Chemical Equilibria: Solutions: Derived Thermodynamic Parameters

A given closed system at fixed temperature and fixed pressure contains a number of chemical substances in chemical equilibrium. The composition of the system depends on temperature and pressure. Key equations describe the dependences of the equilibrium Gibbs energy on temperature and pressure.

\[
H^\text{eq} = -T^2 \left[ \left( \frac{\partial (G/T)}{\partial T} \right)_p \right]^\text{eq} ; \quad V^\text{eq} = \left( \frac{\partial G}{\partial p} \right)_T
\]

The situation is complicated by the fact that both \( H^\text{eq} \) and \( V^\text{eq} \) depend on the equilibrium composition of the system, \( \xi^\text{eq} \; \xi^\text{eq} \; p, T \)

\[
\left( \frac{\partial H}{\partial \xi} \right)^\text{eq}_{T,p} = \sum_{j=1}^{n} \left( \frac{\partial H}{\partial n_j} \right)^\text{eq}_{T,p,n(\neq j)} \left( \frac{\partial n_j}{\partial \xi} \right)^\text{eq}
\]

But partial molar enthalpy, \( H^\text{eq} = \left( \frac{\partial H}{\partial n_j} \right)^\text{eq}_{T,p,n(\neq j)} \)

Further, \( \left( \frac{\partial n_j}{\partial \xi} \right)^\text{eq} = \nu_j \)

Here \( \nu_j \) is the stoichiometry associated with chemical substance \( j \), being positive for products and negative for reactants.

Therefore, \( \left( \frac{\partial H}{\partial \xi} \right)^\text{eq}_{T,p} = \sum_{j=1}^{n} \nu_j \cdot H^\text{eq}_j \)

Similarly, \( \left( \frac{\partial V}{\partial \xi} \right)^\text{eq}_{T,p} = \sum_{j=1}^{n} \nu_j \cdot V^\text{eq}_j \)

\( V^\text{eq}_j \) is the partial molar volume of substance \( j \) in the solution at equilibrium.

The partial molar enthalpy of solute \( j \) can be expressed in terms of a limiting molar enthalpy \( H^\infty_j \) and the dependence of activity coefficient \( \gamma_j \) on temperature.
Therefore, \[
\left( \frac{\partial H}{\partial \xi} \right)_{T,p}^{eq} = \sum_{j=1}^{\infty} v_j \left[ H_j^{\infty} - R \cdot T^2 \cdot \left( \frac{\partial \ln(\gamma_j)}{\partial T} \right)_p^{eq} \right]
\] (f)

In other words the dependence of enthalpy of the system on composition at equilibrium is a function of the limiting molar enthalpies of all chemical substances involved in the equilibrium and the dependences on temperature of their activity coefficients.

By definition, the limiting molar enthalpy of reaction,
\[
\Delta_i H^\infty = \sum_{j=1}^{\infty} v_j \cdot H_j^{\infty}
\] (g)

Then \[1\]
\[
\left( \frac{\partial H}{\partial \xi} \right)_{T,p}^{eq} = \Delta_i H^\infty - \sum_{j=1}^{\infty} v_j \cdot R \cdot T^2 \cdot \left( \frac{\partial \ln(\gamma_j)}{\partial T} \right)_p^{eq}
\] (h)

In some applications, the solutions are quite dilute and the assumption is made that at all temperatures and pressures \(\gamma_j\) for chemical substance \(j\) is unity.

Hence, \[
\left( \frac{\partial H}{\partial \xi} \right)_{T,p}^{eq} = \Delta_i H^\infty
\] (i)

A similar analysis is possible in terms of partial molar volumes. From equation (e), we obtain the following equation for the volume of reaction.
\[
\left( \frac{\partial V}{\partial \xi} \right)_{T,p}^{eq} = \sum_{j=1}^{\infty} v_j \cdot \left[ V_j^{\infty} + R \cdot T \cdot \left( \frac{\partial \ln(\gamma_j)}{\partial p} \right)_T^{eq} \right]
\] (j)

The limiting volume of reaction, \(\Delta_i V^\infty = \sum_{j=1}^{\infty} v_j \cdot V_j^{\infty}\) (k)

Thus \[2\],
\[
\left( \frac{\partial V}{\partial \xi} \right)_{T,p}^{eq} = \Delta_i V^\infty + \sum_{j=1}^{\infty} v_j \cdot R \cdot T \cdot \left( \frac{\partial \ln(\gamma_j)}{\partial p} \right)_T^{eq}
\] (l)

If the solution is dilute, it can often be assumed that the activity coefficient of each chemical substance is independent of pressure. Then,
\[
\left( \frac{\partial V}{\partial \xi} \right)_{T,p}^{eq} = \Delta_i V^\infty
\] (m)
A slight complication to these general equations arises if one of the substances involved in the chemical equilibrium is the solvent. As an example we consider the following equilibrium.

\[
X(aq) + H_2O(aq) \rightleftharpoons Y(aq)
\]  

Then,

\[
(\partial H/\partial \xi)_{T,p}^{eq} = \left[ H_Y^0(aq) - R \cdot T^2 \cdot (\partial \ln \gamma_Y / \partial T)_{p}^{eq} \right]
- \left[ H_X^0(aq) - R \cdot T^2 \cdot (\partial \ln \gamma_X / \partial T)_{p}^{eq} \right]
- \left[ H_Y^*(\lambda) + R \cdot T^2 \cdot M_1 \cdot (m_X + m_Y)^{eq}_p \cdot (\partial \phi / \partial T)_{p}^{eq} \right]
\]  

(\( o \))

If the properties of the solution are ideal (e.g. very dilute), equation (\( o \)) is written in the following form.

\[
(\partial H/\partial \xi)_{T,p}^{eq} = H_Y^0(aq) - H_X^0(aq) - H_Y^*(\lambda)
\]  

(\( p \))

With reference to the limiting volume of reaction, the analogue of equation (\( p \)) is as follows.

\[
(\partial V/\partial \xi)_{T,p}^{eq} = V_Y^0(aq) - V_X^0(aq) - V_Y^*(\lambda)
\]  

(\( q \))

Footnotes

[1] \[ \left( \frac{\partial H}{\partial \xi} \right)_{T,p}^{eq} = [J \text{ mol}^{-1}] + [1 \cdot [J K^{-1} \text{ mol}^{-1}] \cdot [K] \cdot \left( \frac{[1]}{[K]} \right)] = [J \text{ mol}^{-1}] \]

[2] \[ \left( \frac{\partial V}{\partial \xi} \right)_{T,p}^{eq} = [m^3 \text{ mol}^{-1}] + [1 \cdot [J K^{-1} \text{ mol}^{-1}] \cdot [K] \cdot \left( \frac{[1]}{[N \text{ m}^{-2}]} \right)] = [m^3 \text{ mol}^{-1}] \]