

The Gibbs Free Energy

- With the free energies

$$\text{Helmholtz free energy} \quad A = U - TS$$

$$\text{Gibbs free energy} \quad G = H - TS$$

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

$U(S, V)$	\Rightarrow	$dU = TdS - pdV$
$H(S, p)$	\Rightarrow	$dH = TdS + Vdp$
$A(T, V)$	\Rightarrow	$dA = -SdT - pdV$
$G(T, p)$	\Rightarrow	$dG = -SdT + Vdp$

Fundamental equations

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

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

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

The Maxwell relations: $\frac{\partial^2 A}{\partial V \partial T} = \frac{\partial^2 A}{\partial T \partial V}$ and $\frac{\partial^2 G}{\partial p \partial T} = \frac{\partial^2 G}{\partial T \partial p}$

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

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

These can be obtained from an equation of state.

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

$$\left. \begin{aligned} \left(\frac{\partial U}{\partial V}\right)_T &= T\left(\frac{\partial S}{\partial V}\right)_T - p = T\left(\frac{\partial p}{\partial T}\right)_V - p \\ \left(\frac{\partial H}{\partial p}\right)_T &= T\left(\frac{\partial S}{\partial p}\right)_T + V = V - T\left(\frac{\partial V}{\partial T}\right)_p \end{aligned} \right\} \rightarrow U \text{ and } H \text{ from equations of state!}$$

- For an ideal gas $pV = nRT$

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

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

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

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

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

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

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

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

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

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

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

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

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

Can get all the thermodynamic functions from $\mathcal{G}(T,p)$!

- $\mathcal{G}(T,p)$ for liquids, solids, and gases (ideal)

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

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

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

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

- 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 $p_1 = p^\circ = 1 \text{ bar}$

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

(p in bar)

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