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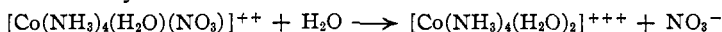
THE VELOCITY OF DECOMPOSITION OF THE CARBONATO-TETRAMMINE-COBALTIC ION AND ITS DEPENDENCE ON THE HYDROGEN-ION CONCENTRATION

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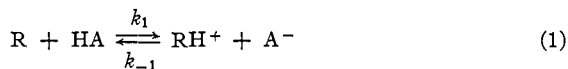
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During the last few years new light has been thrown on the field of hydrogen- and hydroxyl-ion catalysis. The recent progress is to a great extent due to the work of Brönsted and his collaborators.¹ Brönsted's views on catalysis are intimately connected with his theory of acids and bases.² According to this theory, any substance, whether it is a neutral molecule or an ion, is called an acid, if it has a tendency to split off protons, and a base, if it tends to add on protons. Thus if $A \rightleftharpoons B + H^+$, A is an acid and B the corresponding base. In Brönsted's theory of general acid and basic catalysis, catalytic effects are attributed not only to the hydrogen ion and to the hydroxyl ion, but to all substances which are sufficiently strong acids and bases according to the new definition. The magnitude of the catalytic effect increases with increasing acid or basic strength of the catalyst. The existence of general acid or basic catalysis has been experimentally established in a number of cases.¹ However, this fact does not exclude the possibility of cases of specific hydrogen or hydroxyl ion catalysis where only hydrogen or hydroxyl ions but not acids or bases in general are catalysts. The reaction



examined by Brönsted³ may be considered as being a case of specific hydroxyl-ion catalysis.

Let us consider the scheme^{3a}



k_1 , k_{-1} and k_2 are velocity constants. We consider the two special limiting cases

(a) $k_2 \gg k_1 \times c_{\text{HA}}$, $k_2 \gg k_{-1} \times c_{\text{A}^-}$. Reaction 1 from left to right determines the velocity of the total reaction. Practically all the molecules RH^+ react according to (2) before they get time to react with A^- and form $\text{R} + \text{HA}$ again. We have *general acid catalysis*.

(b) $k_{-1} \times c_{\text{A}^-} \gg k_1 \times c_{\text{HA}} \gg k_2$. Equilibrium 1 is maintained all

¹ J. N. Brönsted, *Trans. Faraday Soc.*, **24**, 630 (1928).

² J. N. Brönsted, *J. Phys. Chem.*, **30**, 777 (1926).

³ J. N. Brönsted, *Z. physik. Chem.*, **122**, 383 (1926).

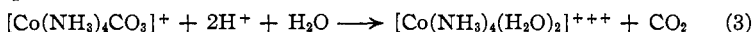
^{3a} Cf. Skrabal, *Trans. Faraday Soc.*, **24**, 687 (1928).

the time. The concentration of RH^+ is small compared with that of R c_{RH^+} and consequently the velocities are only dependent on the hydrogen-ion concentration, when the salt effect is neglected. In this case we have *specific hydrogen-ion catalysis*.

These are special limiting cases. Reactions where both the velocities of (1) as well as that of (2) affect the velocity of the total reaction are quite possible, although their existence has not yet been experimentally established.

The present work was started as a contribution to the study of these different kinds of catalysis.

Carbonato-tetrammine-cobaltic salts have been prepared by S. M. Jørgensen.⁴ He found that they split off carbon dioxide almost instantaneously with cold dilute hydrochloric acid. With very dilute acid ($< 1 N$) only diaquo-tetrammine salt is obtained



With more concentrated hydrochloric acid some chloro-aquo-tetrammine salt is also formed.

In the present work the kinetics of Reaction 3 have been studied at 25° and at different hydrogen-ion concentrations. The experiments fall into 4 series: (1) in glycolate buffer solutions with the total salt concentration 0.11 N . (The hydrogen-ion concentration was here varied within the ratio of 1 to 10); (2) in glycolate buffers with the salt concentration 0.21 N ; (3) in acetate buffers with the salt concentration 0.98 N ; (4) in acetate buffers with the salt concentration 0.11 N .

It will be shown that the velocity may be expressed as the sum of two velocities, one being independent of the hydrogen-ion concentration, the other being proportional to the hydrogen-ion concentration:

$$\frac{dx}{dt} = (k'_0 + k'_1 \times c_{\text{H}^+})(c-x) \quad (4)$$

where c is the initial concentration and $c - x$ the concentration at the time t of the carbonato-tetrammine-cobaltic salt; k'_0 and k'_1 are constants.

This simple relationship only holds when the carbon dioxide pressure is small or the hydrogen-ion concentration comparatively great. However, the following treatment will be based on Equation 4, and we shall see how well the experiments agree with it.

The Apparatus

The rate of Reaction 3 was followed by measuring the pressure of the carbon dioxide above the solution during the reaction. For this purpose a modification of Brønsted's shaking apparatus⁵ was used. In its original form it could be used only in a narrow temperature interval, namely at and a little below room temperature, because a part

⁴ S. M. Jørgensen, *Z. anorg. Chem.*, **2**, 279 (1892).

⁵ Brønsted and King, *THIS JOURNAL*, **47**, 2523 (1925).

of the apparatus is above the water of the thermostat. Above room temperature water distils from the solution in the flask to the top of the apparatus, and the condensed water is apt to run down into the glass spring.

In its new form the apparatus is completely under water except one end of the pressure gage (Fig. 1). The reaction flask A with a capacity of 200 cc. is connected with the mercury manometer C through the elastic glass capillary B, which allows a horizontal shaking of the flask A to prevent supersaturation. The apparatus is made in two separate parts. One piece is the part which is in the thermostat, ending in the horizontal tube which goes through the wall of the thermostat. The second piece is the tube C which is originally open at the top. The two pieces are put in their positions and fused together. Mercury is poured into C through the opening at the top. The apparatus is evacuated to a low pressure simultaneously through C and the tap D. C is sealed off above the spherical part, and the apparatus is ready for use. F is an arrangement to hold and, when desired, to drop a small platinum bucket into the solution in the flask A.

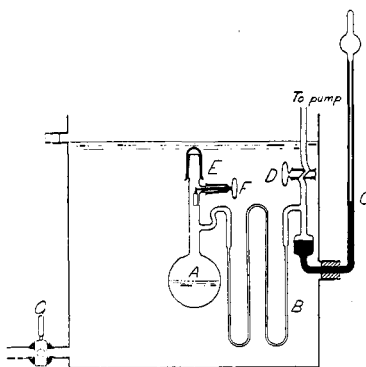


Fig. 1.

It consists of a ground slip-on stopper which has inside a little glass rod ending in a platinum hook. Before the start of an experiment the bucket containing the substance for the reaction is suspended on the hook. When the stopper is turned through 180° the bucket is released and drops into the flask. When an experiment was to be done so much water was removed from the thermostat through the tap G that the opening of the flask A was above the surface. The buffer solution (in each experiment 100 cc.) was poured into the flask. The bucket with the carbonato-tetrammine-cobaltic salt (about 0.001 mole in each experiment) was suspended on the hook. The apparatus was closed by means of the ground slip-on stopper E, and the water which had been removed from the thermostat was poured back. The shaker was started, and the apparatus was evacuated through the tap D. The reaction was started when the substance was dropped into the solution. In all the experiments the temperature was kept constant at $24.95 \pm 0.01^\circ$.

Calculation of the Velocity Constants.—We use the following symbols.

The stoichiometrical initial concentrations of the buffer solution

Acid HA (glycolic or acetic acid)	<i>a</i> molar
Sodium salt NaA (glycolate or acetate)	<i>b</i> molar
Initial concentration of carbonato-tetrammine ion	<i>c</i> molar
Its concentration at the time <i>t</i>	<i>c</i> - <i>x</i> molar
Concentration dissociation constant of the acid of the buffer solution	<i>K</i>
Activity dissociation constant of the same	<i>K</i> ₀
Ratio between the concentrations of undissociated acid (glycolic or acetic) and ion (glycolate or acetate) at the time <i>t</i>	

$$h = \frac{c_{HA}}{c_{A^-}} = \frac{c_{H^+}}{K}$$

At the time $t = 0$ we set $h = h_0$, at the time $t = \infty$ we set $h = h_\infty$. $\frac{1}{2}(h_0 + h_\infty) = h_m$.

The equilibrium constant for the reaction



We now rewrite Equation 4 as follows

$$\frac{dx}{dt} = (k'_0 + k'_1 \times c_{\text{H}^+})(c - x) = (k'_0 + k'_1 \times K \times h)(c - x) \quad (5)$$

Both k'_1 and K vary with the salt concentration, but in a series of experiments where the total salt concentration is kept constant while h varies, k'_1 , K and accordingly also the product $k'_1 \times K$ may be considered as constants. We must, however, take into account that the composition of the buffer solution, expressed by h and determining c_{H^+} , alters during the reaction according to (3). Further, the reaction product $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{+++}$ is a weak acid which has also some effect on h . We have

$$h = \frac{a - hK - 2x + \frac{L}{L+h}x}{b + hK + 2x - \frac{L}{L+h}x}$$

Using the abbreviations

$$A = \frac{a - h_0K}{2 - \frac{(h_0 - h_\infty)K}{c} - \frac{L}{L+h_m}} \quad (6)$$

$$B = \frac{b + h_0K}{2 - \frac{(h_0 - h_\infty)K}{c} - \frac{L}{L+h_m}} \quad (7)$$

we have to a sufficient approximation $h = (A - x)/(B + x)$. In particular $h_0 = A/B$ and $h_\infty = (A - c)/(B + c)$. In order to calculate A and B we must know approximate values of K , L , h_0 and h_∞ .

We can now write the differential Equation 5 in the following form

$$\frac{dx}{dt} = \left(k'_0 + k'_1 K \frac{A - x}{B + x} \right) (c - x)$$

Integrating and noting that $x = 0$ when $t = 0$ we get

$$kt = \log \frac{c}{c-x} - \frac{1+h_\infty}{1-f} \log \frac{fB+A}{fB+A-(1-f)x} \quad (8)$$

where $k = k_0 + K k_1 h_\infty$, $k_0 = 0.4343 k'_0$, $k_1 = 0.4343 k'_1$ and $f = k_0/Kk_1$.

The difference between the manometer readings p_∞ at the time $t = \infty$ and p at the time t is called $P = p_\infty - p$. P is proportional to $c - x$. $P = \varphi(c - x)$. We find the constant φ according to $\varphi = P_0/c$. Formula 8 is now transformed into

$$kt = \log \frac{P_0}{P} - \left(1 + \frac{f+h_\infty}{1-f} \right) \log \frac{\frac{f+h_\infty}{1-f}(B+c)\varphi + P_0}{\frac{f+h_\infty}{1-f}(B+c)\varphi + P} \equiv \psi(P) \quad (9)$$

The second term of $\psi(P)$ expresses the effect of the change in hydrogen-ion concentration during the reaction. Generally this term is small compared with $\log P_0/P$.

The ratio f being unknown, we provisionally plot $\log(P_0/P)$ against t for a whole series of experiments with constant total salt concentration

but with varying h_∞ . In this way we find an approximate value for k for each experiment. We now plot these approximate values against h_∞ . The points fall fairly well on a straight line determining according to the equation $k = k_0 + K \times k_1 \times h_\infty$ approximate values of k_0 and $K \times k_1$. From these we find an approximate value of f which we use in (9). We now plot $\psi(P)$, calculated by means of the approximate value for f against t , and find better values for k_0 , $K \times k_1$ and f . By successive repetitions we continue until a repetition gives the same values again.

For the calculation of A and B , (6) and (7), it is necessary to know K and L . Fortunately they enter the expressions only in small correction terms; consequently only rough values of K and L are necessary. The activity dissociation constants found by conductivity at 25° are for glycolic acid⁶ $K_0 = 1.54 \times 10^{-4}$ and for acetic acid $K_0 = 1.81 \times 10^{-5}$ (recalculated from the measurements of Kendall⁷ by C. W. Davies).⁸ With sufficient approximation except for the 1 N acetate, we may use the formula $-\log K = -\log K_0 - \sqrt{\mu} + \mu$, where μ is the ionic strength. We thus get for the glycolate buffer, salt concentration 0.11 N , $K = 2.6 \times 10^{-4}$, and at the salt concentration 0.21 N , $K = 3 \times 10^{-4}$. For the acetate buffer, salt concentration 0.11 N , we get $K = 3.0 \times 10^{-5}$. Brönsted and Volqvartz⁹ have determined the acid dissociation constant of the diaquo-tetrammine-cobaltic ion



They find at 15°, $-\log K_{\text{Aq.}} = 5.21 + 2\sqrt{\mu} - \mu$. From this and their measurement at 20° $\sqrt{\mu} = 0.29$, $-\log K_{\text{Aq.}} = 5.52$, we find by extrapolation to 25°, $-\log K_{\text{Aq.}} = 4.87 + \sqrt{\mu} - \mu$. By combining this with the K values for glycolic and acetic acid, we find rough values for L .

Glycolate buffers, salt concentration 0.11 N , $L = 0.015$

Glycolate buffers, salt concentration 0.21 N , $L = 0.010$

Acetate buffers, salt concentration 0.11 N , $L = 0.13$

In the acetate buffers with the salt concentration 0.98 N , the change in hydrogen-ion concentration during the reaction is so small that it is sufficient to use $A = a/2$ and $B = b/2$.

Preparation and Purification of the Substances

Carbonato-tetrammine-cobaltic sulfate $[\text{Co}(\text{NH}_3)_4\text{CO}_3]_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ was prepared by the method of S. M. Jörgensen.¹⁰ It was recrystallized from water and again dissolved and precipitated with alcohol. For some of the experiments the nitrate $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3 \cdot 0.5\text{H}_2\text{O}$ was used. My thanks are due to Professor Brönsted for a pure preparation of this salt.

⁶ Böeseken and Kalshoven, *Rec. trav. chim.*, **37**, 130 (1918).

⁷ Kendall, *J. Chem. Soc.*, 101, 1275 (1912).

⁸ Davies, *J. Phys. Chem.*, **29**, 973 (1925).

⁹ Brönsted and Volqvartz, *Z. physik. Chem.*, **134**, 97 (1928).

¹⁰ S. M. Jörgensen, *Ref. 4*, p. 281.

The glycolic acid was purified through the barium salt, which was recrystallized twice from water. To a warm solution of the pure barium glycolate was added a small excess of 4 *N* sulfuric acid. When there is no excess of sulfuric acid the barium sulfate forms a colloidal solution. However, a small excess of the acid makes it easy to filter the barium sulfate from the solution. Afterward all the sulfuric acid could be removed by a little barium glycolate and a new filtration. The filtrate gave a hardly visible reaction with barium ions. The concentration of glycolic acid was determined by titration.

Acetic acid (Merck "Zur Analyse") was used without purification.

The buffer solutions were prepared from the solutions of the acids and sodium hydroxide solution, made of sodium hydroxide Merck "puriss. e natrio." The various glycolate buffer solutions were prepared from a standard solution by adding various amounts of hydrochloric acid and diluting.

The Experimental Data

The experimental results are given in Tables I-IV and Figs. 2-4. Experiments 1-10 and 14-16 were done with carbonato-tetrammine-cobaltic sulfate, while the nitrate was used for Experiments 11-13. In Figs. 2-3 are plotted the values of ψ (*P*) for each reading against the time *t* in minutes. In the experiments on glycolate (Nos. 1-10, Tables I-II, Fig. 2) the points fall well on a straight line for the greatest part of each reaction. However, at the end the velocity is always smaller than that corresponding to the

TABLE I
THE DECOMPOSITION OF THE CARBONATO-TETRAMMINE-COBALTIC ION
Glycolate buffers; total salt concentration, 0.11 *N*; temp., 24.95°

No.	<i>c</i>	<i>a</i>	<i>b</i>	NaCl	<i>h</i> ₀	<i>h</i> _∞	<i>k</i> (found)	<i>k</i> (calcd.)
1	0.01000	0.05106	0.09991	0.00000	0.5091	0.2624	0.00455	0.00449
2	.00979	.06617	.08480	.01511	0.7761	.4481	.00578	.00580
3	.00978	.08128	.06969	.03022	1.157	.6912	.00757	.00750
4	.00990	.08883	.06214	.03777	1.415	.8400	.00848	.00855
5	.00969	.09638	.05459	.04532	1.743	1.037	.00982	.00993
6	.00953	.11148	.03949	.06042	2.754	1.563	.01372	.01362

$k = 0.00265 + 0.00702 h_{\infty}$ (min.⁻¹, decad. logs), or $k = 0.00265 + 45.6 K_0 h_{\infty}$ (min.⁻¹, decad. logs).

TABLE II
THE DECOMPOSITION OF THE CARBONATO-TETRAMMINE-COBALTIC ION
Glycolate buffers; total salt concentration, 0.21 *N*; temp., 24.95°

No.	<i>c</i>	<i>a</i>	<i>b</i>	NaCl	<i>h</i> ₀	<i>h</i> _∞	<i>k</i> (found)	<i>k</i> (calcd.)
7	0.00973	0.1021	0.1998	0.0000	0.5103	0.3779	0.00606	0.00607
8	.00976	.1625	.1394	.0604	1.161	.8983	.01061	.01066
9	.00971	.1990	.1029	.0969	1.920	1.462	.01564	.01560
10	.00988	.0813	.0697	.1302	1.156	0.6861	.00859	(.00895)

$k = 0.00275 + 0.00879 h_{\infty}$ (min.⁻¹, decad. logs), or $k = 0.00275 + 57.1 K_0 h_{\infty}$ (min.⁻¹, decad. logs).

straight line. This drop in velocity is the more pronounced the smaller the hydrogen-ion concentration. The small lines crossing the curves in each experiment show where the reaction is half completed. Owing to this drop in velocity it was always necessary to wait for several days for the infinity reading. In Tables I-II are given the k values determined by the slopes of the straight lines. By plotting k against h_{∞} we find k_0 and $K \times k_1$ for each of the two series of experiments. At the bottom of each table are given the values of k_0 and $K \times k_1$ determined in this way.

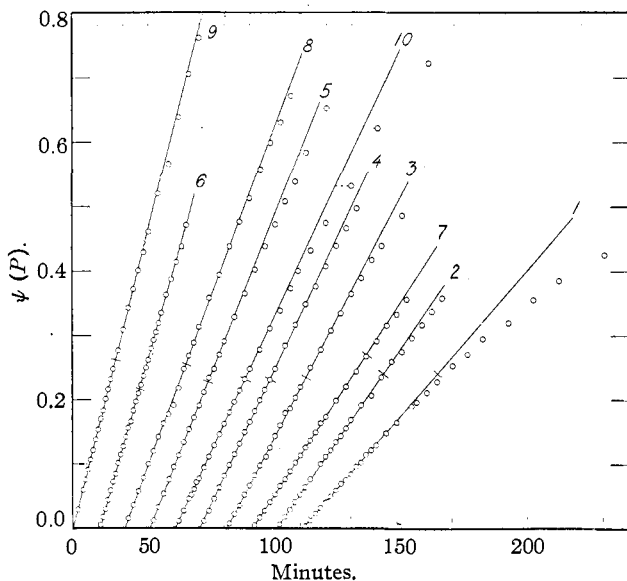


Fig. 2.—The rate of decomposition of the carbonato-tetrammine-cobaltic ion in glycolate buffer solution (Tables I-II).

The last column of the tables gives k calculated from these values. There is a good agreement between k (found) and k (calcd.). All the experiments in glycolate buffer solutions gave practically the same amount of carbon dioxide per equivalent of carbonato salt. Therefore, the reaction may be considered as being practically complete.

TABLE III

THE DECOMPOSITION OF THE CARBONATO-TETRAMMINE-COBALTIC ION
Acetate buffers; total salt concentration 0.98 N ; temp., 24.95°

No.	c	a	b	h_0	h_{∞}	k (found)	k (calcd.)
11	0.00987	1.008	0.974	1.035	0.994	0.00466	0.00466
12	.00957	1.344	.974	1.380	1.332	.00526	.00530
13	.01075	2.013	.974	2.066	2.000	.00660	.00656

$k = 0.00278 + 0.00189 h_{\infty}$ (min.⁻¹, decad. logs), or $k = 0.00278 + 104 K_0 \times h_{\infty}$ (min.⁻¹, decad. logs).

TABLE IV
THE DECOMPOSITION OF THE CARBONATO-TETRAMMINE-COBALTIC ION
Acetate buffers; total salt concentration, 0.11 *N*; temp., 24.95°

(TABLE IVa)						
No.	<i>c</i>	<i>a</i>	<i>b</i>	<i>h</i> ₀	<i>h</i> _∞	<i>k</i> (calcd.)
14	0.00982	0.0939	0.1000	0.939	0.650	0.00319
15	.00998	.1756	.1000	1.756	1.32	.00374
16	.00766	.0939	.1000	0.941	0.718	.00325

(TABLE IVb)									
No.	<i>p</i> CO ₂ (<i>t</i> =0)	<i>p</i> HCO ₃ ⁻ (<i>t</i> =0)	<i>p</i> CO(<i>t</i> =0)	<i>p</i> CO ₂ (<i>t</i> =∞)	<i>p</i> HCO ₃ ⁻ (<i>t</i> =∞)	<i>p</i> CO(<i>t</i> =∞)	<i>α</i>	<i>M</i> × 10 ⁻²	<i>α</i> (calcd.)
14	0.00	0.00	7.23	6.91	0.06	0.26	0.964	4.4	0.968
15	.00	.00	7.59	7.49	.03	.07	.991	4.7	.991
16	19.87	.11	5.63	24.94	.18	.49	.913	5.1	.910

M × 10⁻² = 4.9.

In the acetate buffer solutions with the salt concentration 0.11 *N* (Nos. 14-16, Table IV and Fig. 3), the drop in velocity is so great that no straight

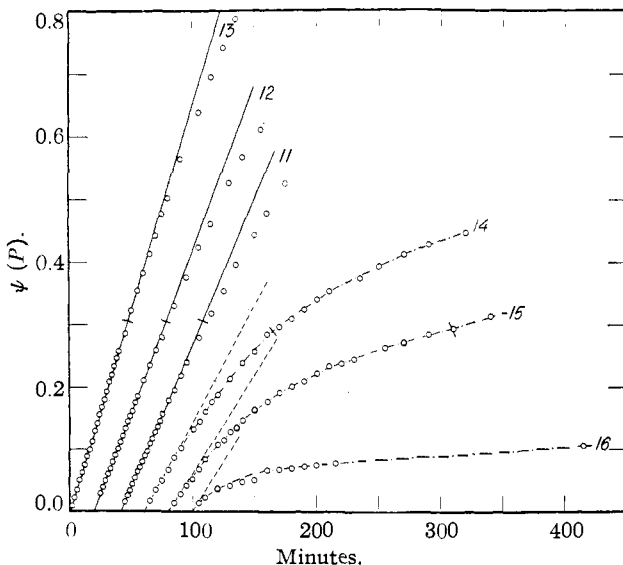


Fig. 3.—The rate of decomposition of the carbonato-tetrammine-cobaltic ion in acetate buffer solutions (Tables III-IV).

line can be drawn. The drop is especially great in Expt. 16. Here the hydrogen-ion concentration is about the same as in Expt. 14, but some carbon dioxide was in the apparatus at the start of the experiment. In order to compare the experiments with those in glycolate at the same salt con-

centration, where Equation 4 holds, we write the velocity constant $k = 0.00265 + 45.6 K_0 h_\infty$. We introduce the activity dissociation constant for acetic acid instead of that for glycolic acid and calculate k values for the different values of h_∞ . In this way we get the k (calcd.) given in the seventh column of Table IVa. The dotted lines in Fig. 3 are drawn with the slopes k (calcd.). They fit quite well as tangents for $t = 0$. The total amount of carbon dioxide evolved in these experiments is a little smaller per equivalent carbonato salt than in the glycolate buffers. Owing to the low hydrogen-ion concentration a little carbon dioxide will be bound as bicarbonate in the solution. However, as will be shown in the following calculation, this is far from being enough to explain the decrease. Consequently, it would seem that the reaction is balanced. In order to show this we try to calculate the equilibrium constant.

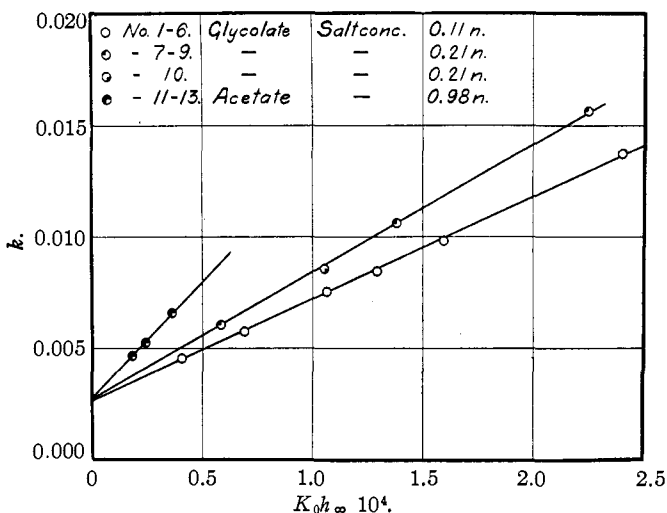


Fig. 4.—The dependence between the velocity constant and the hydrogen-ion concentration.

We denote by p_{CO_2} the carbon dioxide pressure in cm. of mercury. $p_{\text{HCO}_3^-}$ and p_{Co} are the additional pressures which would have been measured if the carbon dioxide were completely liberated from the bicarbonate and the complex cobaltic salt, respectively. Our first object is to calculate $p_{\text{Co}}(t = \infty)$. We have

$$p_{\text{Co}}(t = \infty) = p_{\text{CO}_2}(t = 0) + p_{\text{HCO}_3^-}(t = 0) + p_{\text{Co}}(t = 0) - p_{\text{CO}_2}(t = \infty) - p_{\text{HCO}_3^-}(t = \infty) \quad (10)$$

In Experiments 14 and 15, $p_{\text{CO}_2}(t = 0) = 0$ and $p_{\text{CO}_2}(t = \infty) = P_0$. In 16, where carbon dioxide is present at the start, $p_{\text{CO}_2}(t = 0)$ and $p_{\text{CO}_2}(t = \infty)$ are found by subtracting from the readings at $t = 0$ and $t = \infty$ the reading at $t = 0$ in Expt. 14, which was done in the same apparatus and with the same composition of the solution as in Expt. 16. $p_{\text{Co}}(t = 0) = \varphi c$. For

φ is used the value found in the glycolate experiments; in Expts. 14 and 16, $\varphi = 736$; in Expt. 15, which was done in another apparatus, $\varphi = 761$. It remains to calculate $p_{\text{HCO}_3^-}$ at the times 0 and ∞ . The apparent first dissociation constant of carbonic acid is at 25° 3.12×10^{-7} , found by conductivity by Wilke.¹¹ The ratio between the constants of carbonic acid and acetic acid is $3.12 \times 10^{-7}/1.81 \times 10^{-5} = 0.0172$. Consequently we have

$$\begin{aligned} c_{\text{HCO}_3^-} &= \frac{0.0172}{h} (c_{\text{CO}_2} + c_{\text{H}_2\text{CO}_3}), \text{ or} \\ p_{\text{HCO}_3^-} &= \frac{0.0172}{h} \varphi (c_{\text{CO}_2} + c_{\text{H}_2\text{CO}_3}) \\ c_{\text{CO}_2} + c_{\text{H}_2\text{CO}_3} &= 0.759 \frac{p_{\text{CO}_2} \times 273}{76 \times 22.4 \times 298} \end{aligned}$$

0.759 is the Bunsen absorption coefficient for carbon dioxide in water.¹² We thus get

$$p_{\text{HCO}_3^-} = \frac{0.0172 \times 273 \times 0.759}{76 \times 22.4 \times 298} \frac{\varphi \times p_{\text{CO}_2}}{h} = 7.03 \times 10^{-6} \frac{\varphi p_{\text{CO}_2}}{h}$$

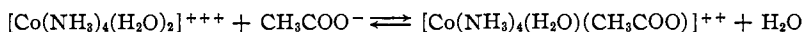
Finally, we find $p_{\text{Co}(t=\infty)}$ by Equation 10. The p values are given in Table IVb. We now calculate the degree of decomposition α of the carbonato salt at equilibrium for the three experiments.

$$1 - \alpha = \frac{p_{\text{Co}(t=\infty)}}{p_{\text{Co}(t=0)}}$$

α is given in the eighth column of Table IVb. In the ninth column is given the equilibrium constant expressed by

$$M = \frac{\alpha \times p_{\text{CO}_2(t=\infty)}}{(1 - \alpha) \times h^2_\infty}$$

The values are constant within the limits of the experimental error. This is seen from the last column, where we have calculated α using the value $M = 4.9 \times 10^2$. In spite of the good constancy, too much weight must not be laid on this result. It is difficult to understand the great drop in velocity without assuming that the equilibrium is reached through two consecutive balanced reactions. If there is an appreciable amount of the intermediate substance present at equilibrium, the above calculation is not unobjectionable. Another objection is that possibly a formation of acetato complexes



may take place. However, rough colorimetric test-tube experiments with different acetate solutions up to 1 *N* acetate left for several days did not support the assumption that acetato complexes were formed.

In the experiments in the more concentrated acetate buffers (salt concentration 0.98 *N*) the decomposition was found to be practically complete,

¹¹ Wilke, *Z. anorg. Chem.*, 119, 365 (1921).

¹² Chr. Bohr, *Wied. Ann.*, 68, 504 (1899).

and the simple equation (4) was found to hold for the greater part of the reaction (Table III and Fig. 3, Expts. 11-13).

Discussion

We first consider the experiments where the fundamental equation (4) holds for a considerable part of the reaction (Expts. 1-13). By means of the equation $k = k_0 + k_1 K h_\infty$, we found for each series of experiments by plotting k against h_∞ the constants k_0 and $K \times k_1$. In order to facilitate a comparison of the experiments in acetate and glycolate buffers we write the equation in the form $k = k_0 + (k_1 F) \times (K_0 h_\infty)$. K_0 is the activity dissociation constant and F a factor expressing the salt effect on K . $F = f_{\text{HA}}/f_{\text{H}^+} f_{\text{A}^-}$, where f_{HA} , f_{H^+} and f_{A^-} are activity coefficients. While K varies with the salt concentration and is not known with sufficient accuracy, K_0 is constant and known with good accuracy. In Fig. 4 k is plotted against $K_0 h_\infty$. For each of the three series of experiments the points fall on a straight line. The slopes determine $k_1 F$, their intercepts on the ordinate axis k_0 . It is seen that all three series give almost the same value of k_0 while $k_1 F$ increases with increasing salt concentration. At the bottom of Tables I-III the equations of the straight lines are given.

No general acid catalysis was found. It is true that an increase in the concentrations of the buffer substances causes an increase in velocity (compare Expts. 1-6 with 7-9). But the same increase is produced by adding sodium chloride to the same total salt concentration (Expt. 10). Consequently the increase may be explained as neutral salt effect. Neither is it possible to detect any general acid catalysis by a comparison with each other of the data of any of the two series (Expts. 1-6 and 7-9). If we did assume an effect of the undissociated glycolic acid, we should have

$$\begin{aligned} k &= k_0 + (k_1 F)(K_0 h_\infty) + k_{\text{HA}} \times c_{\text{HA}} \\ &= k_0 + \left[(k_1 F) + \frac{k_{\text{HA}}}{K_0} c_{\text{A}^-} \right] K_0 h_\infty \end{aligned}$$

Consequently we should get no straight lines in Fig. 4 for the experiments in glycolate, where the concentration of glycolate is varied. If we assume that the values found for $k_1 F$ are constant within each series within an accuracy of 2%, we have

$$\text{(Expts. 1 and 6)} \quad 1.02 \left(k_1 F + \frac{k_{\text{HA}}}{K_0} 0.04 \right) > k_1 F + \frac{k_{\text{HA}}}{K_0} 0.10$$

$$\text{that is, } k_{\text{AH}} < 5 \times 10^{-5} k_1 F$$

$$\text{(Expts. 7 and 9)} \quad 1.02 \left(k_1 F + \frac{k_{\text{HA}}}{K_0} 0.10 \right) > k_1 F + \frac{k_{\text{HA}}}{K_0} 0.20$$

$$\text{that is, } k_{\text{AH}} < 3 \times 10^{-5} k_1 F$$

In order to find how great an effect of the undissociated glycolic acid we should reasonably expect if there were general acid catalysis, we use a method of calculation put forward by Brönsted.¹³ In reactions with

¹³ J. N. Brönsted, *Trans. Faraday Soc.*, **24**, 639 (1928).

general acid catalysis the part of the reaction which is independent of the acid concentration, the so-called "spontaneous" reaction, may be considered as a catalysis of the acid H_2O . Brönsted gives the following formula for a very rough calculation of the effect of an acid if the effects of two other acids (*e. g.*, H_3O^+ and H_2O) are known. The dissociation constants are denoted by K_a , K_b and K_c , the corresponding catalytic coefficients by k_a , k_b and k_c .

$$\log \frac{k_a}{k_b} / \log \frac{k_c}{k_b} = \log \frac{K_a}{K_b} / \log \frac{K_0}{K_b}$$

Acid (a), glycolic acid; $K_a = 1.5 \times 10^{-4}$; $k_a = k_{\text{HA}}$

Acid (b), H_3O^+ ; $K_b = 56$; k_b is roughly $k_1F = 5 \times 10$

Acid (c), H_2O ; $K_0 = (1.05 \times 10^{-14})/56 = 1.9 \times 10^{-16}$; $k_c = 0.0027/56 = 5 \times 10^{-5}$

We find $k_{\text{HA}} = 1.3 \times 10^{-2} \times k_1F$. This value is some hundred times greater than the greatest value $k_{\text{HA}} = 3 \times 10^{-5} k_1F$ which is reconcilable with the experiments.

As a result of this we may say that the rate of reaction is determined only by the hydrogen-ion concentration and a salt effect. The reaction may be considered as the sum of two simultaneous reactions, one being independent of the hydrogen-ion concentration, the other being catalyzed by hydrogen ions. The salt effect is in agreement with Brönsted's theory of kinetic salt effect,¹⁴ according to which a reaction between an ion and an uncharged molecule in dilute solution is almost independent of the salt concentration, while an addition of salt accelerates a reaction between two ions with charges of the same sign and retards a reaction between ions of opposite sign. Consequently k_0 should be only slightly salt sensitive, while k_1 should increase with the salt concentration. Also the factor F should increase with increasing salt concentration. In agreement we found almost the same k_0 at all salt concentrations, while k_1F showed a great increase with increasing salt concentration (Fig. 4).

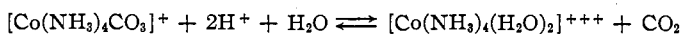
As seen from Figs. 2 and 3 the simple formula (4) holds the better the greater the hydrogen-ion concentration and the smaller the carbon dioxide pressure. In Expts. 14 and 15 and especially 16, where extra carbon dioxide has been added, it fails completely. The reaction is balanced, but the drop in velocity is much greater than can be explained from the assumption that the velocity is determined by a single balanced reaction. A probable explanation seems to be the assumption of consecutive balanced reactions. However, we shall here refrain from suggesting a mechanism owing to the complicated nature of the calculations necessary to test it.

In conclusion the author wishes to thank the Carlsberg Foundation for a grant which has defrayed the expenses of the apparatus, and to express his great indebtedness to Professor Bjerrum for helpful criticism and valuable suggestions.

¹⁴ J. N. Brönsted, *Z. physik. Chem.*, 102, 169 (1922); *Trans. Faraday Soc.*, 14, 630 (1928).

Summary

The kinetics of the decomposition of the carbonato-tetrammine-cobaltic ion



have been studied in glycolate and acetate buffer solutions at 25° and at different salt concentrations.

In the glycolate buffers the decomposition was practically complete. In some acetate buffers it could be shown that the reaction is balanced.

When the carbon dioxide pressure is low and the hydrogen-ion concentration not too small, the velocity may be expressed as the sum of two terms, one being independent of the hydrogen-ion concentration, the other being proportional to the hydrogen-ion concentration. No general acid catalysis was found.

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SOLUBILITIES IN HYDROGEN FLUORIDE

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Solubility relations in non-aqueous inorganic systems have received attention in this Laboratory during several years. Sulfur monochloride, liquid nitrogen tetroxide, thionyl chloride and liquid sulfur dioxide have been employed as solvents.

As one branch of the general problem of solubilities in non-aqueous inorganic systems, the authors set out to develop a technique for the use of liquid anhydrous hydrogen fluoride as a solvent, and to determine some solubilities in this medium. Liquid hydrogen fluoride was chosen for this investigation because of its unusual properties.

The anomalous boiling point of liquid hydrogen fluoride indicates that it is an associated liquid. The anomaly is apparent if one compares the boiling points of the series HI (-35.7°), HBr (-68.7°), HCl (-83.1°) and HF (+19.0°). Water and ammonia show similar anomalous boiling points when compared with the appropriate series. The vapor pressure data of Simons¹ were examined by the use of Hildebrand's modification of the Trouton rule.² The value of the "constant" so determined is about the average of those for normal liquids.

The chemical relationships for hydrogen fluoride indicated that it would prove to be a good solvent. Polar liquids such as ammonia, water and,

¹ J. Simons, *THIS JOURNAL*, **46**, 2179 (1924).

² Hildebrand, "Solubility," The Chemical Catalog Co., Inc., New York, 1924, p. 89.