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Note

The activity coefficient at extremely low concentrations ☆

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Abstract

It is suggested that the activity coefficient of a component approaches unity only in the range of reasonably high dilutions; at extremely low concentration the activity coefficient approaches zero with dilution.

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It is well known that as the concentration of a solid solute in a liquid solvent decreases, the behaviour of both components (the solvent and the solute) becomes more ideal; that is, for the reference states conveniently chosen, the activity of the solvent a_x approaches the mole fraction of the solvent x, and the activity of the solute a_c becomes nearly equal to its concentration c (molarity or molality). It is, therefore, a general practice to extrapolate the behaviour of reasonably diluted solutions to infinite dilutions, so that for the solvent

$$a_x \rightarrow x \quad \text{as} \quad c \rightarrow 0 \tag{1}$$

thus

$$f_x \rightarrow 1 \quad \text{as} \quad c \rightarrow 0 \tag{2}$$

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and for the solute

$$a_c \to c \quad \text{as} \quad c \to 0 \tag{3}$$

thus

$$f_c \to 1 \quad \text{as} \quad c \to 0 \tag{4}$$

where f_x and f_c are the respective activity coefficients.

In this discussion one would like to point out that the extrapolation of the behaviour of a solution to extremely low concentrations is sensible with respect to the solvent only, but not for the solute. Namely, as the concentration of the solute decreases the solution tends towards pure solvent, i.e. to its reference and standard state; thus, in agreement with Eqs. (1) and (2), at infinite dilution $a_x = x = 1$ and $f_x = 1$.

When treating the solute, however, one should note that the validity of Eqs. (3) and (4) has to be limited to moderately high dilutions because in solutions which are not extremely dilute the solute may reveal thermodynamic activity.

In order to support that view let us consider a solution containing one particle (molecule, ion) of a solute in one litre of solvent. In such a case, without further examination, one should assume that this particle of solute will not exhibit any activity at all, viz., it cannot influence any property (vapour pressure, osmotic pressure, electrochemical behaviour, etc.) of the solvent. Increasing the number of particles travelling through the solution to ten, one hundred, or to even a few orders of magnitude more, will not change the situation; the activity of the solute will remain zero.

This is because the activity, as a macroscopic property, always refers to a sufficiently high number of particles per unit volume, so whilst at reasonably high dilution (say 10^{-6} mol l^{-1}) the activity of the solute may be identified with its concentration, at extremely small concentration (say 10^{-20} mol l^{-1}) the solute does not reveal any thermodynamic activity at all. It follows that in some range of very high dilutions the activity of the solute declines with dilution much faster than the corresponding formal concentration, whereby the value of the activity coefficient, being unity at a reasonably low concentration, approaches zero at extremely high dilutions

$$f_c \to 0 \quad \text{as} \quad c \to 0 \tag{5}$$

At this point one should note that qualitative expressions such as extreme or reasonable, low or high concentration and dilution, sufficiently high number of particles, etc., cannot be evaluated explicitly merely for their macroscopic meaning. For this reason the result of the present work, i.e. the relationship (5), cannot be directly used in thermodynamic calculations. Its value lies in the conceptual, mainly didactic, field.

For example, one should realize that actually there exists a quite significant difference between some saturated solutions of various sparingly soluble salts, e.g. AgCl and HgS. In the case of AgCl solution the ion activities may be identified with their concentrations (about 10^{-5} mol l^{-1}) but in the HgS solution the extremely low ion activities (about 10^{-27} mol l^{-1}) cannot be related with certainty to equal concentrations (only one pair of ions per 1660 litres!); with reference to earlier considerations on the macroscopic character of the phenomenon, the corresponding concentration must be several orders of magnitude higher than the activity of HgS dissociation products.

It should be stressed here that the reasoning would be valid even if the activities were significantly higher than the reported ones; the point is that, if they are extremely low, the corresponding concentration must be much higher.

Needless to say, this example is a general illustration of the relationship between activity and concentration of any component at extremely low concentration or partial pressure.

Looking through many textbooks on physical chemistry, however, one cannot find any comment on the problem of the actual concentration related to extremely low activity. On the contrary, customarily it is postulated that Eqs. (3) and (4) are valid without limit at any high dilution.

At this point one should mention Cabral's letter [1] raising just the problem of extremely low concentrations related to very large, or very small, equilibrium constants. He points out the "absurd" meaning of extremely small equilibrium concentrations (e.g. 10^{-28} mol l^{-1}), at the same time encouraging his readers to comment on this question.

It seems that the suggestion in this paper departing from the traditional belief that at infinite dilution $f_c = 1$, may answer the problem of actual concentrations related to extremely low activities.

Reference

[1] J.O. Cabral, Educ. Chem., 16 (1979) 195.