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Abstract

Full Text

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ON THE MAGNITUDES OF THE DISSOCIATION CONSTANTS OF CARBONIC ACID AT ELEVATED TEMPERATURES

(Presented by Academician A. P. Vinogradov, 30 XI 1962)

Carbonic acid is one of the most widespread components of hydrothermal systems. However, up to the present time not a single study has been carried out in which the dissociation constants of carbonic acid at temperatures above 100° would be determined. Meanwhile, knowledge of the dissociation constants would make it possible to clarify such questions as the pH of hydrothermal systems containing carbon dioxide; the hydrolytic decomposition of bicarbonates; the stability of carbonate complexes of various elements; the solubility of carbonates, and many other problems associated with the participation of carbon dioxide in natural processes.

In order to study the dissociation of carbonic acid, the electrical conductivity of aqueous solutions of Na₂CO₃ and NaHCO₃ with concentrations of 0.001-0.05 mole/l was measured at temperatures of 100, 156, and 218° and at a pressure approximately equal to the pressure of saturated vapor over the solution. The construction of the electrolytic cell, the experimental procedure, and the results of determining the electrical conductivity of Na₂CO₃ and NaHCO₃ solutions were reported in paper (1).

For the calculation of the first apparent dissociation constant (K_1) of carbonic acid at temperatures of 100, 156, and 200° in the electrolytic cell described, the electrical conductivity of CO₂ solutions that were under a known partial pressure of carbon dioxide (5-25 atm) was determined; this pressure was calculated as the difference between the measured total pressure and the vapor pressure of water at the temperature of the experiment.

The concentration of CO₂ in the solution was determined using the following values of the solubility of carbon dioxide in water (2): at 100° 0.0102 mole/l · atm, at 156° 0.0076 mole/l · atm, at 200° 0.0072 mole/l · atm. The calculation of the value of K_1 for dissociation was carried out according to the equation

$$K_1 = \frac{\alpha^2 C}{1 - \alpha} \cdot \frac{y_{\text{H}^+} y_{\text{HCO}_3^-}}{y_{\text{CO}_2}} = \frac{\Lambda_c^2 C}{\Lambda_0'(\Lambda_0' - \Lambda_c)} \cdot \frac{y_{\pm 1}^2}{y_{\text{CO}_2}}, \quad (1)$$

where Λ_c is the equivalent electrical conductivity of a CO₂ solution of concen-

tration C (mole/l), Λ'_0 is the equivalent electrical conductivity of carbonic acid in a solution of the ionic strength possessed by the investigated CO_2 solutions, α is the degree of dissociation of carbonic acid, and y_i is the activity coefficient. For calculating the ionic strength of carbonic acid solutions, the degree of dissociation α in the first approximation was determined as the ratio Λ_c/Λ_0 , where Λ_0 is the equivalent electrical conductivity of carbonic acid at infinite dilution. The equivalent conductivities of carbonic acid Λ_0 and Λ'_0 were determined by Kohlrausch's rule from the corresponding equivalent conductivities of NaHCO_3 , $^{(1)}$ NaCl and HCl $^{(3)}$.

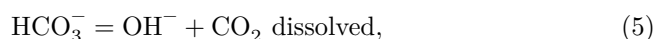
The thermodynamic value of K_I for dissociation was calculated by substituting into equation (1) the ratio $y_{\pm 1}^2/y_{\text{CO}_2}$, with $y_{\pm 1}^2$ calculated from the Debye equation, and y_{CO_2} taken as equal to 1. As a result of processing our own experimental data (at 100, 156, and 200°) and literature data $^{(4)}$ (0-50°) on the values of K_I for dissociation of carbonic acid, the following equations were obtained for the dependence of $\text{p}K_I$ and the enthalpy of dissociation of carbonic acid ...

for the first step ($\Delta H_{(1)}$) on the absolute temperature (T):

$$\text{p}K_I = \frac{2382.8}{T} - 8.153 + 0.02194 T, \quad (2)$$

$$\Delta H_{(1)} = 10901 - 0.1004 T^2. \quad (3)$$

The determination of the second dissociation constant of carbonic acid is based on a study of the hydrolysis of Na_2CO_3 in aqueous solution:



$$K_{1 \text{ hydrolysis}} = \frac{K_W}{K_{II}} = \frac{(\text{OH}^-)(\text{HCO}_3^-)}{(\text{CO}_3^{2-})} = \frac{C h_1^2 (1 - h_2)}{1 - h_1} \frac{y_{\text{OH}^-} y_{\text{HCO}_3^-}}{y_{\text{CO}_3^{2-}}}, \quad (6)$$

$$K_{2 \text{ hydrolysis}} = \frac{K_W}{K_I} = \frac{(\text{OH}^-)(\text{CO}_2)}{(\text{HCO}_3^-)} = \frac{(1 + h_2) c h_1 h_2 \Phi}{1 - h_2} \frac{y_{\text{OH}^-} y_{\text{CO}_2}}{y_{\text{HCO}_3^-}}.$$

where the quantities in parentheses are the equilibrium activities of ions and molecules, h_1 and h_2 are the degrees of hydrolysis of CO_3^{2-} and HCO_3^- ions, Φ is a coefficient accounting for the portion of carbonic acid remaining in the solution out of all the carbonic acid formed during hydrolysis, and C is the initial concentration of Na_2CO_3 .

Fig. 1. Dependence of pK_I and pK_{II} of the dissociation of carbonic acid on the absolute temperature T^{-1}

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According to data on the electrical conductivity of solutions of Na_2CO_3 ⁽¹⁾, NaHCO_3 ⁽³⁾, NaOH ⁽³⁾, and Na_2SO_4 (instead of the hypothetical equivalent electrical conductivity of nonhydrolyzed sodium carbonate), at temperatures of 100, 156, and 218° we determined⁽⁵⁾ the first hydrolysis constant (see equation (6)). Using Noyes' data⁽⁶⁾ on the values of K_W for the indicated temperatures, from the equation $K_{II} = K_W/K_{1 \text{ hydrolysis}}$ we calculated the values of the second dissociation constant (K_{II}) of carbonic acid.

As a result of processing our own experimental data (at 100, 156, and 218°) and literature data^(7,8) (0-90°) on the values of K_{II} of dissociation, the following equations were obtained for the dependence of pK_{II} and of the enthalpy of dissociation of carbonic acid in the second step ($\Delta H_{(2)}$) on absolute temperature:

$$pK_{II} = \frac{2730.7}{T} - 5.388 + 0.02199 T, \quad (8)$$

$$\Delta H_{(2)} = 12493 - 0.1006 T^2. \quad (9)$$

The results of determining K_I and K_{II} of the dissociation of carbonic acid are presented in Fig. 1 in the form of curves of pK_I and pK_{II} as functions of T^{-1} , which have the following extrema: a minimum $pK_I = 6.309$ ($K_I = 4.91 \cdot 10^{-7}$)

occurs at 56.3°, and the minimum $pK_{II} = 10.110$ ($K_{II} = 7.76 \cdot 10^{-11}$) occurs at a temperature of 79.2°.

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Note: Figure translations are in progress. See original paper for figures.

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