

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Determination of the Activity Coefficient of Hydrochloric Acid at High Concentrations from Solubility Measurements

BY GÖSTA ÅKERLÖF AND HARLOW E. TURCK

In a ternary system composed of a solvent and two strong electrolytes the solubilities of the latter when present as pure solid phases are determined by their thermodynamic properties. The changes of their solubilities with changing composition of the solution phase by adding another component may thus be used for the determination of their relative activity coefficients. In case one of the two electrolytes present does not form a solid phase we are unable to calculate directly the changes of its activity coefficient from the composition of the liquid phase. Instead we will endeavor to show in this paper how it may be possible to compute the activity coefficient of an electrolyte of the kind indicated in its own pure solution from the corresponding value for the electrolyte forming the solid phase in a ternary system with the former present as co-solute. The procedure to be given represents a complete reversal of the method previously discussed¹ for the calculation of the activity coefficient of strong electrolytes from solubility measurements at high concentrations.

The method we are referring to is based on two empirical relationships: (1) the ratio of the activity coefficients of two strong electrolytes of the same valence type in pure aqueous solutions and (2) the activity coefficient of a given electrolyte in aqueous solutions of constant total ionic strength. Since at a given temperature the activity of the solid phase is constant, these two relationships give for the solubility μ_s of the solid phase in a ternary system with two homo-ionic, uni-univalent, strong electrolytes the following equation

$$\log \gamma_R(\mu_T) + k_1 \mu_T + k_2(\mu_T - \mu_s) + \frac{1}{2}(\log \mu_T + \log \mu_s) = \log a_s \quad (1)$$

where k_1 is the constant of the first and k_2 the constant for the second one of the two relationships given. The index R indicates the co-solute, μ_T the total ionic strength of the liquid phase and a_s is the activity of the solid phase. Assuming that the values of a_s , k_1 and k_2 are known we

would thus according to equation (1) be able to calculate the activity coefficient of the co-solute in its own pure solution at the total ionic strength μ_T .

The activity coefficient of hydrochloric acid has been measured with greater accuracy and over a larger concentration range than for any other strong electrolyte and therefore was selected as co-solute for an experimental test of the values calculated from equation (1). As electrolyte forming the solid phase sodium chloride was chosen on account of its low temperature coefficient for the solubility and also because its k_1 value is known with comparatively high accuracy. As reference point for the comparison between the values obtained for the activity coefficient of hydrochloric acid according to vapor pressure and electromotive force measurements and those calculated from the solubility data to be given below, has been chosen the value interpolated from the curve obtained by Randall and Young at the saturation concentration of sodium chloride in pure water.² Since the value of the total ionic strength of the liquid phase in our ternary system with increasing acid concentration passes through a minimum, the value of k_2 in equation (1) may be calculated from the solubility measurements themselves and thus only one reference point is necessary.

Experimental Procedure

"Analyzed" sodium chloride was precipitated from its own saturated solution with very pure concentrated hydrochloric acid, filtered off, dried and finally fused partially in a platinum dish. The product was very faintly alkaline although to the extent of less than 0.005%. Three different standard solutions of hydrochloric acid, about 4.0, 9.5 and 16.3 molal, respectively, were made up and analyzed gravimetrically as silver chloride with an accuracy of about 0.02%. The standard solutions were stored in old acid bottles with fully adequate protection against loss of hydrochloric acid by evaporation. Acid solutions of the desired strength were made up by adding the calculated amounts of water. Separate portions of about 200 cc. of a larger quantity of acid solutions thus made up were poured into 250-cc. glass-stoppered bottles containing sufficient sodium chloride to leave 5 to 10 g. undissolved as solid phase. The bottles were sealed with paraffin, mounted in a shaking machine and rotated at a rate of

(1) Åkerlöf and Thomas, *THIS JOURNAL*, **56**, 593 (1934); Åkerlöf, *ibid.*, **56**, 1439 (1934).

(2) Randall and Young, *ibid.*, **50**, 989 (1928).

about 10 p. m. over a period of twenty-four hours in a water thermostat regulated to 25° with a precision of 0.01° and controlled with the same accuracy.

A few hours after the shaking had been finished duplicate samples were taken from each bottle by applying gentle suction to the outlet tube from a small Erlenmeyer flask fitted with a two-holed rubber stopper provided with a short inlet tube coming from the bottle containing the solution to be sampled. The weighed sample was then evaporated to dryness, ignited over a small flame for about two hours, the residue of pure sodium chloride weighed, re-heated and re-weighed to assure constant weight. A summary of the result of the solubility determinations is given in Table I. For acid concentrations between 0 to 9 molal each one of the solubility values represents the mean of at least three separate determinations. Due to the rapidly increasing vapor pressure of very concentrated solutions of hydrochloric acid, it was considered to be impractical to try to make them up to definite concentrations. Therefore the solubility data for acid concentrations be-

tween 9 and 16 molal are values interpolated from a large number of measurements carried out with acid solutions having approximately the desired strength. The solubility measurements of Armstrong and Eyre³ at low acid concentrations and those of Ingham covering a large concentration range agree very closely with the results presented in this paper. When plotted their values fall practically right on the curve representing the solubility data in Table I. In the following all concentrations are given in moles per 1000 g. of water and all weighings have been corrected to vacuum.

The Calculation of the Activity Coefficient of Hydrochloric Acid.—Before we discuss the values given in the third and fourth columns of Table I we are first going to examine the values of the constants used for their calculation. An exhaustive survey of the literature gives as an average of thirty separate values for the solubility of sodium chloride in pure water at 25.00° 6.162 = 0.001 *m*. The "International Critical Tables," Vol. IV, p. 235, gives 6.145 *m* and from our measurements we obtained 6.163 *m*, which latter value, however, is only a fortuitous agreement. The value for the solubility in pure water is used as basis for the calculation of a_s by multiplying with the value for the activity coefficient of sodium chloride at this concentration. The logarithm of this activity coefficient is obtained by adding to the corresponding value for hydrochloric acid the product k_1 6.162. Due to this reason the saturation concentration of sodium chloride in pure water has also been chosen as reference point for all calculations carried out. Interpolation of the data of Randall and Young gives for the logarithm of the activity coefficient of hydrochloric acid at this point the value 0.5300. The value employed for k_1 has been derived from the measurements of Randall and Young and of Harned and Ehlers with solutions of hydrochloric acid and of Harned and of Harned and Nims with solutions of sodium chloride. The value found was $k_1 = -0.0875$ with an estimated error of ± 0.0005 .⁴ The value calculated for k_2 from the interpolated solubility measurements is equal to 0.050. The probable error in k_2 is difficult to estimate since it depends on the combined errors of a_s , k_1 and several solubility measurements.

A graphical comparison between the values for the activity coefficient of hydrochloric acid on one side as calculated according to equation (1) using

(3) Armstrong and Eyre, *Proc. Roy. Soc. (London)*, **A84**, 123 (1911); Ingham, *J. Chem. Soc.*, **128**, 1917 (1928).

(4) Harned and Ehlers, *THIS JOURNAL*, **55**, 2179 (1933); Harned *ibid.*, **48**, 326 (1926); Harned and Nims, *ibid.*, **54**, 423 (1932).

TABLE I

THE ACTIVITY COEFFICIENT OF HYDROCHLORIC ACID AT 25° IN PURE CONCENTRATED AQUEOUS SOLUTIONS AS CALCULATED FROM SOLUBILITY MEASUREMENTS WITH SODIUM CHLORIDE IN THIS ACID

NaCl, <i>m</i>	μ total	Log γ_{HCl} calcd.	Log γ_{HCl} R. and Y.	$\Delta \log \gamma$
6.162	6.162	0.530 ^a	0.530 ^a	(0.000)
5.631	6.131	.523	.526	-.003
5.096	6.096	.518	.521	-.003
4.567	6.067	.515	.517	-.002
4.054	6.054	.515	.516	-.001
3.569	6.069	.519	.517	+.002
3.100	6.100	.526	.521	+.005
2.660	6.160	.537	.529	+.008
2.261	6.261	.553	.543	+.010
1.884	6.384	.574	.559	+.015
1.561	6.561	.599	.583	+.016
1.272	6.772	.630	.610	+.020
1.0203	7.020	.667	.643	+.024
0.8100	7.310	.709	.681	+.028
.6354	7.635	.755	.723	+.032
.4966	7.997	.805	.771	+.034
.3888	8.389	.858	.822	+.036
.3066	8.807	.910	.877	+.033
.2430	9.243	.963	.930	+.033
.1992	9.699	1.011	.984	+.027
.1669	10.167	1.055	1.038	+.017
.1440	10.644	1.094	1.093	+.001
.1262	11.126	1.130	1.147	-.017
.1120	11.612	1.165	1.197	-.032
.1004	12.100	1.197	1.246	-.049
.0908	12.591	1.228	1.297	-.069
.0819	13.082	1.260	1.346	-.086
.0741	13.574	1.293	1.395	-.102
.0670	14.067	1.324	1.443	-.119
.0603	14.560	1.358
.0551	15.055	1.388	1.535	-.147
.0496	15.550	1.428
.0442	16.044	1.459	1.628	-.169

^a Reference point.

our solubility data and the constants just given and on the other side the values obtained by Randall and Young from their critical examination of vapor pressure, electromotive force and other types of measurements to be found in the literature is shown in Fig. 1. As will be shown below, the differences between the two sets of values are in the entire concentration range investigated well within the errors of the different methods used. The experimental errors to be expected in the case of the solubility data themselves at very high acid concentrations due to the action of the acid on the walls of the glass bottles employed were estimated by carrying out a number of blank tests with the pure acid solutions and were found to be insufficient to explain the discrepancies observed. The residues found were only in the case of the highest acid concentrations large enough to cause a maximum error of about 1% in the logarithm of the activity coefficient of hydrochloric acid and dwindled with decreasing acid concentration very rapidly to entirely negligible amounts.

Discussion

The values for the activity coefficient of hydrochloric acid given in the third column of Table I have been computed assuming that the empirical relationships employed are valid even in very concentrated solutions. A strong support for the validity of this assumption has been given for a large number of different strong electrolytes in pre-

vious papers. However, before we make a critical comparison between the data of Randall and Young and the result of the solubility measurements with sodium chloride, we are first going to study some corresponding data for potassium chloride obtained by Ingham.³ Up to a total ionic strength of about 7 his measurements appear to be very accurate but the interpolation of the solubility curve beyond this point is rather uncertain. A summary of the calculation of his data is given in Table II. The values used for k_1 and k_2 were -0.118 and 0.0463 , respectively. Since the total ionic strength of the solutions with increasing acid

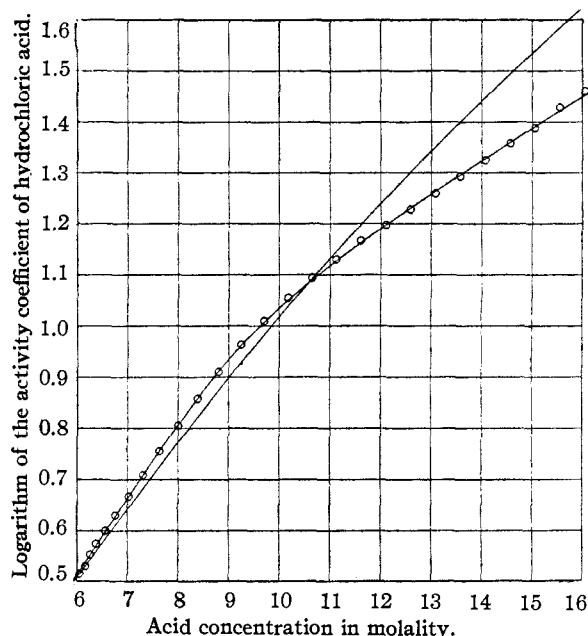


Fig. 1.—Curves for the logarithm of the activity coefficient of hydrochloric acid in pure aqueous solutions at 25°. Curve without points according to Randall and Young and curve with points as calculated from the solubility of sodium chloride in hydrochloric acid.

TABLE II

THE ACTIVITY COEFFICIENT OF HYDROCHLORIC ACID AT 25° IN PURE CONCENTRATED AQUEOUS SOLUTIONS AS CALCULATED FROM SOLUBILITY MEASUREMENTS WITH POTASSIUM CHLORIDE IN THIS ACID

KCl, <i>m</i>	μ total	Log γ_{HCl} calcd.	Log γ_{HCl} R. and Y.	$\Delta \log \gamma$
4.855	4.855	0.358 ^a	0.358 ^a	(0.000)
3.881	4.881	.362	.361	+ .001
3.427	4.927	.369	.367	+ .002
3.010	5.010	.381	.379	+ .002
2.622	5.122	.396	.393	+ .003
2.272	5.272	.415	.413	+ .002
1.961	5.461	.439	.438	+ .001
1.676	5.676	.467	.466	+ .001
1.422	5.922	.499	.498	+ .001
1.210	6.210	.535	.536	- .001
1.029	6.529	.574	.578	- .004
0.877	6.877	.616	.624	- .008
.743	7.243	.660	.671	- .011
.628	7.628	.707	.723	- .016
.473	8.473	.800	.832	- .032
.381	9.381	.886	.945	- .059

^a Reference point.

concentration shows a continuous increase, two reference points were necessary. As one of them was chosen the same point as the one used in the case of sodium chloride solutions and as the other the activity coefficient of hydrochloric acid at the saturation concentration of potassium chloride in pure water. The value found by Ingham was 4.855 *m* while a survey of all data in the literature gives 4.830 ± 0.010 *m*. The temperature coefficient of the solubility of potassium chloride is however quite large and it was considered to be more nearly correct to use the value of Ingham.

Within the accurate concentration range indicated above, the agreement between the solubility

values in Table II and the values interpolated from the data of Randall and Young for the activity coefficient of hydrochloric acid is very good indeed, which, however, is due partly to the use of two reference points. A graphical comparison is shown in Fig. 2. The data of Randall and Young for high acid concentrations are based

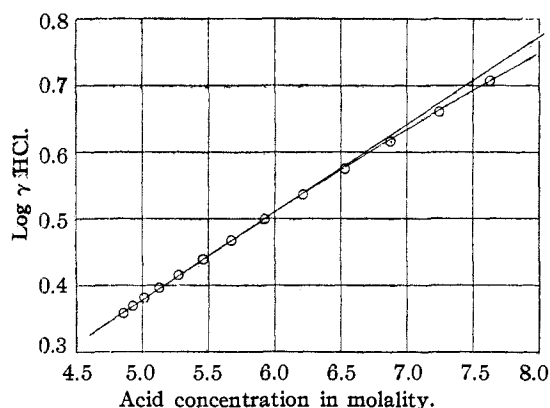


Fig. 2.—Curves for the logarithm of the activity coefficient of hydrochloric acid in pure aqueous solutions at 25°. Curve without points according to Randall and Young and curve with points as calculated from the solubility of potassium chloride in hydrochloric acid.

mainly on the vapor pressure measurements of Bates and Kirschmann⁵ with solutions from 3.2 to 10.0 molal. The average deviation of their experimental points from a smooth curve was 2.8%, indicating that the general form and direction of their curve is quite accurate. At corresponding concentrations the solubility values

(5) Bates and Kirschmann, *THIS JOURNAL*, **41**, 1991 (1919).

show in the case of sodium chloride solutions in the concentration range 6 to 12 molal an average deviation of 2.2% from the vapor pressure points, but these differences have a very definite trend. The same trend is found also for the differences with the solubility values for potassium chloride solutions. It is apparently to some extent caused by experimental errors in the vapor pressure values but probably chiefly due to errors in the k_1 and k_2 constants employed. In the case of sodium chloride solutions these errors are estimated to be able to give a swing of more than 3%, which, up to an acid concentration of about 12 molal, would more than cover the differences found. At still higher concentrations the data of Randall and Young are based on very few measurements, all of unknown accuracy.

Summary

An experimental study has been carried out regarding the possibilities of determining the activity coefficient of strong electrolytes at very high concentrations and in their pure solutions using solubility measurements for a co-solute. The case selected for the investigation was the ternary system hydrochloric acid-sodium chloride-water at 25°. The agreement found between solubility and vapor pressure values of the activity coefficient of hydrochloric acid was as good as reasonably could be expected over the entire concentration range within which an accurate comparison was possible.

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