**Affinity for Spontaneous Reaction: Dependence on Temperature**

Using the definition of the Gibbs energy $G = U + p \cdot V - T \cdot S = H - T \cdot S$, we form an equation for the entropy of a closed system. Thus $T \cdot S = -G + H$. The entropy of the closed system is perturbed by a change in composition/organisation, $\xi$ at fixed $T$ and $p$.

Then, $T \cdot \left( \frac{\partial S}{\partial \xi} \right)_{T,p} = - \left( \frac{\partial G}{\partial \xi} \right)_{T,p} + \left( \frac{\partial H}{\partial \xi} \right)_{T,p}$ \hspace{1cm} (a)

But the affinity for spontaneous reaction, $A = - \left( \frac{\partial G}{\partial \xi} \right)_{T,p}$ \hspace{1cm} (b)

A Maxwell equation requires that, $\left( \frac{\partial S}{\partial \xi} \right)_{T,p} = \left( \frac{\partial A}{\partial T} \right)_{p,\xi}$.

Hence, $T \cdot \left( \frac{\partial A}{\partial T} \right)_{p,\xi} = A + \left( \frac{\partial H}{\partial \xi} \right)_{T,p}$ \hspace{1cm} (c)

Equation (c) is rearranged to yield the following interesting equation.

$$A - T \cdot \left( \frac{\partial A}{\partial T} \right)_{p,\xi} = - \left( \frac{\partial H}{\partial \xi} \right)_{T,p}$$ \hspace{1cm} (d)

The affinity for spontaneous change and its dependence on temperature are simply related to the enthalpy of reaction at fixed $T$ and $p$. We exploit this link by considering the derivative $d(A/T)/dT$ (at fixed $p$ and fixed $\xi$).

$$d(\frac{A}{T})/dT = (1/T) \cdot (dA/dT) - A/T^2$$ \hspace{1cm} (e)

Hence

$$\left[ \frac{\partial (A/T)}{\partial T} \right]_{p,\xi} = - \frac{1}{T^2} \cdot \left[ A - T \cdot \left( \frac{\partial A}{\partial T} \right)_{p,\xi} \right]$$ \hspace{1cm} (f)

Using equation (d),

$$\left[ \frac{\partial (A/T)}{\partial T} \right]_{p,\xi} = \frac{1}{T^2} \cdot \left( \frac{\partial H}{\partial \xi} \right)_{T,p}$$ \hspace{1cm} (g)

The latter equation is an analogue of the Gibbs-Helmholtz Equation relating the change in Gibbs energy to the enthalpy of reaction, $\left( \frac{\partial H}{\partial \xi} \right)_{T,p}$. The background to equation (g) is the definition of the...
dependent variable \((A/T)\) in terms of independent variables, \(T\), \(p\) and \(\xi\).

Thus \((A/T) = (A/T)[T, p, \xi]\) \(\text{(h)}\)

The general differential of the latter equation has the following form.

\[
d(A/T) = \frac{\partial(A/T)}{\partial T} \cdot dT + \frac{1}{T} \cdot \frac{\partial A}{\partial p} \cdot dp + \frac{1}{T} \cdot \frac{\partial A}{\partial \xi} \cdot d\xi \quad \text{(i)}
\]

But, from equation (e)

\[
d(A/T) = -(A/T^2) \cdot dT + (1/T) \cdot dA \quad \text{(j)}
\]

Or, \(dA = T \cdot d(A/T) + (A/T) \cdot dT \quad \text{(k)}\)

We incorporate equation (i) for the term \((A/T)\).

Thus

\[
dA = \left[\frac{1}{T} \cdot \left(\frac{\partial(A/T)}{\partial T}\right)_{p,\xi} + \frac{A}{T}\right] \cdot dT + \left[\frac{\partial A}{\partial p}\right]_{T,\xi} \cdot dp + \left[\frac{\partial A}{\partial \xi}\right]_{T,p} \cdot d\xi \quad \text{(l)}
\]

Then using equation (g),

\[
dA = \left[\frac{1}{T} \cdot \left(\frac{\partial H}{\partial \xi}\right)_{T,p} + \frac{A}{T}\right] \cdot dT - \left[\frac{\partial V}{\partial \xi}\right]_{T,p} \cdot dp + \left[\frac{\partial A}{\partial \xi}\right]_{T,p} \cdot d\xi \quad \text{(m)}
\]

The latter is a general equation for the change in affinity. We rearrange this equation as an equation for a change in extent of reaction.

\[
d\xi = -\left(\frac{\partial \xi}{\partial A}\right)_{T,p} \cdot \left[\frac{1}{T} \cdot \left(\frac{\partial H}{\partial \xi}\right)_{T,p} + \frac{A}{T}\right] \cdot dT + \left[\frac{\partial V}{\partial \xi}\right]_{T,p} \cdot \left(\frac{\partial \xi}{\partial A}\right)_{T,p} \cdot dp
\]

\[
+ \left(\frac{\partial \xi}{\partial A}\right)_{T,p} \cdot dA \quad \text{(n)}
\]

The latter equation has the form of a general differential for the extent of reaction written as,

\[
\xi = \xi[T, p, A] \quad \text{(o)}
\]

Or, \(d\xi = \left(\frac{\partial \xi}{\partial T}\right)_{p,A} \cdot dT + \left(\frac{\partial \xi}{\partial p}\right)_{T,A} \cdot dp + \left(\frac{\partial \xi}{\partial A}\right)_{T,p} \cdot dA \quad \text{(p)}\)

Hence from equation (n),

\[
\left(\frac{\partial \xi}{\partial T}\right)_{p,A} = -\left(\frac{\partial \xi}{\partial A}\right)_{T,p} \cdot \left[\frac{1}{T} \cdot \left(\frac{\partial H}{\partial \xi}\right)_{T,p} + \frac{A}{T}\right] \quad \text{(q)}
\]
Equation (q) describes the dependence of extent of reaction on
temperature at fixed pressure and affinity for spontaneous reaction.

Then from equation (n),

\[
\frac{\partial \xi}{\partial p}_{T,A} = \left[ \frac{\partial V}{\partial \xi} \right]_{T,p} \cdot \left( \frac{\partial \xi}{\partial A} \right)_{T,p},
\]

Equation (r) describes the dependence of extent of reaction at fixed
temperature and fixed affinity for spontaneous change.