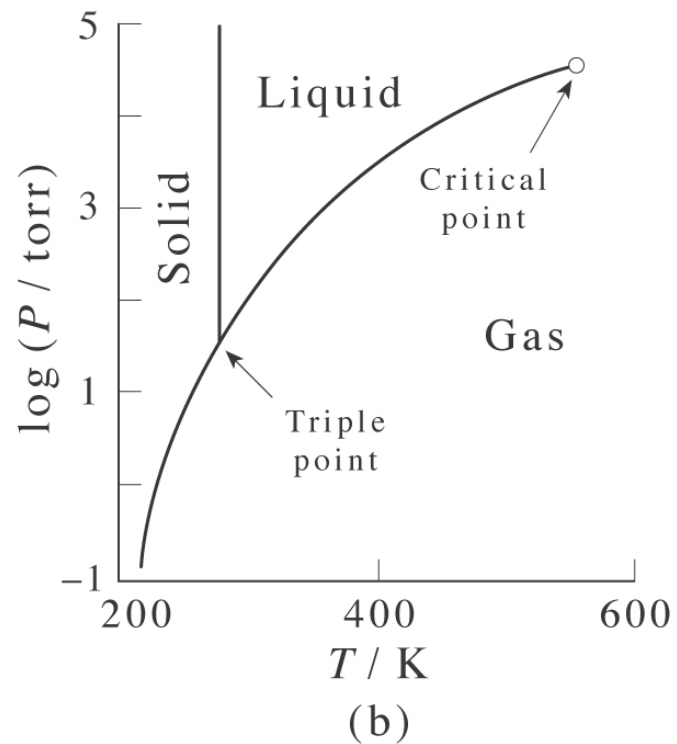
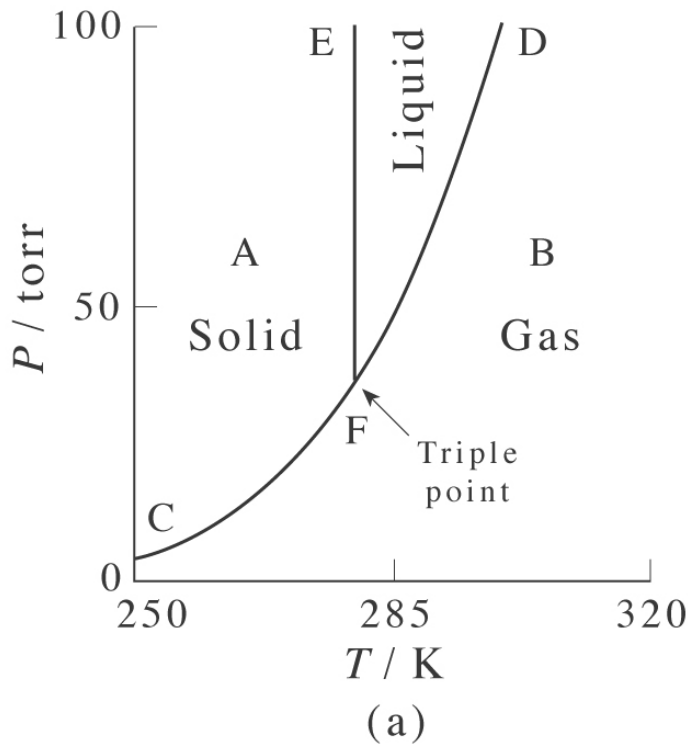
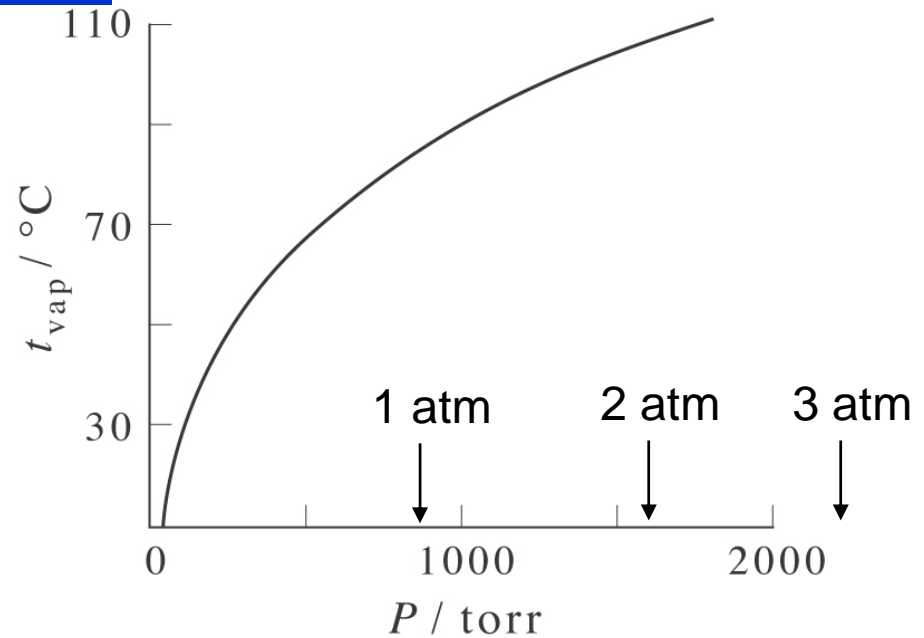
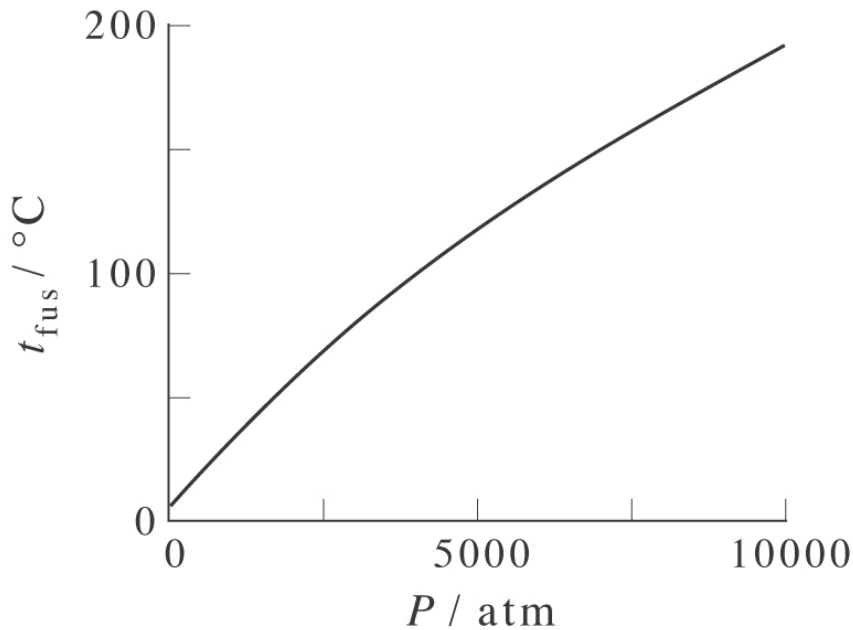


The next portion of this course (minus kinetics) will use the laws of thermodynamics to examine different physical and chemical processes (such as phase equilibria).

## Phase Diagrams of Benzene



## Benzene



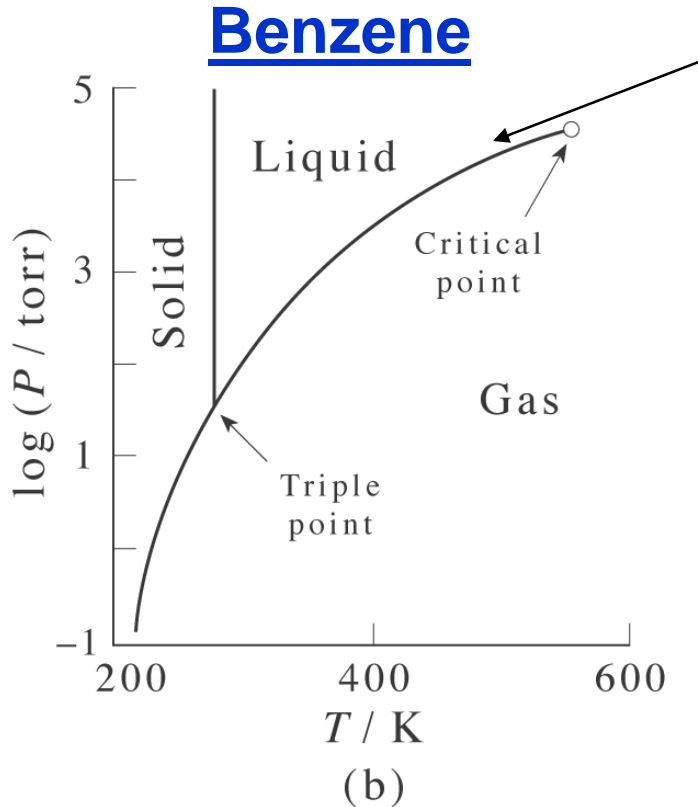
At 1 atm the melting pt is 5.5 °C.  
At 34 atm the melting point is 6.5 °C.

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





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!)

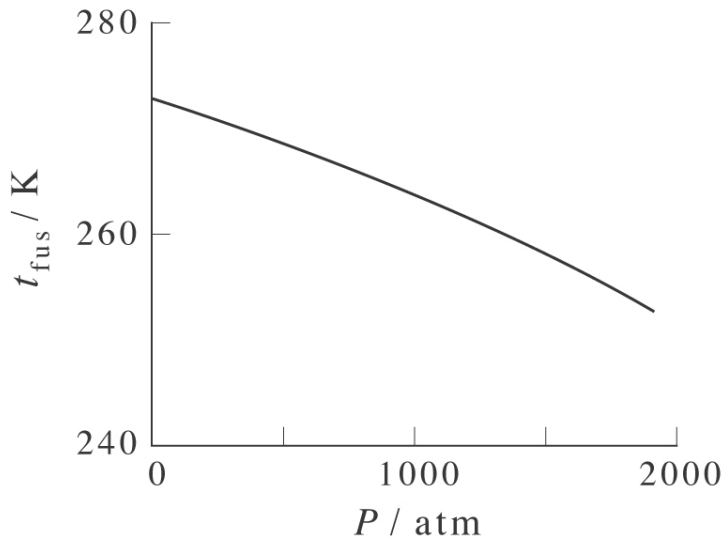
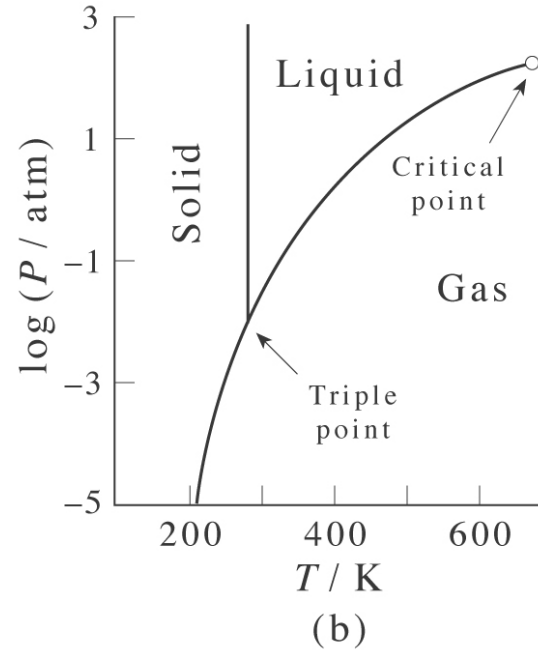
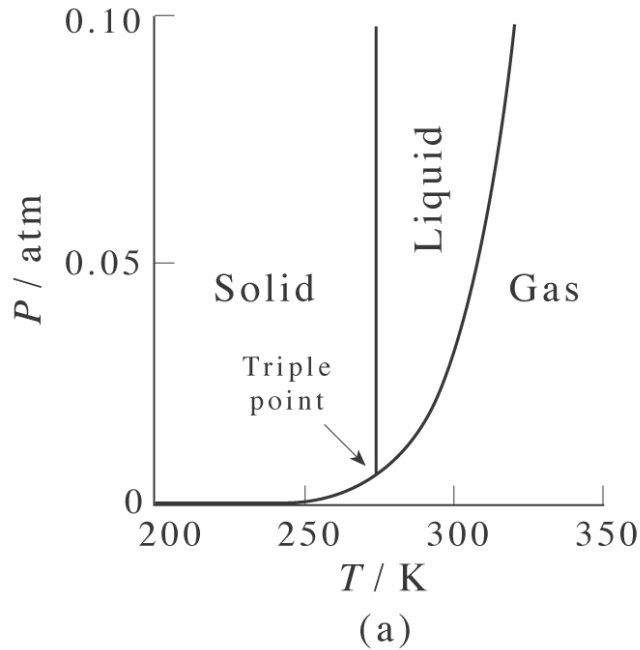
Number of phases  
in coexistence

In single phase region, both T and P must be specified to describe system.

All coexistence curves, only one must be specified.

At triple point?





How does this differ from benzene?

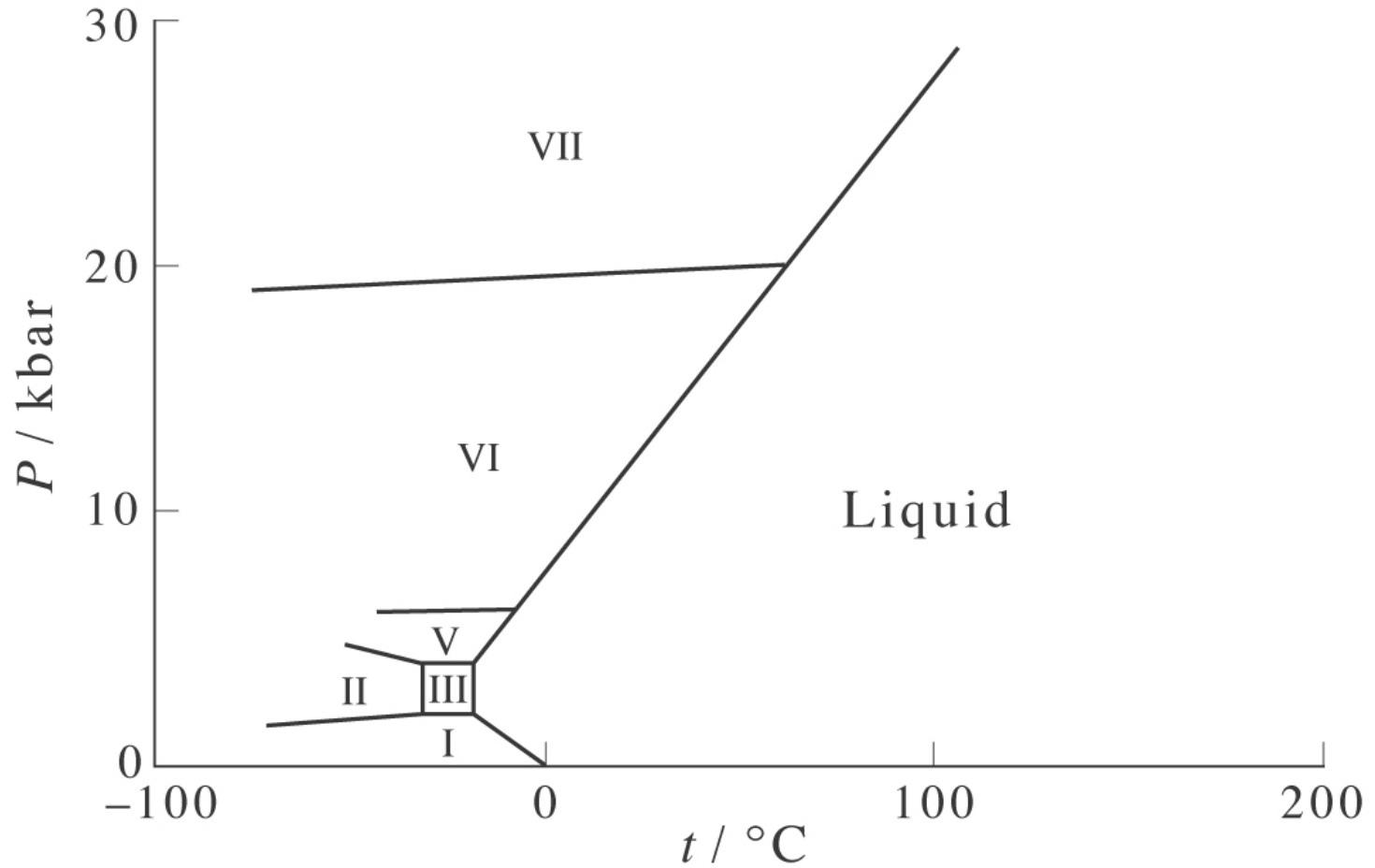
MP of H<sub>2</sub>O decreases with increasing pressure!

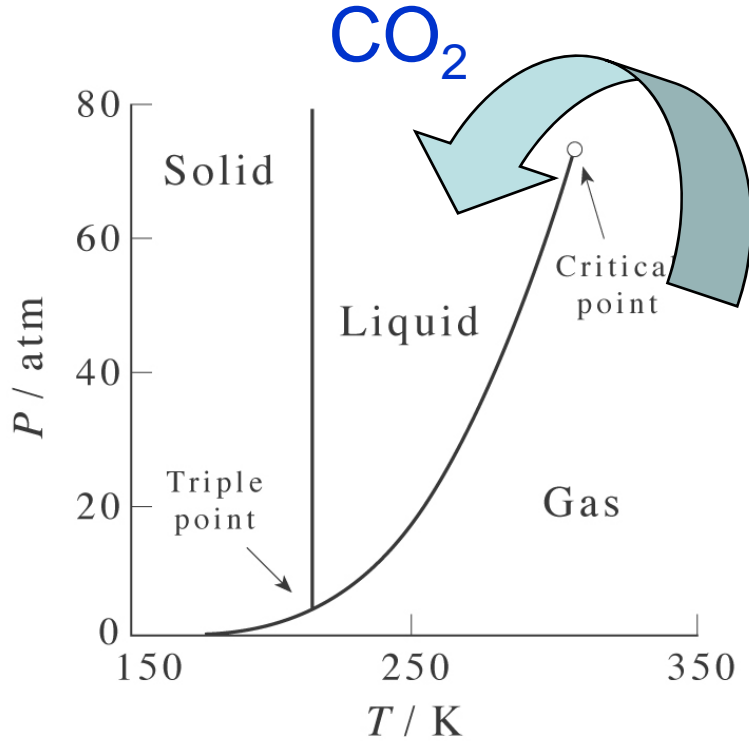
This is because molar volume of ice is greater than that of water at same conditions.



# Is ice always cold?

PE-5

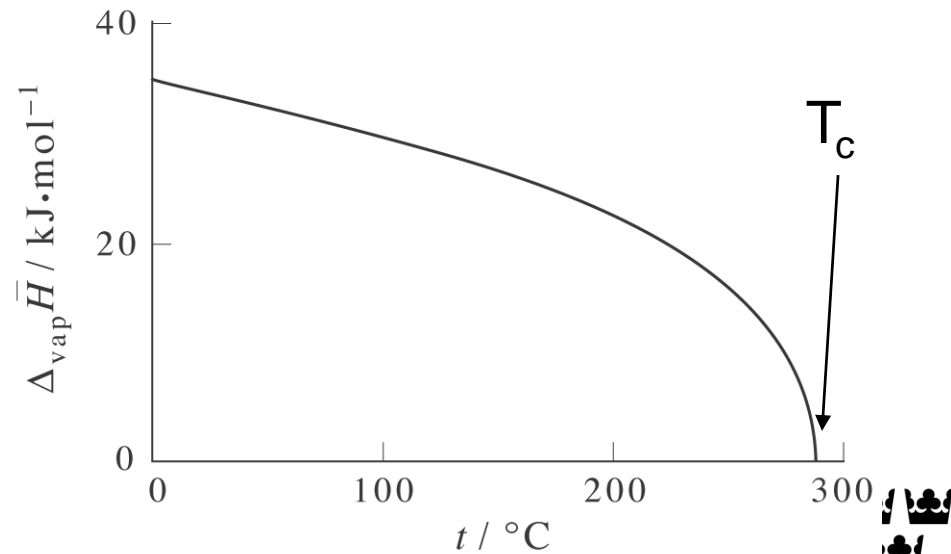




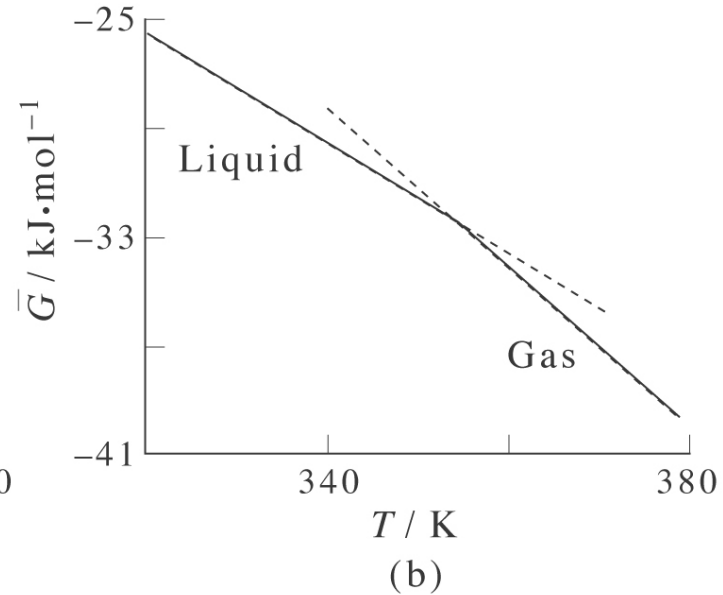
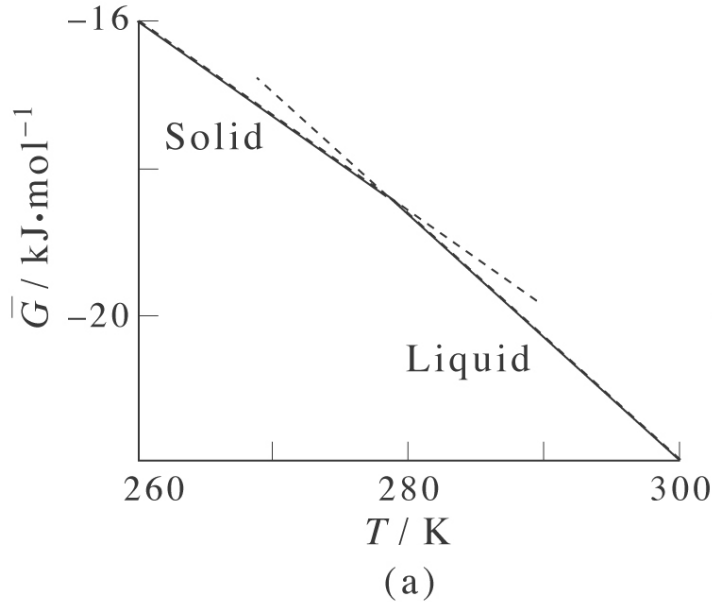
Remember critical points from gas laws?

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

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



## Gibbs at a function of temperature



See Slide A&G-20

Continuous function

Discontinuity in slope at phase transition

Slopes related to entropies

Dashed lines are metastable states

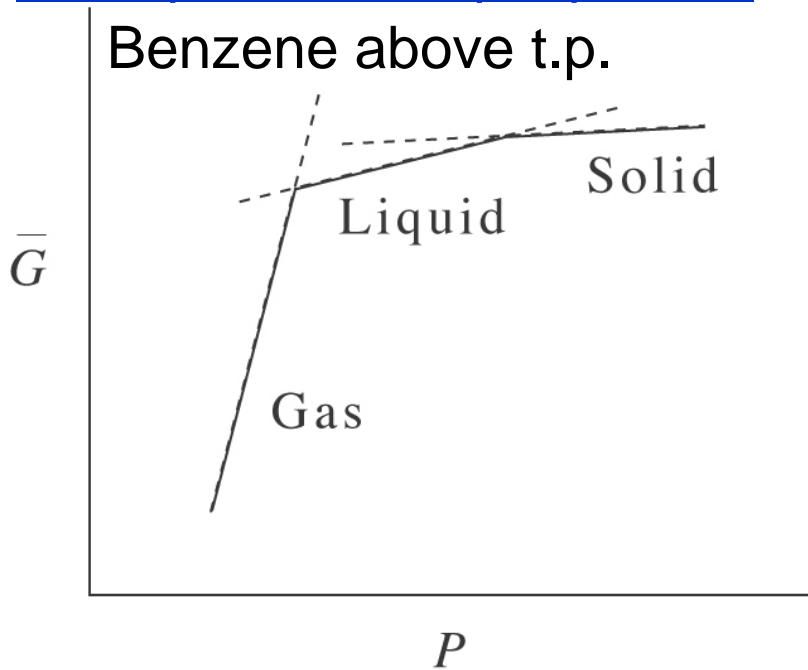
$$\left( \frac{\partial \bar{G}}{\partial T} \right)_P = -S^{phase}$$



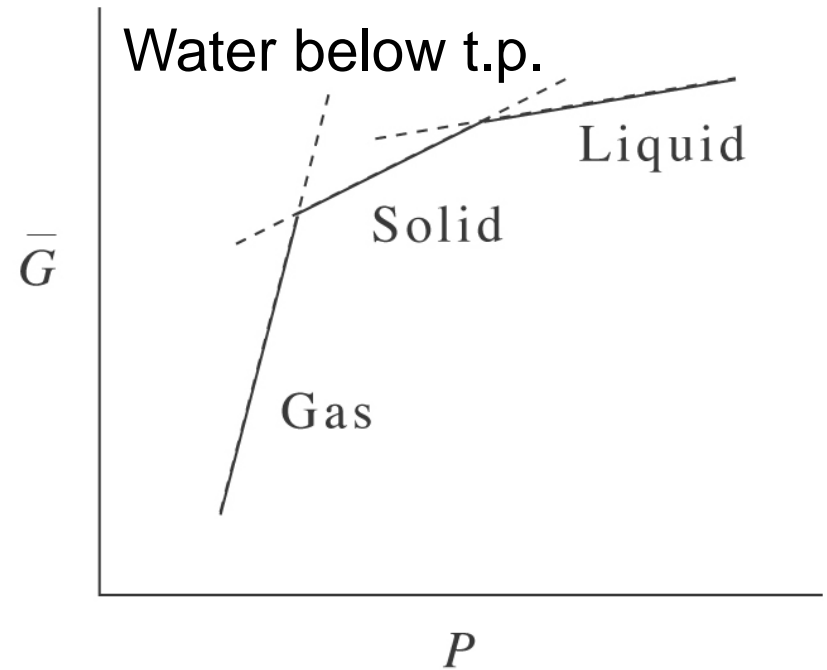
$$\left( \frac{\partial \bar{G}}{\partial P} \right)_T = \bar{V}^{phase}$$

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

Examples near triple point...



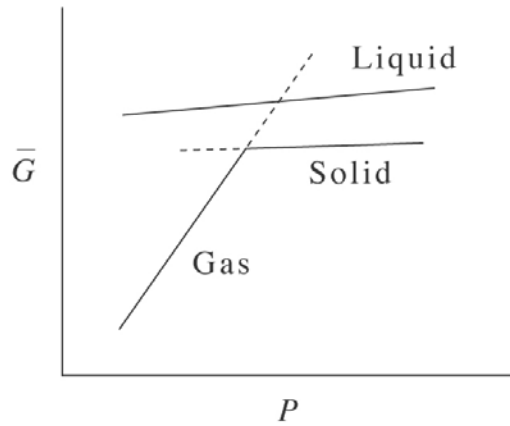
(a)



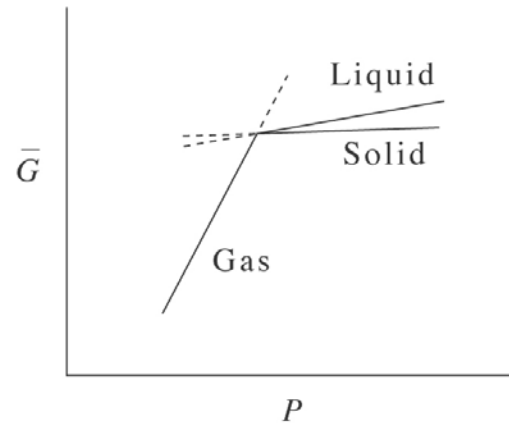
(b)



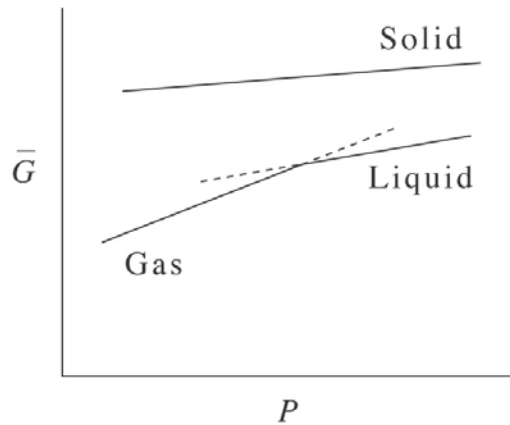
# Can you ID location on phase diagrams?



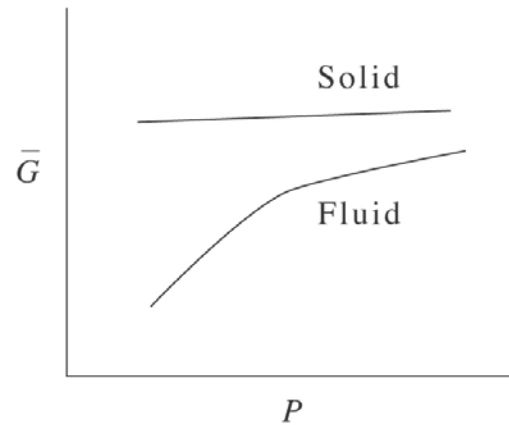
(a)



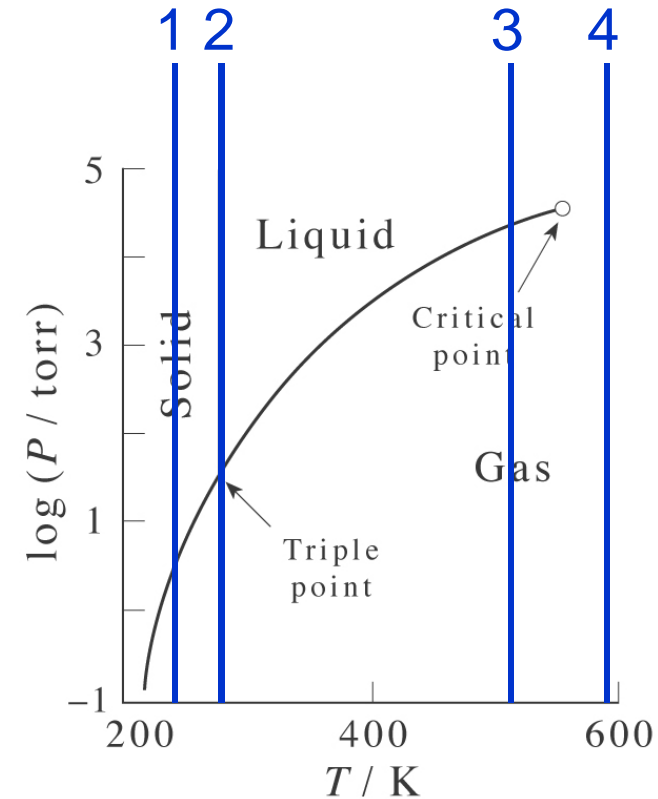
(b)



(c)



(d)



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

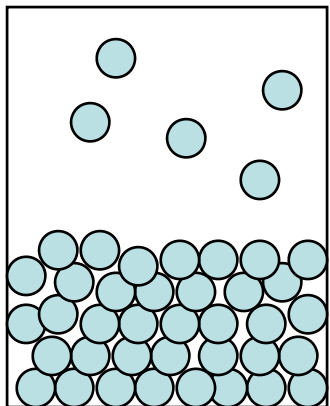


# Consider a two phase system

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:



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

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



WHY?



The partial derivatives in the last expression are called chemical potentials...

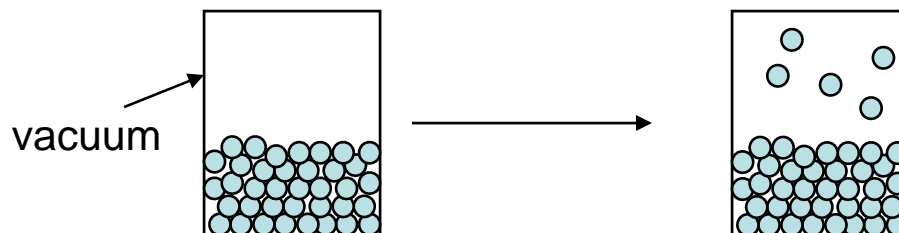
$$\mu^i = \left( \frac{\partial G^i}{\partial n^i} \right)_{P,T}$$

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

What happens at equilibrium?  $dG = 0$

$$\mu^g = \mu^l$$

Out of equilibrium, the transfer of matter occurs so  $dG < 0$ .



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


$$\mu^i = \bar{G}^i$$

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

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

$$\left(\frac{\partial \mu^\alpha}{\partial P}\right)_T dP + \left(\frac{\partial \mu^\alpha}{\partial T}\right)_P dT = \left(\frac{\partial \mu^\beta}{\partial P}\right)_T dP + \left(\frac{\partial \mu^\beta}{\partial T}\right)_P dT$$

$$\left(\frac{\partial \bar{G}^\alpha}{\partial P}\right)_T dP + \left(\frac{\partial \bar{G}^\alpha}{\partial T}\right)_P dT = \left(\frac{\partial \bar{G}^\beta}{\partial P}\right)_T dP + \left(\frac{\partial \bar{G}^\beta}{\partial T}\right)_P dT$$

Recall:  $dG = -SdT + VdP$       What are  $\left(\frac{\partial \bar{G}^\alpha}{\partial P}\right)_T$  &  $\left(\frac{\partial \bar{G}^\alpha}{\partial T}\right)_P$  ? 

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

$$\frac{dP}{dT} = \frac{\bar{S}^{\beta} - \bar{S}^{\alpha}}{\bar{V}^{\beta} - \bar{V}^{\alpha}} \quad \text{OR} \quad \frac{dP}{dT} = \frac{\Delta_{trs} \bar{S}}{\Delta_{trs} \bar{V}}$$

$$\frac{dP}{dT} = \frac{\Delta_{trs} \bar{H}}{T \Delta_{trs} \bar{V}}$$

## 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.

Implicit in equation... 1.

2.



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

**Because molar volume of gas is strongly pressure dependent!**

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

Away from critical point...

$$\bar{V}^g - \bar{V}^l \approx \bar{V}^g$$

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

Assume ideal gas

$$\frac{dP}{dT} = \frac{P\Delta_{vap} \bar{H}}{RT^2}$$

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

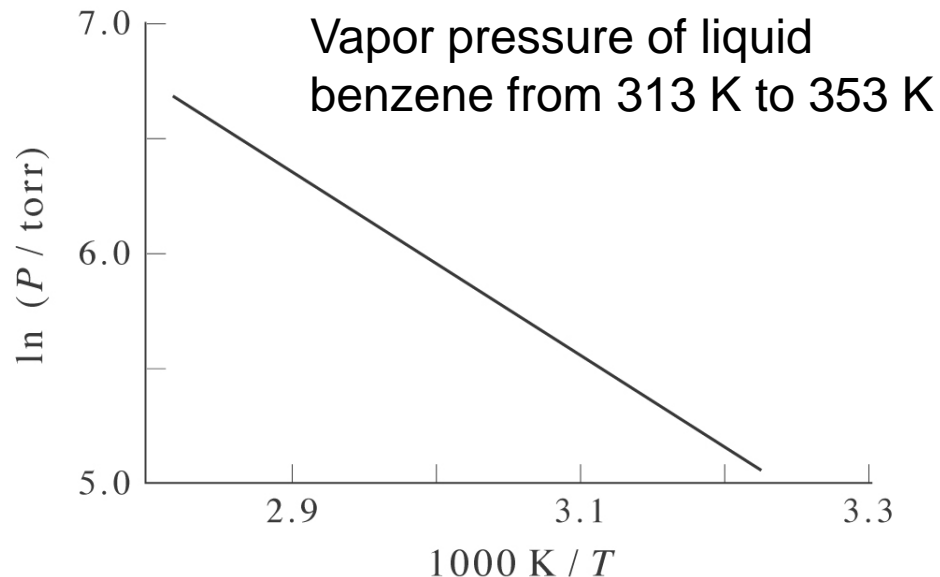
**Clausius-Clapeyron Equation**



Indefinite integral...

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

$$\ln P = -\frac{\Delta_{vap} \bar{H}}{RT} + \text{constant}$$



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

$$\Delta_{vap} \bar{H} = A + BT + CT^2 + \dots$$

$$\ln P = -\frac{A}{RT} + \frac{B}{R} \ln T + \frac{C}{R} T + k + \dots$$

↙ Integration constant



Definite integral

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

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

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,  $\Delta_{vap} H = 30.8 \text{ kJ}\cdot\text{mol}^{-1}$ )? Give answer in torr.

Experimental = 1360 torr

Why the discrepancy?



$$A = U - TS$$

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

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

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

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



- Phase diagrams
- Chemical potential: Matter flows from a higher chemical potential to a lower chemical potential
- Clapeyron and Clausius-Clapeyron Equations
- Connecting chemical potential to stat mech!

