NOTES

Measurements of the Self-diffusion Coefficients of Carbon Dioxide, Hydrogen Carbonate Ions and Carbonate Ions in an Aqueous Solution

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The diffusion coefficients of carbon dioxide in water have been reported by several workers,[1] but the observed values do not agree well with each other.[2] The present authors, therefore, desired to make a contribution to solving the problems of the measurement of the diffusion coefficients of carbon dioxide in water. This paper will report on the diaphragm cell technique as applied to an aqueous carbon dioxide solution and on the details of measurements of the self-diffusion coefficients of carbon dioxide, hydrogen carbonate ions and carbonate ions. The results obtained have been reported in a previous paper[3] except for the value obtained by one additional experiment.

Apparatus and Procedures

The measurements of the self-diffusion coefficients were carried out by a diaphragm cell[4] of a modified Northrop-McBain type, as is shown in Fig. 1. The upper and lower compartments, each containing 20 ml., were filled with solutions of the same chemical composition, containing sodium ions, carbonate ions, hydrogen carbonate ions and carbon dioxide; these solutions were adjusted to pH 4.0, 8.0 and 12.5 at 25°C. These pH values were selected as best for solutions containing almost pure (at least 99%) carbon dioxide, hydrogen carbonate and carbonate ions respectively, as is shown by the calculations using $K_1=4.45\times10^{-7}$ [5] and $K_2=4.69\times10^{-11}$ [6] for the dissociation constants of carbonic acid. The concentration of the latter two ions in the solution was held at ca. 0.1 M, while that of carbon dioxide was ca. 0.06 M. The carbon tracer, C-14, of a 2.3×10^{-2} μc./ml. concentration was contained in the lower compartment.

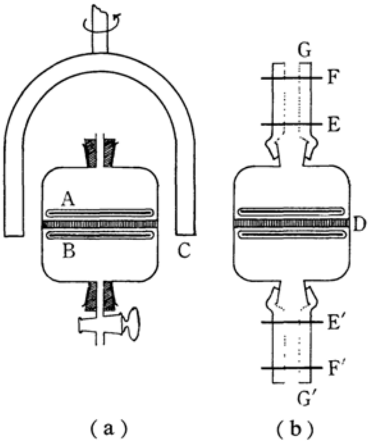

Fig. 1. Diaphragm cells.

a: Used for the solutions with pH>4
b: Used for the solution with pH=4
A and B: Stirrers
C: Magnet (60 r.p.m.)
D: Sintered-glass disk
E, E′, F and F′: Screw clamps
G and G′: Rubber tubes

Before each run, except for the case of the solution with a pH of 4.0, the upper compartment and the diaphragm of the sintered glass disk were filled with a degassed solution and preliminary diffusion was allowed to take place for a few hours in order that a stationary concentration gradient in the diaphragm

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[1] G. Hüfner, *Z. phys. Chem.*, **27**, 227 (1898); T. Carlson, *J. Am. Chem. Soc.*, **33**, 1027 (1911); G. Tammann and V. Jessen, *Z. anorg. u. allgem. Chem.*, **179**, 125 (1929); A. Ringbom, ibid., **238**, 94 (1938); K. H. Gertz and H. H. Loeschcke, *Z. Naturforschg.*, **11b**, 61 (1956).

[2] As is shown in Gertz and Loeschcke's paper.

[3] K. Kigoshi and T. Hashitani, This Bulletin, **36**, 1372 (1963).

[4] R. H. Stokes, *J. Am. Chem. Soc.*, **72**, 763 (1950).

[5] H. S. Harned and R. Davis, Jr., ibid., **65**, 2030 (1943).

[6] H. S. Harned and S. R. Scholes, Jr., ibid., **63**, 1706 (1941).

might be attained. Then the cell was taken out of the bath and the upper compartment was refilled with a non-active solution. In the case of the solution with a pH of 4.0, no preliminary diffusion was allowed because it was difficult to prepare solutions with carbon dioxide of a constant concentration. In this case the results obtained were corrected on the basis of similar diffusion experiments on a potassium chloride solution, which showed that the diffusion coefficient measured without preliminary diffusion was 1.9% less than that measured with preliminary diffussion.

After the diffusion had been allowed to take place for one or two days, the solution in each compartment was taken out and barium carbonate was precipitated by adding barium hydroxide. In the case of pH 4, the escape of carbon dioxide after the diffusion process was prevented by the use of a sodium hydroxide solution. After the run with a solution of pH 4, the rubber tubes shown in Fig. 1(b) were filled with the sodium hydroxide solution and the screw clamps, E and E′, were loosened in order to mix the sodium hydroxide solution with the solution in the cell.

The barium carbonate samples for radioactivity measurements were mounted on dishes of stainless steel. The amounts of barium carbonate were adjusted in order to attain the condition of infinite thickness for β-rays of C-14. A proportional gas flow counter and a G-M counter were used for β countings.

The self-diffusion coefficients were calculated by the formula originally developed by Northrop and Anson:

$$D=(1/Kt)\log(\Delta C_0/\Delta C)$$

where K is a cell constant, and ΔC_0 and ΔC are the differences between the concentration of C-14 in the two compartments of a cell at times zero and t respectively. The cell constant was obtained by diffusion measurements for solutions of potassium chloride and hydrogen chloride of known diffusion coefficients. The diffusion coefficient of potassium chloride from a 0.1 M solution into water of 1.873×10^{-5} cm^2/sec.⁷⁾ at 25°C and that of 0.43 M hydrogen chloride of 1.61×10^{-5} cm^2/sec.⁸⁾ at 0°C were used. The measurements were conducted in a thermostat held at 0, 25, and 30±0.01°C.

Results

Over-all self-diffusion coefficients of a given solution containing carbon dioxide, hydrogen carbonate ions, and carbonate ions can be estimated as a weighted mean of the self-diffusion coefficients of these species. For instance, in the solution of pH 10.0⁹⁾ at 30°C, the concentration ratio, (HCO_3^-) : (CO_3^{2-}), is 66 : 34¹⁰⁾ and a calculated self-diffusion coefficient of carbon compounds becomes $(1.18\pm0.01)\times10^{-5}$, showing good agreement with the observed value in this measurement $(1.21\pm0.013)\times10^{-5}$.

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7) R. H. Stokes, *J. Am. Chem. Soc.*, **73**, 3527 (1951).

8) J. D. R. Scheffer, *Z. phys. Chem.*, **2**, 390 (1888).

9) Buffer solution containing 0.025 M Na_2CO_3 and $NaHCO_3$ respectively per liter.

10) This concentration ratio is calculated on the basis of the dissociation constant: $K_2=5.13\times10^{-11}$ (30°C).⁶⁾