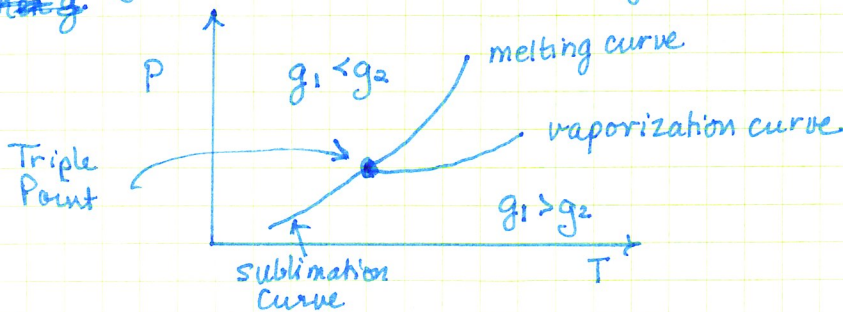
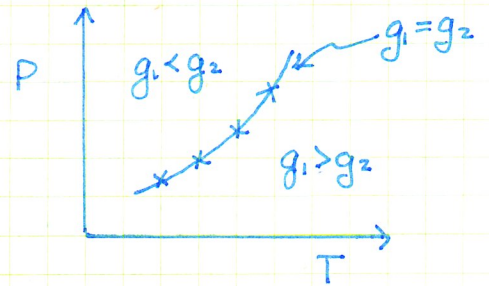


Phase equilibrium $g_1(T, P) = g_2(T, P)$

$$G = N_1 g_1(T, P) + N_2 g_2(T, P)$$

to minimize G:

if $g_1 < g_2$ all should be N_1
 if $g_2 < g_1$ all should be N_2
 when $g_1 = g_2$ then N_1, N_2 can take on any value



not all substances have a triple point

Taylor Expansion

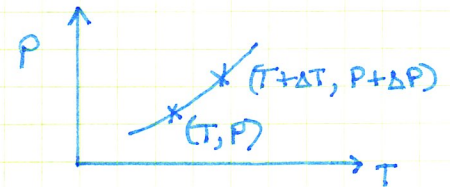
$$g_1(T, P) = g_2(T, P)$$

$$g_1(T + \Delta T, P + \Delta P) = g_2(T + \Delta T, P + \Delta P)$$

$$g_1(T, P) + \left(\frac{\partial g_1}{\partial T}\right)_P dT + \left(\frac{\partial g_1}{\partial P}\right)_T dP = g_2(T, P) + \left(\frac{\partial g_2}{\partial T}\right)_P dT + \left(\frac{\partial g_2}{\partial P}\right)_T dP$$

$$dP \left[\left(\frac{\partial g_1}{\partial P}\right)_T - \left(\frac{\partial g_2}{\partial P}\right)_T \right] = dT \left[\left(\frac{\partial g_2}{\partial T}\right)_P - \left(\frac{\partial g_1}{\partial T}\right)_P \right]$$

$$\frac{dP}{dT} = \frac{- \left[\left(\frac{\partial g_2}{\partial T}\right)_P - \left(\frac{\partial g_1}{\partial T}\right)_P \right]}{\left[\left(\frac{\partial g_2}{\partial P}\right)_T - \left(\frac{\partial g_1}{\partial P}\right)_T \right]} = - \frac{\Delta \left(\frac{\partial g}{\partial T}\right)_P}{\Delta \left(\frac{\partial g}{\partial P}\right)_T}$$



It doesn't look useful on RHS but let's look at the definition of G

$$G(T, P, N) = N g(T, P)$$

Thermodynamic Fundamental Identity with N as a variable

$$dS = \left(\frac{\partial S}{\partial E}\right)_{V, N} dE + \left(\frac{\partial S}{\partial V}\right)_{E, N} dV + \left(\frac{\partial S}{\partial N}\right)_{E, V} dN$$

$$dS = \frac{1}{T} dE + P dV - \mu dN$$

$dE = T ds - P dV + \mu dN$
<div style="display: flex; justify-content: space-around;"> heat work change in internal identity </div>

$$G = E + PV - TS$$

$$dG = dE + PdV + VdP - TdS - SdT$$

$$dG = (TdS - PdV + \mu dN) + PdV + VdP - TdS - SdT$$

$$dG = VdP - SdT + \mu dN$$

by inspection $\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}$

integrate $G = N\mu + \chi(T, P)$

$$\lim_{N \rightarrow 0} G = 0 = \chi(T, P) \rightarrow 0$$

$$\therefore \mu = \frac{G}{N} \equiv g \quad G = Ng(T, P)$$

$$G = Ng(T, P)$$

$$dG = Ndg + gdN = VdP - SdT + \mu dN$$

$$Ndg = VdP - SdT$$

$$dg = \frac{V}{N} dP - \frac{S}{N} dT = \left(\frac{\partial g}{\partial T}\right)_P dT + \left(\frac{\partial g}{\partial P}\right)_T dP \quad \text{compare coefficients}$$

$$\therefore \frac{V}{N} = \left(\frac{\partial g}{\partial P}\right)_T \quad \frac{S}{N} = -\left(\frac{\partial g}{\partial T}\right)_P$$

Expression for $\frac{dP}{dT}$ is as good as the 2nd law

$$\frac{dP}{dT} = -\frac{\Delta\left(\frac{\partial g}{\partial T}\right)_P}{\Delta\left(\frac{\partial g}{\partial P}\right)_T} = \frac{\Delta\left(\frac{S}{N}\right)}{\Delta\left(\frac{V}{N}\right)} = \frac{\Delta S}{\Delta V} = \frac{\text{change in entropy per mole (or gram)}}{\text{change in volume per mole (or gram)}}$$

watch units on ΔS , ΔV

Lecture 12 continued... Latent Heat

Latent heat for melting / vaporization

$$\Delta S = \frac{L_{12}}{T} \quad \boxed{\frac{dP}{dT} = \frac{L_{12}}{T \Delta V}} \quad \text{Clausius Clapeyron Equation}$$

Shows that you can change the melting point of ice by changing the pressure

p 94, 230 more vacant sites in liquid water but water has less density than water

Phase 1 = solid Phase 2 = liquid $\frac{dP}{dT} = \frac{L_{12}}{T \Delta V}$ $L_{12} = 3.35 \cdot 10^5 \frac{\text{J}}{\text{kg}} \sim \frac{80 \text{ cal}}{\text{g}}$ water ice

$\rho_{\text{liquid water}}^{-1} = 1.0907 \frac{\text{cm}^3}{\text{g}}$ $\rho_{\text{ice}}^{-1} = 1.00013 \frac{\text{cm}^3}{\text{g}}$

$V_1 = 1.0907 \text{ cm}^3$ $V_2 = 1.00013 \text{ cm}^3$ $\Delta V = V_2 - V_1 = -0.0906 \cdot 10^{-3} \frac{\text{m}^3}{\text{kg}}$

Why ice floats!

$$\frac{dP}{dT} = \frac{-3.35 \cdot 10^5 (\text{J/kg})}{273.2 \text{ K} (0.0906 \cdot 10^{-3} \text{ m}^3/\text{kg})} = -1.35 \cdot 10^7 \text{ Nm}^{-2} (\text{°C})^{-1} = -134 \text{ atm/°C}$$

as pressure increases, the melting point decreases explains

- glacier melts when it hits a large rock
- lubrication of ice skater

Vapor Pressure Curve (p. 231)

Pressure dependence of the Boiling Point of water

Phase 1 = liquid Phase 2 = vapour $L_{12} = 2.257 \cdot 10^6 \frac{\text{J}}{\text{kg}}$ it takes more energy to change liquid to gas than solid to liquid

"volume density" $V_1 = 1.043 \frac{\text{cm}^3}{\text{g}}$ liquid at 1 atm 100°C

$V_2 = 1673 \frac{\text{cm}^3}{\text{g}}$ vapour at 1 atm 100°C = 373.15K

$\therefore \Delta V \sim V_2$

$$\frac{dP}{dT} = \frac{L_{12}}{T \Delta V} = \frac{2.257 \cdot 10^6}{(373.15)(1.672)} = 3.62 \cdot 10^3 \frac{\text{N}}{\text{m}^2 \text{°C}} = 27 \frac{\text{mmHg}}{\text{°C}}$$

1 atm = $1.0132 \cdot 10^5 \text{ N/m}^2$

at the top of mount Everest, Pressure gets lower
 $P = 3.6 \cdot 10^4 \text{ N/m}^2$ less pressure, less oxygen

$\Delta P = -6.5 \cdot 10^4 \text{ N/m}^2$ $\frac{dP}{dT} = \frac{\Delta P}{\Delta T} = 3.62 \cdot 10^3 \frac{\text{N}}{\text{m}^2 (\text{°C})}$



$$\Delta T = \frac{\Delta P}{3.62 \cdot 10^3 (\text{N/m}^2)(^\circ\text{C})^{-1}} = \frac{-6.5 \cdot 10^4 \text{ N/m}^2 \text{ } ^\circ\text{C}}{3.62 \cdot 10^3 \text{ N/m}^2} = -18^\circ\text{C}$$

So at the top of Mount Everest, water boils at $T = 100^\circ\text{C} + \Delta T = \sim 80^\circ\text{C}$

Vapor Pressure Curve

$$\Delta V = V_2 - V_1 \sim V_2$$

$$\frac{dP}{dT} = \frac{L_{12}}{T \Delta V} \sim \frac{L_{12}}{T V_2}$$

$$P V_2 = RT \text{ for one mole}$$

$$P V_2 = nRT \text{ for } n \text{ moles}$$

$$V_2 = \frac{nRT}{P}$$

$$\frac{dP}{dT} = \frac{1}{nR} \frac{L_{12} P}{T^2}$$

$$\int \frac{dP}{P} = \int \frac{1}{nR} \frac{L_{12} dT}{T^2}$$

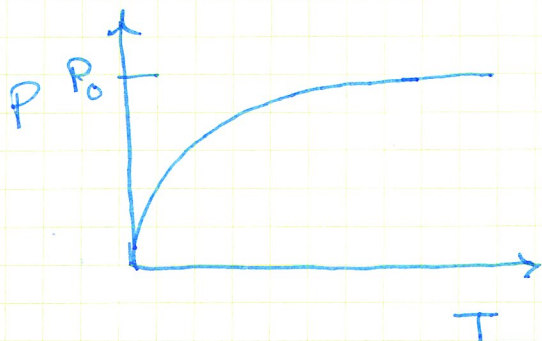
$$\ln P = -\frac{L_{12}}{nRT} + \text{constant}$$

or

$$\ln P = \frac{-(L_{12})_{\text{molar}}}{RT} + \text{constant}$$

$$P = P_0 e^{-(L_{12})_{\text{molar}} / RT}$$

damped exponential



If the temperature decreases, the pressure will decrease.