The fundamental equations

$dU = dq_{rev} + dw_{rev} = TdS - pdV \rightarrow$ applicable to any process since dU is a state function

For irr. Changes, $TdS > dq$ and $-pdV > dw$, but the sum $dq + dw$ remains the same.

Seems $U(S, V)$ is a natural choice

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV; \quad \left(\frac{\partial U}{\partial S}\right)_V = T \quad and \quad \left(\frac{\partial U}{\partial V}\right)_S = -p$$

Since U is a state function, the above equation gives, $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$

$$dH = dU + d(pV) = TdS - pdV + pdV + Vdp = TdS + Vdp$$

$$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dp; \quad \left(\frac{\partial H}{\partial S}\right)_p = T \quad and \quad \left(\frac{\partial H}{\partial p}\right)_S = V$$

Since H is a state function, the above equation gives, $\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$

$$dA = dU - d(TS) = TdS - pdV - TdS - SdT = -pdV - SdT$$

$$dA = \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial T}\right)_V dT; \quad \left(\frac{\partial A}{\partial T}\right)_V = -S \quad and \quad \left(\frac{\partial A}{\partial V}\right)_T = -p$$

Since A is a state function, the above equation gives, $\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$

$$dG = dH - d(TS) = TdS + Vdp - TdS - SdT = Vdp - SdT$$

$$dG = \left(\frac{\partial G}{\partial p}\right)_T dp + \left(\frac{\partial G}{\partial T}\right)_p dT; \quad \left(\frac{\partial G}{\partial T}\right)_p = -S \quad and \quad \left(\frac{\partial G}{\partial p}\right)_T = V$$

Since G is a state function, the above equation gives, $\left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial S}{\partial p}\right)_T$

The equations in blue are the Maxwell relations.

Table 3.5 The Maxwell relations

From U:	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$
From H:	$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$
From A:	$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$
From G:	$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$

Some examples

We saw the variation of U as a function of V.

$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$ gives, $\quad \left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_T + \left(\frac{\partial U}{\partial V}\right)_S \rightarrow \quad \pi_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$. This is a thermodynamic equation of state.

For an I.G. $\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial (nRT/V)}{\partial T}\right)_V = \frac{nR}{V} \quad \therefore \quad \pi_T = \frac{nRT}{V} - p = 0$

For a van der Waals gas, $p = \frac{nRT}{V-nb} - \frac{an^2}{V^2} \rightarrow \left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial (nRT/(V-nb))}{\partial T}\right)_V = \frac{nR}{V-nb}$

$$\therefore \quad \pi_T = \frac{nRT}{V-nb} - p = \frac{nRT}{V-nb} - \left(\frac{nRT}{V-nb} - \frac{an^2}{V^2}\right) = \frac{an^2}{V^2}$$

Focusing on the Gibbs Free Energy

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \quad and \quad \left(\frac{\partial G}{\partial p}\right)_T = V$$

S is always +ve. G dec. as T is increased

      G dec. more if entropy is large. It dec. more for gases than solids

Since $V > 0$, G always inc. when p is inc., G being more sensitive when the V is large (i.e. gases)

G as a function of T

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

The equilibrium constant is related to G/T

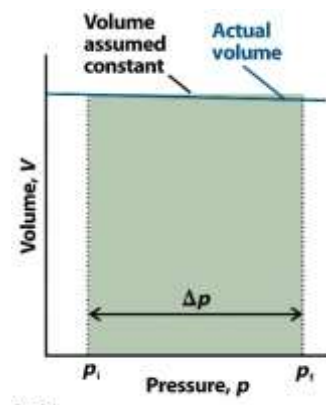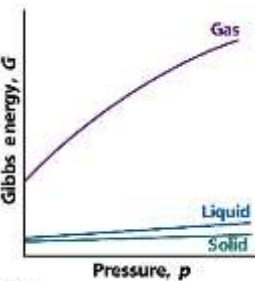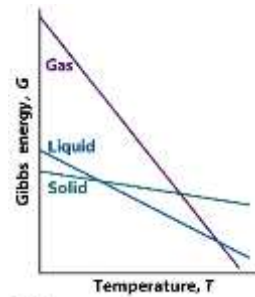$$\left(\frac{\partial (G/T)}{\partial T}\right)_p = -\frac{H}{T^2} \quad Gibbs - Helmholtz \; equation$$

$$\left(\frac{\partial (G/T)}{\partial T}\right)_p = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p + G\frac{d(1/T)}{dT} = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T^2} = \frac{1}{T}\left\{\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T}\right\} = \frac{1}{T}\left\{\frac{G-H}{T} - \frac{G}{T}\right\} = -\frac{H}{T^2}$$

$$\left\{\frac{\partial (\Delta G/T)}{\partial T}\right\}_p = -\frac{\Delta H}{T^2}$$

G as a function of p

At constant T, $\left(\frac{\partial G}{\partial p}\right)_T = V$. $G_m(p_f) = G_m(p_i) + \int_{p_i}^{p_f} V_m dp$

For condensed phases V_m is essentially constant. So not much change in G_m

Gibbs energy, G vs Temperature, T (Gas, Liquid, Solid)

Gibbs energy, G vs Pressure, p (Gas, Liquid, Solid)

Volume, V vs Pressure, p (Volume assumed constant, Actual volume, Δp, p_i, p_f)

For gases it does. For an I.G.,

$$G_m(p_f) = G_m(p_i) + RT \int_{p_i}^{p_f} \frac{1}{p} \, dp = G_m(p_i) + RT \ln \frac{p_f}{p_i}$$

Set $p_i = p^0$ (standard pressure)
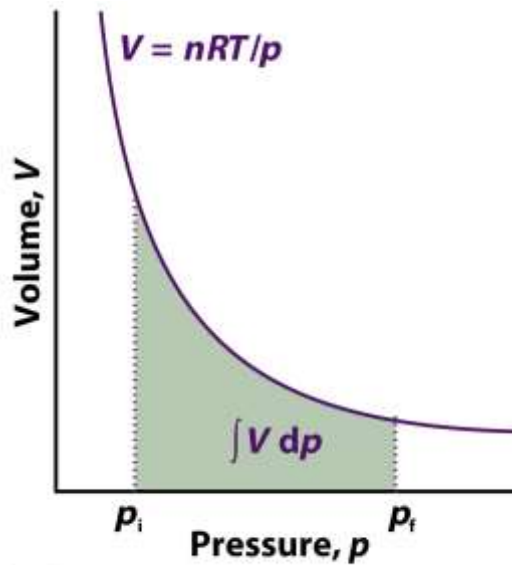
$$G_m(p) = G_m^0 + RT \ln \frac{p}{p^0}$$

Figure 3-22
Atkins Physical Chemistry, Eighth Edition
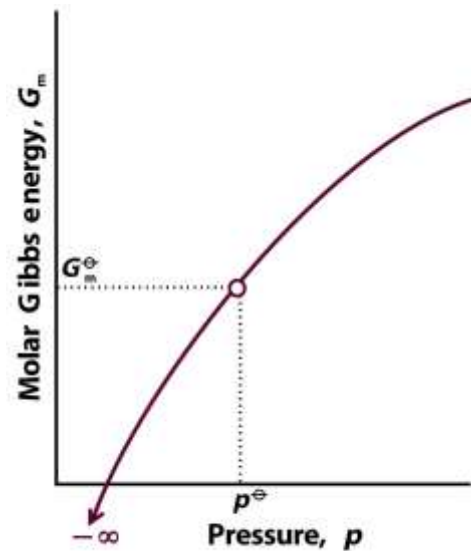© 2006 Peter Atkins and Julio de Paula

Figure 3-23
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