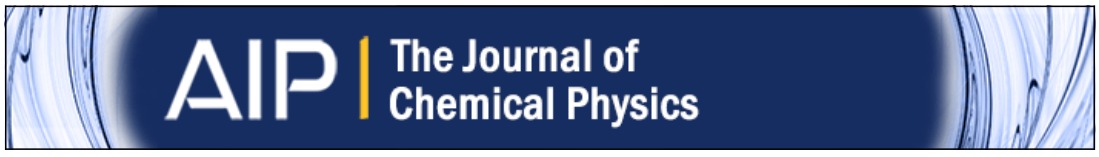

Erratum: ``Note on the Conditions of Equilibrium for Systems of Many Constituents''

Stuart R. Brinkley Jr.

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constant so that

$$P(v, K+1)-P(v, K)=P_r(K+1) -P_r(K)=\alpha(2K+1).$$

Hence,

$$\alpha=\frac{P(v, K+1)-P(v, K)}{2K+1}. \quad (27)$$

By use of the data of Table XVI for band 3, this formula gives an average value of $\alpha=0.0156 \pm 0.0003$. Hence,

$$P_r=0.0156K^2 \text{ (empirical)}.$$

It may be significant that if the numbering were reduced by one, as is suggested by the ΔF values, this empirical coefficient of K^2 becomes 0.0165 which is in better agreement with the theoretical coefficient of K^2. However, the linear term in K, which varies with v', may contribute to the isotope effect.

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Erratum: "Note on the Conditions of Equilibrium for Systems of Many Constituents"

[J. Chem. Phys. 14, 563 (1946)]

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THE paragraphs given below should be inserted following the paragraph containing Eq. (8) in the second column of page 564. The author did not receive proof and was, therefore, unable to supply this correction before publication of the article.

The derivation by means of the method employed by Gibbs,[4] subject to the constraints of Eqs. (8), of the conditions for equilibrium is straight forward, and it is unnecessary to reproduce it here. The usual conditions for thermal and mechanical equilibrium are obtained, and the conditions for chemical equilibrium take the form,

$$\mu_j^{(k)}=\lambda_j, \quad (9)$$

$$\mu_j^{(k)}=\sum_{j=1}^{c}\nu_{ij}\lambda_j, \quad (10)$$

$k=1, 2, \cdots p; j=1, 2, \cdots c; i=c+1, c+2, \cdots s,$

where $\mu_i^{(k)}$ and $\mu_j^{(k)}$ are the chemical potentials in the kth phase of the ith and jth substances, respectively, the λ_j are constants which may be eliminated from Eqs. (9), and where it has been assumed for simplicity that each substance of the system is included in every phase.[8]

[8] If a particular component, say the j'th, is a possible but not an actual constituent of a particular phase, say the k'th, then the determination of the conditions for equilibrium is subject to the additional constraint, $\delta n_{j'}^{(k')} \geqslant 0$, and the corresponding number of Eqs. (7) becomes $\mu_{j'}^{(k')} \geqslant \lambda_j$. A similar additional constraint must be applied if a particular dependent constituent, say the i'th, is a possible but not an actual constituent of the k'th phase, the corresponding member of Eqs. (9) becoming $\mu_{i'}^{(k')} \geqslant \sum_{j=1}^{c}\nu_{i'j}\lambda_j$. If the j'th component is excluded *a priori* from the k'th phase, the corresponding member of Eqs. (9) disappears as being without meaning, and similar considerations obtain if the i'th dependent constituent is excluded *a priori* from the k'th phase. The number of relations in Eqs. (9) and (10) is reduced by the number of such additional constraints, and the number of variables upon which the chemical potentials depend is reduced by the same number, thereby producing no effect upon the phase rule, Eq. (11). See Gibbs, reference 3, pp. 66, 67.

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