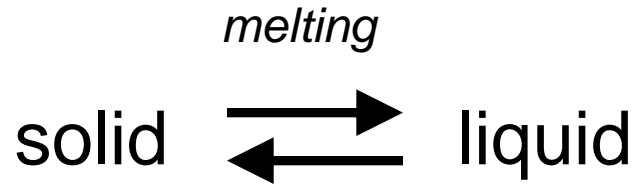


Chemistry 163B

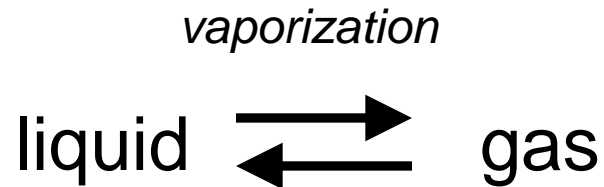
One-Component

Phase Diagram Basics

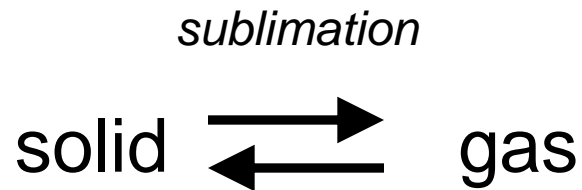
qualitative factors in phase changes



freezing/fusion



condensation



deposition

ENDOTHERMIC



EXOTHERMIC

vapor pressure over **PURE** liquid (notation)



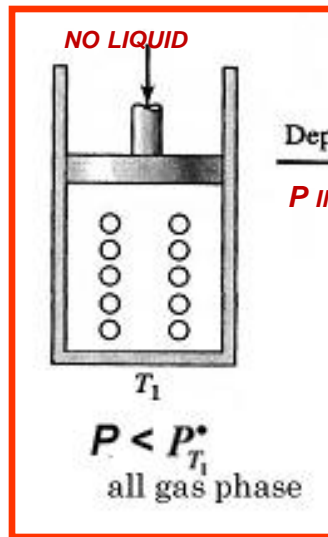
$$P^\bullet \equiv P^* \equiv P^0$$

Gene
(many others)

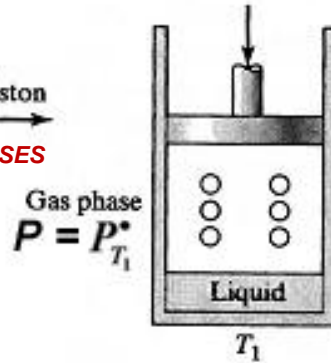
E&R

Raff

gas \rightleftharpoons liquid as pressure increases (vary P , const T)

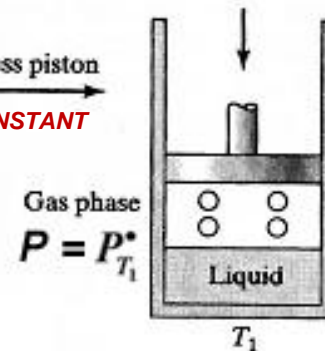


Depress piston
 P INCREASES



SOME LIQUID
 \rightleftharpoons v EQUILIB

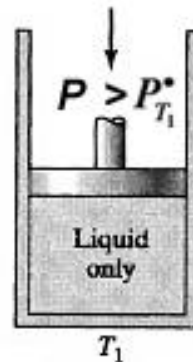
Depress piston
 P CONSTANT



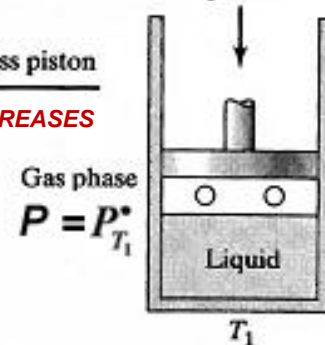
MORE LIQUID
Depress piston
 P CONSTANT

$P_{T_1}^*$ = vapor pressure of pure liquid at T_1

Depress piston
 P INCREASES

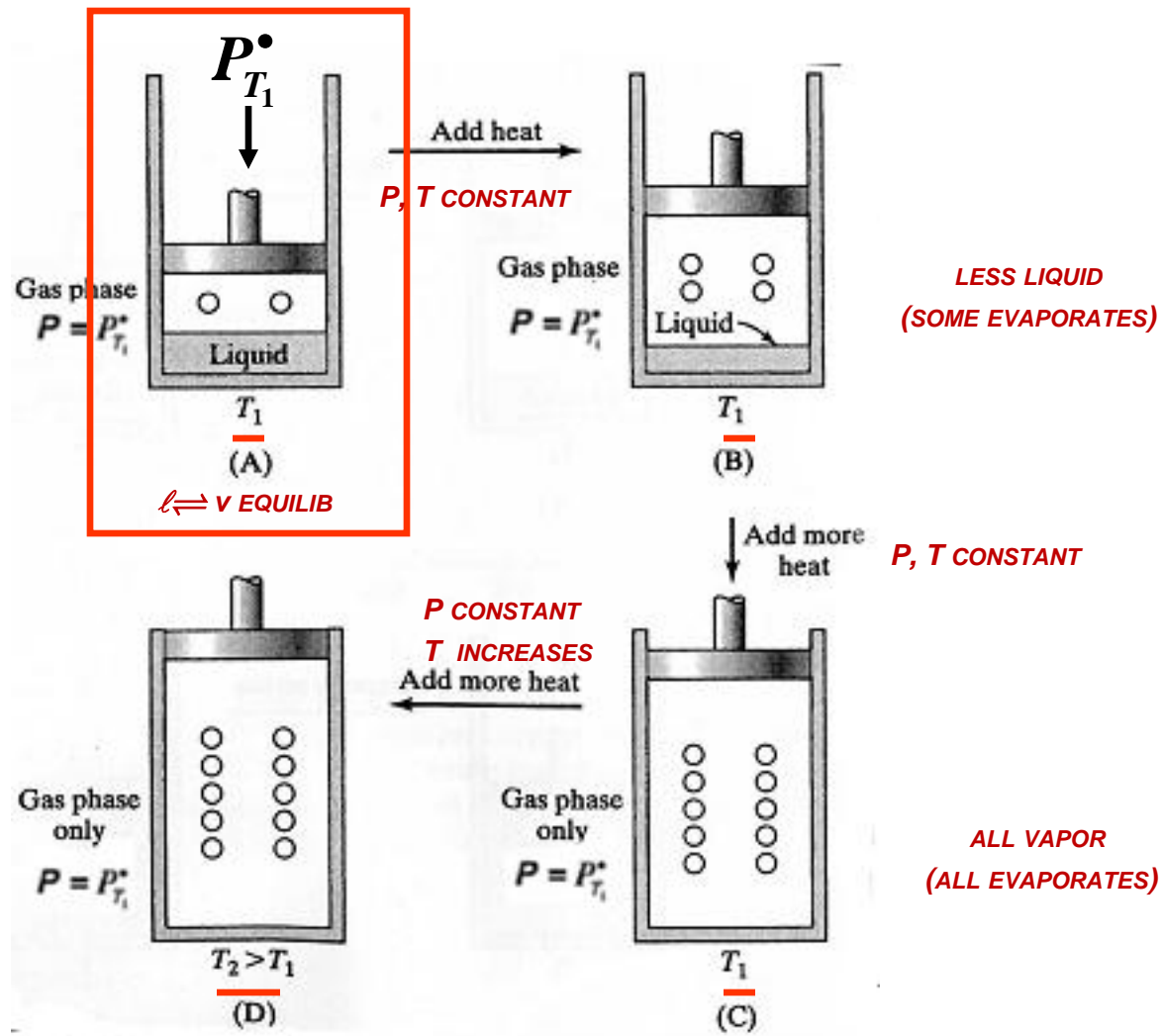


ALL LIQUID

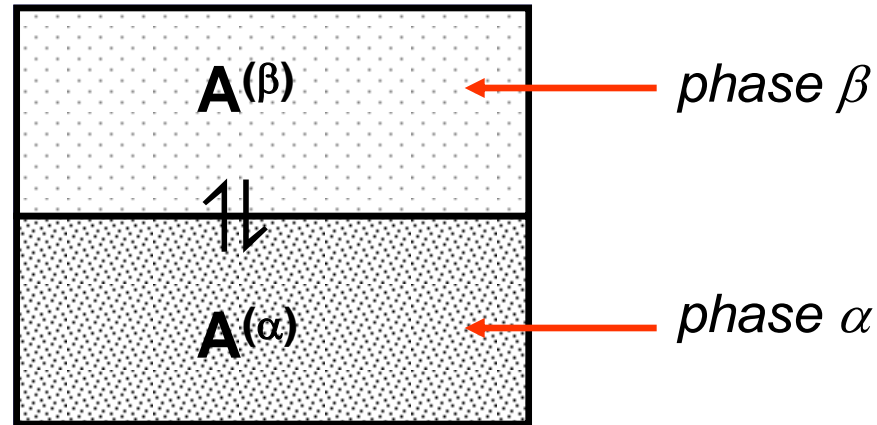


EVEN MORE LIQUID

liquid \rightleftharpoons vapor as **heat added** (vary T , const P)



dG for phase change at constant T,P



same T,P for each phase

$$dG = -SdT + VdP + \sum_i \mu_i dn_i$$

one component 'A' in *phases* α and β constant T,P

$$dG_{T,P} = \mu_A^{(\alpha)} dn_A^{(\alpha)} + \mu_A^{(\beta)} dn_A^{(\beta)}$$

$$dn_A^{(\beta)} = -dn_A^{(\alpha)}$$

$$dG_{T,P} = \left(\mu_A^{(\alpha)} - \mu_A^{(\beta)} \right) dn_A^{(\alpha)}$$

at equilibrium $\mu^{(\alpha)} = \mu^{(\beta)}$; μ is **ESCAPING TENDENCY**

$$dG_{T,P} = \left(\mu_A^{(\alpha)} - \mu_A^{(\beta)} \right) dn_A^{(\alpha)}$$

at equilibrium $dG_{T,P} = 0$

$$\mu_A^{(\alpha)} = \mu_A^{(\beta)}$$

for spontaneity $dG_{T,P} < 0$

$$dG_{T,P} = \left(\mu_A^{(\alpha)} - \mu_A^{(\beta)} \right) dn_A^{(\alpha)} < 0$$

$$\mu_A^{(\alpha)} > \mu_A^{(\beta)} \Rightarrow dn_A^{(\alpha)} < 0 \quad \text{molecules lost from phase } \alpha$$

$$\mu_A^{(\beta)} > \mu_A^{(\alpha)} \Rightarrow dn_A^{(\alpha)} > 0 \quad \text{molecules gained by phase } \alpha$$

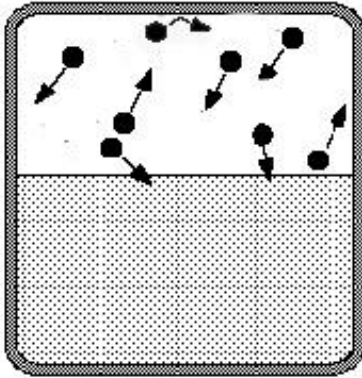
$\mu_A^{(\alpha)}$ is the **ESCAPING TENDENCY**
for molecules in phase α

high $\mu \rightarrow$ low μ

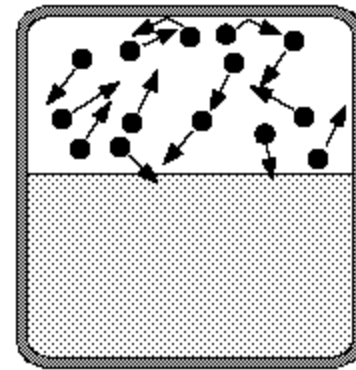
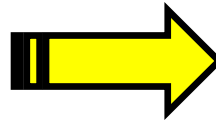
hyper \rightarrow mellow

Question:

can my pressure cooker heat water to 200C
without exploding?

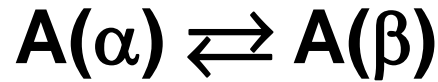


$T=298\text{ K}$
 $P = 0.032\text{ bar}$



$T=473\text{ K}$
 $P = 15.5\text{ bar}$

phase equilibrium one-component systems (i.e pure substances)



at equilibrium $\Delta\mu = 0 \Rightarrow \mu_A^{(\alpha)} = \mu_A^{(\beta)}$

How can P and T covary to maintain equilibrium?

$$\begin{array}{ccc} \mu^{(\alpha)}(T_1, P_1) = \mu^{(\beta)}(T_1, P_1) & & \\ \downarrow d\mu^{(\alpha)} & & \downarrow d\mu^{(\beta)} \\ \mu^{(\alpha)}(T_2, P_2) = \mu^{(\beta)}(T_2, P_2) & & \end{array}$$

T and P covary *T and P covary*

$$\boxed{\mu^{(\alpha)}(\underline{T_1}, \underline{P_1}) = \mu^{(\beta)}(\underline{T_1}, \underline{P_1})} \xrightarrow{dT, dP} \boxed{\mu^{(\alpha)}(\underline{T_2}, \underline{P_2}) = \mu^{(\beta)}(\underline{T_2}, \underline{P_2})}$$

before

after

*conditions for remaining at phase equilibrium (one-component),
covary T and P*

$$\mu^{(\alpha)}(T_1, P_1) = \mu^{(\beta)}(T_1, P_1) \xrightarrow{dT, dP} \mu^{(\alpha)}(T_2, P_2) = \mu^{(\beta)}(T_2, P_2)$$

$$d\mu^{(\alpha)} = -\bar{S}^{(\alpha)}dT^{(\alpha)} + \bar{V}^{(\alpha)}dP^{(\alpha)} = -\bar{S}^{(\beta)}dT^{(\beta)} + \bar{V}^{(\beta)}dP^{(\beta)} = d\mu^{(\beta)}$$

with

$$T^{(\alpha)} = T^{(\beta)} = T \quad dT^{(\alpha)} = dT^{(\beta)} = dT$$

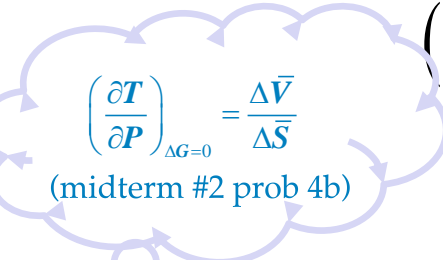
$$P^{(\alpha)} = P^{(\beta)} = P \quad dP^{(\alpha)} = dP^{(\beta)} = dP$$

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


$$\left(\bar{S}^{(\beta)} - \bar{S}^{(\alpha)}\right)dT = \left(\bar{V}^{(\beta)} - \bar{V}^{(\alpha)}\right)dP$$

phase equilibrium (one-component)

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


$$\left(\frac{\partial T}{\partial P}\right)_{\Delta G=0} = \frac{\Delta \bar{V}}{\Delta \bar{S}}$$

(midterm #2 prob 4b)


$$\left(\frac{dP}{dT}\right)_{\text{phase equilibrium}}$$

$$= \frac{\Delta \bar{S}_{\phi}}{\Delta \bar{V}_{\phi}}$$

$\phi = \text{phase change}$

eqn. 8.13 E&R

since phase change is an equilibrium (reversible) process

$$\Delta \bar{S}_{\phi} = \frac{\Delta \bar{H}_{\phi}}{T}$$

$$\left(\frac{dP}{dT}\right)_{\text{phase equilibrium}} = \frac{\Delta \bar{H}_{\phi}}{T \Delta \bar{V}_{\phi}}$$

I. application to liquid \rightleftharpoons gas (vapor) or solid \rightleftharpoons gas

$$\left(\frac{dP}{dT}\right)_{\text{phase equilibrium}} = \frac{\Delta\bar{H}_\phi}{T\Delta\bar{V}_\phi}$$

vaporization – condensation	liquid \rightleftharpoons gas (vapor)
or	
sublimation – deposition	solid \rightleftharpoons gas

\bar{V}_{solid} and \bar{V}_{liquid} are small compared to \bar{V}_{vapor} $\Delta\bar{V}_\phi \approx \bar{V}_{\text{vapor}}$

assume ideal gas $\Delta\bar{V}_\phi = \bar{V}_{\text{vapor}} = \frac{RT}{P}$

$$\left(\frac{dP}{dT}\right)_{\ell \text{ or } s \rightleftharpoons g} = \frac{\Delta\bar{H}_\phi}{T\left(\frac{RT}{P}\right)} = \frac{P\Delta\bar{H}_\phi}{RT^2}$$

$$\left(\frac{d(\ln P)}{dT}\right) = \frac{\Delta\bar{H}_{\text{vap or sub}}}{RT^2}$$

I. application to liquid \rightleftharpoons gas (vapor) or solid \rightleftharpoons gas

$$\left(\frac{dP}{dT}\right)_{\ell \text{ or } s \rightleftharpoons g} = \frac{\Delta \bar{H}_{\phi}}{T \left(\frac{RT}{P}\right)} = \frac{P \Delta \bar{H}_{\phi}}{RT^2}$$

$$\left(\frac{d(\ln P)}{dT}\right)_{\text{equilibrium}} = \frac{\Delta \bar{H}_{\text{vap or sub}}}{RT^2}$$

Clausius-Clapeyron
 \approx eqn. 8.19 E&R

I. application to liquid \rightleftharpoons gas (vapor) or solid \rightleftharpoons gas

$$\left(\frac{d(\ln P)}{dT} \right)_{\text{equilibrium}} = \frac{\Delta \bar{H}_{\text{vap or sub}}}{RT^2} \quad \text{for } s \text{ or } \ell \rightleftharpoons \text{gas} \quad K_P = P_{\text{gas}}$$

$$\left(\frac{d(\ln K_P)}{dT} \right)_{\text{equilibrium}} = \frac{\Delta \bar{H}_{\text{vap or sub}}}{RT^2}$$

$$\int_{P_1}^{P_2} d(\ln P) = \int_{T_1}^{T_2} \frac{\Delta \bar{H}_{\phi}}{RT^2} dT \quad (\text{assume } \Delta \bar{H} \text{ independent of } T)$$

$$\ln \left(\frac{P_2}{P_1} \right) = -\frac{\Delta \bar{H}_{\phi}}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

E&R eqn 8.20 where ϕ is vaporization similar for sublimation

application to problems:

normal b.p. (1 atm), standard b.p. (1 bar)

to get vapor pressure given $T_{\text{boiling}}^{\circ}$ and ΔH_{vap} :

$$\text{at } T_1 = T_{bp}^{\circ} \quad P_1 = P_{\text{vapor}} = \mathbf{1 atm}$$

$$\ln \left(\frac{P_{\text{vapor}}(T)}{1 atm} \right) = -\frac{\Delta \bar{H}_{\text{vap}}}{R} \left[\frac{1}{T} - \frac{1}{T_{bp}^{\circ}} \right] = \frac{\Delta \bar{H}_{\text{vap}}}{R} \left[\frac{1}{T_{bp}^{\circ}} - \frac{1}{T} \right]$$

I. application to liquid \rightleftharpoons gas (vapor) or solid \rightleftharpoons gas

application to problems:

to get T_{boiling} when $P_{\text{atm}} \neq 1 \text{ atm}$:

$$\ln\left(\frac{P_{\text{atm}}}{1 \text{ atm}}\right) = -\frac{\Delta\bar{H}_{\text{vap}}}{R} \left[\frac{1}{T_{\text{bp}}} - \frac{1}{T_{\text{bp}}^{\circ}} \right]$$

$$T_{\text{bp}}^{\circ} \left(\ln\left(\frac{P_{\text{atm}}}{1 \text{ atm}}\right) \right) = -\frac{\Delta\bar{H}_{\text{vap}}}{R} \left[\frac{T_{\text{bp}}^{\circ}}{T_{\text{bp}}} - 1 \right]$$

$$T_{\text{bp}}^{\circ} \left(\ln\left(\frac{P_{\text{atm}}}{1 \text{ atm}}\right) \right) - \frac{\Delta\bar{H}_{\text{vap}}}{R} = -\frac{\Delta\bar{H}_{\text{vap}}}{R} \left[\frac{T_{\text{bp}}^{\circ}}{T_{\text{bp}}} \right]$$

$$\left[T_{\text{bp}}^{\circ} \left(\ln\left(\frac{P_{\text{atm}}}{1 \text{ atm}}\right) \right) - \frac{\Delta\bar{H}_{\text{vap}}}{R} \right] \left[\frac{R}{\Delta\bar{H}_{\text{vap}}} \right] = - \left[\frac{T_{\text{bp}}^{\circ}}{T_{\text{bp}}} \right]$$

$$\left[\frac{T_{\text{bp}}}{T_{\text{bp}}^{\circ}} \right] = \frac{1}{\left[1 - \frac{RT_{\text{bp}}^{\circ}}{\Delta\bar{H}_{\text{vap}}} \ln\left(\frac{P_{\text{atm}}}{1 \text{ atm}}\right) \right]}$$

I. application to liquid \rightleftharpoons gas (vapor) or solid \rightleftharpoons gas

application to problems: to get T_{boiling} when $P_{\text{atm}} \neq 1 \text{ atm}$:

$$\left[\frac{T_{bp}}{T_{bp}^{\circ}} \right] = \frac{1}{\left[1 - \frac{RT_{bp}^{\circ}}{\Delta \bar{H}_{vap}} \ln \left(\frac{P_{atm}}{1 \text{ atm}} \right) \right]}$$



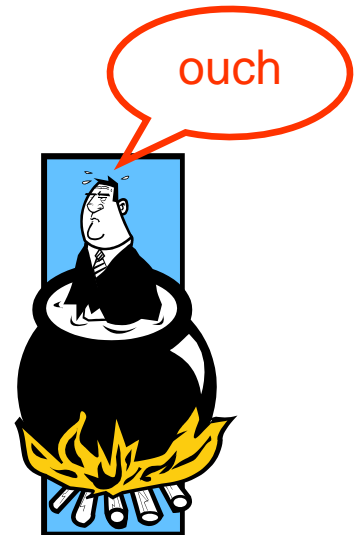
Denver: elev=1610m $P=0.822 \text{ atm}$

$$P < 1 \text{ atm} \Rightarrow \left[\frac{T_{bp}}{T_{bp}^{\circ}} \right] < 1 \Rightarrow T_{bp} < T_{bp}^{\circ}$$



Death Valley: elev = -82.5 m, $P=1.010 \text{ atm}$

$$P > 1 \text{ atm} \Rightarrow \left[\frac{T_{bp}}{T_{bp}^{\circ}} \right] > 1 \Rightarrow T_{bp} > T_{bp}^{\circ}$$



II. application to solid \rightleftharpoons liquid

$$\left(\frac{dP}{dT}\right)_{\text{phase equilibrium}} = \frac{\Delta\bar{H}_{\phi}}{T\Delta\bar{V}_{\phi}} \quad T_{\text{melting}}^{\circ} \text{ for phase equilibrium at } P = 1 \text{ atm}$$

what is T_{melting} at other pressures?

$$\frac{dT}{T} = \frac{\Delta\bar{V}_{\phi}}{\Delta\bar{H}_{\text{melting}}} dP \Rightarrow \ln\left(\frac{T_{\text{melting}}}{T_{\text{melting}}^{\circ}}\right) = \frac{\Delta\bar{V}_{\phi}}{\Delta\bar{H}_{\text{melting}}} [P - 1 \text{ atm}]$$

$$\ln\left(\frac{T_{\text{melting}}}{T_{\text{melting}}^{\circ}}\right) = \frac{\bar{V}_{\text{liquid}} - \bar{V}_{\text{solid}}}{\Delta\bar{H}_{\text{melting}}} [P - 1 \text{ atm}]$$

will increased pressure raise or lower T_{melting} ?

$$\Delta H_{\text{melting}} > 0$$

(usual) $V_{\text{liquid}} > V_{\text{solid}}$ T_{melting} increases

(when??) $V_{\text{liquid}} < V_{\text{solid}}$ T_{melting} decreases

phase rule one-component system (save proof for later)

f= degrees of freedom

p=phases simultaneously present

2 variables : T, P (same for each phase)

p-1 restrictions: $\mu^{(\alpha)} = \mu^{(\beta)} = \mu^{(\gamma)} = \dots$

f: degrees of freedom = (variables-restrictions)

$$f = 2 - (p - 1) = 3 - p$$

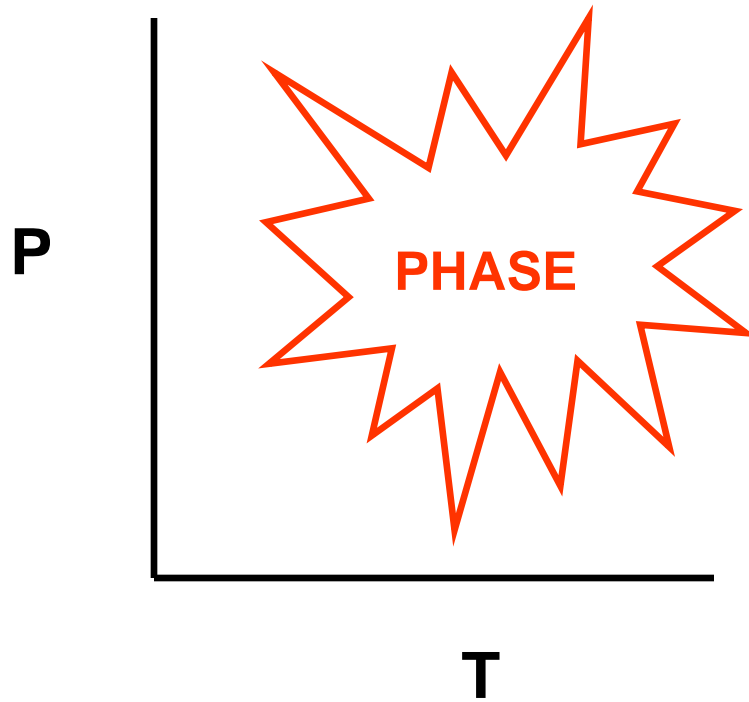
$f = 3 - p$

1 phase: T,P vary independently

2 phases present: T and P covary

3 phases present: fixed T and P

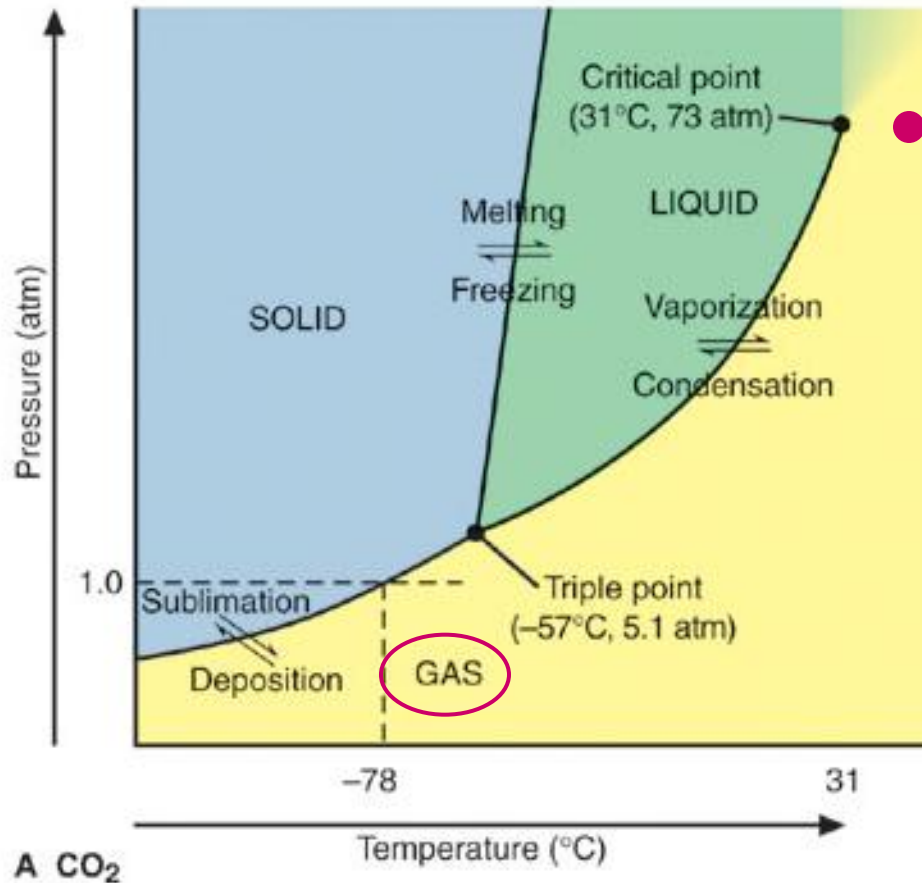
phase diagrams one component: phase vs (P,T)



BE[A]WARE: when we study multicomponent phase diagrams the axis variables may not be P,T

phase diagrams (f=3-p)

“state” or “phase” as a function of P, T



high T

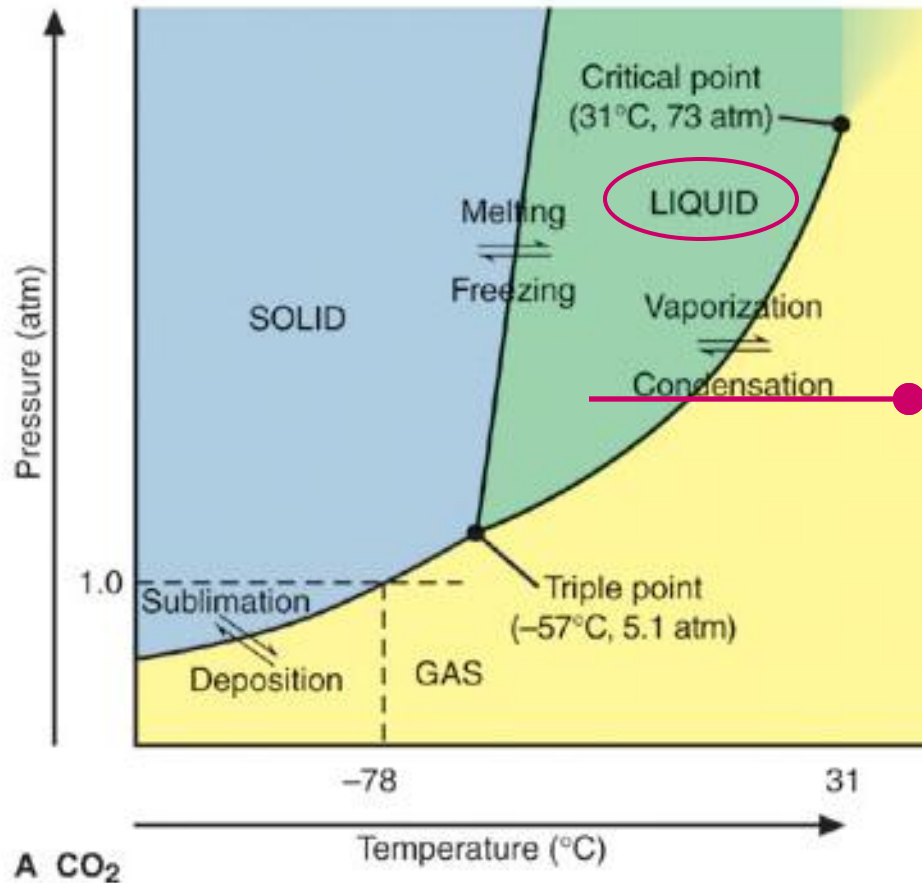
gas

1 phase, f=2
vary both T,P

CO₂

phase diagrams (f=3-p)

“state” or “phase” as a function of P, T



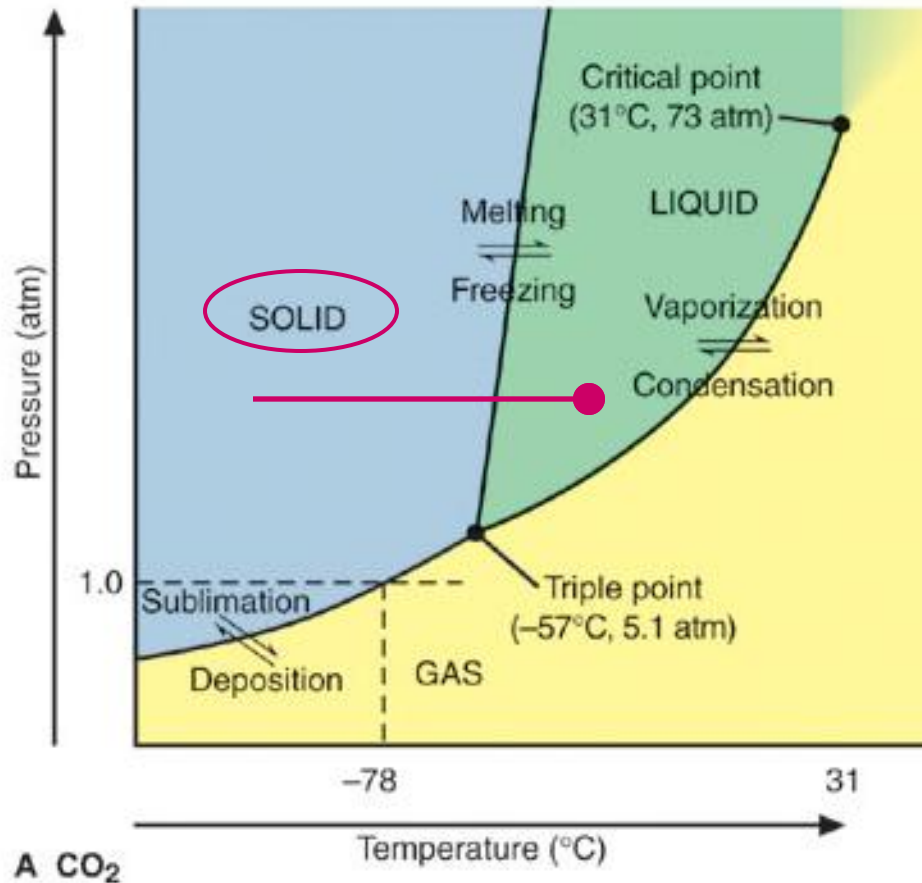
lower T

liquid

1 phase, $f=2$
vary both T,P

CO₂

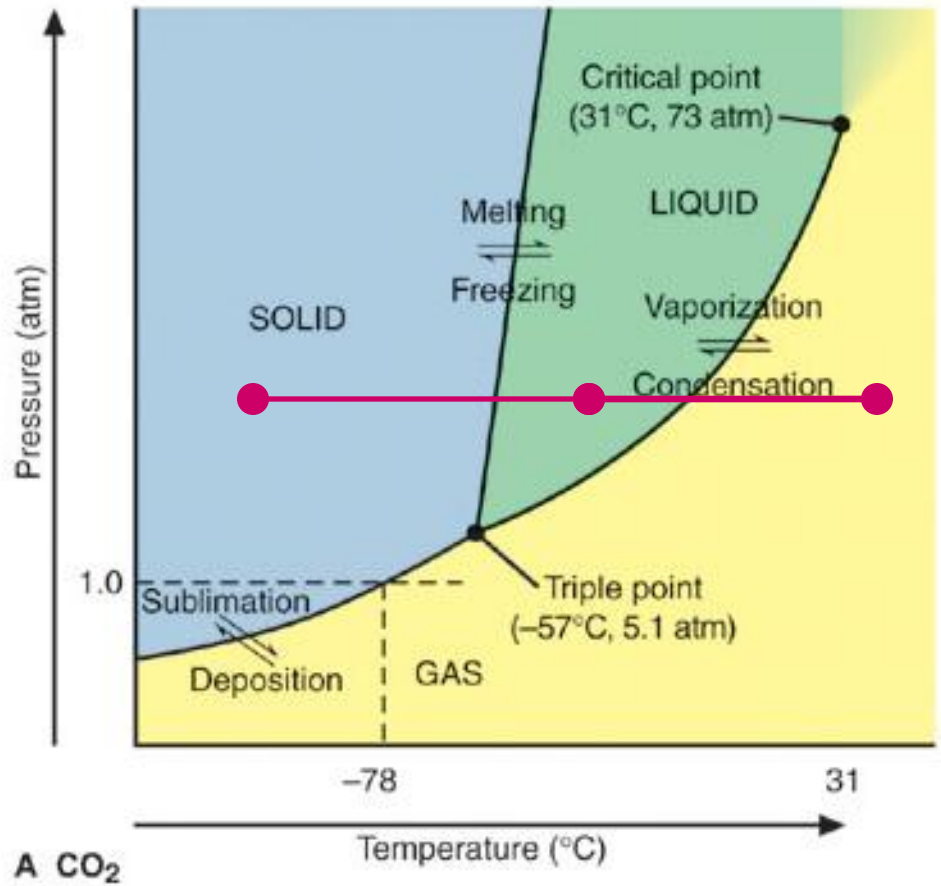
“state” or “phase” as a function of P, T



lower T more
solid

CO₂

“state” or “phase” as a function of P, T



high T
gas

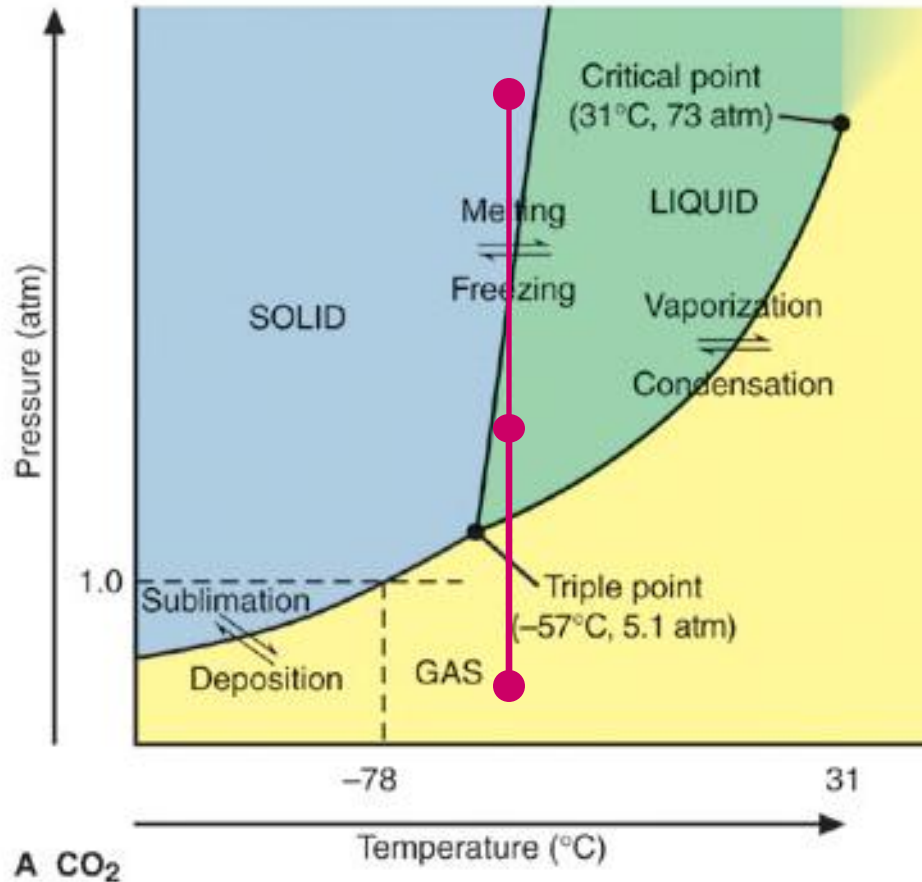
lower T
liquid

lower T more
solid

A CO₂

CO₂

“state” or “phase” as a function of P, T



low P
gas

raise P
liquid

raise P more
solid

A CO₂

CO₂

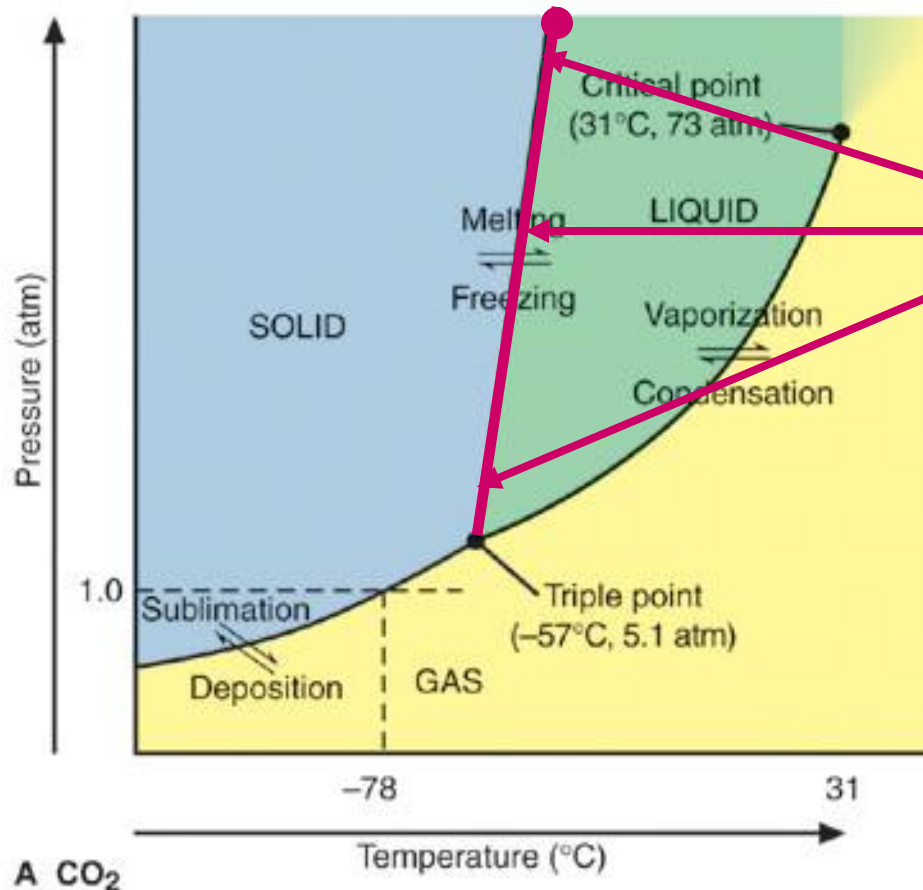
two-phase equilibrium (p=2)

$$f=3-p =1$$

$$\left(\frac{dP}{dT}\right)_{equilib} = \frac{\Delta\bar{H}_\phi}{T\Delta\bar{V}_\phi}$$

phase diagrams (f=3-p)

liquid ↔ solid equilibrium line (melting, freezing or fusion)



T's and P's

for liquid ↔ solid equilibrium

**2 phases,
f=3-2=1**

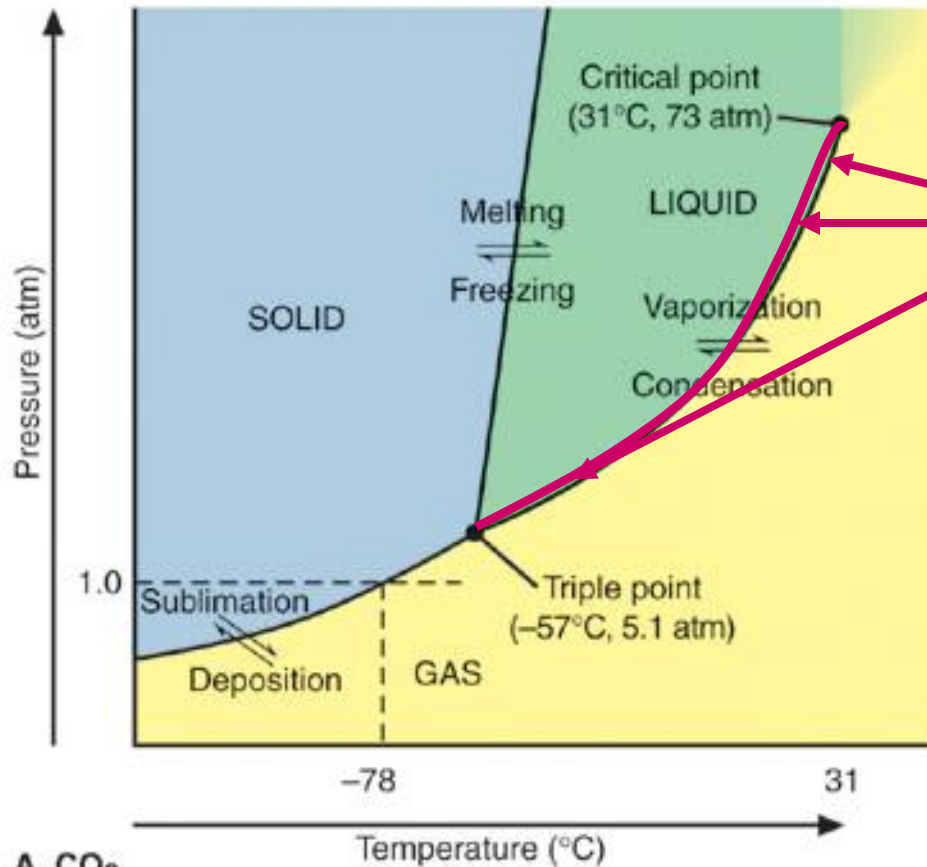
T and P covary

$$\left(\frac{dP}{dT}\right)_{s \rightleftharpoons l} = \frac{\Delta \bar{H}_{fus}}{T \Delta \bar{V}_{fus}}$$

CO₂

phase diagrams (f=3-p)

liquid ↔ gas equilibrium line (vaporization, condensation)



T's and P's

for liquid ↔ gas equilibrium

**2 phases,
f=3-2=1**

T and P covary

**[select T, then P determined
select P, then T determined]**

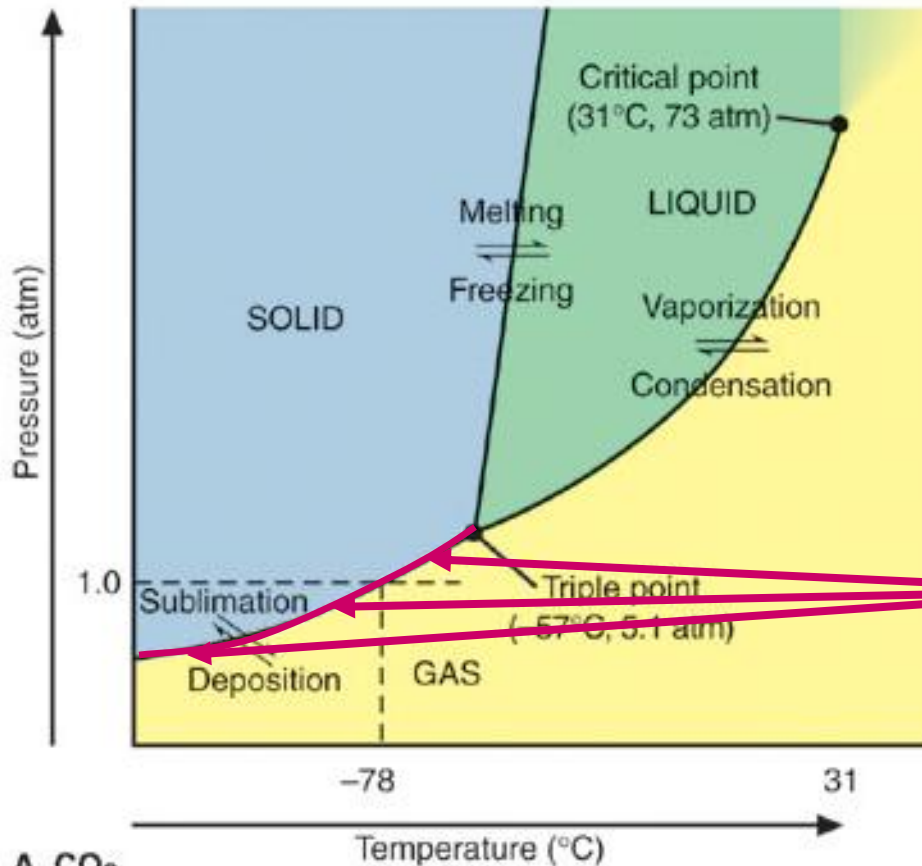
$$\left(\frac{dP}{dT}\right)_{l \rightleftharpoons g} = \frac{\Delta \bar{H}_{\phi}}{T \Delta \bar{V}_{\phi}} \approx \frac{\Delta \bar{H}_{vap}}{RT^2}$$

A CO₂

CO₂

phase diagrams

solid ↔ gas equilibrium line (sublimation, deposition)




2 phases,
 $f=3-2=1$
 T and P covary

T's and P's
 for solid ↔ gas
 equilibrium

$$\left(\frac{dP}{dT}\right)_{eq} = \frac{\Delta\bar{H}_{\phi}}{T\Delta\bar{V}_{\phi}} \approx \frac{\Delta\bar{H}_{sub}}{RT^2}$$

CO₂

critical point and triple point

- Triple point: for a pure substance, there is only one point (value of T and P) where all three phases (solid, liquid, and gas) can simultaneously exist in equilibrium 
- Critical point: point (value of T and P) above which liquid and gas become one phase (fluid or supercritical fluid)



movie: benzene critical point  
A B

originally from: jchemed.chem.wisc.edu/jcesoft/cca/samples/cca2benzene.html

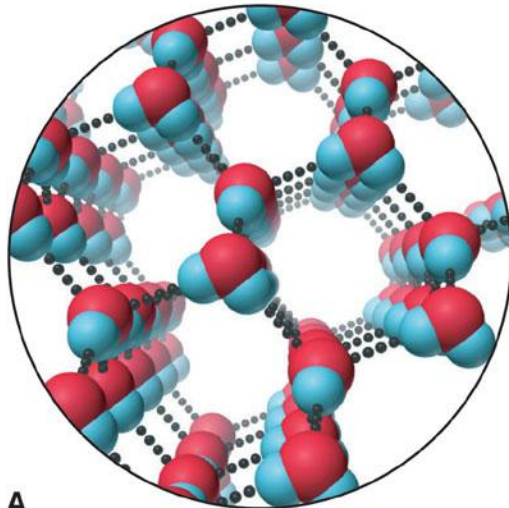
http://www.youtube.com/watch?v=79H2_QVBMGA



why does ice float ?

- H_2O is polar and can form hydrogen bonds (macho intermolecular forces)
- High surface tension and capillarity
- Hydrogen bonds form very open structure in solid H_2O (ice) giving ice a lower density than H_2O liquid. ICE FLOATS!!

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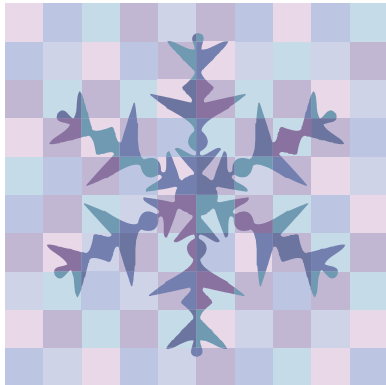


A



B

ice bomb !!!!



<http://www.ice.divched.org/JCESoft/CCA/pirelli/pages/cca2icebomb.html>

remember for CO₂ : P increases gas → liquid → solid

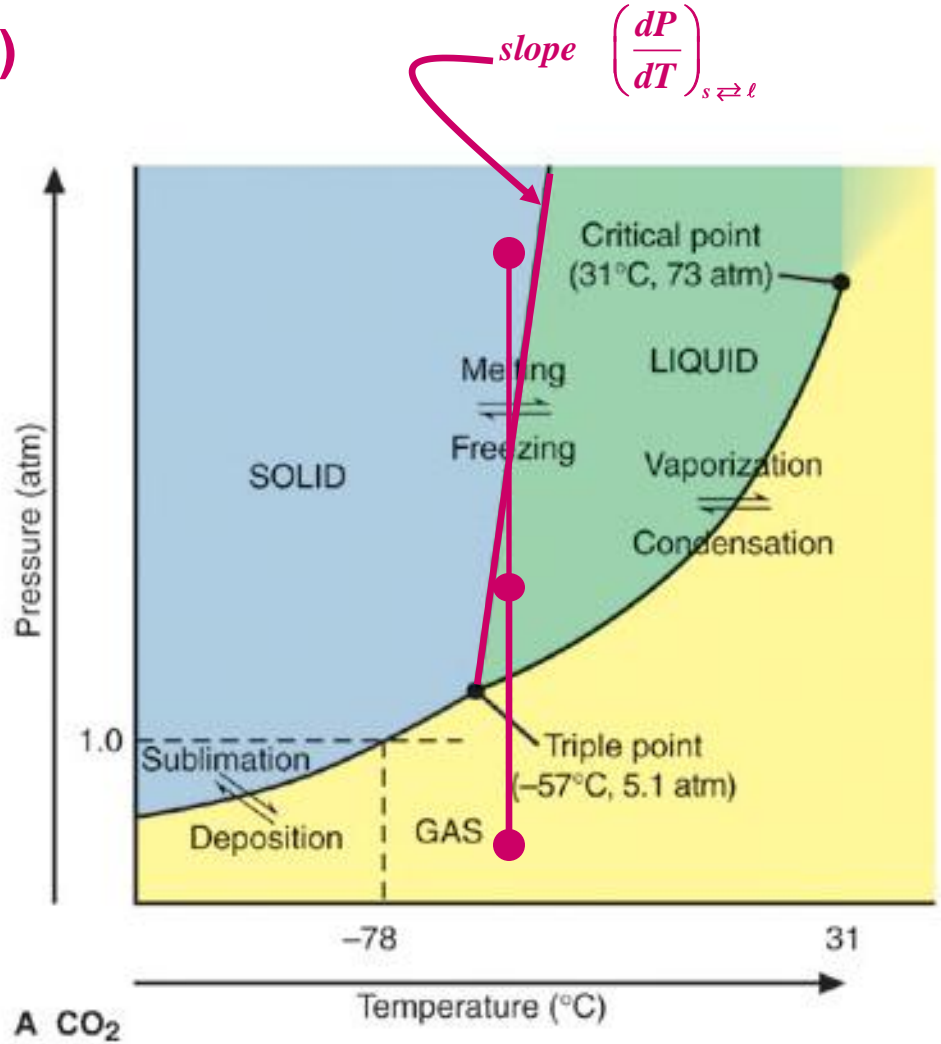


$$\left(\frac{dP}{dT}\right)_{s \rightleftharpoons l} = \frac{\Delta \bar{H}_{melt}}{T \Delta \bar{V}_{melt}};$$

$\Delta \bar{H}_{melt} > 0;$

$V_l > V_s \quad \Delta V > 0$

$$\Rightarrow \left(\frac{dP}{dT}\right)_{s \rightleftharpoons l} > 0$$



low P
gas

raise P
liquid
(more dense)

raise P more
solid
(most dense)

A CO₂

CO₂

phase diagram for water

remember for CO₂: P increases gas → liquid → solid

but for H₂O
as P increases:

gas



solid

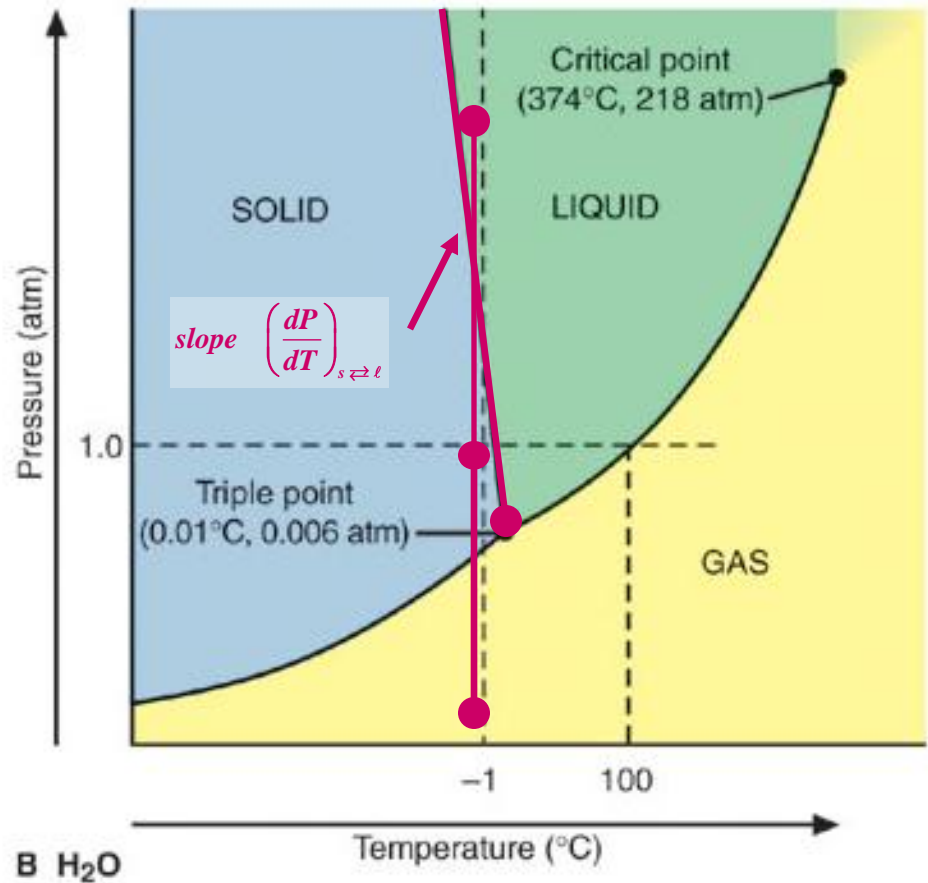


liquid

WHY?

$$\left(\frac{dP}{dT}\right)_{s \rightleftharpoons l} < 0$$

for ice ⇌ water



$$\left(\frac{dP}{dT}\right)_{s \rightleftharpoons l} = \frac{\Delta \bar{H}_{melt}}{T \Delta \bar{V}_{melt}} ; \Delta \bar{H}_{melt} > 0$$

$$V_s > V_l \quad \Delta V_{melt} < 0 \Rightarrow \left(\frac{dP}{dT}\right)_{s \rightleftharpoons l} < 0$$

H₂O

ice skater myth

Does the weight of an ice skater create a pressure that melts ice to form a liquid groove for skate?



$$\ln \frac{T_{melt}}{T_{1atm}} = \frac{(\bar{V}_\ell - \bar{V}_s)}{\Delta \bar{H}_{fusion}} (P - 1 atm)$$
$$(\bar{V}_\ell - \bar{V}_s) < 0 \Rightarrow \textit{pressure 'melts' ice}$$

E&R_(3rd) Problem P8.8

582 bar for -4°

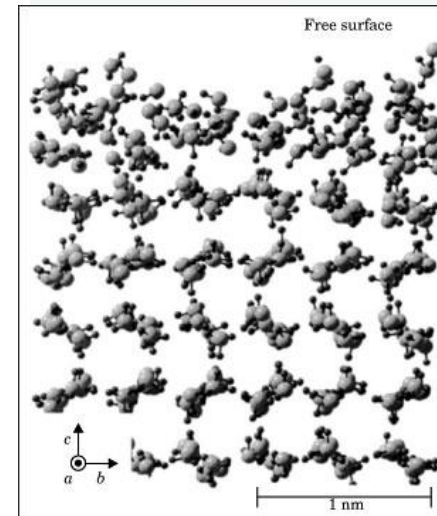
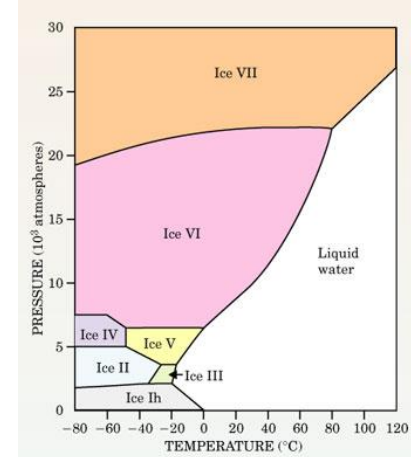
'thin blade'; 78kg \approx 172lb; -1.5°

NO, not even if they are quite 'weighty'!
(not enough pressure and further details of
water-ice phase diagram)

e.g. Rosenberg, Robert (December 2005). "Why is ice slippery?". [*Physics Today*](#): 50–54.

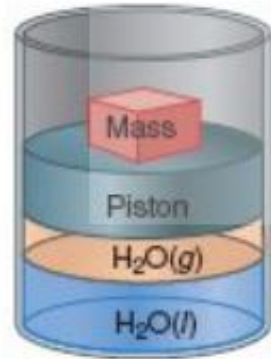


Figure 1. An [ice skater](#) exerts pressures on the order of a few hundred atmospheres on the ice surface, enough to reduce the melting temperature by only a few [degrees](#). Premelting—the development of a liquid-like surface layer at temperatures below freezing—and frictional heating of the ice as skaters move around must account for ice's slipperiness at the wide variety of [subzero](#) temperatures found in nature. (*Ice Skating*, by Hy Sandham, 1885, courtesy of the Library of Congress)

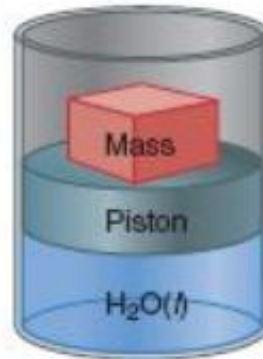


The nature of the liquid-like layer is not clear from experimental measurements, so theorists have tried to clarify the situation.

effects of inert gas (increased total pressure) on vapor pressure
E&R sec. 8.7



$P_{\text{external}} = 0.0316 \text{ bar}$
(b)



$P_{\text{external}} = 1.00 \text{ bar}$
(a)

pure H_2O
at 298K

$$P_{\text{H}_2\text{O}} = 0.0316 \text{ bar}$$

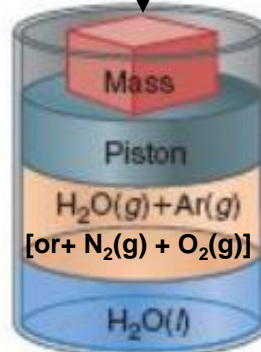
$$\left(\frac{\partial \mu_{\text{H}_2\text{O}}^{(\ell)}}{\partial P} \right)_T = \bar{V}_{\text{H}_2\text{O}}^{(\ell)}$$

$\mu_{\text{H}_2\text{O}}^{(\ell)}$ increases at P_{total} increase

$P_{\text{H}_2\text{O}(g)}$ must increase to restore $\mu^{(\ell)} = \mu^{(g)}$

$$RT \ln \left(\frac{P^{(g)}}{P^*} \right) = \int_{P^*}^{P_{\text{total}}} \bar{V}_{\text{H}_2\text{O}}^{(\ell)} dP$$

$P=1 \text{ bar}$

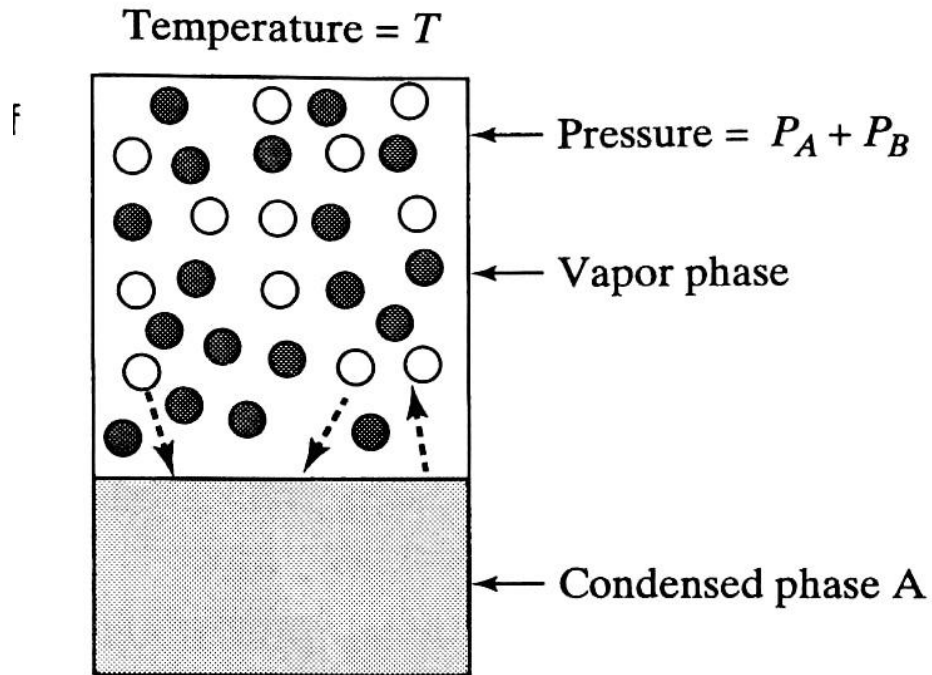


$P_{\text{external}} = 1.00 \text{ bar}$
(c)

'normal' H_2O in $P_{\text{total}}=1 \text{ bar}$
 $[\text{H}_2\text{O}(g) + \text{N}_2(g) + \text{O}_2(g)]$
at 298K

$$P_{\text{H}_2\text{O}} = 0.031622 \text{ bar}$$

E&R section 8.7 (effect of inert gas on vapor pressure)



H₂O at 300 K

$$P_{\text{H}_2\text{O}} = 0.328 \text{ atm}$$

add air (inert N₂ + O₂)
to raise $P_{\text{total}} = 1 \text{ atm}$

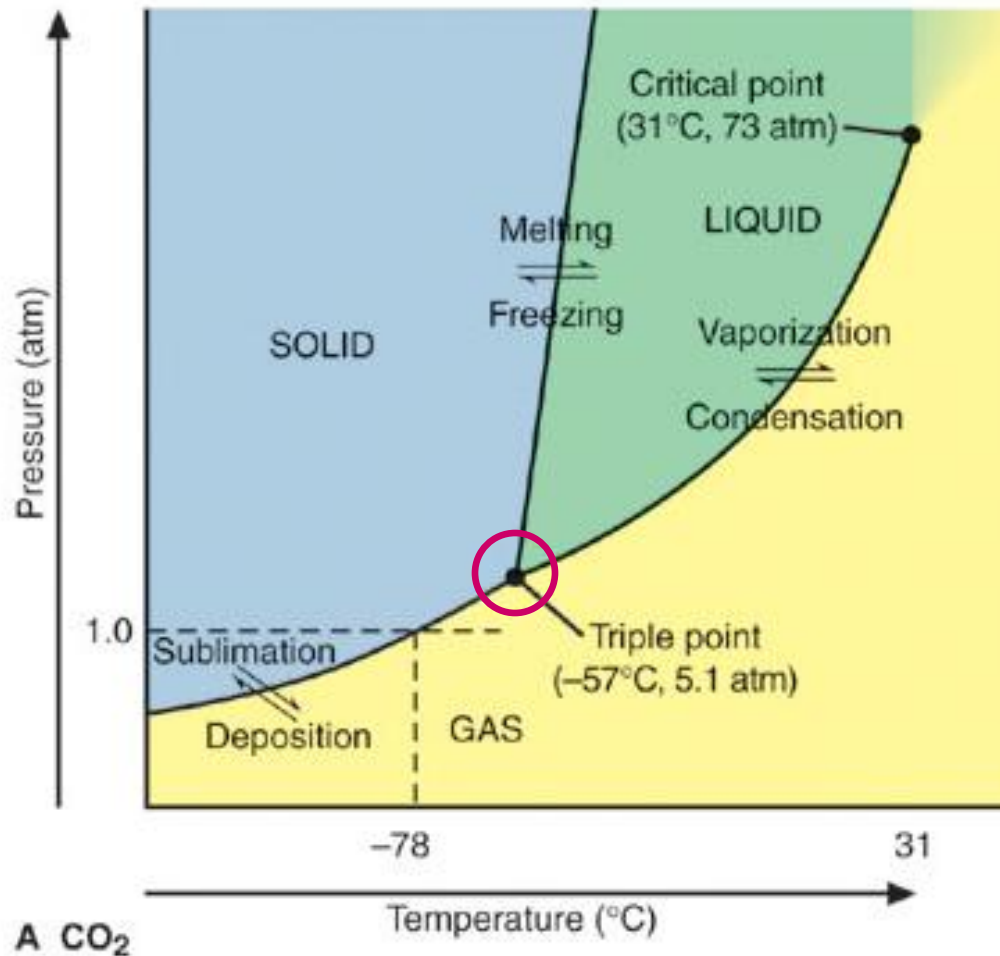
$$\text{new } P_{\text{H}_2\text{O}} = 0.32832 \text{ atm}$$

$$(P/P)_{\text{H}_2\text{O}} = 1.00071$$

End of Lecture

triple point

triple point: simultaneous equilibrium of gas, liquid solid



3 phases,
 $f=3-p$
 $f=3-3=0$
T and P fixed



vary T and P through critical point

