

Phase Transitions

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- First-Order Phase Transitions
 - Three Phases: Solid, Liquid, Gas (Vapor)
 - Liquid and Gas/Vapor are known as fluids
 - From liquid to gas, solid to gas, and solid to liquid, the process would be isothermal
 - Phase Changes:
 - * Solid to Liquid \rightarrow Melting
 - * Liquid to Solid \rightarrow Crystalization
 - * Solid to Gas \rightarrow Sublimation
 - * Gas to Solid \rightarrow Deposition
 - * Liquid to Gas \rightarrow Boiling
 - * Gas to Liquid \rightarrow Condensation
- Coexistence of two phases (l and g)

$$G = G_l + G_g = N_l \mu_l(P, \tau) + N_g \mu_g(P, \tau)$$
$$N_g + N_l = N \quad (\text{constant})$$

- This expression may be rewritten as:

$$G = N_l(\mu_l - \mu_g) + N\mu_g$$

- If l and g coexist, then:
 - * $\tau_l = \tau_g$ (thermal equilibrium)
 - * $P_l = P_g$ (mechanical equilibrium)
 - * $\mu_l = \mu_g$ (chemical equilibrium)
- Thus, for coexistence of l and g , we may write:

$$\mu_l(\tau, P) = \mu_g(\tau, P)$$

- The pressure differential with respect to τ may be written as:

$$\frac{dP}{d\tau} = \frac{\left(\frac{\partial\mu_l}{\partial\tau}\right)_P - \left(\frac{\partial\mu_g}{\partial\tau}\right)_P}{\left(\frac{\partial\mu_g}{\partial\tau}\right)_\tau - \left(\frac{\partial\mu_l}{\partial\tau}\right)_\tau}$$

- Furthermore, implementing pressure and volume per molecules (s and v), we may write:

$$\frac{dP}{dt} = \frac{s_g - s_l}{v_g - v_l}$$

- We can recall that, in a reversible process:

$$\delta Q = \tau d\sigma$$

$$\Delta Q = \tau \Delta\sigma$$

$$\Delta Q = \tau(s_g - s_l)$$

- Thus, we may described the heat gained from moving 1 molecule from g to l
- This ΔQ term is referred to as L , or the latent heat of vaporization per molecule

- This leads us to the Clausius-Clapeyron Equation:

$$\frac{dP}{d\tau} = \frac{L}{\tau(v_g - v_l)}$$

- This is used in liquid-gas coexistence
- We assume the gas is ideal
- We also assume $v_l \ll v_g$
- Also, L is assumed to be constant
- In assuming this, we may write:

$$\frac{dP}{d\tau} = \frac{LP}{\tau^2}$$

- Solving this, we get:

$$P(\tau) = P_o e^{-\frac{L}{\tau}}$$

- Van der Waals Equation of state

- As a reminder, the free energy for an ideal gas is:

$$F_{ideal} = -N\tau \left(\ln \left(\frac{n_Q}{n} \right) + 1 \right)$$

$$P = - \left(\frac{\partial F}{\partial V} \right)_{\tau, N} \rightarrow PV = N\tau$$

- In the above, V must be replaced with $V - bN$, where b is the volume of a single molecule, and N is the total number of molecules
- To find the interaction between particles, we use a mean field approximation

$$\Delta U = \frac{1}{2} \sum_{i \neq j=1}^N \phi(|\bar{r}_i - \bar{r}_j|) = \frac{1}{2}(N^2 - N)\langle \phi(r) \rangle$$

- Assume that the molecules are uniformly distributed in the accessible volume, $V - bN$, and average overall the positions of all molecules
- We can approximate it to:

$$\frac{1}{2}(N^2 - N) \int_V \frac{\phi(r)}{V - bN} d^3r$$

$$\Delta U = -\frac{N^2 a}{V}, \quad a > 0$$

- from here, we can write the free energy:

$$F_{VdW} = -N\tau \left(\ln \left(\frac{n_Q(V - bN)}{N} \right) + 1 \right) - \frac{N^2 a}{V}, \quad a, b > 0$$

$$P = \frac{\tau N}{V - bN} - \frac{N^2 a}{V^2}$$

- The equation of state may be simplified as:

$$\left(P + \frac{N^2 a}{V} \right) (V - bN) = N\tau$$

- * The term dependent on a is the reduction in pressure due to attractive interactions between molecules
- * The term dependent on b is the excluded volume due to molecule volume
- Critical points may be defined as:

$$\tau_c = \frac{8a}{27b}$$

$$P_c = \frac{a}{27b^2}$$

$$V_c = 3Nb$$

- The Gibbs Free Energy for this Van der Waals gas is:

$$G = F + PV = F + P(V - bN)$$

$$G = -N\tau \ln \left(\frac{n_Q(V - bN)}{N} \right) - \frac{2N^2a}{V}$$

- We find the following relations:

$$\left(\frac{\partial G}{\partial P} \right)_{\tau, N} = \frac{V}{N}$$

$$\left(\frac{\partial G}{\partial \tau} \right)_{P, N} = -\frac{\sigma}{N} = -S$$

- Ferromagnetism

- There are N magnetic moments μ in a binary-spin system. From this, we get:

$$U = -$$

- Assume that M is the magnetization of the volume — net magnetic moment per volume

$$B_E = \lambda M$$

- Is the effective magnetic field due to M (mean field approximation)

$$\bar{M} = \frac{1}{V} \sum_{i=1}^N \bar{\mu}_i$$

- The magnetization may be defined as:

$$M = \mu n \tanh \left(\frac{\mu \lambda M}{\tau} \right)$$

- * If $\tau > \tau_c \rightarrow M = 0$
- * If $\tau < \tau_c \rightarrow M = 0$ (unstable) or $M \neq 0$ (stable) ferromagnetic
- * We can define the critical value as $\tau_c = n\mu^2\lambda$ (this value is known as the Curie temperature, and is an example of a 2nd order phase transition)

- Kinetic Theory

- Ideal Gas Law

- * The average force due to a particle on a wall can be written as:

$$F_{ix} = \frac{2mv_x}{\Delta t}$$

* The pressure can then be expressed as:

$$P = \frac{N}{A} \langle F_{ix} \rangle$$

* The time between collisions may be expressed as:

$$\Delta t = \frac{2L_x}{v_x}$$

* Combining these three, we get:

$$P = \frac{Nm}{AL_x} \langle v_x^2 \rangle$$

* If we assume isotropy, we can get:

$$PV = \frac{2}{3}U$$

* As we know from statistical physics, we can write:

$$U = \frac{3}{2}N\tau$$

* This brings us back to the ideal gas law:

$$PV = N\tau$$

- Important Topics

- Ideal Gas

$$P = n\tau$$

$$\mu = \tau \ln \left(\frac{n}{n_Q} \right), \quad n_Q = \left(\frac{m\tau}{2\pi\hbar^2} \right)^{\frac{3}{2}}$$

$$U = \frac{3}{2}N\tau$$

$$\sigma = N \left(\ln \left(\frac{n_Q}{n} \right) + \frac{5}{2} \right)$$

$$F = -N\tau \left(\ln \left(\frac{n_Q}{n} \right) + 1 \right)$$

- Calculating Partition Function

$$z = \sum_{\text{q states}} e^{-\frac{\epsilon_q}{\tau}}$$

$$z_N = \frac{z_1^N}{N!} \text{ or } z_1^N \text{ omit the } N! \text{ if particles are distinguishable}$$

$$z \rightarrow F = -\tau \ln(z)$$

$$F \rightarrow P \text{ or } \mu \text{ or } U$$

$$P = - \left(\frac{\partial F}{\partial V} \right)_{\tau, N}$$

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{\tau, V}$$

$$U = \tau^2 \left(\frac{\partial \ln(z)}{\partial \tau} \right)_{N, V}$$

$$\sigma = \frac{U - F}{\tau}$$

– Gibbs Sum

$$Z(\mu, \tau, N) = \sum_{N=0}^{\infty} \sum_{S(N)} \lambda^N e^{-\frac{\varepsilon_S(N)}{\tau}}$$

– Cycles for an Ideal Gas (Carnot)

* Calculate Q , W , for each part of cycle

* Calculate efficiency, $\eta = \frac{W_{tot}}{Q_{in}}$

– First Order Phase Transitions

* Working with the coexistence curve (Clayperon-Clausius)

$$\frac{dP}{dt}$$

– Chemical Reactions

* Calculate pH

$$\text{pH} = -\log_{10} ([\text{H}^+])$$

* Mass action law

– Thermal Radiation

– Thermodynamic Identities

– Fermi and Bose Gasses

– Van der Waal's Gas