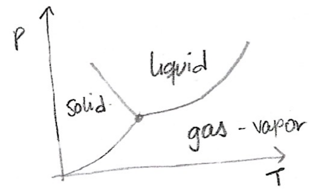
SM-2 January 2012

Water

a) Sketch P-T phase diagram



b) Find L_{vap}

$$L_{vap} = \Delta(TS)$$ → at interface T is constant

$$= T\Delta S$$ $\Delta S = S_{vap} - S_{liq}$

$$L_{vap} = T(S_{vapor} - S_{liquid})$$

c. Show that along liquid-vapor line, chemical potentials are equal.

$$\frac{\partial \mu}{\partial p} = V \qquad \frac{\partial \mu}{\partial T} = -S_i \qquad PV = nk_BT$$

$$\frac{\partial \mu}{\partial p} = \frac{nk_BT}{P} \rightarrow \mu_f = nk_BT \ln\left(\frac{P_f}{P_i}\right) + \mu_0$$

$P_f = P_v$
$P_i = P_L$

say $C = \mu_0$

$$\mu_v = nk_BT \ln\left(\frac{P_v}{P_L}\right) + \mu_0$$

→ at liquid-vapor line → $P_v = P_L$

$\ln(1) = 0$

$$\mu_v = \mu_0$$

$$\mu_L = nk_BT \ln\left(\frac{P_L}{P_v}\right) + \mu_0 = \mu_0$$

$$\mu_L = \mu_v$$

→ since P is the same for both, $\ln\left(\frac{P_f}{P_0}\right) = 0$ and both chemical potentials will be the same along L-V line

d. Prove Clausius-Clapeyron

$$d\mu = -S\,dT + V\,dP$$ → at boundary $\mu_v = \mu_L$

$$-S_v\,dT + V_v\,dP = -S_L\,dT + V_L\,dP$$

$$0 = (S_L - S_v)dT - (V_L - V_v)dP = \Delta S\,dT - \Delta V\,dP$$

$$\frac{\Delta S}{\Delta V} = \frac{dP}{dT} = \frac{L}{T\Delta V} = \frac{L_{vap}}{T(V_{vap} - V_{liq})}$$

$\Delta S = \frac{L_{vap}}{T}$ from part a.

$$\frac{dP}{dT} = \frac{L_{vap}}{T(V_{vap} - V_{liq})}$$