

# Phase Diagrams of Pure Substances

CHEM 323 Physical Chemistry I

---

---

---

---

---

---

---

---

## Phase Diagrams

- Review Definitions
  - Phase (allotropes, metastable phases)
  - State
  - Vapor pressure vs. sublimation vapor pressure
  - Transition temperature
  - Normal vs. standard
  - Critical pressure, critical temperature, critical point

---

---

---

---

---

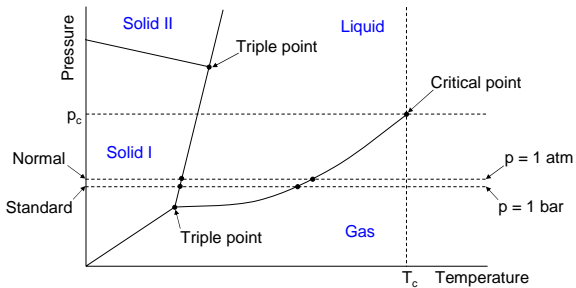
---

---

---

## Phase Diagram

- Show Conditions of T and p where different States and Phase (co)exist



---

---

---

---

---

---

---

---

## Equations

- Lines on Phase Diagram show conditions of  $T$  and  $p$  where Phases coexist
  - These lines must have equations that describe them
- Define the Chemical Potential,  $\mu$ , for a pure Substance:  $\mu = G_m$ 
  - Measure of potential that a substance has for bringing about change in a system
- If two Phases coexist  $\mu_1 = \mu_2$ 
  - Thermodynamic criterion for equilibrium

---

---

---

---

---

---

---

---

## Thermodynamic Description of Phase Changes

- Phase Change occurs when  $\mu_1 = \mu_2$ 
  - How do we bring about these changes?
- Remember  $G = H - TS = U + pV - TS$ 
  - $G$  (and  $\mu$ ) depend on  $p$  and  $T$
  - Changing  $p$  and/or  $T$  can bring about change
  - $S$  and  $V$  determine how  $p/T$  changes affect  $\mu$

$$\left(\frac{\partial\mu}{\partial T}\right)_p = -S_m \quad \left(\frac{\partial\mu}{\partial p}\right)_T = V_m$$

---

---

---

---

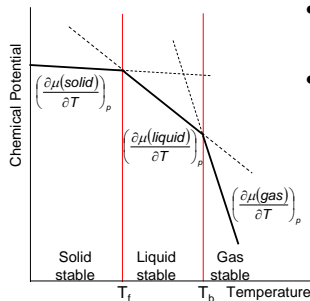
---

---

---

---

## Dependence on $T$ at Constant $p$



- Most stable State has lowest  $G_m$  ( $\mu$ )
- Why do Phase Changes occur?
  - Slope of each line is different ( $S_m$ )
  - Lines intersect
  - Energy as heat overcomes energy of arrangement

---

---

---

---

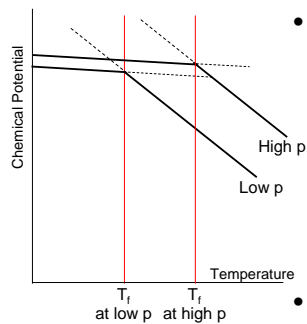
---

---

---

---

## Dependence on $p$ at constant $T$



- Case 1: Melting
  - In general  $\mu$  varies with  $p$  as  $V_m$
  - For most substances  $V_{m,liquid} > V_{m,solid}$
  - So  $\mu_{solid}$  changes less than  $\mu_{liquid}$  as  $p$  rises
  - $T_f$  increases as  $p$  increases
- Exception

---

---

---

---

---

---

---

---

## Dependence on $p$ at constant $T$

- Case 2: Vaporization (Sublimation)
- Observation: raising  $p$  on Condensed Phase increases Vapor Pressure
  - Partial vapor pressure
  - Gas dissolution
  - Gas solvation
- Described by Equations

$$p = p^* e^{V_m \Delta p / RT} \quad p \approx p^* \left( 1 + \frac{V_m \Delta p}{RT} \right)$$

When  $V_m \Delta p / RT \ll 1$ .

---

---

---

---

---

---

---

---

## Phase Boundaries

- Now know Slopes of Lines describing Phase Boundaries, but can we predict where they occur?
- Clapeyron Equation  $\frac{dp}{dT} = \frac{\Delta_{trs} S}{\Delta_{trs} V}$ 
  - Rearrange to  $\frac{dp}{dT} = \frac{\Delta_{trs} H}{T \Delta_{trs} V}$
  - Integrate for each case
- Ehrenfest Classification

---

---

---

---

---

---

---

---

## Phase Boundaries

- Case 1: Solid-Liquid
  - Graph of p vs. T is steeply-sloped straight line
  - Slope of line determined by  $\Delta V_m$

$$p = p^* + \frac{\Delta_{fus}H}{T^* \Delta_{fus}V} (T - T^*)$$

- Case 2: Liquid-Vapor
  - Graph of p vs. T is exponential ends at  $T_c$

$$p = p^* e^{-\Delta_{vap}H \left( \frac{1}{T} - \frac{1}{T^*} \right)}$$

- Case 3: Solid-Vapor  $p = p^* e^{-\Delta_{sub}H \left( \frac{1}{T} - \frac{1}{T^*} \right)}$

---

---

---

---

---

---

---

---

## Physical Boundaries

- Bubbles, Cavities, Droplets, Capillary Action
- Work needed to create Surface  $dw = \gamma d\sigma$ 
  - Surface tension,  $\gamma$
  - Tendency of surfaces to minimize surface area ( $dA < 0$ )

- Important Equations

- Laplace equation

$$p_{in} = p_{out} + \frac{2\gamma}{r}$$

- Kelvin equation  $p = p^* e^{\frac{2\gamma V_m}{rRT}}$

---

---

---

---

---

---

---

---