

Recap:

We considered  $r$  components in  $v$  phases. By counting degrees of freedom and constraints we got the Gibbs Phase Rule

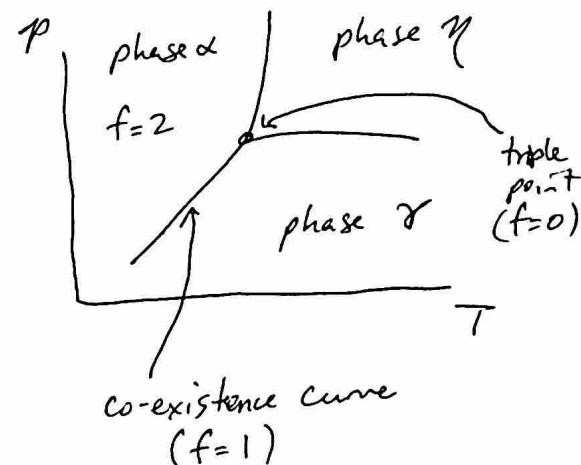
$f = 2 + r - v$ , where  $f$  is the # of independently tunable degrees of freedom from the set  $T, p, \mu_1, \mu_2, \dots$

One component phase diagrams ( $r=1$ )

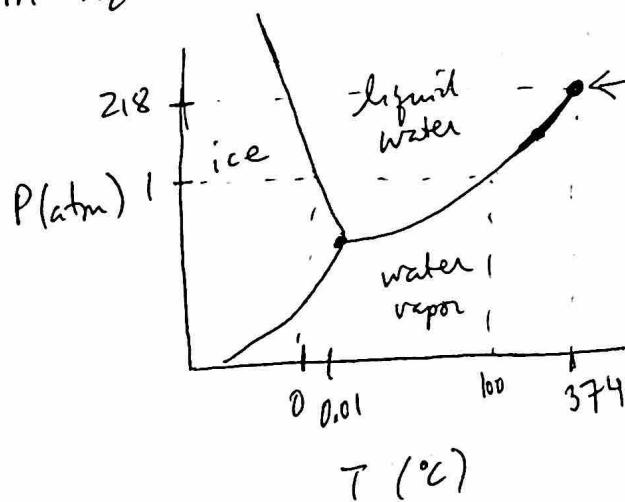
$v=1 \Rightarrow f=2$  Can independently vary  $T + p$

$v=2 \Rightarrow f=1$  There are lines in  $p-T$  space along which 2 phases can coexist

$v=3 \Rightarrow f=0$  There is a point in  $p-T$  space at which three phases can coexist.



In  $\text{H}_2\text{O}$ ...



What's up with this?  
Is it liquid or vapor to the right of the critical point?

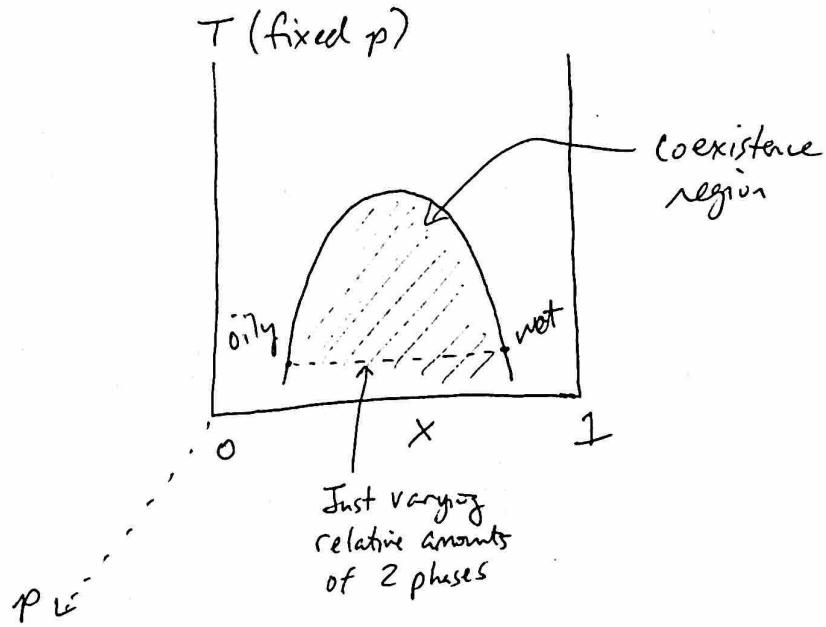
Many component ( $r > 1$ ) can get very messy!

Simple case: oil/water ( $r = 2$ )

$$f = 2 + r - v$$

$$v = 2 \Rightarrow f = 2$$

$$x_{\text{coex}}^{(1)}(T, p), x_{\text{coex}}^{(2)}(T, p)$$
$$\uparrow$$
$$x = \frac{N_{\text{wt}}}{N}$$



Remember the conditions for being in equilibrium in a coexistence region is that each phase must have equal chemical potential for all components.

We used lattice models to find ideal gas/ideal solution chemical potentials. Let's see that another way...

What is the partition function for a non-interacting gas of  $N$  particles?

Canonical

Single particle:  $g = g^{\text{trans}} g^{\text{int}}$  ← vbs, rotates

Why is it a product?

$N$  particles:  $\Omega = \frac{g^N}{N!}$  ← why is it a product?

← why is there an  $N!$   
(bosons, fermions, classical limit)

$$-\beta A = \ln Q = -(N \ln N - N) + N \ln g$$

$$= -(N \ln N - N) + N \ln g_{\text{int}} + N \ln g_{\text{trans}}$$

$$g_{\text{trans}} = \sum_{\substack{\text{regions} \\ \text{of space}}} e^{-\beta E(\text{spatial region})} = 1 \left( \frac{\text{how many regions of}}{\text{space}} \right) \propto V$$

↑  
translational symmetry

turns out the proportionality  
has to do with quantum mechanics  
- Planck cell

$$g_{\text{trans}} = \frac{V}{\lambda^3}, \text{ where } \lambda = \left( \frac{h}{\sqrt{2\pi m k_B T}} \right) \text{ the deBroglie/ thermal wavelength}$$

$$\Rightarrow -\beta A = -(N \ln N - N) + N \ln \frac{V g_{\text{int}}}{\lambda^3}$$

$$A = E - TS \rightarrow dA = -SdT - pdV + \mu dN$$

$$\left( \frac{\partial \ln Q}{\partial V} \right)_{T, N} = \beta p = \frac{N}{V} \Rightarrow \beta p = \rho \quad \text{ideal gas law}$$

$$\left( \frac{\partial \ln Q}{\partial \beta} \right)_{T, N} = -\langle E \rangle = N \frac{\partial}{\partial \beta} \ln \left( \frac{g_{\text{int}}}{\lambda^3} \right) = N \times (\text{fn of } T)$$

$$\left( \frac{\partial \ln Q}{\partial N} \right)_{T, V} = -\beta \mu = -(\ln N + 1/T) + \ln \frac{V g_{\text{int}}}{\lambda^3}$$

$$\Rightarrow \beta \mu = \ln \frac{\rho \lambda^3}{g_{\text{int}}}$$

$$\Rightarrow \mu = k_B T \ln \rho V_0 + \underbrace{k_B T \ln \left( \frac{\lambda^3}{g_{\text{int}} V_0} \right)}_{\mu^{(0)}(T)} = \mu^{(0)}(T) + k_B T \ln (\rho V_0)$$

defines  
standard state

Consequences of the ideal form for  $\mu$

① Partitioning b/w phases as in exam

② Chemical equilibrium



$$N_B \rightarrow N_B - b\Delta N, \quad N_c \rightarrow N_c + c\Delta N$$

$$\Delta G = \left( \frac{\partial G}{\partial N_B} \right)_{T, P, N_c} (-b\Delta N) + \left( \frac{\partial G}{\partial N_c} \right)_{T, P, N_B} (c\Delta N)$$

= 0 at equilibrium

$$\Rightarrow -b\mu_B + c\mu_c = 0$$

$$\underline{b\mu_B = c\mu_c}$$

Assume dilute (ideal)

$$b(k_B T \ln \rho_B V_0 + \mu_B^{(0)}) = c(k_B T \ln \rho_C V_0 + \mu_c^{(0)})$$

$$\Rightarrow \frac{(\rho_c)^c}{(\rho_B)^b} = V_0^{b-c} e^{-\beta \Delta \mu_{rxn}^{(0)}} = K_{eq}(T) \leftarrow \text{law of mass action}$$

$$\text{w/ } \Delta \mu_{rxn}^{(0)} = c\mu_c^{(0)} - b\mu_B^{(0)}$$

$$\left. \begin{aligned} & \text{for } bB \rightleftharpoons cC + dD \\ & b\mu_B = c\mu_c + d\mu_D \end{aligned} \right\}$$

## Crossovers and Phase Transitions

For a simple chemical equilibrium  $B \rightleftharpoons C$

$$\frac{P_C}{P_B} = e^{-\beta \Delta \mu^{(0)}} \text{ at equl, } \Delta \mu^{(0)} = \mu_C^{(0)} - \mu_B^{(0)}$$

If  $P_B + P_C = \bar{P}$  fixed

$$P_C = P_C \frac{\bar{P}}{P_B + P_C} = \frac{\bar{P}}{1 + e^{\beta \Delta \mu^{(0)}}}$$

Take  $\Delta \mu^{(0)} = \underbrace{\Delta h^{(0)}}_{\text{Both positive, ind. of } T, \text{ large}} - T \underbrace{\Delta S^{(0)}}_{\text{Both positive, ind. of } T, \text{ large}}$

At low  $T$ ,  $P_C = 0$ , at high  $T$ ,  $P_C = \bar{P}$

