5.60 Thermodynamics & Kinetics
Spring 2008

<u>The Gibbs Free Energy</u>

- With the free energies

         Helmholtz free energy $A = U - TS$
         Gibbs free energy $G = H - TS$

we've introduced all our state functions. For closed systems,

$$
\begin{array}{ll}
U(S,V) & \Rightarrow \quad dU = TdS - pdV \\
H(S,p) & \Rightarrow \quad dH = TdS + Vdp \\
A(T,V) & \Rightarrow \quad dA = -SdT - pdV \\
G(T,p) & \Rightarrow \quad dG = -SdT + Vdp
\end{array}
$$
Fundamental equations

From $dA = \left(\dfrac{\partial A}{\partial T}\right)_V dT + \left(\dfrac{\partial A}{\partial V}\right)_T dV$

and $dG = \left(\dfrac{\partial G}{\partial T}\right)_p dT + \left(\dfrac{\partial G}{\partial p}\right)_T dp$

$$
\begin{array}{ll}
\left(\dfrac{\partial A}{\partial T}\right)_V = -S & \qquad \left(\dfrac{\partial A}{\partial V}\right)_T = -p \\[3mm]
\left(\dfrac{\partial G}{\partial T}\right)_p = -S & \qquad \left(\dfrac{\partial G}{\partial p}\right)_T = V
\end{array}
$$

The <u>Maxwell relations</u>: $\dfrac{\partial^2 A}{\partial V \partial T} = \dfrac{\partial^2 A}{\partial T \partial V}$ and $\dfrac{\partial^2 G}{\partial p \partial T} = \dfrac{\partial^2 G}{\partial T \partial p}$

now allow us to find how S depends on V and p.

$$
\Rightarrow \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \qquad \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p
$$

These can be obtained from an equation of state.

We can now also relate T and H to p-V-T data.

$$\left.\begin{array}{l} \left(\dfrac{\partial U}{\partial V}\right)_T = T\left(\dfrac{\partial S}{\partial V}\right)_T - p = T\left(\dfrac{\partial p}{\partial T}\right)_V - p \\[4mm] \left(\dfrac{\partial H}{\partial p}\right)_T = T\left(\dfrac{\partial S}{\partial p}\right)_T + V = V - T\left(\dfrac{\partial V}{\partial T}\right)_p \end{array}\right\} \rightarrow U \text{ and } H \text{ from equations of state!}$$

-     For an ideal gas $pV = nRT$

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V} = \frac{p}{T} \qquad \Rightarrow \qquad \left(\frac{\partial U}{\partial V}\right)_T = 0$$

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{nR}{p} = \frac{V}{T} \qquad \Rightarrow \qquad \left(\frac{\partial H}{\partial p}\right)_T = 0$$

This <u>proves</u> that for an ideal gas $U(T)$ and $H(T)$, functions of T only. We had <u>assumed</u> this was true from Joule and Joule-Thomson expansion experiments. Now we know it is rigorously true.

-     For a van der Waals gas

$$\left(p + \frac{a}{\bar{V}^2}\right)\left(\bar{V} - b\right) = RT$$

$$p = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{RT}{\bar{V} - b} - p = \frac{a}{\bar{V}^2} \neq 0 \qquad \Rightarrow \qquad U(T,V)$$

- The special role of $G(T,p)$:   If you know $G(T,p)$,
                                        you know everything!

$$\boxed{S = -\left(\frac{\partial G}{\partial T}\right)_p}, \qquad \boxed{V = \left(\frac{\partial G}{\partial p}\right)_T}$$

$$H = G + TS \qquad \Rightarrow \qquad \boxed{H = G - T\left(\frac{\partial G}{\partial T}\right)_p}$$

$$U = H - pV \qquad \Rightarrow \qquad \boxed{U = G - T\left(\frac{\partial G}{\partial T}\right)_p - p\left(\frac{\partial G}{\partial p}\right)_T}$$

$$A = U - TS \qquad \Rightarrow \qquad \boxed{A = G - p\left(\frac{\partial G}{\partial p}\right)_T}$$

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p \qquad \Rightarrow \qquad \boxed{C_p = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_p}$$

Can get all the thermodynamic functions from $G(T,p)$!

- $G(T,p)$ for liquids, solids, and gases (ideal)

    From $V = \left(\dfrac{\partial G}{\partial p}\right)_T$

    $$\Rightarrow \qquad \bar{G}(T,p_2) = \bar{G}(T,p_1) + \int_{p_1}^{p_2} \bar{V}dp$$

    - <u>Liquids</u> and <u>solids</u> $\Rightarrow$ $\bar{V}$ is <u>small</u>

        $$\bar{G}(T,p_2) = \bar{G}(T,p_1) + \bar{V}(p_2 - p_1) \approx \bar{G}(T,p_1) \qquad \Rightarrow \qquad \boxed{\bar{G}(T)}$$

- ## Ideal gases

$$\bar{G}(T,p_2) = \bar{G}(T,p_1) + \int_{p_1}^{p_2} \frac{RT}{p}\,dp = \bar{G}(T,p_1) + RT\ln\frac{p_2}{p_1}$$

Take $p_1 = p^\circ = 1$ bar

$$\bar{G}(T,p) = \bar{G}^\circ(T) + RT\ln\frac{p}{p_0} \quad \text{or} \quad \bar{G}(T,p) = \bar{G}^\circ(T) + RT\ln p$$

$$\nearrow$$
$$(p \text{ in bar})$$

From $\qquad S = -\left(\dfrac{\partial G}{\partial T}\right)_p \qquad \Rightarrow \qquad \bar{S}(T,p) = \bar{S}^\circ(T) - R\ln p$