59-240 Lecture 14 - Phase Diagrams and Physical Transformations of Substances

Location of Phase Boundaries

$\mu_\alpha(p,T) = \mu_\beta(p,T)$

Clapeyron equation

$$\frac{dp}{dT} = \frac{\Delta_{trs}S}{\Delta_{trs}V}$$

$$\frac{dp}{dT} = \frac{\Delta_{fus}H}{T\,\Delta_{fus}V}$$

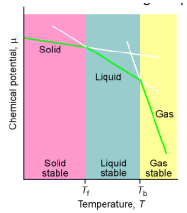
- ΔV term is constant — solid/liquid
- $p = p^* + \frac{\Delta_{fus}H}{\Delta_{fus}V}\ln\left(\frac{T}{T^*}\right)$ — solid/solid

$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T\,\Delta_{vap}V}$$

- $\Delta_{vap}V = V_m(g) - V_m(l) \approx V_m(g)$, (since $V_m(g) \gg V_m(l)$) — vapour/liquid
- $p = p^* e^{-\chi}$, $\chi = \frac{\Delta_{vap}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$ — vapour/solid

Phase at given p, T

- molar Gibbs energies, G_m
- chemical potentials, μ
- lowest μ indicates most thermodynamically stable phase
- phase — form of pure matter that is uniform in terms of **composition** and **physical state**
- phase transition — **spontaneous conversion** from one phase to another at a specific T_{trs}

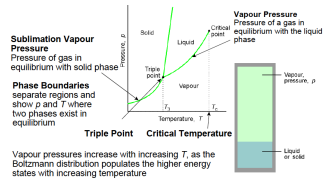


- μ vs. T plots
  - at a phase transition, μ values are equal
  - e.g., when ice melts μ(s) = μ(liq)

Thermo vs. kinetic

- Thermodynamics
  - predicts spontaneity
  - does not predict rate
- Kinetics
  - predicts the rate of reaction or process
  - connected to Gibbs energies and temperatures
- Diamond. vs. graphite example
  - μ(g) < μ(d)
  - graphite thermodynamically stable
  - diamond kinetically stable
  - metastable phases (e.g., diamond)

Phase boundaries



- Terms and definitions
  - open vs. closed vessel
  - boiling/free vaporization
  - normal bp, 1 atm
  - standard bp, 1 bar
  - critical temp and pressure, T_c and p_c
  - supercritical fluid
  - triple point, T_3

Phase diagram examples

- Water
  - Slope of s/l boundary vs. s/g or l/g boundaries
  - high pressure multiple phases
- CO_2
  - phase diagram
  - fire extinguishers
  - J-T throttle
  - snow
  - decaffeination
  - supercritical CO_2 as solvent
    - oil removal (e.g., snacks)
    - removal of toxins from water
    - chemotherapeutic natural product extraction
- ^4He
  - bcc
  - hcp
  - multiple solid phases
  - liquid-I phase
  - superfluid
  - liquid-II phase
- metastable — diamonds
- metals
  - iron
  - s/l slopes similar to water
  - bismuth

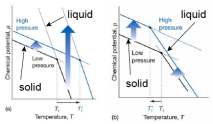
Phase stability and phase transitions

μ1 = μ2 at equilibrium

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

$S_m(g) > S_m(l) > S_m(s)$

- Pressure response

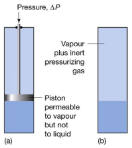


$V_m(s) < V_m(l)$

$V_m(s) > V_m(l)$

- sample calculation

Applied pressure and vapour pressure



$$p = p^* e^{V_m \Delta P/RT}$$

- proof of above equation
- estimating effects of pressure (calc)