The Gibbs Free Energy

- 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,

\[
\begin{align*}
U(S,V) & \Rightarrow dU = TdS - pdV \\
H(S,p) & \Rightarrow dH = TdS + Vdp \\
A(T,V) & \Rightarrow dA = -SdT - pdV \\
G(T,p) & \Rightarrow dG = -SdT + Vdp
\end{align*}
\]

Fundamental equations

From

\[
\begin{align*}
dA &= \left( \frac{\partial A}{\partial T} \right)_V dT + \left( \frac{\partial A}{\partial V} \right)_T dV \\
dG &= \left( \frac{\partial G}{\partial T} \right)_p dT + \left( \frac{\partial G}{\partial p} \right)_T dp
\end{align*}
\]

and

\[
\begin{align*}
\left( \frac{\partial A}{\partial T} \right)_V &= -S & \left( \frac{\partial A}{\partial V} \right)_T &= -p \\
\left( \frac{\partial G}{\partial T} \right)_p &= -S & \left( \frac{\partial G}{\partial p} \right)_T &= V
\end{align*}
\]

The Maxwell relations:

\[
\frac{\partial^2 A}{\partial V \partial T} = -\frac{\partial^2 A}{\partial T \partial V} \quad \text{and} \quad \frac{\partial^2 G}{\partial p \partial T} = \frac{\partial^2 G}{\partial T \partial p}
\]

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

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

These can be obtained from an equation of state.
We can now also relate $T$ and $H$ to $p$-$V$-$T$ data.

$$\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial S}{\partial V} \right)_T - p = T \left( \frac{\partial p}{\partial T} \right)_V - p$$

$$\left( \frac{\partial H}{\partial p} \right)_T = T \left( \frac{\partial S}{\partial p} \right)_T + V = V - T \left( \frac{\partial V}{\partial T} \right)_p$$

$\Rightarrow U$ and $H$ from equations of state!

- For an ideal gas $pV = nRT$

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

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

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

- For a van der Waals gas

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

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

$$\left( \frac{\partial U}{\partial V} \right)_T = \frac{RT}{V - b} - p = \frac{a}{V^2} \neq 0 \Rightarrow U(T, V)$$
• The special role of $G(T,p)$: If you know $G(T,p)$, you know everything!

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

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

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

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

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

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

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

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

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

• Liquids and solids $\Rightarrow \bar{V}$ is small

$$\bar{G}(T,p_2) = \bar{G}(T,p_1) + \bar{V}(p_2 - p_1) \approx \bar{G}(T,p_1) \quad \Rightarrow \quad \bar{G}(T)$$
• **Ideal gases**

\[ \bar{G}(T, p_2) = \bar{G}(T, p_1) + \int_{p_1}^{p_2} \frac{R T}{p} \, dp = \bar{G}(T, p_1) + R T \ln \frac{p_2}{p_1} \]

Take \( p_1 = p^o = 1 \text{ bar} \)

\[ \bar{G}(T, p) = \bar{G}^o(T) + R T \ln \frac{p}{p_0} \quad \text{or} \quad \bar{G}(T, p) = \bar{G}^o(T) + R T \ln p \]

\[ \text{(p in bar)} \]

From \[ S = -\left( \frac{\partial G}{\partial T} \right)_p \quad \Rightarrow \quad \bar{S}(T, p) = \bar{S}^o(T) - R \ln p \]

Earlier derivation assumed \( U(T) \), now we see this is rigorously true.