Chemical Equilibria: Cratic and Unitary Quantities

We comment on the term ‘equilibrium constant’ where the composition of the solution under examination is expressed in terms of solute molalities, solute concentrations and solute mole fractions. [1-5] We consider a closed system in which the solvent is water ($\lambda$) at defined temperature and pressure where the pressure is ambient and close to the standard pressure $p^0$. The solution contains $n_1$ moles of water and $n_{j}^{eq}$ moles of each chemical substance $j$, solutes, where the composition is described in terms of a chemical equilibrium. The latter is described in the following general terms where $\nu_j$ is the stoichiometry for chemical substance $j$, being positive for products and negative for reactants.

$$\sum_{j=1}^{\infty} \nu_j \cdot \mu_j^{eq}(aq) = 0 \quad (a)$$

The sum is taken over all i-solutes in solution with respect to the equilibrium chemical potentials of each chemical substance $j$.

Molalities

The equilibrium molality of solute $j$ is given by the ratio $(n_j / n_1 \cdot M_i)$ where $M_i$ is the molar mass of water. From equation (a),

$$\sum_{j=1}^{\infty} \nu_j \cdot [\mu_j^0(aq;T) + R \cdot T \cdot \ln(m_j^{eq} \cdot \gamma_j^{eq} / m^0)] = 0 \quad (b)$$

By definition for each solute $j$,

$$\lim_{m_j \to 0} \gamma_j = 1.0 \quad \text{at all } T \text{ and } p. \quad (c)$$

A standard equilibrium constant $K_m^0$ is defined using equation (d) where the subscript ‘m’ is a reminder that we are using molalities to express the composition of the solution under examination.

$$\Delta_r G^0(T;\text{m-scale}) = -R \cdot T \cdot \ln[K_m^0(T)] = \sum_{j=1}^{\infty} \nu_j \cdot \mu_j^0(aq;T) \quad (d)$$

At temperature $T$, $K_m^0(T)$ is related to the equilibrium composition of the solution using equation (e).

$$K_m^0(T) = \prod_{j=1}^{\infty} (m_j^{eq} \cdot \gamma_j^{eq} / m^0)^{\nu_j} \quad (e)$$

Also by definition, $pK_m^0(T) = -\log[K_m^0(T)] \quad (f)$
From the Gibbs –Helmholtz Equation,

\[
\Delta r H_m^0 = -T^2 \cdot \left[ \frac{\partial}{\partial T} \left( \frac{\Delta r G_m^0}{T} \right) \right]_p = R \cdot T^2 \cdot \left[ \frac{\partial \ln(K_m^0)}{\partial T} \right]_p = -R \cdot \left[ \frac{\partial \ln(K_m^0)}{\partial T^{-1}} \right]_p \quad (g)
\]

\[
\Delta r C_{pmn}^0 (T) = [\partial\Delta r H_m^0 / \partial T]_p \quad (h)
\]

\[
\Delta r S_m^0 = T^{-1} \cdot [\Delta r H_m^0 - \Delta r G_m^0] \quad (i)
\]

The algebra is a little tortuous but the points are clearly made if we confine attention to chemical equilibria in solutions having thermodynamic properties which are ideal. For a chemical equilibrium involving \( j \) chemical substances in solution where the solvent is chemical substance 1, at fixed temperature and pressure,

\[
K^0 = \prod_{j=2}^{m} \left( \frac{m_j^{eq}}{m_j^0} \right)^{v_j} \quad (j)
\]

Also \( K_m^0 = \prod_{j=2}^{m} \left( \frac{m_j^{eq}}{m_j^0} \right)^{v_j} \quad (k) \)

\[
\Delta r G^0 = -R \cdot T \cdot \ln K^0 \quad (\lambda)
\]

\[
\Delta r G^0 = -R \cdot T \cdot \ln \left[ \prod_{j=2}^{m} \left( \frac{m_j^{eq}}{m_j^0} \right)^{v_j} \right] \quad (m)
\]

\[
\Delta r G^0 = -R \cdot T \cdot \ln \left[ \prod_{j=2}^{m} \left( \frac{m_j^{eq}}{m_j^0} \right)^{v_j} \right] + v \cdot R \cdot T \cdot \ln(m^0) \quad (n)
\]

\[
\Delta r G^0 = -R \cdot T \cdot \ln K_m^0 + v \cdot R \cdot T \cdot \ln(m^0) \quad (o)
\]

\[
\Delta r G_m^0 = \Delta r G_m^0 + v \cdot R \cdot T \cdot \ln(m^0) \quad (p)
\]

\[
\Delta r G_m^0 = -R \cdot T \cdot \ln K_m^0 \quad (q)
\]

This rather dull analysis has merit in showing that the lost units in the equation \( \Delta r G^0 = -R \cdot T \cdot \ln K_m^0 \) are found in the term \( v \cdot R \cdot T \cdot \ln(m^0) \) where \( v = \sum_{j=2}^{m} v_j \).

This concern arises because for correct dimensions the logarithm operation should operate on a pure number. No such problems emerge if \( v \) is zero as is the case for a stoichiometrically balanced equilibrium. Moreover if we probe the dependence of \( K^0 \) or \( K_m^0 \) on temperature we have that,
\[
\frac{d}{dT} \left[ \nu \cdot R \cdot T \cdot \ln \left( \frac{m^0}{T} \right) \right] = 0 \quad \text{(r)}
\]

If we are interested in the dependence of either \( K^0 \) or \( K_m^0 \) on pressure, we have that,

\[
\frac{d}{dp} \left[ \nu \cdot R \cdot T \cdot \ln \left( m^0 \right) \right] = 0 \quad \text{(s)}
\]

**Mole Fraction Scale**

The total amount of all chemical substances in the closed system, an aqueous solution, at chemical equilibrium is given by equation (t).

\[
n_{eq}^T = n_1 + \sum n_{eq}^j \quad \text{(t)}
\]

For a given chemical substance, solute \( k \)

\[
x_{eq}^k = \frac{n_{eq}^k}{[n_1 + \sum n_{eq}^j]} \quad \text{(u)}
\]

In terms of mole fractions, the equilibrium chemical potential for solute \( j \), \( \mu_{eq}^j (aq; T; p) \) is related to the equilibrium mole fraction \( x_{eq}^j (aq) \) using equation (v).

\[
\mu_{eq}^j (aq; T; p) = \mu_{eq}^j (x \text{ - scale}; aq; T) + R \cdot T \cdot \ln(x_{eq}^j \cdot f_{eq}^j) \quad \text{(v)}
\]

By definition, at all \( T \) and \( p \), \( \lim (x_j \to 0) f_{eq}^j = 1.0 \). \( \text{(w)} \)

Further, \( \mu_{eq}^j (x \text{ - scale}; aq; T) \) is the chemical potential of substance \( j \) in aqueous solution at temperature \( T \) in a solution where the mole fraction of solute \( j \) is unity. Here therefore \( \mu_{eq}^j (x \text{ - scale}; aq; T) \) is the reference chemical potential.

From equation (a),

\[
\sum_{j=1}^{n} v_j \cdot [\mu_{eq}^j (x \text{ - scale}; aq; T) + R \cdot T \cdot \ln(x_{eq}^j \cdot f_{eq}^j)] = 0 \quad \text{(x)}
\]

\[
\Delta G_x^0 (T) = -R \cdot T \cdot \ln[K_x^0 (T)] = \sum_{j=1}^{n} v_j \cdot \mu_{eq}^j (x \text{ - scale}; aq; T) \quad \text{(y)}
\]

At temperature \( T \), \( K_x^0 (T) \) is related to the equilibrium mole fractions of the solutes.

\[
K_x^0 (T) = \prod_{j=1}^{n} (x_{eq}^j \cdot f_{eq}^j)^{v_{eq}^j} \quad \text{(z)}
\]
From the Gibbs–Helmholtz Equation,

\[
\Delta_r H_x^0 = -T^2 \cdot \left[ \frac{\partial}{\partial T} \left( \frac{\Delta_r G_x^0}{T} \right) \right]_{p} = R \cdot T^2 \cdot \left[ \frac{\partial \ln(K_x^0)}{\partial T} \right]_{p} = -R \left[ \frac{\partial \ln(K_x^0)}{\partial T^{-1}} \right]_{p} \tag{za}
\]

\[
\Delta_r C_{p_1}^0 (T) = [\partial \Delta_r H_x^0 / \partial T]_p \tag{zb}
\]

\[
\Delta_r S_x^0 = T^{-1} \cdot [\Delta_r H_x^0 - \Delta_r G_x^0] \tag{zc}
\]

We note a complication. We suppose that the composition of a given closed system, an aqueous solution, is described in terms of the formation of a dimer by a solute Z in aqueous solution at defined T and p

\[
2Z(aq) \rightleftharpoons Z_2(aq) \tag{zd}
\]

At equilibrium, the solution contains \( n_1 \) moles of water, \( n_{eq}(Z) \) moles of monomer and \( n_{eq}(Z_2) \) moles of dimer.

\[
x(Z)^{eq} = n(Z)^{eq} / [n_1 + n(Z)^{eq} + n(Z_2)^{eq}] \tag{ze}
\]

\[
x(Z_2)^{eq} = n(Z_2)^{eq} / [n_1 + n(Z)^{eq} + n(Z_2)^{eq}] \tag{zf}
\]

Further, \( x_1^{eq} = n_1 / [n_1 + n(Z)^{eq} + n(Z_2)^{eq}] \tag{zg} \)

As a result of a change in temperature \( n_{eq}(Z) \) and \( n_{eq}(Z_2) \) change; \( n_1 \) does not.

For example \( x(Z)^{eq} \) changes as a result of changes in both numerator and denominator in equation (ze). This unwelcome complication is not encountered if we use the molality scale. The way forward is to confine attention to dilute solutions such that at all temperatures, \( \sum_{j=2}^{Z} n_{j}^{eq} << n_1 \).

**Mole Fraction and Molality Scales**

The complication noted in conjunction with equation (zd) also emerges when equilibrium constants on these two scales are compared. If the thermodynamic properties of the solutions are ideal, we obtain the following two equations.

\[
K_{m}^0 (T) = \prod_{j=1}^{Z} (m_j^{eq} / m^0)^{v(j)} \tag{zh}
\]

\[
K_x^{0} (T) = \prod_{j=1}^{Z} (x_j^{eq})^{v(j)} \tag{zi}
\]

\[
K_{m}^0 (T) / K_x^{0} (T) = \prod_{j=1}^{Z} (m_j^{eq} / m^0 \cdot x_j^{eq})^{v(j)} \tag{zj}
\]

But \( m_j^{eq} = n_j^{eq} / w_i = n_j^{eq} / n_1 \cdot M_i \)

For dilute solutions \( x_j^{eq} = n_j^{eq} / n_1 \)
\[
\frac{m_j}{m^0 \cdot x^j} = \frac{n^\text{eq}_j}{n_1 \cdot M_1 \cdot m^0 \cdot n^\text{eq}_j} \cdot \frac{n_j}{n^\text{eq}_j}
\]

\[
\prod_{j=1}^{m} \left[ \frac{n^\text{eq}_j}{n_1 \cdot M_1 \cdot m^0} \cdot \frac{n_j}{n^\text{eq}_j} \right]^{v(j)} = \prod_{j=1}^{m} \left[ \frac{1}{M_1 \cdot m^0} \right]^{v(j)}
\]

The product \((M_1 \cdot m^0)\) is dimensionless; i.e. \((\text{kg mol}^{-1}) \cdot (\text{mol kg}^{-1})\).

Hence, \(K^0_j(T) = K^0_m(T) \cdot \prod_{j=1}^{m} (M_1 \cdot m^0)^{v(j)}\) \((zl)\)

Consider a chemical equilibrium which has the following form,

\[
A(aq) \rightleftharpoons B(aq)
\]

\(K^0_j(T) = K^0_m(T) \cdot (M_1 \cdot m^0)^{z_l} \cdot (M_1 \cdot m^0)^{z_0}\) \((zn)\)

In fact for all symmetric equilibria in dilute solution, the numerical values of \(K^0_j(T)\) and \(K^0_m(T)\) are equal.

**Concentration Scale**

The main advantage from a thermodynamic standpoint in expressing the composition of a solution in terms of molalities, \(m_j\) is the fact that the definition does not require specification of either temperature or pressure. The latter is a consequence of using a definition based on the masses of solvent and solute. Nevertheless from a practical standpoint there are many advantages in expressing the composition of a solution in terms of concentration \(c_j\) \((= n_j/V\) where \(V\) is the volume of a solution). Many experimental techniques are based on ‘counting’ the amount of solute \(j\) in a given volume of system. This is certainly true of uv/visible spectrophotometric methods based on Beer’s Law. Similarly electrical conductivities count the amount of conducting ions in a given volume of solution. Further when these methods are used, the actual densities of the solutions are only rarely measured so that conversion from concentration \(c_j\) to molality \(m_j\) is not straightforward.

We may find it convenient to characterise the composition of a given aqueous solution in terms of equilibrium concentrations of each solute \(j\). Therefore the volume of the aqueous solution \(V_{\text{aq}}(T;p)\) is given by equation \((zp)\).

\[
V_{\text{aq}}(T;p) = n_1 \cdot V^\text{aq}_1(aq;T;p) + \sum_{j=2}^{m} n^\text{eq}_j \cdot V^\text{eq}_j(aq;T;p)
\]
For solute j, $c_j^{eq} = n_j^{eq} / V^{eq}(aq; T; p)$ \quad (zq)

At this point a problem emerges. Even in the event that $n_j^{eq}$ does not change when the temperature is changed, $c_j^{eq}$ changes because for real solutions $V^{eq}(aq; T; p)$ is dependent on temperature. Furthermore at fixed T, p and composition, the volume of the corresponding ideal solution differs from $V^{eq}(aq; T; p)$ and hence $c_j^{id} \neq c_j^{eq}$. The way forward explores chemical equilibria in very dilute solutions.

$$\sum_{j=2}^{n} n_j^{eq} \cdot V_j^{eq}(aq; T; p) \ll n_1 \cdot V_1^{eq}(aq; T; p) \quad (zr)$$

Hence, $V^{eq}(aq; T; p) = n_1 \cdot V_1^* (\lambda; T; p) \quad (zs)$

Therefore, $c_j^{eq} = n_j^{eq} / n_1 \cdot V_1^* (\lambda) \quad (zt)$

We express the chemical potential $\mu_j^{eq}(aq)$ using equation (zu).

$$\mu_j^{eq}(aq; T; p) = \mu_j^0 (c - \text{scale}; aq; T) + R \cdot T \cdot \ln(c_j^{eq} \cdot y_j^{eq} / c_r) \quad (zu)$$

Here $c_r = 1 \text{ mol dm}^{-3}$, $c_j^{eq}$ being expressed using the unit, mol dm$^{-3}$; $y_j^{eq}$ is the activity coefficient for solute j on the concentration scale, describing the impact of solute-solute interactions in the aqueous solution. By definition at all T and p,

$$\lim_{c_j \to 0} y_j = 1.0 \quad (zv)$$

From equation (a),

$$\sum_{j=1}^{n} v_j \cdot [\mu_j^0 (c - \text{scale}; aq; T) + R \cdot T \cdot \ln(c_j^{eq} \cdot y_j^{eq} / c_r)] = 0 \quad (zw)$$

By definition,

$$\Delta_r G_c^0 (T) = -R \cdot T \cdot \ln[K_c (T)] = \sum_{j=1}^{n} v_j \cdot \mu_j^0 (c - \text{scale}; aq; T) \quad (zx)_{-}$$

$$K_c (T) = \prod_{j=1}^{n} (c_j^{eq} / c_r)^{y_j^{eq}} \quad (zy)$$

For dilute solutions we might assume that $y_j^{eq}$ is unity for all solutes.

$$K_c (T) = \prod_{j=1}^{n} (c_j^{eq} / c_r)^{y_j^{eq}} \quad (zz)$$

From the Gibbs - Helmholtz Equation,

$$\Delta_r H_c^0 = -T^2 \cdot \left[ \frac{\partial}{\partial T} \left( \frac{\Delta_r G_c^0}{T} \right) \right]_p = R \cdot T^2 \cdot \left[ \frac{\partial \ln(K_c)}{\partial T} \right]_p = -R \cdot \left[ \frac{\partial \ln(K_c)}{\partial T} \right]_p \quad (zza)$$
$\Delta_c C^0_p(T) = [\partial \Delta_c H^0 / \partial T]_p$  \hspace{1cm} (zzb)

$\Delta_c S^0_c = T^{-1} \cdot [\Delta_c H^0 - \Delta_c G^0_c]$  \hspace{1cm} (zzc)

**Molality and Concentration Scales**

If the thermodynamic properties of the solutions are ideal, we obtain the following two equations.

$$K_m^0(T) = \prod_{j=1}^{i=1} \left( m_j^i / m_0^i \right)^{v(j)}$$  \hspace{1cm} (zzd)

$$K_c^0(T) = \prod_{j=1}^{i=1} \left( c_j^i / c_0^i \right)^{v(j)}$$  \hspace{1cm} (zze)

$$K_m^0(T) / K_c^0(T) = \prod_{j=1}^{i=1} \left( m_j^i \cdot c_i / c_j^i \cdot m_0^i \right)^{v(j)}$$  \hspace{1cm} (zzf)

But $m_j^i / w_i = n_j^i / n_i \cdot M_i$

And for dilute solutions, $c_j^i = n_j^i / V(aq) = n_j^i / n_i \cdot V_1^*(\lambda)$

$m_j^i / c_j^i = V_1^*(\lambda) / M_i = 1 / \rho_i^*(\lambda)$  \hspace{1cm} (zzg)

By definition, $\rho^0 = c_i / m_0^i = [\text{mol dm}^{-3}] / [\text{mol kg}^{-1}] = [\text{kg dm}^{-3}]$

By introducing the property $\rho^0$ we overcome the problem with units.

$$K_m^0(T) / K_c^0(T) = \prod_{j=1}^{i=1} \left( \rho_i^*(\lambda) / \rho^0 \right)^{v(j)}$$  \hspace{1cm} (zzh)

A scale factor of $10^3$ often occurs in these equations because concentrations are conventionally quoted using the unit, mol dm$^{-3}$ and densities are expressed using the unit, g cm$^{-3}$.

In summary care should be taken when using equilibrium constants based on different composition scales. [1-4] A classic example [5] from the field of kinetics shows how misleading conclusions can be drawn from, for example, comparison of standard entropies of activation and reaction expressed using different composition scales. [6]

**Footnotes**

[5] As Guggenheim remarked the units of ln(V) are ln(m$^3$). If V = 100 m$^3$, then log(V) = log(100) + log(m$^3$), log(V)-log(m$^3$) = 2; log(V/m$^3$)=2.