

Chapter Seven: Gibbs Free Energy

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,

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

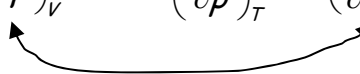
From $dA = \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV$

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

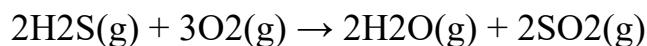
$$\bar{G}(T, p) = \bar{G}^\circ(T) + RT \ln \frac{p}{p_0} \quad \text{or} \quad \bar{G}(T, p) = \bar{G}^\circ(T) + RT \ln p$$

\nearrow
(p in bar)

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

Eexample(6. 1):

Calculate the Gibbs free energy change for the reaction below at 25°C if the standard enthalpy of the reaction is -187.8 kJ/mol and the standard entropy change is -97.96 J/(mol.K).



Solution:

The Gibbs free energy change (ΔG) can be calculated using the following formula:

$$\Delta G = \Delta H - T\Delta S$$

where

ΔH = standard enthalpy change

T = temperature (in Kelvin)

ΔS = standard entropy change

Substituting the given values, we get:

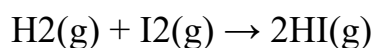
$$\Delta G = (-187.8 \text{ kJ/mol}) - (298 \text{ K})(-97.96 \text{ J/(mol.K)})/1000 \text{ J/kJ}$$

$$\Delta G = -187.8 \text{ kJ/mol} + 29.5 \text{ kJ/mol}$$

$$\Delta G = -158.3 \text{ kJ/mol}$$

Therefore, the Gibbs free energy change for the reaction is -158.3 kJ/mol.

Example (6.2) : Calculate the change in Gibbs free energy for a chemical reaction given the following information, and determine if the reaction takes place spontaneously:



$$\Delta H = -51.8 \text{ kJ/mol}$$

$$\Delta S = -116.2 \text{ J/mol}\cdot\text{K}$$

$$T = 298 \text{ K}$$

Solution:

To calculate the change in Gibbs free energy, we use the equation:

$$\Delta G = \Delta H - T\Delta S$$

Plugging in the values given:

$$\Delta G = -51.8 \text{ kJ/mol} - (298 \text{ K})(-116.2 \text{ J/mol}\cdot\text{K})/(1000 \text{ J/kJ})$$

$$\Delta G = -51.8 \text{ kJ/mol} + 34.6 \text{ kJ/mol}$$

$$\Delta G = -17.2 \text{ kJ/mol}$$

Since ΔG is negative, this means that the reaction is spontaneous under standard conditions (1 atm and 298 K). This is because the reaction results in a decrease in free energy, and a spontaneous process must have a decrease in free energy.

Therefore, the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$ is spontaneous under standard conditions