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LETTERS TO THE EDITOR

Acid–Base Equilibrium in the K_2SO_3–Methanol System

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Earlier we found that mixing of potassium carbonate with methanol gives the corresponding alcoholate [1]. It can be assumed that in the alkali metal carbonate–alcohol system there exists an acid–base equilibrium.

$$\mathrm{ROH + M_2CO_3 \rightleftarrows ROM + MHCO_3},$$

$$\mathrm{M = alkali\ metal,\ R = Alk.}$$

We considered it of interest to estimate the constant of this reaction with methanol (R = Me) and potassium carbonate (M = K). The equilibrium concentrations of the components of the K_2CO_3–methanol system were determined titrimetrically. To this end, the suspension obtained by continuous 6-h stirring of freshly calcined potassium carbonate in absolute methanol in a temperature-controlled cell at a specified temperature (298 ± 0.05 and 308 ± 0.05 K) was passed under pressure through a filter with a porous plate. The separated solid and liquid phases were treated with water and analyzed for K_2CO_3, $KHCO_3$, and CH_3OK by acidometric titration; therewith, potassium methylate was titrated as KOH [1].

The equilibrium constant of the process studied were calculated with the activity coefficient of methanol, determined from data on the vapor–liquid equilibrium in the system, obtained by GLC by the equilibrium vapor analysis [2]. The activity coefficients, calculated by the UNIQUAC equation with account for the Debye–Huckel theory [3] and on the assumption of complete dissociation of the components of the system into ions, fail to fit the coefficients estimated from experimental vapor–liquid equilibrium data. Calculation by a classical UNIQUAC model [4] gives better results. The energetic parameters of the interaction between the components of the system were estimated from data on the liquid–vapor equilibria in the corresponding alcohol–salt systems.

The equilibrium constants of the reaction is 3.7×10^{-5} at 298 K; an increase of the temperature by 10 K reduces the constant to $2.6–10^{-5}$. The standard deviation is 4×10^{-6} (confidence level 0.95).

It was found that the potassium hydrocarbonate formed by this reaction is more than by 99% is in the solid phase. Apparently, this circumstance is a factor operating to shift the equilibrium to the right. As the temperature is increased, the solubility of $KHCO_3$ in methanol increases, thereby shifting the equilibrium in the opposide direction.

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