59-240 Lecture 13 Second Law - Machinery

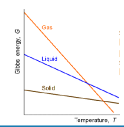
- **Fugacity, f**
  - effective pressure of a real gas
  - $\mu = \mu^{o} + RT\ln\left(\frac{f}{p^{o}}\right)$
  - $f = \phi p$
    - φ is the **fugacity coefficient**
      - $\mu = \mu^{o} + RT\ln\left(\frac{p}{p^{o}}\right) + RT\ln\phi$
      - $\ln\phi = \int_0^p \left(\frac{Z-1}{p}\right) dp$
  - perfect or low p gas
    - $Z = 1$, $\varphi = 1$, $f = p$
  - real intermediate p gas
    - $Z < 1$, $\varphi < 1$, $f < p$, $\mu < \mu^{o}$
    - escape tendency lessened
    - particles attracted to one another
  - real high p gas
    - $Z > 1$, $\varphi > 1$, $f > p$, $\mu > \mu^{o}$
    - escape tendency heightened
    - particles repelled from one another

- **Fundamental Equation of Thermodynamics (U)**
  - $dU = dq + dw$
  - $dw_{rev} = -p\,dV$
  - $dq_{rev} = T\,dS$
  - $dU = TdS - pdV$
    - FET $dU = TdS - pdV$
    - TDE $dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$
    - ThDef $\left(\frac{\partial U}{\partial S}\right)_V = T$ $\quad \left(\frac{\partial U}{\partial V}\right)_S = -p$
    - Maxwell relation $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$
    - using **exact differentials**
    - Example use of Maxwell relations: $\pi_T = \left(\frac{\partial U}{\partial V}\right)_T$

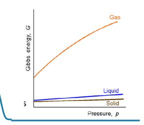
- **Chemical potential, μ**
  - $\mu = \left(\frac{\partial nG_m}{\partial n}\right)_{T,p} = G_m$
  - $\mu = \mu^{o} + RT\ln\left(\frac{p}{p^{o}}\right)$
  - Lowest μ indicates the most stable phase, spontaneity, reaction path, etc.

- **FET(H, A)**
  - Make sure you know derivations for all 4 FET (U, H, G, A)
  - For each FET:
    - Write the TDE
    - State the ThDef's
    - Using the ED, state the appropriate Maxwell relation (MR)

- **FET (G)**
  - $dG = Vdp - SdT$
    - $\left(\frac{\partial G}{\partial T}\right)_p = -S$
      - basic graph



    - $\left(\frac{\partial G}{\partial p}\right)_T = V$
      - basic graph



  - Gibbs Helmholz equation
    - $\left(\frac{\partial}{\partial T}\left(\frac{G}{T}\right)\right)_p = -\frac{H}{T^2}$
  - Pressure dependence of G
    - incompressible fluid, V_m constant
    - gas, $V_m = nRT/p$
    - geological high p example
    - $G_m(p) = G_m^{o} + RT\ln\left(\frac{p}{p^{o}}\right)$