

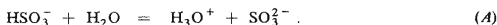
pH-CONCENTRATION DEPENDENCE IN SYSTEM  $\text{NH}_3\text{-SO}_2\text{-H}_2\text{O}$ 

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The system  $\text{NH}_3\text{-SO}_2\text{-H}_2\text{O}$  is employed on an industrial scale as an absorption solution for removing sulphur oxides from flue gases. For this reason the knowledge of its pH-concentration dependence is of practical interest. The system undergoes a number of chemical reactions, for example, the dissociation of the ion  $\text{HSO}_3^-$



The equilibrium constant of the reaction (A) is defined by the relation

$$K = a_{\text{H}_3\text{O}^+} a_{\text{SO}_3^{2-}} / a_{\text{HSO}_3^-} a_{\text{H}_2\text{O}} \quad (1)$$

where  $a_i$  denotes the (equilibrium) activity of the constituent  $i$  ( $i = \text{H}_3\text{O}^+$ ,  $\text{SO}_3^{2-}$ ,  $\text{HSO}_3^-$ ,  $\text{H}_2\text{O}$ ).

If a very diluted solution is chosen as the reference system, the activity of hydrogen ions can be expressed as follows:

$$a_{\text{H}_3\text{O}^+} = K \frac{a_{\text{HSO}_3^-} a_{\text{H}_2\text{O}}}{a_{\text{SO}_3^{2-}}} = K \frac{x_{\text{HSO}_3^-} x_{\text{H}_2\text{O}}}{x_{\text{SO}_3^{2-}}} \frac{\gamma_{\text{HSO}_3^-} \gamma_{\text{H}_2\text{O}}}{\gamma_{\text{SO}_3^{2-}}} \quad (2)$$

where  $x_i$  denotes the mole fraction and  $\gamma_i$  the rational activity coefficient of the constituent  $i$ .

Solutions of molalities from 6 and 20 between normal and hydrogen ammonium sulphites are interesting from a practical point of view. That's why it is necessary to express the dependence of the activity coefficients on composition by means of a procedure adequate to this very high concentration region.

Vapour-liquid equilibria in systems of electrolytic components can be characterized over a wide concentration range using a thermodynamically consistent method<sup>1,2</sup>. If we modify this method for our purpose we obtain the following equation as a first approximation:

$$Q_{\pm} = cJ^{3/2} + \dots \quad (3)$$

where  $Q_{\pm}$  is the excess function,  $c$  constant which can be evaluated from experimental data and  $J$  the concentration variable defined by means of the equation

$$J = \frac{1}{2} \left( \frac{n_{\text{NH}_4^+}}{n_{\text{H}_2\text{O}}} + \frac{n_{\text{HSO}_3^-}}{n_{\text{H}_2\text{O}}} + \frac{4n_{\text{SO}_3^{2-}}}{n_{\text{H}_2\text{O}}} \right) \quad (4)$$

where  $n_i$  is the number of moles of the constituent  $i$  in the solution.

Relations expressing the dependence of activity coefficients on composition of the solution can be obtained by means of partial differentiation of Eq. (3)

$$\log \gamma_{\text{HSO}_3^-} = \frac{\partial}{\partial n_{\text{HSO}_3^-}} (n_{\text{H}_2\text{O}} Q_{\pm}) = \left(\frac{2}{3}\right) cJ^{1/2}, \quad (5)$$

$$\log \gamma_{\text{H}_2\text{O}} = \frac{\partial}{\partial n_{\text{H}_2\text{O}}} (n_{\text{H}_2\text{O}} Q_{\pm}) = -\left(\frac{1}{2}\right) cJ^{3/2}, \quad (6)$$

$$\log \gamma_{\text{SO}_3^{2-}} = \frac{\partial}{\partial n_{\text{SO}_3^{2-}}} (n_{\text{H}_2\text{O}} Q_{\pm}) = 3cJ^{1/2}. \quad (7)$$

From Eqs (5) to (7) we obtain

$$\log (\gamma_{\text{HSO}_3^-} \gamma_{\text{H}_2\text{O}} / \gamma_{\text{SO}_3^{2-}}) = -\frac{1}{2} cJ^{1/2} \left(\frac{2}{3} + J\right). \quad (8)$$

TABLE I  
pH-Concentration Dependence in System  $\text{NH}_3$  (1)- $\text{SO}_2$  (2)- $\text{H}_2\text{O}$  (3) at 20°C

$r_{13}$	$r_{23}$	pH		$\Delta\text{pH}$
		found	calculated	
Data by Johnstone <sup>4</sup>				
0.2236	0.1571	5.96	5.76	-0.20
0.2214	0.1761	5.55	5.46	-0.09
0.2221	0.1892	5.27	5.26	0.01
0.2228	0.2035	4.92	4.97	0.05
0.10566	0.07616	5.84	5.79	-0.05
0.10621	0.08615	5.43	5.48	0.05
0.10680	0.10000	4.74	4.88	0.14
0.05869	0.04274	5.85	5.80	-0.05
0.05866	0.04863	5.43	5.46	0.03
0.05809	0.05230	5.13	5.15	0.02
0.05826	0.05575	4.71	4.75	0.04
Data by Berdjanskaja and coworkers <sup>5</sup>				
0.190	0.162	5.29	5.28	-0.01
0.192	0.174	5.15	5.00	-0.15
0.205	0.188	4.98	4.96	-0.02
0.196	0.187	4.60	4.68	0.08
0.225	0.203	5.03	5.03	0.00
0.222	0.204	4.80	4.94	0.14
0.217	0.208	4.23	4.63	0.20

The next step is to express the mole fractions in Eq. (2) and mol ratios in Eqs (3) and (8) by means of analytical concentrations of the components.

If we take into account conditions of electroneutrality, the following relations can be written

$$n_1 = n_{\text{NH}_4^+} = n_{\text{HSO}_3^-} + 2n_{\text{SO}_3^{2-}},^* \quad (9)$$

$$n_2 = n_{\text{HSO}_3^-} + n_{\text{SO}_3^{2-}}, \quad (10)$$

$$n_3 = n_{\text{H}_2\text{O}} = n_{\text{HSO}_3^-} + n_{\text{SO}_3^{2-}}, \quad (11)$$

where  $n_1$ ,  $n_2$  and  $n_3$  denote the analytically determined numbers of moles of  $\text{NH}_3$ ,  $\text{SO}_2$  and  $\text{H}_2\text{O}$  in the solution.

Equations (9) and (11) can be rearranged

$$n_{\text{HSO}_3^-} = 2n_2 - n_1, \quad (12)$$

$$n_{\text{SO}_3^{2-}} = n_1 - n_2, \quad (13)$$

$$n_{\text{H}_2\text{O}} = n_3 - n_2 \quad (14)$$

and the product at the right side of Eq. (2) written in the form

$$\frac{x_{\text{HSO}_3^-} x_{\text{H}_2\text{O}}}{x_{\text{SO}_3^{2-}}} = \frac{(2n_2 - n_1)(n_3 - n_2)}{(n_1 + n_3)(n_1 - n_2)} = \frac{(2r_{23} - r_{13})(1 - r_{23})}{(1 + r_{13})(r_{13} - r_{23})}, \quad (15)$$

where

$$r_{13} = n_1/n_3, \quad (16)$$

$$r_{23} = n_2/n_3. \quad (17)$$

Similarly the concentration variable,  $J$ , defined by Eq. (4) can be expressed as follows:

$$J = \frac{2n_1 - n_2}{n_3 - n_2} = \frac{2r_{13} - r_{23}}{1 - r_{23}}, \quad (18)$$

if we assume pH as  $(-\log a_{\text{H}_3\text{O}^+})$ ,\*\* we can write according to Eqs (2), (8), (15) and (18)

$$\begin{aligned} \text{pH} = -\log a_{\text{H}_3\text{O}^+} = & -\log K - \log \frac{(2r_{23} - r_{13})(1 - r_{23})}{(1 + r_{13})(r_{13} - r_{23})} + \\ & + \frac{1}{2}c \left( \frac{2r_{13} - r_{23}}{1 - r_{23}} \right)^{1/2} \left( \frac{9}{2} + \frac{2r_{13} - r_{23}}{1 - r_{23}} \right). \end{aligned} \quad (19)$$

After introducing adjustable parameters

$$A = -\log K, \quad (20)$$

\* The number of moles of hydrogen ion,  $n_{\text{H}_3\text{O}^+}$ , is very low in comparison with  $n_{\text{NH}_4^+}$  and can be neglected.

\*\* For the exact definition of pH see<sup>3</sup>.

$$C = \frac{1}{2}c, \quad (21)$$

we arrive to the final equation

$$\text{pH} = A - \log \frac{2r_{23} - r_{13}(1 - r_{23})}{(1 + r_{13})(r_{13} + r_{23})} + C \left( \frac{2r_{13} - r_{23}}{1 - r_{23}} \right)^{1/2} \left( \frac{9}{2} + \frac{2r_{13} - r_{23}}{1 + r_{23}} \right), \quad (22)$$

where  $A$  and  $C$  are constants which can be evaluated from experimental data.

The application of the method just described is illustrated on an example. In Table I direct experimental data of Johnstone<sup>4</sup> and Berdjanskaja and coworkers<sup>5</sup> are presented and compared with values calculated by means of Eq. (22) with constants  $A = 6.20$ ,  $C = -0.164$ . The agreement can be considered as satisfactory.

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## CALCULATION OF THE INTEGRAL ISOTHERMAL HEAT OF VAPORIZATION OF MIXTURES

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An exact thermodynamic relation for calculating the integral isothermal heat of vaporization of mixtures is derived in this paper. Relations and formulations of the given problem published in the literature are often inaccurate. The dependence of the pure substance enthalpy on pressure at a given temperature  $T < T_k$  is illustrated in Fig. 1. Experimentally accessible parts of the curve consist of the dependence of the vapour phase enthalpy on pressure for  $P < P^\circ$ , the dependence of the liquid phase enthalpy on pressure for  $P > P^\circ$ , and the difference between the enthalpies of the liquid and the vapour at  $P = P^\circ$ . These parts of the curve are represented by solid lines in the figure. The heat of vaporization  $L_v$  at the temperature  $T$  is given by the relation

$$L_v = [H^{(g)} - H^{(l)}]_{P^\circ} = T[S^{(g)} - S^{(l)}]_{P^\circ}, \quad (1)$$

where the subscript  $P^\circ$  denotes that we are dealing with the change of enthalpy or entropy at the constant pressure  $P = P^\circ$ .