

INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION

COMMISSION ON ELECTROANALYTICAL CHEMISTRY

**PROPOSED TERMINOLOGY AND
SYMBOL FOR THE
QUANTITY REPRESENTING
THE TRANSFER OF
SOLUTES FROM ONE
SOLVENT TO ANOTHER**

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PERGAMON PRESS
OXFORD · NEW YORK · PARIS · FRANKFURT

Analytical Chemistry Division

Commission on Electroanalytical Chemistry[†]

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SCOPE OF THE PROBLEM

The following problems are either equivalent or closely related: splitting the Gibbs free energies of solvation of electrolytes into the components for the ions involved; evaluating the corresponding quantities for the transfer of individual ions from one solvent to another; evaluating single ion activities, inner (Galvani) potentials and liquid junction potentials; and establishing a normalized electromotive force series for the correlation of potentials in different solvents. Estimates of these quantities must be based on extrathermodynamic procedures and cannot be fully verified experimentally, but are nevertheless of considerable value in the elucidation of ion-solvent interactions and for practical reasons.

The terminology and symbols used for the quantity representing the transfer of solutes from one solvent to another have developed into a state of chaos. Among terms used are the following: distribution coefficient (Bjerrum, 1927, and Kolthoff, 1959); degenerate activity coefficient (Grunwald, 1961); medium effect (Bates, 1964, and Popovych, 1970); medium activity coefficient (Coetzee, 1967); solvent activity coefficient (Parker, 1967); solvation activity coefficient (Charlot, Vedel, and Trémillon, 1968); and transfer coefficient (Courtot-Coupez). Likewise, several symbols have been used, most often γ or Γ with a variety of super- and subscripts. In "Electrochemical Symbols and Definitions"¹ the term "medium effect" and the symbol $\gamma_{S_2}^{S_1}(B)$ are used.

In this report, we are recommending an alternate term. The terminology and symbol are consistent with the "Manual of Symbols and Terminology for Physicochemical Quantities and Units"².

THERMODYNAMIC QUANTITIES FOR THE TRANSFER OF A SOLUTE FROM A REFERENCE TO ANOTHER SOLVENT

According to ref. 2, paragraph A.I.12, the (relative) activity of a solute B, a_B , at a molality m_B in any dilute liquid solution (in any solvent) is defined as follows:

$$a_B = \gamma_B (m_B/m_B^\theta) \quad (T, p \text{ const.}) \quad (1)$$

where m_B^θ is a standard value of molality (usually 1 mol kg⁻¹). Here, γ_B is the activity coefficient of solute B, given by

$$\gamma_B = (\lambda_B/m_B)/(\lambda_B/m_B)^\infty \quad (2)$$

where λ_B is the absolute activity of solute B and the superscript ∞ refers to infinite dilution. The relative activity of solute B is related to its chemical potential, μ_B , as follows:

$$RT \ln a_B = \mu_B - [\mu_B - RT \ln (m_B/m_B^\theta)]^\infty \quad (3)$$

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Case I. Solute B is uncharged. Solutions of B in two solvents R and S are in equilibrium when μ_B has the same value in the two solvents, i.e.,

$$RT \ln [(a_B)_R / (a_B)_S] = [\mu_B - RT \ln (m_B/m^\theta)]_S^\infty - [\mu_B - RT \ln (m_B/m^\theta)]_R^\infty \quad (4)$$

The right-hand side of this equation represents the change in Gibbs free energy occurring in the transfer of one mole of solute B (in the state of an infinitely dilute solution) from R (the reference solvent) to another solvent, S. This quantity is the standard Gibbs free energy of transfer of B from R to S, which is the difference in the standard Gibbs free energies of solvation of B in R and S, and we propose to represent it by the symbol $\Delta G_t^\circ(B)_{R \rightarrow S}$. It follows that a solute B in solvent S, at the molality $(m_B)_S$ corresponding to the relative activity $(a_B)_S$, has the same absolute activity as in the reference solvent R at the molality $(m_B)_R$ corresponding to the relative activity $(a_B)_R$, where

$$(a_B)_R = (a_B)_S \exp[(RT)^{-1} \Delta G_t^\circ(B)_{R \rightarrow S}] \quad (5)$$

Case II. Solute B is ionic. Consider a solute MX_n which is completely dissociated into M and X ions in both solvents. Here it is necessary to substitute the mean relative activity, a_{\pm} , for the relative activity a_B , and the mean activity coefficient, γ_{\pm} , for the activity

coefficient γ_B , so that $a_{\pm} = \gamma_{\pm} m$, where $\gamma_{\pm}^\infty = 1$. In this case, the only measurable quantity which can be defined is the standard Gibbs free energy of transfer from R to S of one mole of the electrolyte as a whole: $\Delta G_t^\circ(MX_n)_{R \rightarrow S}$. While it is operationally useful to consider that this quantity consists of individual ionic components, i.e.,

$$\Delta G_t^\circ(MX_n)_{R \rightarrow S} = \Delta G_t^\circ(M)_{R \rightarrow S} + n \Delta G_t^\circ(X)_{R \rightarrow S} \quad (6)$$

it is important to realize that a split of this kind falls outside the realm of rigorous thermodynamics and requires the adoption of extrathermodynamic models.

PROPOSED TERMINOLOGY AND SYMBOL

Relative activity scales in different pure and mixed solvents can be correlated through the quantity $\exp[(RT)^{-1} \Delta G_t^\circ(B)_{R \rightarrow S}]$. It is desirable to assign a term and a symbol to it. It seems to be impossible to find a term which will be (all at once) accurate, fully descriptive, and concise. All terms used in the past, and other possibilities considered, have one or more limitations, and a compromise is necessary. It seems desirable to incorporate the word "transfer", even though this at first might imply to some a nonequilibrium transport process. After consultation with a number of workers in the field, we recommend the term

"transfer activity coefficient" and the symbol $\gamma_{R2}^{S1}(B)$ or, alternatively, $\gamma_R^S(B)$. Since this

symbol is somewhat cumbersome, it would be convenient to contract it to γ_t , provided the nature of B, R, and S already has been specified. In many cases it will also be convenient to use the symbol $p\gamma_t$ to represent $-\log \gamma_t$.

NOTES

1. When S and R are two totally immiscible solvents, the quantity $\gamma_R^S(B)$ becomes the partition constant, K_D^0 , for the case of an uncharged solute, and the distribution coefficient, D, for an ionic solute in a single, definite form.³

2. The quantity $\gamma_R^S(B)$ behaves as an activity coefficient in expressing a "medium change effect", just as the conventional activity coefficient, γ_B , expresses a "salt effect". The composition of a mixed solvent medium can be varied continuously, just as the salt effect can be varied in a given solvent.

3. The transfer of an ion of charge z_B from a solvent R of inner electric potential ϕ_R to another solvent S of inner electric potential ϕ_S requires electric work equal to $z_B F(\phi_S - \phi_R)$, which cannot be separated experimentally from the chemical energy change. Equilibration of an ion B between two solvents requires equal values of the electrochemical potential $\bar{\mu}_B = \mu_B + z_B F\phi$, and not merely of the chemical potential μ_B . As a result, the definition of a transfer activity coefficient for a single ion is purely hypothetical. Its evaluation would require the determination of the junction potential, $\phi_S - \phi_R$, between the two solvents. Since this quantity cannot be determined experimentally at present, the only recourse is to base estimates of the transfer activity coefficient for a single ion on extrathermodynamic models.

4. In equations (3) and (4) the difficulty of defining μ_B^∞ was circumvented. The following definition is sometimes encountered:

$$\mu_B^\infty = \lim [\mu_B - RT \ln (m_B/m^\theta)]$$

(T and p const., $m_B \rightarrow 0$)

whence

$$\Delta G_t^\circ(B)_{R \rightarrow S} = \mu_B^\infty(S) - \mu_B^\infty(R)$$

REFERENCES

1. "Electrochemical Definitions and Symbols", Pure Appl. Chem. - in press.
2. "Manual of Symbols and Terminology for Physicochemical Quantities and Units", Pure Appl. Chem. 21 (1970), pp. 1-44.
3. "Recommended Nomenclature for Liquid-Liquid Distribution", Pure Appl. Chem. 21 (1970), pp. 109-114.