-h_n t}\right] \qquad (7)$$

From (5) and (7) by subtraction

$$\delta = (P_0 - \delta_0)\cdot\left[\frac{k_n}{h_n - k_n}\cdot e^{-k_nt} - \left(\frac{k_n}{h_n - k_n} - \frac{\delta_0}{P_0 - \delta_0}\right) e^{-h_nt}\right] \tag{8}$$

Using decadic logarithms, (7) and (8) can be written as follows

$$P = (P_0 - \delta_0)\cdot\left[\frac{h}{h - k}\,10^{-kt} - \left(\frac{k}{h - k} - \frac{\delta_0}{P_0 - \delta_0}\right) 10^{-ht}\right] \tag{9}$$

$$\delta = (P_0 - \delta_0)\left[\frac{k}{h - k}\,10^{-kt} - \left(\frac{k}{h - k} - \frac{\delta_0}{P_0 - \delta_0}\right) 10^{-ht}\right] \tag{10}$$

(9) can be written as

$$kt = \log (P_0 - \delta_0) + \log \frac{h}{h - k} - \log\left[P + (P_0 - \delta_0)\left(\frac{k}{h - k} - \frac{\delta_0}{P_0 - \delta_0}\right) 10^{-ht}\right] \tag{11}$$

If $t = 0$ is the time when the reaction is started, and if we assume that there is no C present at $t = 0$, we have $\delta = 0$, in which case (11) simplifies to

$$kt = \log P_0 + \log \frac{h}{h - k} - \log\left[P + P_0\,\frac{k}{h - k}\cdot 10^{-ht}\right] \tag{12}$$

If we ignore the supersaturation, the following simple formula would hold

$$kt = \log P_0 - \log P \tag{13}$$

When the shaking is kept uniform, and accordingly h is a constant, $\log \dfrac{h}{h - k}$ in (12) is constant and without importance for the determination of k. The other correction $\Delta = P_0\,\dfrac{k}{h - k}\,10^{-ht}$ decreases rapidly as t increases. If we require $\Delta < 0.01$ cm., before we take readings of p, we are sure to attain this by waiting until the time t determined by

$$\Delta < 10\cdot 10^{-ht} < 10^{-2}. \quad ht > 3. \quad t > 3/h$$

(we assume $P_0 < 10$ cm. and $h > 2k$).

In Fig. 2, AB is the straight line we should get by plotting log P against t if there were no supersaturation ($P_0 = 8$ cm., $k = 0.03$, $h = \infty$). With supersaturation, say $h = 0.3$, we get the curve AB_1 by plotting log P against t. AB_1 very quickly fuses into the straight line A_1B_1. Thus the supersaturation only causes a parallel displacement of the straight line. The magnitude of this displacement is determined by the term $\log h/(h-k)$. Δ determines how quickly the curve AB_1 fuses into the straight line A_1B_1.

If Reaction II had taken place in a homogeneous phase, h would be constant at constant temperature. In the present case Reaction II is a heterogeneous reaction and h varies with the rate of shaking. We shall find what influence it will have if h changes to h' at the time t_1 during the reaction. From (11) we get

$$k(t - t_1) = \log (P_1 - \delta_1) + \log \frac{h'}{h' - k} - \log \left[P + (P_1 - \delta_1)\left(\frac{k}{h' - k} - \frac{\delta_1}{P_1 - \delta_1}\right) 10^{-h(t-t_1)}\right] \qquad (14)$$

From (5) we get, putting $\delta_0 = 0$,

$$\log (P_1 - \delta_1) = \log P_0 - kt_1 \qquad (15)$$

and from (5) and (10)

$$\frac{\delta_1}{P_1 - \delta_1} = \frac{k}{h - k} - \frac{k}{h - k} 10^{-(h-k)t_1} \qquad (16)$$

If we substitute (15) and (16) in (14) we get

$$kt = \log P_0 + \log \frac{h'}{h' - k} - \log \left[P + P_0 \frac{k}{h - k}\left(10^{-(h'(t-t_1) + ht_1)} - \frac{h' - h}{h' - k} 10^{-(h'(t-t_1) + kt_1)}\right)\right] \qquad (17)$$

which gives an expression for k when $t \geqq t_1$. It shows that the change in supersaturation due to the change in h at $t = t_1$ causes a new parallel displacement of the straight line whose slope determines k. If $P_0 = 8$ cm., $k = 0.03$, $h = 0.3$, when $t < 5$ min., but $h = 0.6$ when $t > 5$ min., we get the curve ACB$_2$ in Fig. 2. CB$_2$ fuses into the straight line A$_2$B$_2$ parallel to AB. The magnitude of the extra displacement is determined by the change in the constant term of equation (17) compared with that of (12) which holds for $t \leqq t_1$. The correction

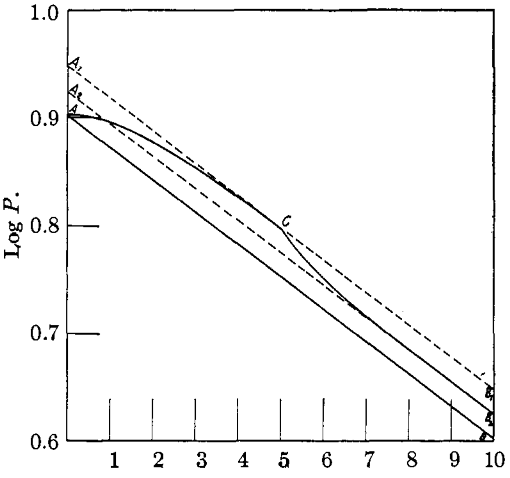

Fig. 2.—The effect of supersaturation on a unimolecular reaction.

$$\Delta_2 = -P_0 \frac{k}{h - k} \frac{h' - h}{h_1 - k} 10^{-(h'(t-t_1) + kt_1)}$$

shows how quickly this second displacement takes place, while

$$\Delta_1 = P_0 \frac{k}{h - k} 10^{-(h'(t-t_1) + ht_1)}$$

expresses the changed velocity for the first displacement for $t > t_1$. Of course Δ_1 will only play a part when the change in h to h' occurs very soon after the start, that is, before the first displacement has finished.

If we wish to calculate how great a change in h we can allow during the reaction, it is obviously sufficient to consider the corrections in the constant term. We, therefore, put $\Delta_1 = \Delta_2 = \Delta = 0$. We get instead of (12) and (17) the simpler formulas

$$0 < t < t_1: \quad kt = \log P_0 + \log \frac{h}{h-k} - \log P \tag{18}$$

$$t_1 < t: \quad kt = \log P_0 + \log \frac{h'}{h'-k} - \log P \tag{19}$$

(19) can be written as follows

$$t_1 < t: \; kt = \log P_0 + \log \frac{h}{h-k} - \log \left(P \frac{h}{h-k} \frac{h'-k}{h'} \right)$$

which by comparison with (18) gives

$$\frac{\Delta P}{P} = \frac{h}{h-k} \frac{h'-k}{h'} - 1 = \frac{k}{h-k} \frac{h'-h}{h'}$$

$$\frac{\Delta h}{h} = \left(\frac{h}{k} - 1 \right) \frac{\Delta P}{P}$$

If we require that $\Delta P/P < 0.2\%$, the permissible variation in h is determined by

$$\frac{\Delta h}{h} < \left(\frac{h}{k} - 1 \right) 0.2\%$$

Examples

While the free undissociated nitro-acetic acid is stable in aqueous solution, the decomposition of the nitro-acetate ion follows the unimolecular law.[4] The constants are at 18° 0.0241 and at 20° 0.0316 (min.$^{-1}$, decad. logs).

1. In an experiment on the decomposition of the nitro-acetate ion we have $k < 0.03$. $P_0 < 10$ cm. We use 100 cc. of solution. We shake so that we get as little supersaturation as possible: $l = 18$ mm., $n = 158$ (the maximum of Curve I in Fig. 1). From the figure we find $h = 0.94$. We have $\Delta < 10\ (0.03/0.9)\ 10^{-0.94\,t}$. $t = 1$, gives $\Delta < 0.04$, $t \geqq 2$, gives $\Delta < 0.005$. If we allow an error of 0.01 cm. in P, we can start the readings two minutes after the dissolution of the nitro-acetic acid.

In h we can allow a variation of $((0.94/0.03) - 1)\ 0.2 = 6\%$. From Curve I we find that n must be kept within the limits $152 < n < 163$.

2. If we shake more rapidly, say $n = 190$, $l = 12$ mm., the conditions become much less favorable for a good result, as seen from the following calculations. From Curve II in Fig. 1 we find $h = 0.43$; $\Delta < 10\ (0.03/0.40)\ 10^{-0.43\,t}$.

The induction period is much longer

t	1	2	3	4	5
Δ	0.28	0.10	0.04	0.014	0.006

We must wait five minutes for the first reading. The permissible variation in h is $((0.43/0.03) - 1)\ 0.2 = 2.6\%$. From the curve we find that n

---

[4] Pedersen, *Trans. Faraday Soc.*, **23**, 316 (1927).

must be kept within the limits $189 < n < 191$. A comparison of the two examples makes clear of how great importance it may be to know how to do the shaking in order to get the best effect.

In conclusion I wish to thank Professor Dr. Niels Bjerrum, whose advice and helpful criticism of my work have been of great value.

Summary

The supersaturation error in measurements of velocity of chemical reactions by rate of gas evolution has been examined.

The velocity of the evolution of carbon dioxide from supersaturated solution follows the unimolecular law. The dependence of its velocity constant h on the number of horizontal shakings n per minute has been determined. h has a maximum and falls rapidly when n is diminished or increased.

A mathematical expression for the velocity of the evolution of gas in the course of the reaction $A \longrightarrow B + C$ (dissolved), followed by the reaction C (dissolved) $\rightleftarrows$ C (gas), has been derived.

The importance of the results for the measurement of a fairly quick unimolecular reaction has been discussed.

COPENHAGEN, DENMARK

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY, NO. 557]

SILVER ION CATALYSIS OF PERSULFATE OXIDATIONS. I SALT EFFECT ON THE VELOCITY OF OXIDATION OF AMMONIA. II. COMPARISON OF THE VELOCITY WITH VARIOUS REDUCING AGENTS

BY CECIL V. KING

RECEIVED MAY 16, 1927 PUBLISHED NOVEMBER 5, 1927

I. Introduction

It has been shown that persulfates react with ammonia, in alkaline solutions, in the presence of silver salts, with a measurable velocity,[1] and Yost has represented the reaction as taking place in two steps, as follows (the silver ion, however, being in an ammonia complex):

$$S_2O_8^{--} + Ag^{+} \longrightarrow 2SO_4^{--} + Ag^{+++} \text{ measurable} \qquad (1)$$

$$3Ag^{+++} + 2NH_3 \longrightarrow 3Ag^{+} + N_2 + 6H^{+} \text{ extremely rapid} \qquad (2)$$

There seems to be no question that trivalent silver is formed, as indicated by two things: the analysis of the insoluble compound formed when persulfates and silver salts are mixed, and the fact that the reaction rate, when ammonia or chromic salts are oxidized, is proportional to the *first* power of the silver-ion concentration.

---

[1] (a) Marshall, *Proc. Roy. Soc. Edinburgh*, **23**, 163 (1900). (b) Yost, THIS JOURNAL, **48**, 374 (1926).