ACTIVITY COEFFICIENTS IN CONCENTRATED SOLUTIONS CONTAINING SEVERAL ELECTROLYTES

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IN problems connected with concentrated solutions involving several electrolytes, it is necessary to have a knowledge of the activity coefficients of the separate salts. The determination of these activities in mixtures is usually a major experimental difficulty, and it is desirable to have a method for their calculation.

An important step in this direction was made by Guggenheim[1] in 1935, who derived the following equation for the activity coefficient $f\binom{X_1Y_1}{X_2Y_2}$ of an electrolyte X_1Y_1, in the presence of another electrolyte X_2Y_2 (in different notation)

$$\log_{10} f\binom{X_1Y_1}{X_2Y_2} = \frac{-0.5\,x_1y_1}{(1+I^{-1/2})} + \frac{x_1}{x_1+y_1}\sum_X \lambda_{XY_1}[X] + \frac{y_1}{x_1+y_1}\sum_Y \lambda_{X_1Y}[Y],$$

(1)

where x and y are the ionic charges of X and Y, taken positive irrespective of sign, $[X]$, $[Y]$ are the molar concentrations of the ions, I is ionic strength $= \frac{1}{2}\Sigma(x^2[X] + y^2[Y])$, and λ_{XY} are constants. The subscripts 1 and 2 refer to the solutes X_1Y_1 and X_2Y_2, respectively.

As shown by Guggenheim, this equation with a suitable choice of constants gives excellent agreement with the observations up to an ionic strength of about 0.3 mol./l., but does not apply at higher concentrations.

An analysis of the properties of Guggenheim's equation shows that its application is restricted mainly by the assumption that the 'specific' part of the activity coefficient, represented by the λ terms, is linear in the concentrations.

However, if we assume that the λ's are not constant, but are functions of the ionic strength I, then a much wider range of application is possible. We can now eliminate the λ's from the known values of the activity coefficients of the pure solutes at this ionic strength. This leads to a relationship between the activity coefficients in a mixed solution $\left(f\binom{X_1Y_1}{X_2Y_2}\right)$ and those of the pure solutes ($f^{X_1Y_1}$, $f^{X_2Y_2}$, etc.) at the total ionic strength I of the solution.

In the most interesting case, that of two ionic solutes with a common ion, we obtain the simple relationship :

$$\log_{10} f\binom{X_1Y}{X_2Y} = \log_{10} f^{X_1Y} - \frac{[X_2]}{4I}\left[K_1\log_{10} f^{X_1Y} - K_2\log_{10} f^{X_2Y} - \frac{K_3}{(1+I^{-1/2})}\right],$$

(2)

where $K_1 = x_2(2x_2-x_1+y)$, $K_2 = x_1(x_2+y)^2(x_1+y)^{-1}$, $K_3 = \frac{1}{2}x_1x_2y(x_1-x_2)^2(x_1+y)^{-1}$, which permits the calculation of activity coefficients in mixed solutions if those of the pure solutes are known.

Similar equations can be obtained for solutions in which all the ions are different, and for more than two solutes ; and it should be emphasized that none of these equations contains freely adjustable constants.

Within the limits of the experimental error, equation 2 is obeyed equally well if used with the 'practical' activity coefficients (γ, for use with molalities), instead of the 'rational' ones (f, for use with mole-fractions).

The agreement of equation 2 with the experimental data is shown by the example of the activity coefficients of hydrochloric acid for mixtures of 0.01 M acid and barium chloride (0.03–3 molar ionic strength), representing the influence of a 2 : 1 electrolyte on the activity of a 1 : 1 electrolyte (see Table 1).

Table 1. Activity coefficients of hydrochloric acid in the presence of barium chloride at 25° C.

Ionic strength (molal) I	$\left[\gamma^{HCl}_{(BaCl_2)}\right]_{m_{HCl}=0.01}$		γHCl[5]	$\gamma BaCl_2$[5]
	Calc. from equation 2	found[4]		
0.03	0.854	0.854	0.855	0.723
0.05	0.823	0.826	0.8304	0.670
0.10	0.782	0.786	0.7964	0.595
0.5	0.708	0.705	0.7571	0.457
1.0	0.698	0.699	0.8090	0.406
2.0	0.743	0.743	1.009	0.385
3.0	0.821	0.823	1.316	0.392

The knowledge of activity coefficients in the presence of multiple solutes renders possible the application of mass-law equations to the solubilities of highly soluble electrolytes. Table 2 shows the constancy of the solubility product of barium chloride in the presence of hydrochloric acid, if use is made of the activity coefficients calculated by equation 2. It speaks for the correctness of the theory that the same solubility product (2.1 ± 0.05) is obtained if sodium chloride is used as a salting-out agent. These examples represent the influence of 1 : 1 electrolytes on the activity of a 2 : 1 salt.

Table 2. Solubility product of barium chloride in the presence of hydrochloric acid

Molalities[6]		$\left(\gamma^{BaCl_2}_{(HCl)}\right)$ calc. from refs. 2,3	$[Ba^{++}].[Cl^-]^2.\gamma^3$
HCl	BaCl₂		
—	1.784	0.090	2.0
0.423	1.548	0.108	2.1
0.772	1.366	0.124	2.0
0.890	1.280	0.131	2.0
1.306	1.065	0.153	1.9
1.686	0.846	0.182	1.8
2.078	0.678	0.217	1.7
2.600	0.487	0.286	1.8
3.750	0.205	0.620	2.2
4.410	0.110	0.890	2.1
5.30	0.650	1.620	2.1

Another important application of the theory consists in the use of equation 2 for the calculation of activity coefficients of pure solutes in very greatly supersaturated solutions. After obtaining $\gamma\binom{X_1Y}{X_2Y}$ from solubility products in the presence of a second

solute, equation 2 can be solved for the activity coefficients of the pure solute (γ^{X_1Y}) at the ionic strengths of the mixed solutions, which are often greater than the saturation strength I of the pure salt X_1Y. As the activity coefficients so obtained must be independent of the nature of the second solute, agreement of the values of γ^{X_1Y} obtained from different combinations of solutes provides a very stringent test for the theory.

The accompanying diagram shows the activity coefficients of supersaturated solutions of pure barium nitrate calculated from its solubility data in the presence of barium chloride, potassium, sodium, calcium and ammonium nitrates, and nitric acid[5], all of which agree perfectly in spite of the greatly differing effect of these solutes on the solubility of barium nitrate. The method is particularly suitable for the calculation of activity coefficients in supersaturated solutions of salts of medium and low solubility, and it promises a considerable extension of our knowledge of activity coefficients by the application of equation (2) to the enormous mass of existing solubility data.
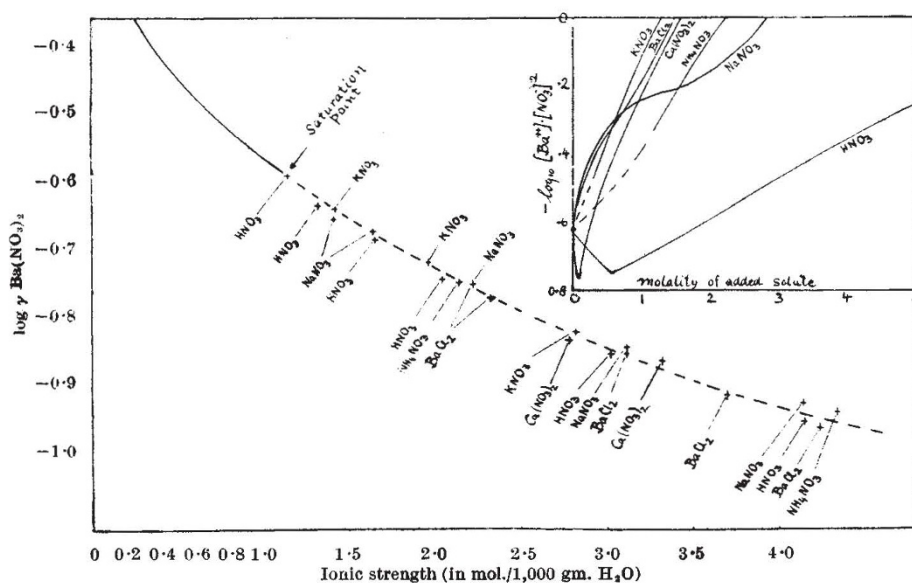
Activity coefficients of pure Ba(NO₃)₂ in supersaturated solutions calculated from solubilities in the presence of other solutes. Inset : solubility product of Ba(NO₃)₂ in mixed solutions

This extension of the theory to high concentrations does not, of course, improve other shortcomings which are inherent in the basic assumptions employed in the derivation of Guggenheim's equation, in particular the Bronsted[6] assumption : "that ions are 'specifically' influenced only by ions of opposite sign"; and in a number of cases equation (2) is only very imperfectly obeyed and apparently requires the introduction of an additional term. But in those cases where Brönsted's postulate is fulfilled, the new assumptions lead to equations which fully represent the 'specific' ion effects and cover the whole range up to and beyond the saturation concentrations.

Further details, including applications and critical discussion, will be published in due course.

[1] Guggenheim, E. A., *Phil. Mag.*, **19**, 606 (1935) (equation 52, symbols changed).

[2] Harned, H. S., and Owen, B. B., "Physical Chemistry of Electrolytic Solutions", table 11–4–1A, p. 547 (1943).

[3] Robinson, R. A., and Stokes, R. H., *Trans. Farad. Soc.*, **36**, 735 (1940).

[4] Harned, H. S., and Geary, C. G., *J. Amer. Chem. Soc.*, **59**, 2032 (1937).

[5] Solubility data from Gmelin's "Handbook" (8th edit.).

[6] Brönsted, T., *J. Amer. Chem. Soc.*, **44**, 877 (1922).

RIVER-FLOW SURVEY AND RECORDS

A GEOPHYSICAL Discussion on the subject of "River-Flow Survey and Records" was held by the Royal Astronomical Society in its rooms at Burlington House, London, W.1, on January 28, 1949, with Sir Roger Hetherington in the chair.

Mr. H. J. F. Gourley opened the discussion. He said that rivers have always played a very important part in the life of the community. In Great Britain the upland tributaries, which are free of contamination, form the chief source of water supply. The larger tributaries and main streams determine the sites of villages and towns and provide the necessary water for industrial development. Thus, quite apart from its scientific interest, an accurate knowledge of river flow is of great importance. The minimum flow is of special significance, for it determines the amount of water available for industrial processes such as cooling, and limits the amount of effluent which may be discharged without excessive contamination. In areas liable to flooding, the maximum flow is also of obvious importance.

The Land Drainage Act of 1930 made no provision for Government grants towards the expenses involved in gauging the flow in British rivers, but the River Boards Act (1947) has now remedied this. It also empowers the Ministry of Health to make recommendations to the various river boards. At present, the Thames is the only river in Great Britain for which day to-day records exist. In other cases, the Meteorological Office provides good estimates of the rainfall, but lack of knowledge of evaporation and storage makes estimates of run-off somewhat uncertain. They form the principal data from which the engineer can work, and provide a valuable means of obtaining advance information of floods. Nevertheless, they cannot replace accurate gauging, and it is to be hoped that the Ministry of Health will, in future, give every encouragement to this type of work.

Dr. J. Glasspoole, of the Meteorological Office, described how estimates of river flow can be made from rainfall data. Great Britain is remarkably well equipped with rain gauges, and analysis of the records from these has led to a good understanding of the effect of topography on the distribution of rainfall. The actual precipitation over a given basin can usually be determined to within a few per cent. but to derive the run-off in the river requires, in addition, a knowledge of storage and evaporation. Neither is accurately known, but, even so, the correlation coefficient between rainfall and run-off is 0·9, indicating that 80 per cent of the observed