Thermochimica Acta, 111 (1987) 321–324
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

GIBBS ENERGY AND EQUILIBRIUM: DIMENSIONS IN THE LEWIS EQUATION

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(Received 14 April 1986; in final form 15 July 1986)

ABSTRACT

The well-known relationship between the Gibbs energy change and the equilibrium constant for a chemical reaction, $\Delta G^0 = -RT \ln K$, seemingly has either extensive dimensions, ΔG^0, or intensive dimensions, RT. The discrepency is explained on the basis of an ellipsis, the omission of $n = 1$ as a multiplier, and the relationship is explicitly $\Delta G^0 = -RT \times (n = 1) \ln K$ and hence extensive.

INTRODUCTION

The elegant and useful thermodynamic relation $\Delta G^0 = -RT \ln K$, (the Lewis Equation [1], $\Delta G = \Delta G^0 + RT \ln Q$, applied to reaction equilibrium at constant temperature and pressure), has subtleties not always immediately apparent, particularly the role of the solvent in liquid solutions [2,3]. Another kind of subtlety is that of dimensional consistency: ΔG clearly has extensive dimensions, energy, whereas the pre-logarithmic factor RT, taken simply as it stands, has intensive dimensions, energy per mol. If the dimensions are given as intensive, the implication is that there is an inherent Gibbs energy change for a chemical reaction independent of the stoichiometry represented by the balancing coefficients even though these are arbitrary. In textbooks and other places this leads to confusing and inconsistent interpretation.

Two examples which follow bring out the dimensional inconsistencies found in many, probably most, textbooks in discussion or applying the Lewis Equation. The authors of a well-known physical chemistry textbook [4] state "ΔG^0 is the change in standard Gibbs energy when the indicated numbers of moles in the *unmixed* reactants in their standard states at temperature T and 1 atm pressure react to form *unmixed* products in their standard states at the same temperature and pressure." Clearly ΔG^0 in this statement is extensive. The disscussion proceeds to the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

0040-6031/87/$03.50

and using 1 mol l^{-1} standard state a calculation at 400°C yields $K = 0.500$. Subsequently they write "$\Delta G^0 = -RT \ln K_c = -(1.987 \text{ cal K}^{-1} \text{ mol}^{-1})$ $(673 \text{ K})\ln 0.500 = 927 \text{ cal mol}^{-1}$" and arrive at a result with intensive dimensions. The author of a very recent textbook on thermodynamics [5] discussing the same reaction first writes "if we compute K_p from $\Delta G^0(298.2) = -32$ kJ, as obtained from tabulated thermodynamic data;" later, in a problem he writes "With $\Delta G^0_{300} = -33.0 \text{ kJ mol}^{-1}$, compute K_p at 300 K."

The purpose of this article is to show that ΔG^0 in the Lewis equation whether derived as by Lewis and Randall [6] or through the degree of advancement must be dimensionally extensive and that RT seemingly intensive is instead extensive. Although the derivation of the Lewis Equation is well known, in the development which follows elementary steps are elucidated in order to bring out the dimensional subtlety.

DISCUSSION

Consider a chemical reaction represented by

$$a\text{A} + b\text{B} \leftrightharpoons c\text{C} + d\text{D} \tag{1}$$

ΔG for the reaction is defined as the total Gibbs energy of the unmixed products less the total Gibbs energy of the unmixed reactants or

$$\Delta G = \tilde{G}_p - \tilde{G}_r \tag{2}$$

where $\tilde{G}$ is the total Gibbs energy and p and r denote product side and reactant side. μ_i is defined as $(\partial G/\partial n_i)_{P,T,n_j \neq n_i}$, and by Euler's theorem

$$\Delta G = \left(\sum n_i \mu_i\right)_p - \left(\sum n_i \mu_i\right)_r$$

and

$$\Delta G^0 = \left(\sum n_i \mu_i^0\right)_p - \left(\sum n_i \mu_i^0\right)_r \tag{3}$$

The activity is defined by

$$\mu_i = RT \ln a_i + B \tag{4}$$

with B a function of temperature only; at constant temperature and pressure

$$\mu_i - \mu_i^0 = RT \ln\left(a_i/a_i^0\right) \tag{5}$$

and

$$n_i \mu_i - n_i \mu_i^0 = n_i RT \ln\left(a_i/a_i^0\right) \tag{6}$$

Substitution of eqn. (6) in eqn. (3) yields

$$\Delta G - \Delta G^0 = RT\left\{\left[\sum n_i \ln\left(a_i/a_i^0\right)\right]_p - \left[\sum n_i \ln\left(a_i/a_i^0\right)\right]_r\right\} \tag{7}$$

Clearly both sides of eqn. (7) have extensive dimensions; RT, intensive, multiplied by number of moles, n_i, is extensive.

If eqn. (1) is written as

$$0 = -a\mathrm{A} - b\mathrm{B} + c\mathrm{C} + d\mathrm{D} \tag{8}$$

and $-a$, $-b$, c, and d are identified as dimensionless coefficients, ν_i, with positive values for products and negative values for reactants, for each product $n_i = \nu_i \times (n = 1)$ and for each reactant $n_i = -\nu_i \times (n = 1)$. Equation (7) may then be written as

$$\Delta G - \Delta G^0 = RT \times (n = 1) \sum \nu_i \ln\left(a_i/a_i^0\right) \tag{9}$$

or

$$\Delta G - \Delta G^0 = RT \times (n = 1) \sum \ln\left(a_i/a_i^0\right)^{\nu_i} \tag{10}$$

or

$$\Delta G - \Delta G^0 = RT \times (n = 1) \ln Q \tag{11}$$

and for equilibrium at constant pressure and temperature

$$\Delta G^0 = -RT \times (n = 1) \ln K \tag{12}$$

Equation (12) is dimensionally congruent and shows explicitly that there is an ellipsis, $n = 1$, in the Lewis Equation.

A contemporary trend in textbooks is to approach chemical equilibrium through the degree of advancement variable, ξ. Its use leads to a form of the Lewis Equation in which the same ellipsis as above appears not once but twice.

The degree of advancement is defined by

$$n_i = n_{i,0} + \nu_i \xi \tag{13}$$

and hence ξ has dimensions of n, moles. From eqn. (13), $\mathrm{d}n_i = \nu_i \mathrm{d}\xi$ yielding

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \sum \nu_i \mu_i \tag{14}$$

The De Donder affinity [7],

$$A = -\left(\frac{\partial G}{\partial \xi}\right)_{T,P}$$

is a minimum at equilibrium, and hence eqn. (14) yields $\Sigma \nu_i \mu_i = 0$ as the equilibrium condition; $\Sigma \nu_i \mu_i$ is numerically equal to ΔG but is not equivalent to ΔG which is $\Sigma \nu_i \times (n = 1)\mu_i$. The resulting expression $(\partial G/\partial \xi) = \Delta G^0 + RT \ln Q$ is explicitly

$$(n = 1) \times (\partial G/\partial \xi) = \Delta G^0 + RT \times (n = 1) \ln Q \tag{15}$$

with the same ellipsis embodied twice. Of course $(n = 1) \times (\partial G/\partial \xi)$ is simply ΔG.

Although there is no inherent ΔG^0 for a chemical reaction independent of the coefficients used in balancing, an inherent intensive property is defined if the extensive ΔG^0 is divided by the coefficients taken as representing number of moles: $\Delta G^0/a$; $\Delta G^0/b$; $\Delta G^0/c$; $\Delta G^0/d$. $\Delta G^0/n_i$ is then intensive and there is a referent component.

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