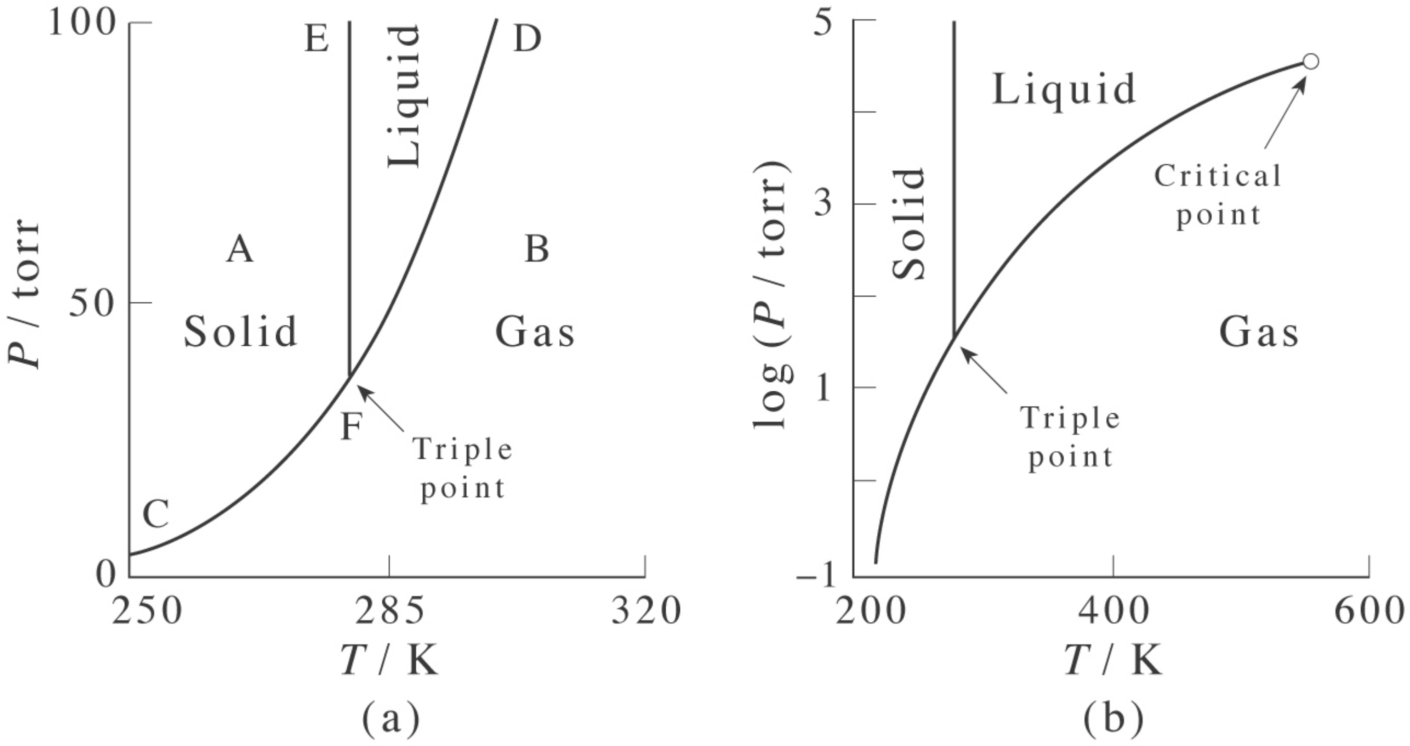
Phase Behavior and Equilibria

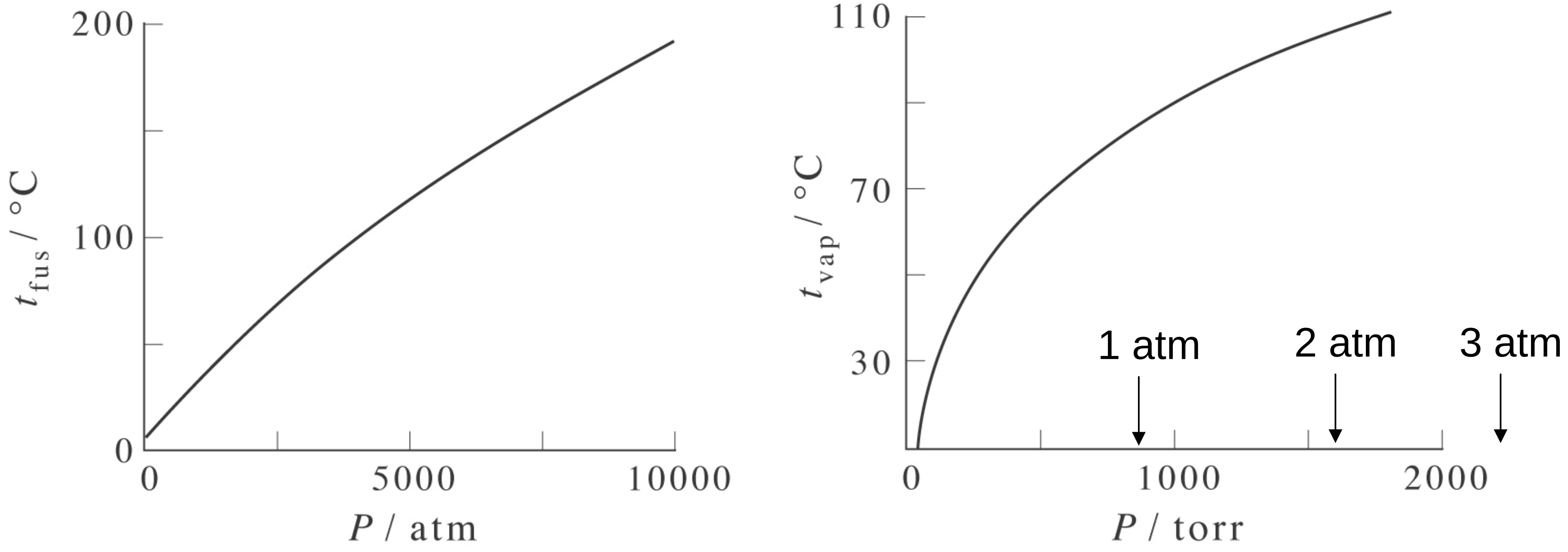
The next portion of this course (minus kinetics) will use the laws of thermodynamics to examine different physical and chemical processes (such as phase equilibria).

Phase Diagrams of Benzene



Phase transitions as function of P

Benzene



At 1 atm the melting pt is 5.5 °C.
At 34 atm the melting point is 6.5 °C.

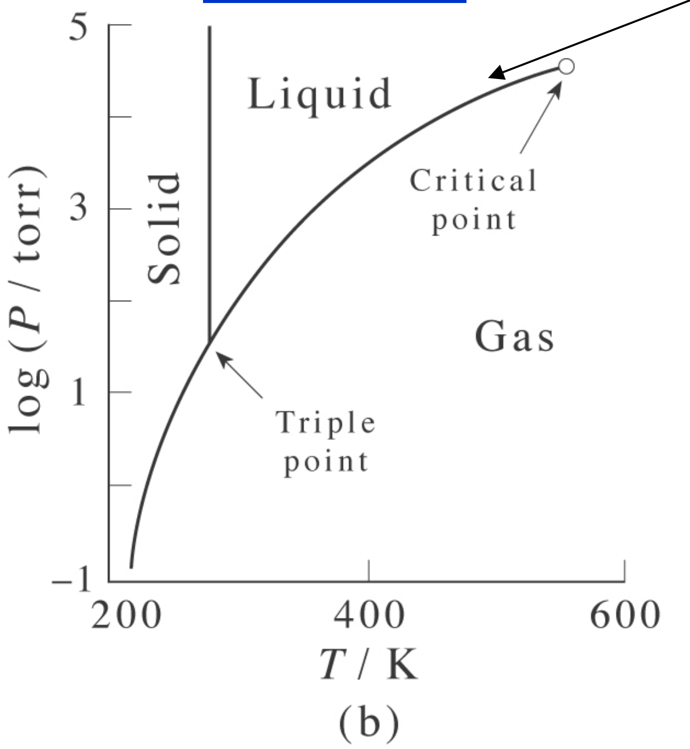
At 1 atm the boiling pt is 80.1 °C.
At 0.66 atm the boiling point is 67 °C.

MP at 1 atm = Normal melting point
MP at 1 bar = Standard melting point

BP at 1 atm = Normal boiling point
BP at 1 bar = Standard boiling point

Some definitions

Benzene



Coexistence curve can be thought of as the pressure dependence of a certain phase transition (melting).

Triple point: S-L-G all coexist.
Benzene 5.5 °C and 36.1 torr

Phase rule

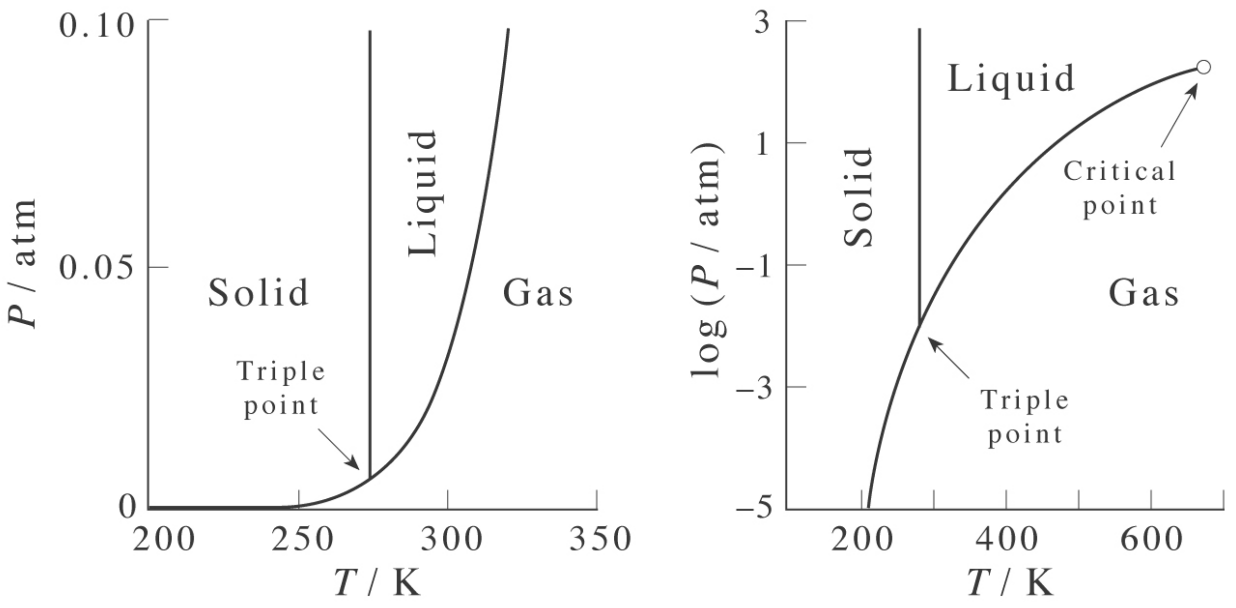
$$f = 3 - p$$

Degrees of freedom
(different than previous!)

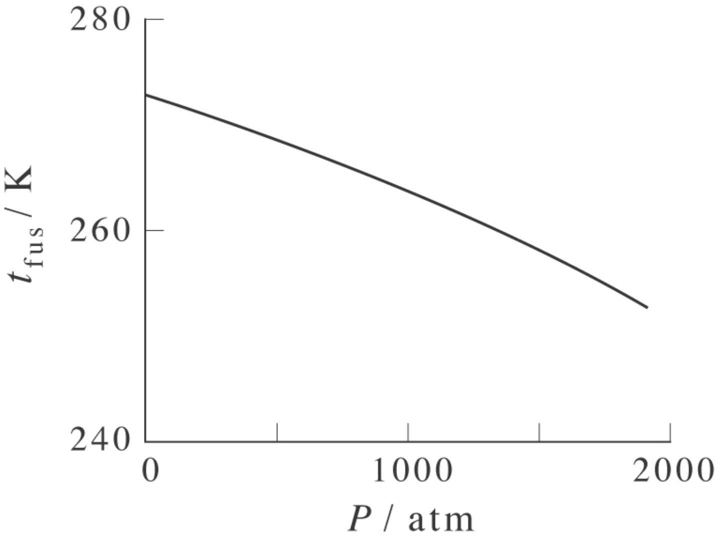
Number of phases
in coexistence

In single phase region, both T and P must be specified to describe system.
All coexistence curve, only one must be specified.
At triple point?

Phase transitions for H_2O

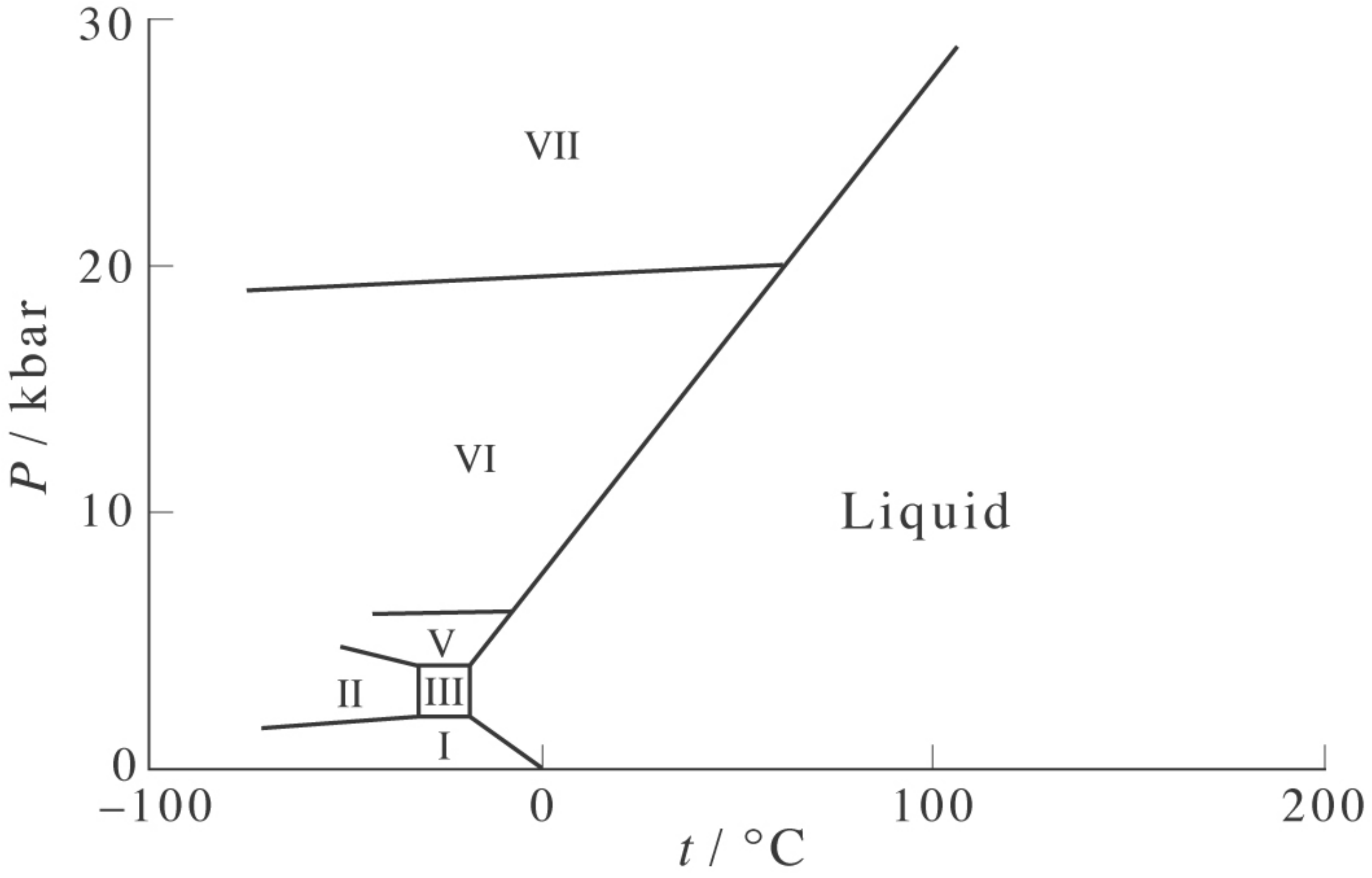


(a) (b)

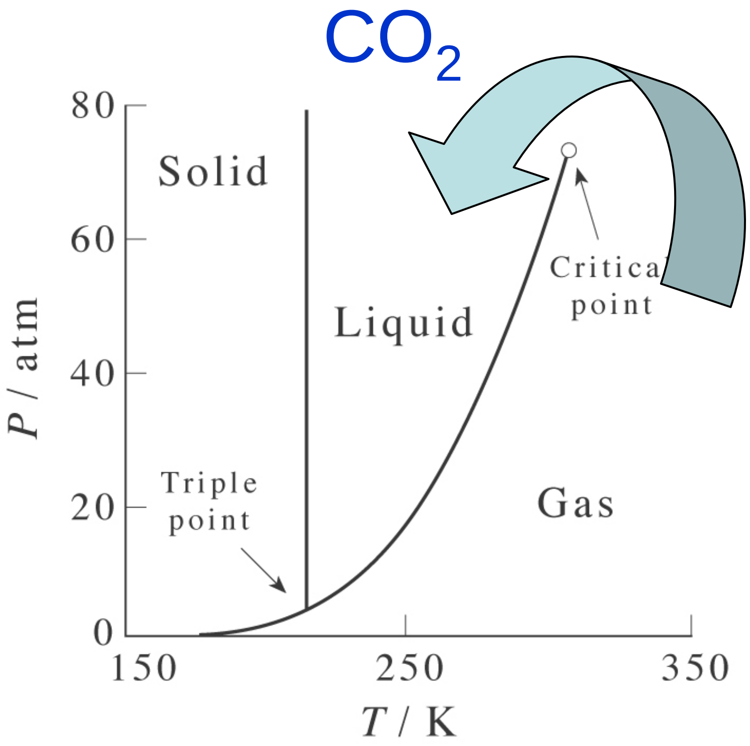


How does this differ from benzene?

Is ice always cold?



Critical Point



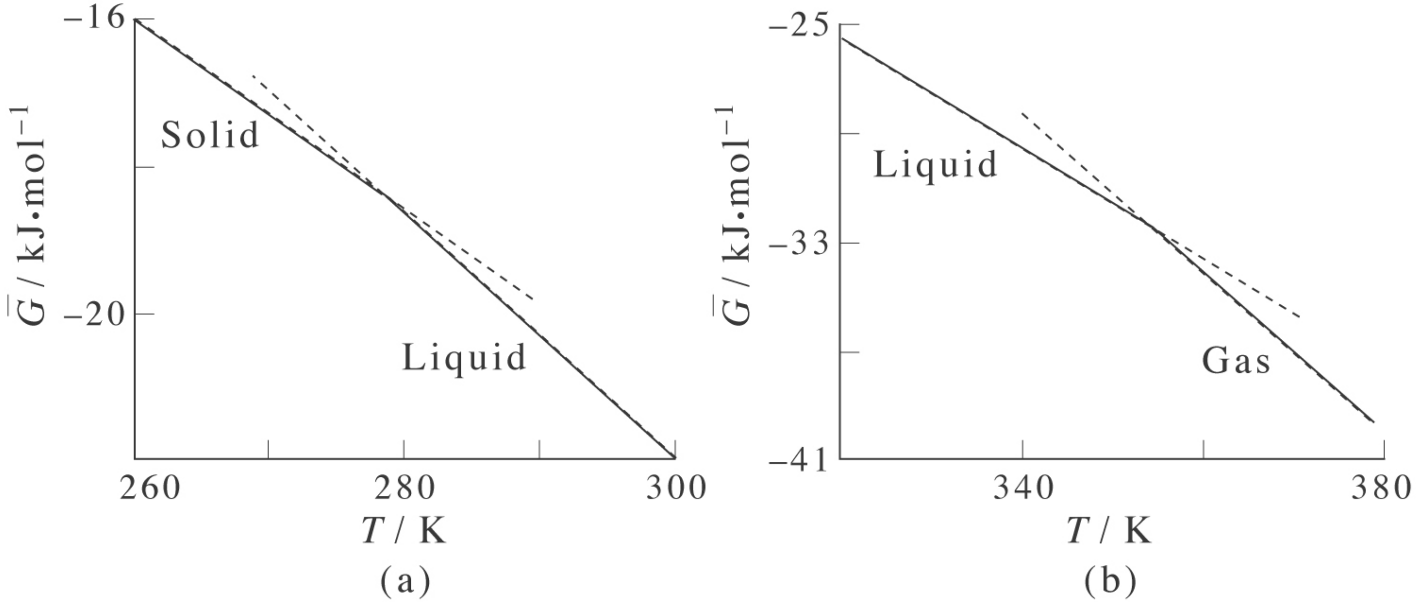
Remember critical points from gas laws?

If you follow blue arrow, the gas can be transformed into a liquid without every passing through a two-phase state.

What happens to $\Delta_{vap}H$?

Phase diagrams and Gibbs energy

Gibbs at a function of temperature



See Slide A&G-20

$$\left(\frac{\partial \overline{G}}{\partial T}\right)_P = -S^{phase}$$

Continuous function
Discontinuity in slope at phase transition
Slopes related to entropies
Dashed lines are metastable states

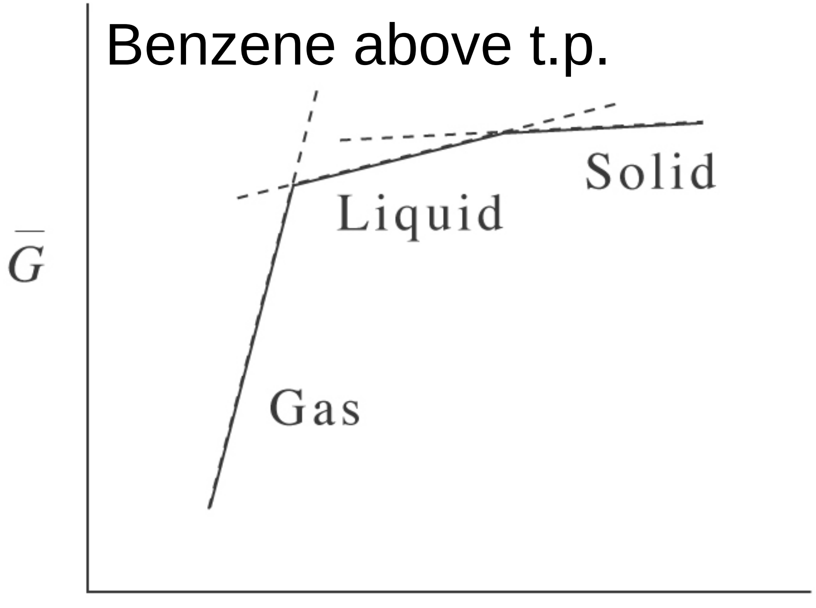
Gibbs as a function of P

$$\left(\frac{\partial \overline{G}}{\partial P}\right)_T = \overline{V}^{\,phase}$$

Always positive (slopes +)
Magnitude of slopes depends on substance
Imagine T-P phase diagram and ↑ P

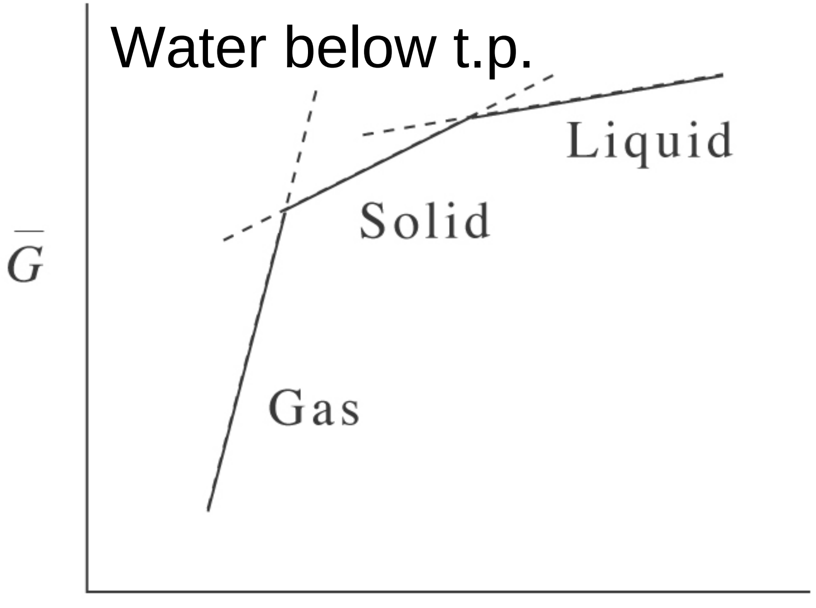
Examples near triple point…

Benzene above t.p.



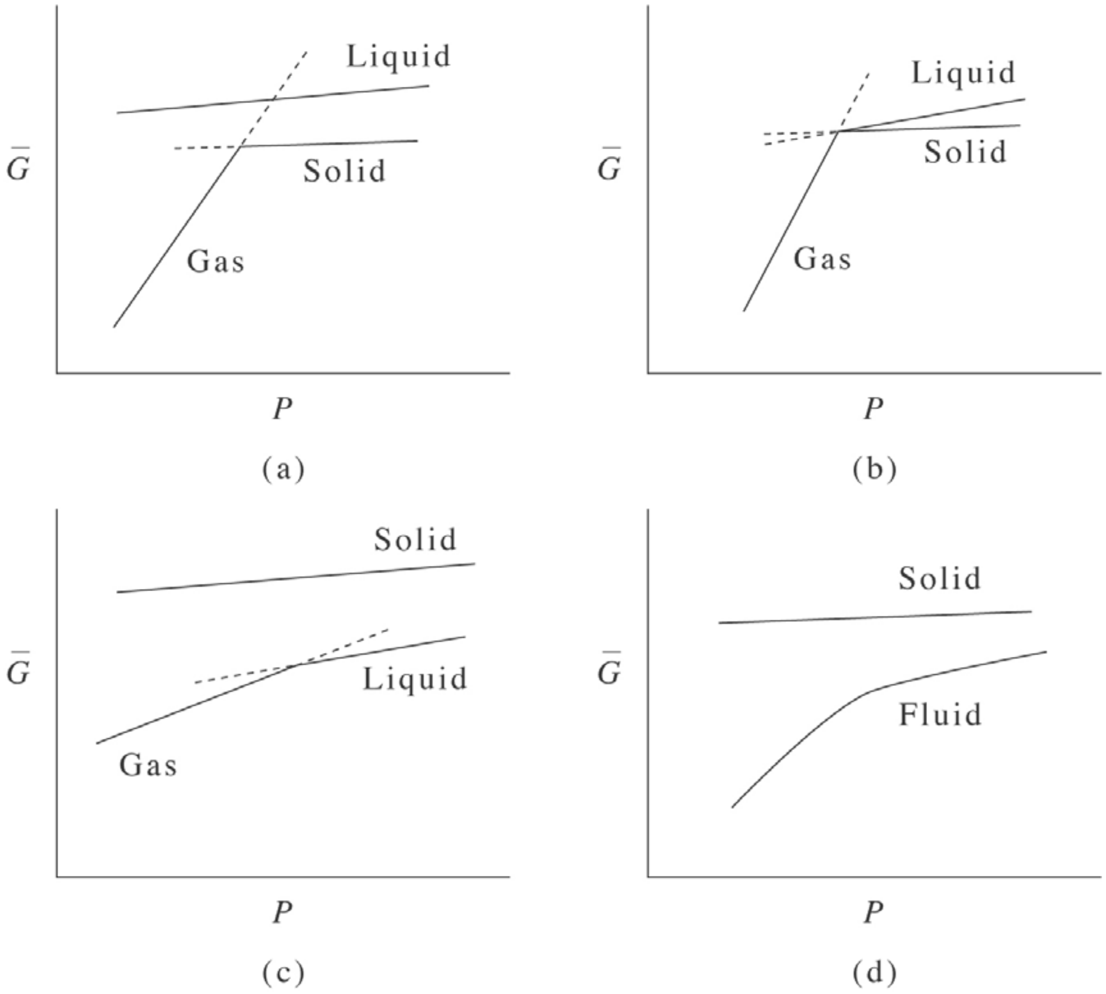
(a)

Water below t.p.

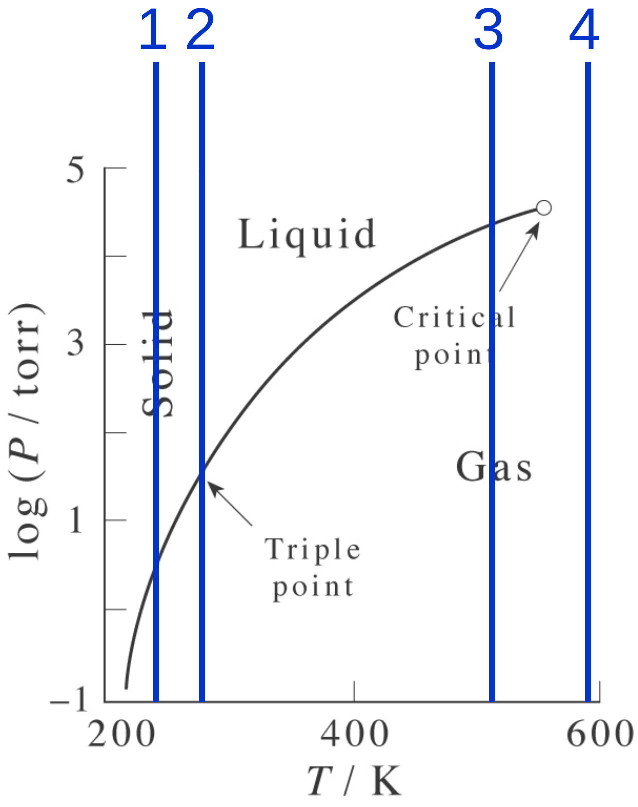


(b)

Can you ID location on phase diagrams?



(a) (b) (c) (d)



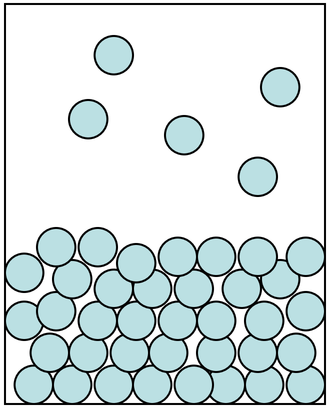
Identify the line on phase diagram that corresponds to figure on left…
What is the difference between these lines?

Consider a two phase system

The Gibbs energy of two phases in equilibrium with each other is simply the sum of the individual Gibbs energies.

$$G = G^g + G^l$$

Now imagine *dn* moles are transferred from the liquid phase to the gas phase with T and P held constant. We can write the change in Gibbs energy as:



$$dG = \left(\frac{\partial G^g}{\partial n^g}\right)_{P,T} dn^g + \left(\frac{\partial G^l}{\partial n^l}\right)_{P,T} dn^l$$

WHY?

$$dG = \left[\left(\frac{\partial G^g}{\partial n^g}\right)_{P,T} - \left(\frac{\partial G^l}{\partial n^l}\right)_{P,T}\right] dn^g$$

Chemical potentials

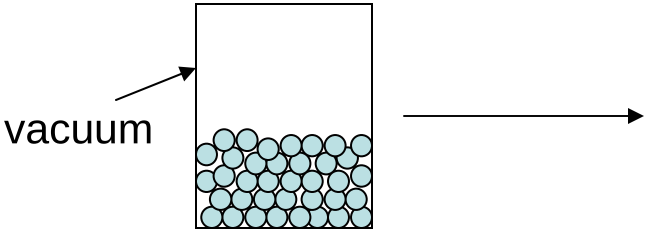
The partial derivatives in the last expression are called *chemical potentials*…

$$\mu^i = \left(\frac{\partial G^i}{\partial n^i} \right)_{P,T}$$

$$dG = \left[\mu^g - \mu^l \right] dn^g$$

What happens at equilibrium?

“Matter flows from a higher chemical potential to a lower chemical potential”



Simple form of the chemical potential

For a pure substance, the chemical potential is simply the molar Gibbs energy, an intensive quantity.

$$\mu^i = \overline{G}^{\,i}$$

At equilibrium…

$$\mu^\alpha(T,P) = \mu^\beta(T,P)$$

Also true that the total derivatives are equal to each other…

Recall: $dG = -SdT + VdP$

What are $\left(\dfrac{\partial \overline{G}^{\,\alpha}}{\partial P}\right)_T$ & $\left(\dfrac{\partial \overline{G}^{\,\alpha}}{\partial T}\right)_P$?

Clapeyron Equation

$$\overline{V}^{\alpha} dP - \overline{S}^{\alpha} dT = \overline{V}^{\beta} dP - \overline{S}^{\beta} dT$$

$$\frac{dP}{dT} = \frac{\overline{S}^{\beta} - \overline{S}^{\alpha}}{\overline{V}^{\beta} - \overline{V}^{\alpha}}$$

OR

$$\frac{dP}{dT} = \frac{\Delta_{trs}\overline{S}}{\Delta_{trs}\overline{V}}$$

Clapeyron Equation

In words… Relationship between the slope of the two-phase boundary line in a phase diagram with the change in molar enthalpy and molar volume.

Clausius-Clapeyron Equation

Clapeyron Equation works well for fusion but not vaporization or sublimation. Why??

$$\frac{dP}{dT} = \frac{\Delta_{vap}\overline{H}}{T(\overline{V}^{g} - \overline{V}^{l})}$$

Away from critical point…

$$\frac{dP}{dT} = \frac{\Delta_{vap}\overline{H}}{T(\overline{V}^{g} - \overline{V}^{l})} \approx \frac{\Delta_{vap}\overline{H}}{T\overline{V}^{g}}$$

Assume ideal gas →

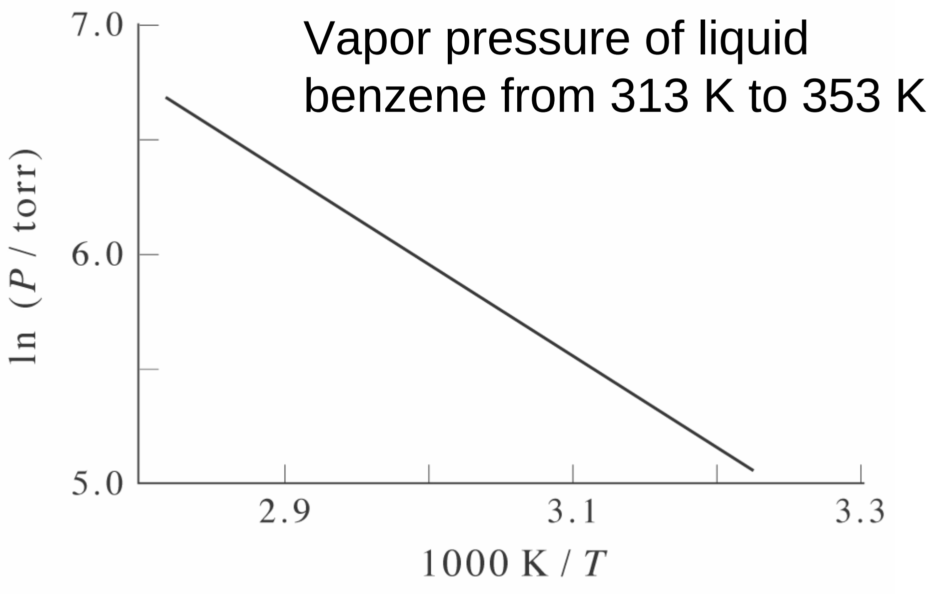
$$\frac{1}{P}\frac{dP}{dT} = \frac{d\ln P}{dT} = \frac{\Delta_{vap}\overline{H}}{RT^{2}}$$

Clausius-Clapeyron Equation

Integrated form of CC Equation: Part 1

Indefinite integral…

$$\int \frac{1}{P} dP = \int \frac{\Delta_{vap}\overline{H}}{RT^2} dT$$



Vapor pressure of liquid benzene from 313 K to 353 K

But we know that the molar enthalpy of vaporization does vary with temperature ($dH=C_p dT$). We can model this (statistically)…

$$\Delta_{vap}\overline{H} = A + BT + CT^2 + \ldots$$

↙ Integration constant

Integrated form of the CC Equation: Part 2

Definite integral

$$\int_{P_1}^{P_2} \frac{1}{P}\,dP = \int_{T_1}^{T_2} \frac{\Delta_{vap}\overline{H}}{RT^2}\,dT$$

$$\ln\frac{P_2}{P_1} = -\frac{\Delta_{vap}\overline{H}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

The above equation can be used to calculate the vapor pressure at some temperature given the molar enthalpy of vaporization and vapor pressure at some other temperature.

Example: Benzene

What is vapor pressure at 373.2 K for benzene (normal boiling point = 353.2 K, $\Delta_{vap}H$ = 30.8 kJ·mol^{-1})?

μ from *q*

$$A = U - TS$$

$$U = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} \qquad S = k_B T \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} + k_B \ln Q$$

$$A = -k_B T \ln Q$$

Recall: $\mu = \left(\frac{\partial G}{\partial n} \right)_{T,P} = \left(\frac{\partial A}{\partial n} \right)_{T,V}$

$$\boxed{\mu = -k_B T \left(\frac{\partial \ln Q}{\partial n} \right)_{V,T} = -RT \left(\frac{\partial \ln Q}{\partial N} \right)_{V,T}}$$