**Topic 2040**

**Gibbs - Helmholtz Equation**

The Gibbs energy and enthalpy of a closed system are related:

\[ G = H - T \cdot S \]  

(a)

The two properties \( G \) and \( H \) are also related by the Gibbs - Helmholtz equation through the dependence of \( G \) on temperature at fixed pressure. We envisage a situation in which a closed system at equilibrium having Gibbs energy \( G \) is displaced to a neighbouring equilibrium state by a change in temperature at constant pressure.

We are interested in the partial derivative, \[ \left[ \frac{\partial (G / T)}{\partial T} \right] \_{p,A=0} \]. In general terms we consider the isobaric differential dependence of \( (G/T) \) on temperature.

\[ \frac{d}{dT} \left( \frac{G}{T} \right) = \frac{1}{T} \cdot \left( \frac{\partial G}{\partial T} \right) \_p - \frac{G}{T^2} \]  

(b)

\[ T^2 \cdot \frac{d}{dT} \left( \frac{G}{T} \right) = T \cdot \left( \frac{\partial G}{\partial T} \right) \_p - G \]  

(c)

But \( S = - \left( \frac{\partial G}{\partial T} \right) \_p \)  

(d)

For an equilibrium change, equations (b) and (c) yield equation (e).

\[ T^2 \cdot \frac{d}{dT} \left( \frac{G}{T} \right) \_p = -(G + T \cdot S) \]  

(e)

But \( H = G + T \cdot S \). Then, \( H = -T^2 \cdot \frac{d}{dT} \left( \frac{G}{T} \right) \_p \)  

(f)

For an equilibrium change,

\[ \Delta H(A = 0) = -T^2 \cdot \frac{d}{dT} \left( \frac{\Delta G}{T} \right) \_{p,A=0} \]  

(g)

or, \( \Delta H(A = 0) = \frac{d}{dT^{-1}} \left( \frac{\Delta G}{T} \right) \_{p,A=0} \)  

(h)

In a similar manner we obtain the Gibbs-Helmholtz equation for a system perturbed at constant composition [1].

\[ \Delta H(\text{fixed } \xi) = \frac{d}{dT^{-1}} \left( \frac{\Delta G}{T} \right) \_{p,A=0} \]  

(i)
Equation (f) is the starting point for the development of another important equation.

Thus, \[ H = -T^2 \cdot \left[ -\frac{G}{T^2} + \frac{1}{T} \cdot \frac{dG}{dT} \right] \] \hspace{1cm} (j)

Hence, \[ H = G - T \cdot \left[ \frac{dG}{dT} \right] \] \hspace{1cm} (k)

Equation (k) is differentiated with respect to temperature at constant pressure and at \( \text{'}A=0\text{'} \).

\[ \left( \frac{\partial H}{\partial T} \right)_{p,A=0} = \left( \frac{\partial G}{\partial T} \right)_{p,A=0} - T \cdot \left( \frac{\partial^2 G}{\partial T^2} \right)_{p,A=0} - \left( \frac{\partial G}{\partial T} \right)_{p,A=0} \] \hspace{1cm} (l)

Hence, \[ \left( \frac{\partial H}{\partial T} \right)_{p,A=0} = -T \cdot \left( \frac{\partial^2 G}{\partial T^2} \right)_{p,A=0} \] \hspace{1cm} (m)

But \[ \left( \frac{\partial^2 G}{\partial T^2} \right)_{p,A=0} = \frac{\partial}{\partial T} \left( \frac{\partial G}{\partial T} \right) = \frac{\partial S}{\partial T} \left( \frac{\partial G}{\partial T} \right)_{p,A=0} \] \hspace{1cm} (n)

Also the equilibrium isobaric heat capacity,

\[ C_p(A = 0) = \left( \frac{\partial H}{\partial T} \right)_{p,A=0} \] \hspace{1cm} (o)

Equations (m), (n) and (o) yield equation (p).

\[ \left( \frac{\partial S}{\partial T} \right)_{p,A=0} = \frac{C_p(A = 0)}{T} \] \hspace{1cm} (p)

Equation (p) relates the isobaric equilibrium dependence of entropy of a closed system on temperature to the isobaric heat capacity.

Also starting from, \( H = G + T \cdot S \),

then \( \left( \frac{\partial H}{\partial p} \right)_T = \left( \frac{\partial G}{\partial p} \right)_T + T \cdot \left( \frac{\partial S}{\partial p} \right)_T \) \hspace{1cm} (q)

Using a Maxwell Equation, \( \left( \frac{\partial H}{\partial p} \right)_T = V - T \cdot \left( \frac{\partial V}{\partial T} \right)_p \) \hspace{1cm} (r)

Similarly, \( \left( \frac{\partial U}{\partial T} \right)_V = C_v = T \cdot \left( \frac{\partial S}{\partial T} \right)_V \) \hspace{1cm} (s)

And \( \left( \frac{\partial U}{\partial V} \right)_T = -p - T \cdot \left( \frac{\partial V}{\partial T} \right)_p \cdot \left( \frac{\partial p}{\partial V} \right)_T \) \hspace{1cm} (t)

**Footnote**

[1] There are many thermodynamic equations which are of the Gibbs-Helmholtz type. As a common feature they conform to the following calculus property.

Given \( f = f(x, y) \)
Then 
\[ \left( \frac{\partial (f / x)}{\partial (1 / x)} \right)_y = -x^2 \cdot \left( \frac{\partial (f / x)}{\partial x} \right)_y = f - x \cdot \left( \frac{\partial f}{\partial x} \right)_y \]

Similarly, 
\[ \left( \frac{\partial (f / y)}{\partial (1 / y)} \right)_x = -y^2 \cdot \left( \frac{\partial (f / y)}{\partial y} \right)_x = f - y \cdot \left( \frac{\partial f}{\partial y} \right)_x \]

Normally f stands for a thermodynamic potential and x and y for its natural variables. Thus a total of 8 equations of the Gibbs-Helmholtz type holding for closed systems can be constructed from

\[ U = U(S, V), F = F(T, V), H = H(S, P) \text{ and } G = G(T, P). \]