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ORNL-3471

Contract No. W-7405-eng-26

CHEMISTRY DIVISION

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Date Issued

JUL 15 1963

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The Activity Coefficients of Hydrochloric Acid and Sodium Chloride in Hydrochloric Acid-Sodium Chloride Mixtures

M. H. Lietzke and R. W. Stoughton

ABSTRACT

The activity coefficients of HCl and NaCl in HCl-NaCl mixtures have been computed from literature data. The calculations are based on the observation that at constant ionic strength and temperature the logarithm of the activity coefficient of HCl in HCl-NaCl mixtures varies linearly with NaCl concentration.

The Activity Coefficients of Hydrochloric Acid and Sodium Chloride in Hydrochloric Acid-Sodium Chloride Mixtures*

M. H. Lietzke and R. W. Stoughton

In a recent study[1] of the cell

$$Pt - H_{2(p)} \mid HBr_{(m_2)}, KBr_{(m_3)} \mid AgBr - Ag$$

it was shown that at constant temperature and ionic strength the logarithm of the activity coefficient of HBr in HBr-KBr mixtures varies linearly with the molality of KBr. It was also shown that with the parameters describing this variation it is possible to calculate the activity coefficient of the KBr in the mixtures. Previously it had been shown[2] that at constant ionic strength and temperature the logarithm of the activity coefficient of HCl in HCl-NaCl mixtures varies linearly with NaCl molality. This paper deals with the calculation of the parameters describing the activity coefficients of both HCl and NaCl in HCl-NaCl mixtures by using literature data on the activity coefficient of HCl in pure solutions[3] and in NaCl solutions[4] and of NaCl[2,2a] in pure solutions. For these calculations the values of the activity coefficient of HCl($\underline{m}$ = 0.01) in NaCl solutions[4] for 0 to 50° were extrapolated to 60°.

In carrying out the computation it was assumed that the ionic strength dependence of the logarithms of the activity coefficients of HCl, of NaCl, and of HCl($\underline{m}$ = .01) in NaCl solutions could be described at each temperature

*This work was supported in part by the Office of Saline Water, U. S. Department of the Interior.

by equation (1)

$$\ln \gamma\pm = \frac{-\mathcal{S}\sqrt{I}}{1 + 1.5\sqrt{I}} + BI + CI^2 + DI^3 \qquad (1)$$

In this equation $\mathcal{S}$ is the appropriate Debye-Hückel limiting slope which contains as a factor the square root of the density of water; I is the ionic strength (on a molality basis); and B, C, and D are adjustable parameters. The values of the parameters were determined in each instance by the method of least squares and are given in Table I. For convenience, the value of the parameter in the denominator of the Deybe-Hückel expression was taken in all cases to be 1.5.

Table I

Values of the Parameters of Equation (1) Giving the Ionic Strength Dependence of the Activity Coefficients of HCl and NaCl

NaCl*

Temp.	$B \times 10^2$	$C \times 10^2$	$D \times 10^3$	σ^2_{fit} **
0	-3.73852	3.56644	-3.03349	1.5×10^{-5}
10	-0.701016	2.95583	-2.43814	8.9×10^{-6}
20	1.02915	2.81899	-2.50491	7.2×10^{-6}
25	2.41390	2.29369	-1.96781	1.7×10^{-6}
30	2.65655	2.56721	-2.45514	8.1×10^{-6}
40	4.17905	2.11154	-1.97467	9.1×10^{-6}
50	5.53079	1.68468	-1.53191	8.5×10^{-6}
60	6.28909	1.95709	-2.28398	5.3×10^{-6}

*The equations hold to 4 m.

**Variance of fit.

Table I (Contd.)

HCl*

Temp.	B x 10	C x 10^2	D x 10^3	σ^2_{fit}
0	2.53049	2.33598	-2.02789	1.7 x 10^{-5}
10	2.47702	2.13754	-1.83070	6.2 x 10^{-6}
20	2.41086	1.92351	-1.56655	2.9 x 10^{-6}
25	2.37579	1.82248	-1.45024	2.8 x 10^{-6}
30	2.22354	3.38269	-6.73504	2.2 x 10^{-6}
40	2.18233	2.50886	-4.14886	3.2 x 10^{-6}
50	2.14575	1.82417	-1.81932	1.7 x 10^{-6}
60	2.13183	0.589944	2.96181	2.1 x 10^{-6}

*At 25° and below the equations hold to 4 m, above 25° to 2 m.

HCl (m=.01) in NaCl*

Temp.	B x 10	C x 10^2	D x 10^3	σ^2_{fit}
0	1.39450	4.28343	-6.23885	1.9 x 10^{-5}
10	1.48713	3.59159	-4.98155	8.5 x 10^{-6}
20	1.50904	3.33731	-4.62235	7.0 x 10^{-6}
25	1.56031	2.91288	-3.89802	4.4 x 10^{-6}
30	1.54654	2.95854	-4.11460	6.5 x 10^{-6}
40	1.57406	2.57192	-3.64777	5.7 x 10^{-6}
50	1.60227	2.07142	-2.89576	1.1 x 10^{-5}
60	1.63973	1.61486	-2.50417	1.7 x 10^{-5}

*The equations hold to 3 m.

At constant ionic strength and temperature it may be assumed that

$$\ln \gamma_{HCl} = \ln \gamma^{o}_{HCl} - \alpha\, m_{NaCl}, \qquad (2)$$

where α is a function only of total ionic strength and temperature. In equation (2) γ_{HCl} is the activity coefficient of HCl in the HCl-NaCl mixture and γ^{o}_{HCl} is the activity coefficient of HCl in an HCl solution of the same ionic strength. The parameters in Table I giving the ionic strength dependence of the logarithm of the activity coefficients of HCl and HCl(m=.01) in NaCl may be used to calculate values of the parameter α in equation (2). These values are given in Table II.

Table II

Values of the Parameter α in Equation (2) for HCl-NaCl Mixtures

I \ t(°C)	0	10	20	25	30	40	50	60
.02	.22642	.19740	.17980	.16266	.13557	.12163	.10860	.09801
.03	.16953	.14783	.13464	.12183	.10174	.09121	.08141	.07336
.06	.13493	.11775	.10721	.09708	.08153	.07294	.06504	.05834
.11	.12266	.10717	.09753	.08842	.07495	.06683	.05950	.05296
.21	.11518	.10088	.09172	.08333	.07190	.06371	.05657	.04966
.51	.10686	.09424	.08544	.07816	.07057	.06158	.05443	.04629
1.01	.09921	.08839	.07981	.07376	.07000	.06028	.05348	.04478
2.01	.09193	.08290	.07448	.06987	.06597	.05782	.05400	.05054
3.01	.09344	.08405	.07556	.07114	.05691	.05457	.05685	.06721

In order that the values of $\underline{\alpha}$ shown in Table II could be used to compute the activity coefficient of NaCl in the HCl-NaCl mixtures they were fitted by the method of least squares to equation (3) for ionic strength values above 0.11.

$$\alpha = a_0 + a_1 I + a_2 I^2 + a_3 t + a_4 I t \qquad (3)$$

Because the activity coefficient values appeared to be more precise at 25° and below two separate fits of the $\underline{\alpha}$-values were made: (1) using the α-values from 0-25°, and (2) using the $\underline{\alpha}$-values from 25-60°. The parameters of equation (3) for the two fits are given in Table III.

Table III

Parameters of Equation (3)*

$$\alpha = a_0 + a_1 I + a_2 I^2 + a_3 t + a_4 I t$$

Temp. range	$a_0 \times 10$	$a_1 \times 10^2$	$a_2 \times 10^3$	$a_3 \times 10^3$	$a_4 \times 10^4$
0 - 25°	1.20661	-2.53234	5.32570	-1.22881	1.40681
30 - 60°	1.08192	-2.11277	4.45109	-0.962928	1.88598

*Equation holds over the ionic strength range .11 to 3.01 $\underline{m}$ at 0-25° and .11 to 2.01 above 25°.

Equation (3) may be used in equation (2) to calculate the values of γ_{HCl} in HCl-NaCl mixtures between 0 and 60° for a total ionic strength as low as 0.11. It may also be used in calculating the activity coefficient of NaCl in the HCl-NaCl mixtures, since according to the rules of partial differentiation it follows from the equation for the total free energy of the system in terms of the partial molal quantities that[5]

$$\left(\frac{\partial \ln a_3}{\partial m_2}\right)_{m_3} = \left(\frac{\partial \ln a_2}{\partial m_3}\right)_{m_2} \qquad (4)$$

This equation may be expressed in terms of the variable I:

$$\left(\frac{\partial \ln \gamma_3}{\partial m_2}\right)_{m_3} = \left(\frac{\partial \ln \gamma_3}{\partial I}\right)_{m_3} = \left(\frac{\partial \ln \gamma_2}{\partial m_3}\right)_{m_2} = \left(\frac{\partial \ln \gamma_2}{\partial I}\right)_{m_2} \qquad (5)$$

Upon differentiating[6] equation (2) with respect to the total ionic strength $\underline{I}$ at constant $\underline{m_2}$

$$\left(\frac{\partial \ln \gamma_2}{\partial I}\right)_{m_2} = \frac{d \ln \gamma_2^{o}}{d I} - \alpha - m_3 \frac{d\alpha}{dI} \tag{6}$$

Equation (6) may be inserted into equation (5) and the latter integrated with respect to $\underline{I}$ between the limits $\underline{m}_3$ and $\underline{m}_2 + \underline{m}_3$; whence

$$\ln \gamma_3 (m_2 + m_3) - \ln \gamma_3^{o} (m_3) = \ln \gamma_2^{o} (m_2 + m_3) - \ln \gamma_2^{o} (m_3)$$

$$- \int_{I=m_3}^{I=m_2 + m_3} \alpha dI - \int_{I=m_3}^{I=m_2 + m_3} m_3 \frac{d\alpha}{dI} dI \tag{7}$$

The second term on the left and the first two terms on the right of equation (7) may be evaluated by the use of equation (1) and the parameters given in Table I for the pure components HCl and NaCl. The substitution of equation (3), which gives the ionic strength and temperature dependence of α, into equation (7) permits the evaluation of the remaining integrals and hence the calculation of the activity coefficient of NaCl in HCl-NaCl mixtures. Values of the activity coefficients of HCl and NaCl in pure solution and in a 50-50% mixture at 0, 10, 25, 40, and 60° are given in Table IV.

As expected, (1) at any temperature and ionic strength the activity coefficients are in the order (greatest to least) γ_{HCl}^{o}, $\gamma_{HCl}(m_2 = m_3)$, $\gamma_{NaCl}(m_2 = m_3)$, γ_{NaCl}^{o}; (2) at any temperature the changes of activity coefficients with ionic strength are in the same order.

Table IV

The Activity Coefficients of HCl and NaCl in Pure Solution and in a 50-50% Mixture

	$m_{HCl} = I$	$m_{HCl} = m_{NaCl} = \frac{1}{2} I$		$m_{NaCl} = I$
I	γ_{HCl}	γ_{HCl}	γ_{NaCl}	γ_{NaCl}
		$t = 0^{\circ}$		
.2	.780	.771	.749	.736
.5	.777	.756	.704	.674
1.0	.840	.799	.694	.636
1.5	.943	.878	.714	.625
2.0	1.078	.984	.748	.628
2.5	1.247	1.114	.793	.642
3.0	1.455	1.266	.843	.662
		$t = 10^{\circ}$		
.2	.775	.767	.748	.737
.5	.769	.750	.706	.679
1.0	.826	.790	.700	.648
1.5	.921	.865	.722	.642
2.0	1.046	.964	.759	.650
2.5	1.202	1.085	.805	.668
3.0	1.391	1.225	.856	.692
		$t = 25^{\circ}$		
.2	.768	.762	.746	.736
.5	.758	.743	.705	.682
1.0	.809	.780	.703	.656
1.5	.895	.850	.728	.656
2.0	1.008	.942	.767	.668
2.5	1.148	1.054	.815	.688
3.0	1.318	1.182	.866	.715
		$t = 40^{\circ}$		
.2	.758	.753	.740	.732
.5	.743	.731	.699	.679
1.0	.785	.762	.698	.657
1.5	.861	.824	.722	.660
2.0	.960	.904	.757	.675
		$t = 60^{\circ}$		
.2	.745	.741	.730	.723
.5	.723	.715	.689	.673
1.0	.754	.737	.686	.654
1.5	.818	.790	.710	.661
2.0	.907	.864	.749	.680

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