

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Strength of Carbonic Acid. The Rate of Reaction of Carbon Dioxide with Water and Hydroxyl Ion

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A value of the order of 4×10^{-7} is accepted by most chemists as the first ionization constant of aqueous carbonic acid. If K_1 is defined as equal to

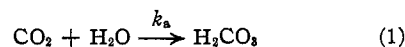
$$\frac{(H^+)(HCO_3^-)}{(\text{total } CO_2 \text{ in solution})}$$

this value is correct. For certain types of work such as those where bicarbonate ion or carbonic acid is used as a catalyst for reactions, it is necessary to distinguish between the total amount of carbon dioxide in solution and that fraction of it which is present as carbonic acid, a distinction emphasized by Brönsted.¹ In some of our unpublished work on the hydrolysis of β -butyrolactone, the catalytic character of bicarbonate ion indicated that carbonic acid was about ten times stronger than acetic acid, and so the literature was searched for information bearing on this point.

McBain² noted a slow neutralization of carbonic acid with phenolphthalein as indicator, an observation amplified by Vorländer and Strube³ and by Thiel.⁴ By colorimetric measurements Thiel, together with Strohecker, made a detailed study of the reactions involved, but, since much of this work was superseded in accuracy by Faurholt's, it is pertinent here to recall only one of Thiel's experiments. Thiel set the amount of carbonic acid present as equivalent to the amount of base neutralized by a given carbon dioxide solution in less than 0.4 second, which at 4° he found to be 0.67%, corresponding to a first dissociation constant of 5×10^{-4} (recalculated by Faurholt as 1.9×10^{-4}). The value 7.4×10^{-4} obtained by Lotte Pusch⁵ through conductivity measurements was dismissed by Faurholt as doubtful.

Faurholt⁶ determined the amount of carbonic acid present in carbon dioxide solutions by adding excess of dimethylamine to combine with the carbon dioxide in solution as carbamate so that the carbonic acid could be precipitated by barium

chloride. By analyses at measured time intervals he followed the reaction of carbon dioxide with water



and with hydroxyl ion



His value for k_a was checked by Stadie and O'Brien,⁷ by Brinkman, Margaria and Roughton⁸ using manometric and flow techniques, and by Urey and Mills⁹ in a study of O¹⁸ exchange between carbon dioxide and water.

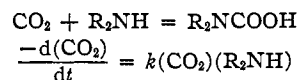
From Faurholt's results at 0 and 18° we calculate for reaction (1)

$$RT^2 \frac{\Delta \ln K}{\Delta t} = \Delta H = 0.7 \text{ kcal. per mole}$$

$$RT^2 \frac{\Delta \ln k_a}{\Delta t} = \Delta E = 19 \text{ kcal. per mole}$$

For the reaction with hydroxyl ion, the activation energy is from 10 to 13 kcal. per mole, according to the data used.

The velocity with which carbon dioxide adds to bases depends upon the strength of the base, as is shown by the following figures from Faurholt¹⁰ for the reaction



Base	NH ₃	MeNH ₂	Me ₂ NH
k (18°, time in hours)	2.3×10^6	5×10^6	4×10^7

These figures also serve to justify Faurholt's method of analysis, which involved essentially a competition between two bases for the carbon dioxide.

Roughton and Booth¹¹ published approximate figures for the catalytic effect of bases on reaction (1). Their results conform roughly to a typical Brönsted diagram. Catalysis by bicarbonate ion corresponds to an acid strength for carbonic acid of about 5×10^{-5} , showing approximate agreement with our results.

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(1) Brönsted, *Z. physik. Chem.*, **108**, 215 (1924).

(2) McBain, *J. Chem. Soc.*, **101**, 814 (1912).

(3) Vorländer and Strube, *Ber.*, **46**, 172 (1913).

(4) Thiel, *ibid.*, **46**, 241 (1913).

(5) Lotte Pusch, *Z. Elektrochem.*, **22**, 206 (1916).

(6) Faurholt, *J. chim. phys.*, **21**, 400 (1924).

(7) Stadie and O'Brien, *J. Biol. Chem.*, **203**, 521 (1933).

(8) Brinkman, Margaria and Roughton, *Phil. Trans. Roy. Soc.*, **232A**, 65 (1932).

(9) Urey and Mills, *THIS JOURNAL*, **61**, 534 (1939).

(10) Faurholt, *J. chim. phys.*, **22**, 1 (1925).

(11) Roughton and Booth, *Biochem. J.*, **32**, 2049 (1938).

Summary

The catalytic efficiency of HCO_3^- confirms the statements found in various published articles that the first ionization constant for carbonic acid is about 2×10^{-4} .

From the rates of the reaction $\text{CO}_2 + \text{H}_2\text{O} =$

H_2CO_3 at various temperatures, the heat of activation is found to be 19 kcal./mole.

For the reaction $\text{CO}_2 + \text{OH}^- = \text{HCO}_3^-$ the heat of activation is found to be from 10 to 13 kcal./mole.

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The Solubility of Cadmium and Zinc Oxalates in Salt Solutions

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In the determination of the ionization constants of cadmium and zinc oxalates by Clayton and Vosburgh¹ there were two sources of uncertainty. One was the value used for the second ionization constant of oxalic acid and the other the interpretation of the solubility data for cadmium oxalate in cadmium sulfate solutions. The redetermination of the second ionization constant of oxalic acid by Harned and Fallon² has made it advisable to recalculate some of the data of Clayton and Vosburgh,¹ and some new experiments have led to a better interpretation of the solubility data.

Materials.—Cadmium oxalate was prepared by precipitation as described by Clayton and Vosburgh.¹

Potassium perchlorate was prepared from potassium hydroxide and perchloric acid. It was recrystallized three times and dried at 100°.

Cadmium perchlorate was prepared by addition of an excess of cadmium oxide to a known quantity of 60% perchloric acid solution. The solution was separated from the excess oxide and heated, whereupon some cadmium hydroxide precipitated. Filtration and dilution gave a stock solution with a pH of about 7 as measured by a glass electrode. The concentration determined by an electrolytic cadmium determination agreed with the concentration as calculated from the original quantity of perchloric acid. Dilution of the cadmium perchlorate solution caused a decrease in pH, the largest decrease observed being about one unit.

Potassium sulfate was recrystallized twice. Solutions of this and of potassium perchlorate were prepared by weight, and analysis was considered unnecessary.

Solubility Determinations.—Solutions of potassium and cadmium perchlorates and potassium sulfate were saturated with cadmium oxalate at $25 \pm 0.02^\circ$ (in an oil-bath) by stirring mechanically for at least two hours. Experiments showed that saturation could be attained in one hour. A large sample was drawn through a filter of Pyrex glass wool and portions of 200 ml. each were taken for analysis, without allowing the temperature to fall appreciably below 25°. The oxalate was titrated with 0.05

N permanganate solution by the use of a 5-ml. semi-micro buret. The permanganate solution was standardized frequently against sodium oxalate from the National Bureau of Standards under conditions similar to those used in the oxalate determinations. Experiments showed that the solvent salts did not interfere with the analyses. The results of the solubility determinations are given in Tables I-IV in the columns headed "total oxalate." It is believed that errors were within 1.5%.

The values reported for the solubility of cadmium oxalate in water by Clayton and Vosburgh¹ differ from the one in this paper by more than 1.5%, but it is believed that the latter is the more reliable and is accurate within the limit claimed.

Discussion

For the interpretation of the solubility data it is necessary to recalculate the solubility product of cadmium oxalate. Use of the value 5.18×10^{-5} for the second ionization constant of oxalic acid² and the experimental data of Clayton and Vosburgh¹ gives 1.44×10^{-8} for the activity solubility product.

By means of the solubility product and the activity coefficients of Kielland³ the concentration of oxalate ion in the salt solutions was calculated. In potassium perchlorate and potassium sulfate solutions allowance was made for a small amount of autocomplex formation. For potassium perchlorate solutions the data in Table I were obtained.

TABLE I
SOLUBILITY OF CADMIUM OXALATE IN POTASSIUM PERCHLORATE SOLUTIONS

KClO ₄ <i>m</i> × 10 ³	Total oxalate <i>m</i> × 10 ³	$\sqrt{\mu}$	C ₂ O ₄ ²⁻ <i>m</i> × 10 ³	CdC ₂ O ₄ un-ionized <i>m</i> × 10 ³
None	0.289	0.0232	0.133	0.154
5	.316	.0752	.163	.150
10	.341	.104	.179	.159
20	.365	.144	.208	.153
40	.413	.203	.247	.161
80	.475	.285	.303	.166

(1) Clayton and Vosburgh, *THIS JOURNAL*, **59**, 2414 (1937).

(2) Harned and Fallon, *ibid.*, **61**, 3111 (1939).

(3) Kielland, *THIS JOURNAL*, **59**, 1677 (1937).