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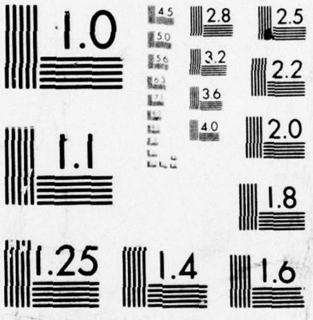
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ON THE UNITS OF THE EQUILIBRIUM CONSTANT

J. M. Heimerl

June 1977

USA ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
USA BALLISTIC RESEARCH LABORATORY
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A straightforward explicit derivation of the equilibrium constant is presented together with a discussion of the dimensional relationships that exist among equilibrium constants commonly used.

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INTRODUCTION

Some standard text discussions on the equilibrium constant are terse to the point of confusion while others are succinct to the point of error. It is the purpose of this note to present a derivation of the equilibrium constant, carrying those terms commonly treated implicitly and to demonstrate the dimensional relationships that exist among the various equilibrium constants presently in use in the literature. The sources for this eclectic presentation are listed in the bibliography.

THE EQUILIBRIUM CONSTANT

The first and second laws of thermodynamics can be written

$$dE \geqslant \delta Q - \delta W, \tag{1a}$$

and

$$\delta Q/T \leqslant dS, \tag{2a}$$

where dE is the change in the internal energy of a closed system, δQ the heat supplied to that system, δW the work done by the system, T the temperature of the system and dS the change in entropy of the system. For reversible processes and mechanical work done by hydrostatic pressure we can write

$$dE = \delta Q - PdV \tag{1b}$$

and

$$\delta Q/T = dS\ , \tag{2b}$$

where P is the pressure and dV the change in volume. Combining equations 1b and 2b we find

$$dE = TdS - PdV\ . \tag{3}$$

The enthalpy and gibbs free energy are defined

$$H \equiv E + PV \tag{4}$$

and

$$G \equiv H - TS\ , \tag{5}$$

respectively. The differential forms of equations (4) and (5) are

$$dH = dE + d(PV) \tag{6}$$

and

$$dG = dE + d(PV) - d(TS), \tag{7}$$

where equation 6 has been substituted for dH in equation 7. Adding d(PV) - d(TS) to both sides of equation 3, using equation (7) on the

LHS and collecting terms on the RHS we find

$$dG = -SdT + VdP \; ; \tag{8}$$

or for an isothermal process

$$dG = VdP. \tag{9}$$

Substituting in equation (9) for V from the ideal gas law written in the form

$$PV = nRT \; , \tag{10}$$

where n is the number of moles and R the universal gas constant, we have

$$dG = \frac{nRT\,dP}{P} \; , \tag{11}$$

or

$$dg = RT\,d(\ln P) \tag{12}$$

where g is the gibbs free energy per mole. Integrating equation (12) from a reference pressure, $P^\dagger$, to some arbitrary pressure, P, we have

$$g(P) - g(P^\dagger) = RT \ln(P/P^\dagger). \tag{13}$$

Equation (13) relates the gibbs free energy per mole at pressure P to the gibbs free energy per mole at reference pressure $P^\dagger$.

The change in free energy per mole for a reaction, not necessarily in equilibrium, is given by

$$\Delta g_r = \Sigma\, \nu_i g_i , \tag{14}$$

where by convention the stoichiometric coefficient of the ith species is positive if a product and negative if a reactant. Substituting equation (13) into equation (14) we find

$$\Delta g_r = RT\, \Sigma\, \nu_i \ln(P_i/P^\dagger) + \Sigma\, \nu_i g_i(P^\dagger) \; , \tag{15a}$$

where P_i is the partial pressure of the ith species. The last term in equation (15a) represents the net change in free energy per mole in the reaction for all species referred to the reference pressure $P^\dagger$. This term is defined as $\Delta g°$. Equation (15a) can be written as

$$\Delta g_r = RT[\ln \Pi(P_i/P^\dagger)^{\nu_i}] + \Delta g° , \tag{15b}$$

where Π denotes a continued product and logarithmic identities have been employed. Up to this point the P_i have been arbitrary; if now we require that they be the partial pressures at equilibrium, then the net change in the gibbs free energy per mole must be zero; and we have

$$\Delta g^\circ = - RT \ln K \ , \tag{16}$$

where

$$K = \Pi(P_i/P^\dagger)^{\nu_i}. \tag{17}$$

Equation (17) is the definition of the equilibrium constant. There are other derivations of equations (16) and (17), based on partition functions and the idea of a chemical potential but they will not be treated here. What we have chosen to do here is explicitly carry the reference pressure, $P^\dagger$, so that one can see that K is the log of a dimensionless number. The reference state is arbitrary and the numerical value of K will depend upon that state.

Equation (17) can be written

$$K = K_p/K^\dagger \ , \text{ where} \tag{18}$$

$$K_p = \Pi(P_i)^{\nu_i} \quad \text{and} \tag{19}$$

$$K^\dagger = \Pi(P^\dagger)^{\nu_i} \ . \tag{20}$$

In equation (20), $K^\dagger$ is a function only of the reference pressure; in equation (19), K_p is a function only of the partial pressures of the system. Both K_p and $K^\dagger$ have dimensions of pressure raised to some power.

The selection $P^\dagger = 1$ (in some units) produces the following effects. The magnitude of $K^\dagger$ in equation (20) is unity, although it still is a dimensioned quantity. Then the magnitude of the dimensionless equilibrium constant K in equation (18) is identical to the magnitude of the dimensioned quantity K_p in equation (19). Operationally one may: (1) compute K_p, (2) ignore the dimensions, and (3) use the value so computed for K. This procedure provides numerically correct results. (For the particular circumstance $\Sigma\nu_i = 0$, both $K^\dagger$ and K_p are dimensionless with the result that substitution of K_p for K is rigorously correct.)

The most commonly used reference pressure, $P^\dagger$, is one atmosphere; hence the dimensions of K_p (and $K^\dagger$) are atmospheres to some power. This power is determined by the reaction itself and how the stoichiometric coefficients are written. For example, consider the overall reaction

$$2H_2 + O_2 = 2H_2O. \tag{21a}$$

From equation (19) we have

$$K_p = \frac{P^2_{H_2O}}{P^2_{H_2} P_{O_2}} \ (\mathrm{atm})^{-1} . \tag{22a}$$

But reaction (21a) can be written as

$$H_2 + 1/2\ O_2 = H_2O , \tag{21b}$$

then

$$K_p = \frac{P_{H_2O}}{P_{H_2} P^{1/2}_{O_2}} \ (\mathrm{atmos})^{-1/2} . \tag{22b}$$

Had we selected $P^\dagger = 1$ Pascal = 1 Pa = 1 Newton/meter^2 = 1 Nm^{-2}, the dimensions of *the equilibrium constants* in equations (22a) and (22b) would have been (Pa)$^{-1}$ and (Pa)$^{-1/2}$, respectively. (1 atmos = 1.01325×10^5 Nm^{-2}).

OTHER FORMS OF THE EQUILIBRIUM CONSTANT

Equation (17) is based on partial pressures and is not always the most convenient form for the equilibrium constant. Other forms include equilibrium constants based on moles (or mole fractions) or on concentrations. To express equation (17) in terms of moles we note that from equation (10) we have

$$P_i/P_t = n_i/n_t \tag{23}$$

where the subscript t indicates "total." Substituting into equation (17) for P_i from equation (23), we find

$$K = K_n\ [P_t/(n_t\ P^\dagger)]^{\Delta\nu}, \tag{24}$$

where $K_n = \Pi n_i^{\nu_i}$ and $\Delta\nu = \Sigma\nu_i$. Since the mole fraction is defined as $x_i = n_i/n_t$ we have from equation (24)

$$K = K_x(P_t/P^{\dagger})^{\Delta\nu} \quad , \tag{25}$$

where $K_x = \Pi x_i^{\nu_i}$. In Equation (25) P_t must be expressed in the same units as $P^{\dagger}$.

To express equation (17) in terms of concentrations ("number densities"), we recall the ideal gas law in the form PV = NkT, where k is Boltzmann's constant (= 1.3806×10^{-23} J deg^{-1}). Then

$$P = c\ kT \tag{26}$$

where c = N/V is the concentration. Substituting into equation (17) for P_i from equation (26), we find

$$K = K_c(kT/P^{\dagger})^{\Delta\nu} , \tag{27}$$

where $K_c = \Pi c_i^{\nu_i}$. In equation (27) kT must be expressed in the same system of units as $P^{\dagger}$.

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