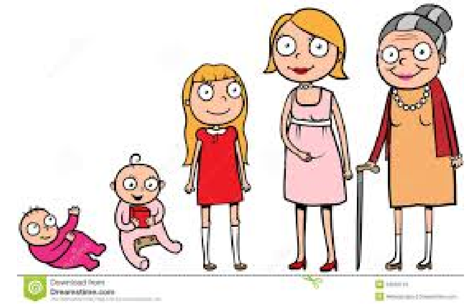
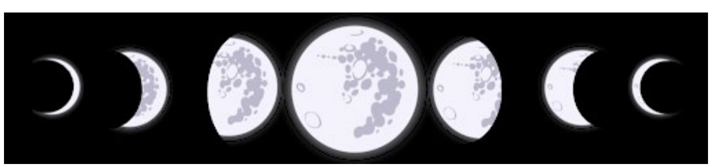
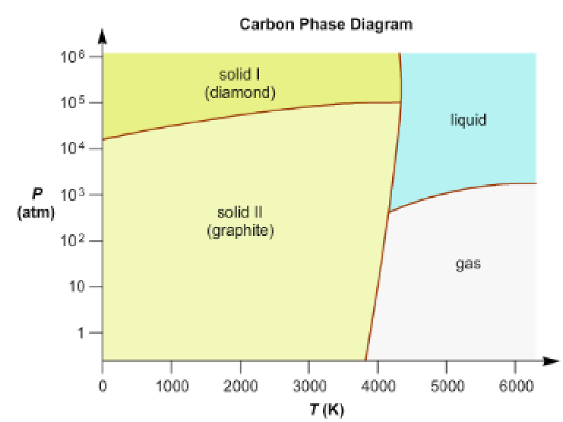


Lectures 18-19
Chemistry 163B

One-Component
Phase Diagram Basics





qualitative factors in phase changes

melting

solid ⇌ liquid

freezing/fusion

vaporization

liquid ⇌ gas

condensation

sublimation

solid ⇌ gas

deposition

ENDOTHERMIC

⇌

EXOTHERMIC

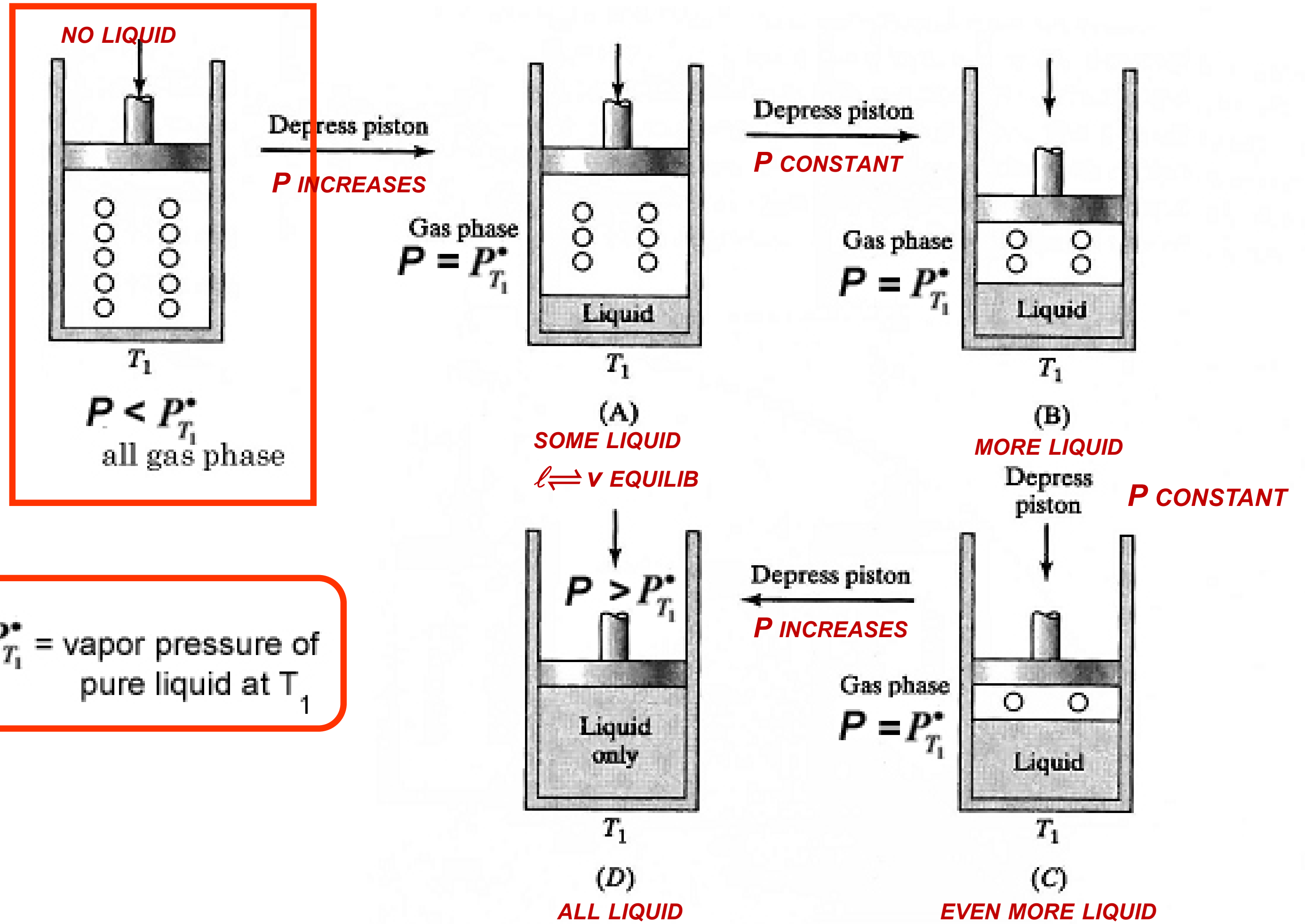
*vapor pressure over **PURE** liquid (notation)*

☑

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

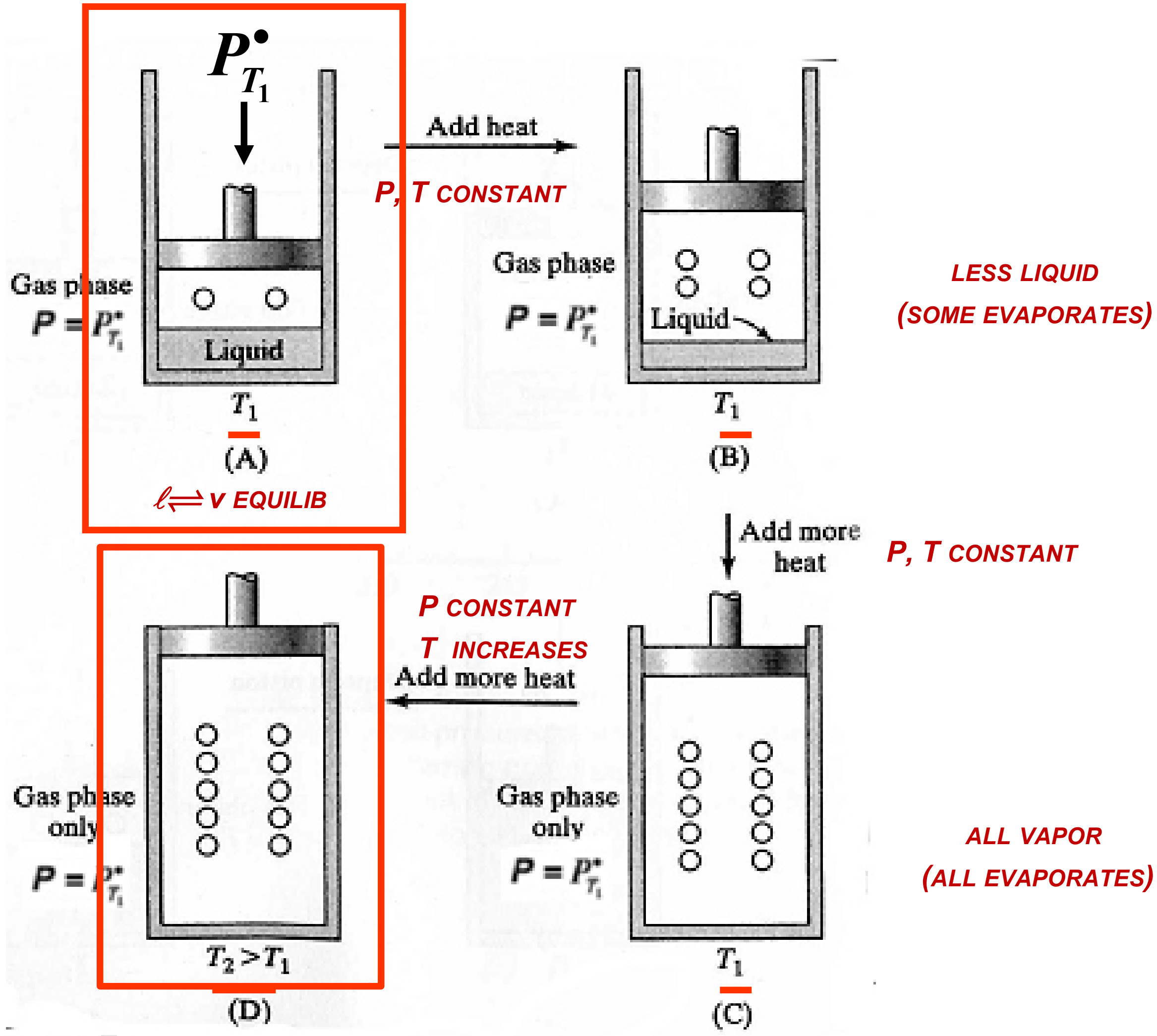
Gene	**E&R**	**Raff**
(many others)		

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

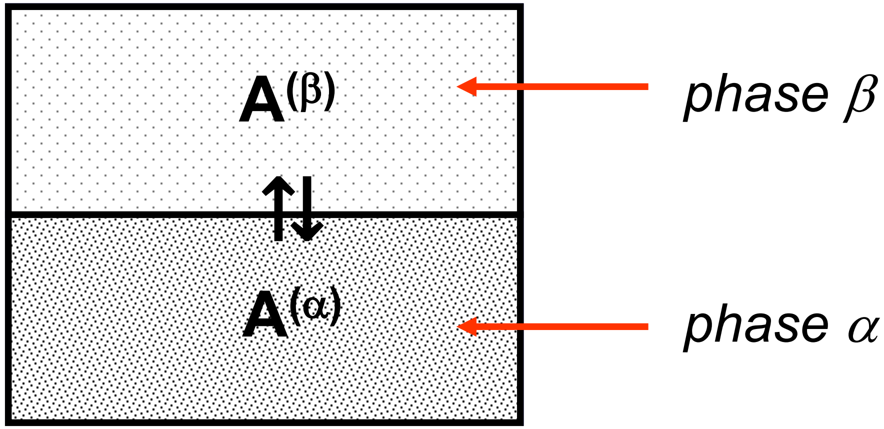


$P^{\bullet}_{T_1}$ = vapor pressure of pure liquid at T_1

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



dG for phase change at constant T,P *$X^{(y)}$ property X, phase y*



same T,P for each phase

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

one component 'A' in $phases\ \alpha\ and\ \beta\ constant\ T, P$

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

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

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

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 $dG_{T,P} < 0$

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

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

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

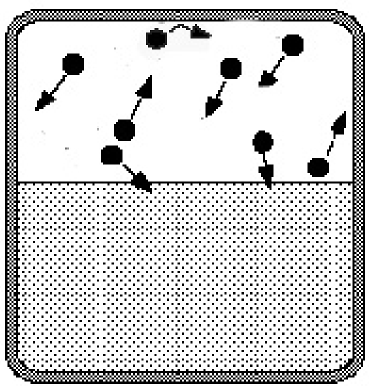
$\mu_A^{(\alpha)}$ is the **ESCAPING TENDENCY**
for molecules in phase α

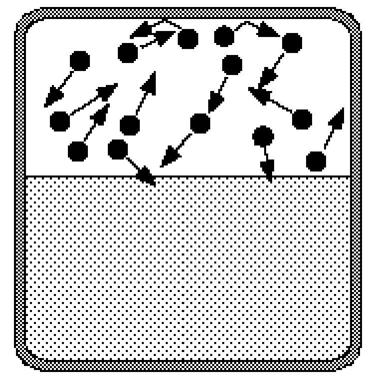
high $\mu \rightarrow$ low μ

hyper $\rightarrow$ *mellow*

Question:

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





T=298 K
$P^{\bullet}$=0.032 bar

T=473 K
$P^{\bullet}$=15.5 bar

https://www.engineeringtoolbox.com/water-vapor-saturation-pressure-d_599.html

https://www.engineeringtoolbox.com/water-properties-d_1573.html

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

A(α) ⇄ A(β)

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

How can P and T covary to maintain equilibrium?

$$\mu^{(\alpha)}(T_1, P_1) = \mu^{(\beta)}(T_1, P_1)$$

T and P covary $\quad d\mu^{(\alpha)} \downarrow \qquad \downarrow d\mu^{(\beta)} \quad$ *T and P covary*

$$\mu^{(\alpha)}(T_2, P_2) = \mu^{(\beta)}(T_2, P_2)$$

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

before $\qquad\qquad$ ***after***

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

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

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

with

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

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

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

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

phase equilibrium (one-component)

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

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

ϕ = phase change

eqn. 8.13 E&R_{4th}

since phase change is an equilibrium (reversible) process

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

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

I. application to liquid ⇄ gas (vapor) or solid ⇄ gas

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

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

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

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

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

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

I. application to liquid ⇄ gas (vapor) or solid ⇄ gas

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

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

Clausius-Clapeyron

≈ eqn. 8.19 E&R$_{4th}$

So just like 'before'

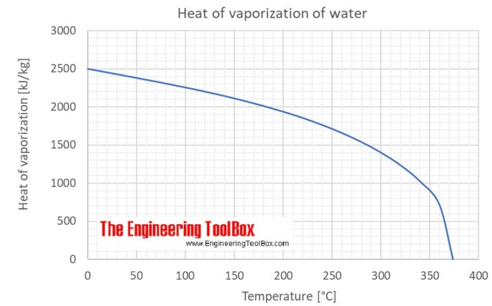
$$for\ s\ or\ \ell \rightleftarrows gas \quad K_P = \left(a_{gas}/a_{s,\ell}\right) \cong \left(P_{gas}/1\right)$$

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

midterm 2

I. application to liquid ⇄ gas (vapor) or solid ⇄ gas

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



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

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

E&R$_{4th}$ 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 $T^o_{boiling}$ and ΔH_{vap} :

$$at\ T_1 = T^o_{bp} \quad P_1 = P_{vapor} = 1\,atm$$

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

application to problems:

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

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

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

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

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

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

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

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

Denver: elev=1610 m P=0.822 atm

$$P < 1atm \quad ln\left(\frac{P_{atm}}{1\,atm}\right) < 0 \quad \Rightarrow \quad \left[\frac{T_{bp}}{T^{\circ}_{bp}}\right] < 1 \quad \Rightarrow \quad T_{bp} < T^{\circ}_{bp}$$

Death Valley: elev =-82.5 m, P=1.010atm

$$P > 1atm \quad ln\left(\frac{P_{atm}}{1\,atm}\right) > 0 \quad \Rightarrow \quad \left[\frac{T_{bp}}{T^{\circ}_{bp}}\right] > 1 \quad \Rightarrow \quad T_{bp} > T^{\circ}_{bp}$$

Denver vs Death Valley

$$\left[\frac{T_{bp}}{T^\circ_{bp}}\right] = \frac{1}{\left[1 - \frac{RT^\circ_{bp}}{\Delta\bar{H}_{vap}} ln\left(\frac{P_{atm}}{1\,atm}\right)\right]}$$

$$\left[\frac{T_{bp}}{373}\right] = \frac{1}{\left[1 - \frac{(8.3245\, J\, K^{-1} mol^{-1})(373K)}{40.65\times 10^{3}\, J\, mol^{-1}} ln\left(\frac{P_{atm}}{1\,atm}\right)\right]} = \frac{1}{\left[1 - .0763\, ln\left(\frac{P_{atm}}{1\,atm}\right)\right]}$$

Denver: elev 1610m P=.822 atm T_{bp}=367.5K

Sea level: elev 0m P=1.00 atm T_{bp}=373 K

Death Valley : elev -82.5m P=1.01 atm T_{bp}=373.28K

II. application to solid ⇄ liquid

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

$T^o_{melting}$ *for phase equilibrium at* $P = 1\ atm$

what is $T_{melting}$ *at other pressures?*

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

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

will increased pressure raise or lower $T_{melting}$?

$\Delta H_{melting} > 0$

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

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

phase rule one-component system (save proof for later; f=c-p+2, c=1)

f= degrees of freedom

p=phases simultaneously present

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

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

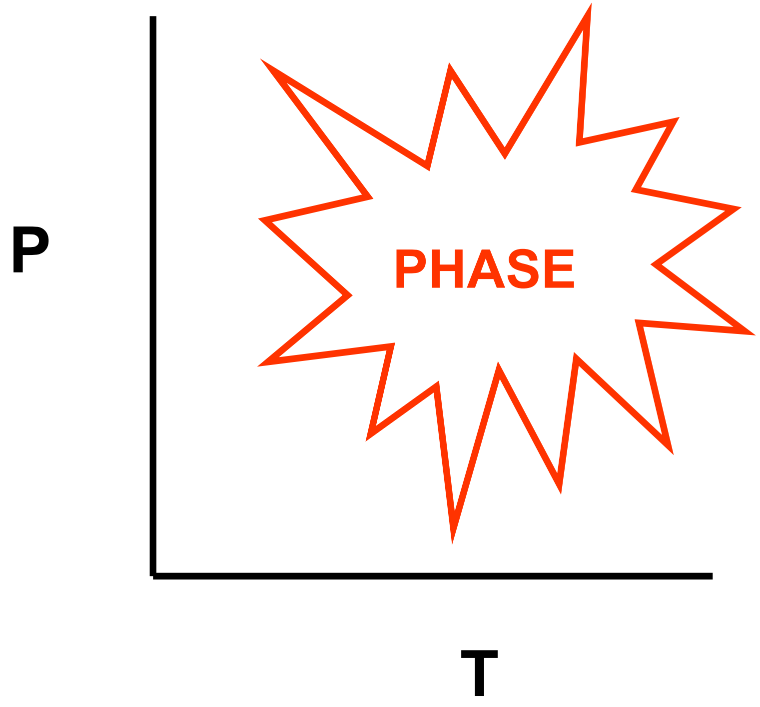
f: degrees of freedom = (variables-restrictions)

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

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

HW7 #45 (phase diagram but note log P axis scaling)

45. E&R4th P8.1

Within what range can you restrict the values of P and T if the following information is known about CO_2? Use Figure 8.12 to answer this question.

NOTE: The critical point is at T_c=31.1°C and P_c= 72.8 atm.

a. As the temperature is increased, the solid is first converted to the liquid and subsequently to the gaseous state.

b. As pressure on a cylinder containing pure CO_2 is increased from **5** to 80. atm, no interface delineating liquid and gaseous phases is observed. *(note the 5 atm here differs from E&R4th USE THIS VALUE, it makes more sense)*

c. Solid, liquid, and gas phases coexist at equilibrium.

d. An increase in pressure from 10. to 50. atm converts the liquid to the solid.

e. An increase in temperature from -80.° to 20.°C converts a solid to a gas with no intermediate liquid phase.

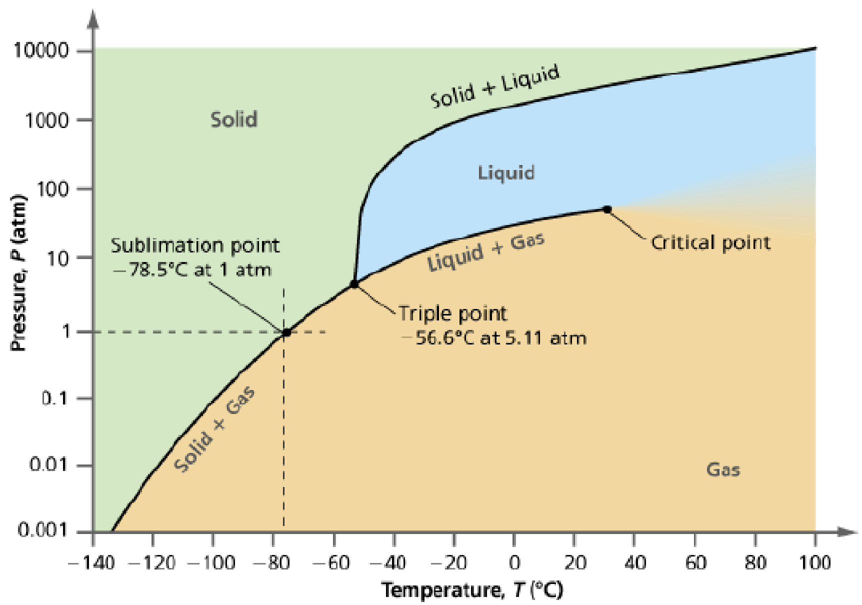
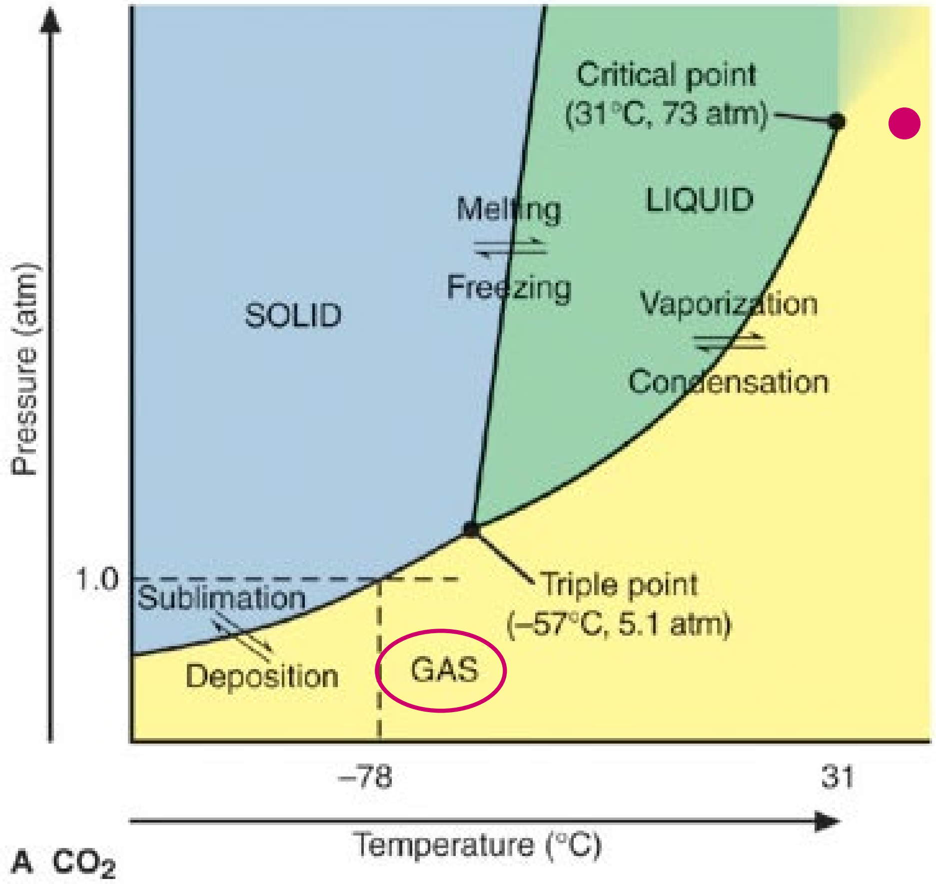


Figure 8.12 The P–T phase diagram for CO2

"state" or "phase" as a function of P, T



high T

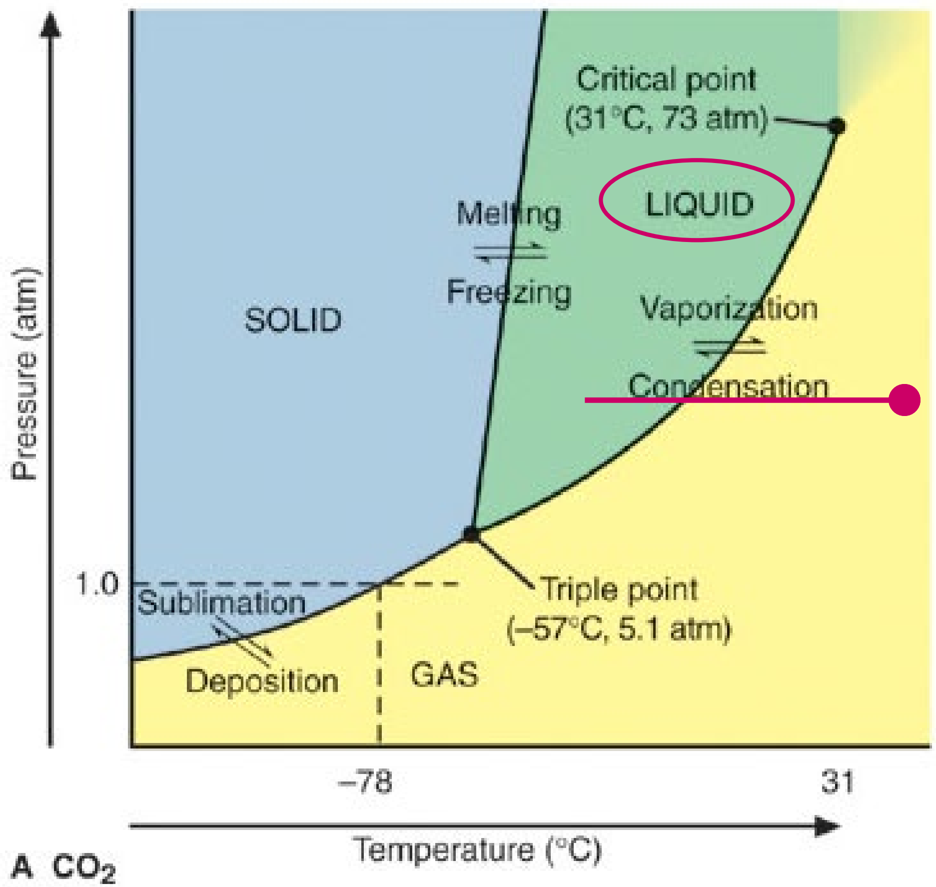
gas

1 phase, f=2

vary both T,P

CO_2

"state" or "phase" as a function of P, T



lower T

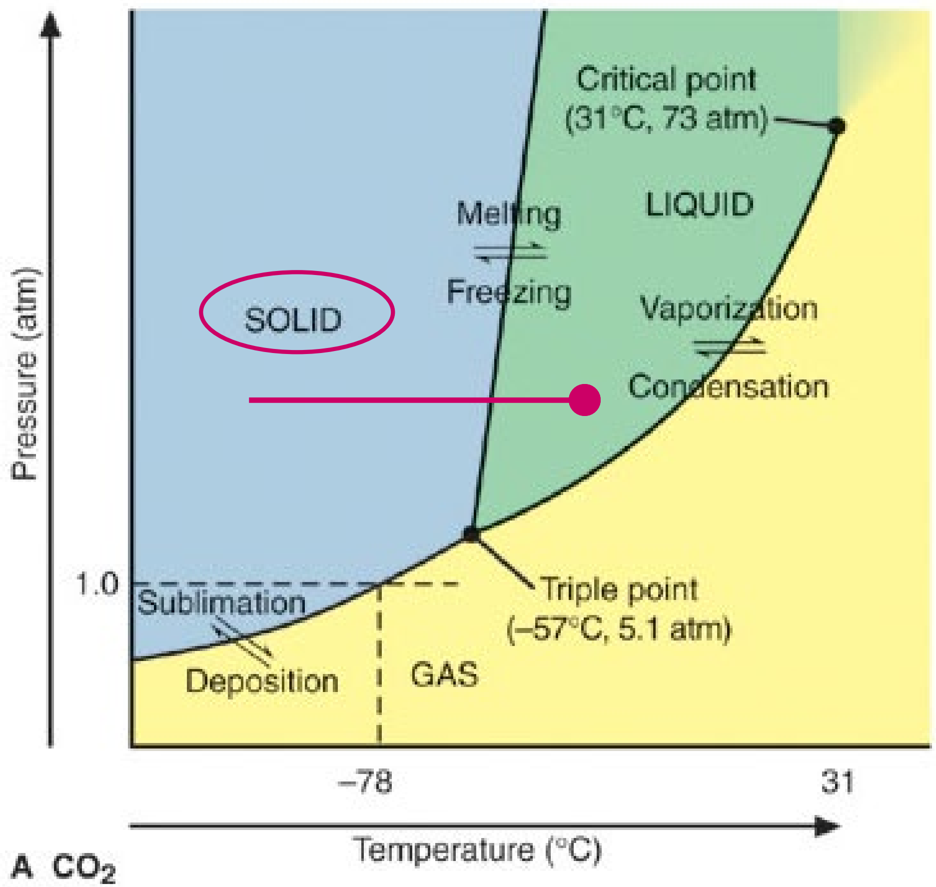
liquid

1 phase, f=2

vary both T,P

CO_2

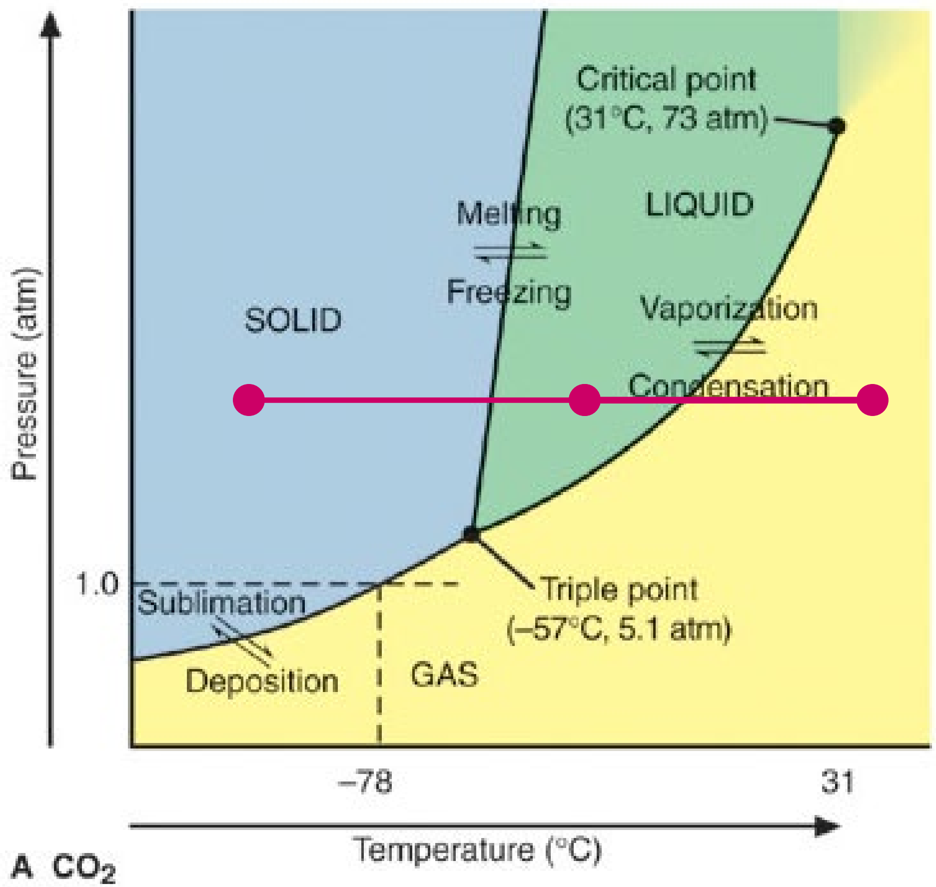
"state" or "phase" as a function of P, T



lower T more solid

CO_2

"state" or "phase" as a function of P, T



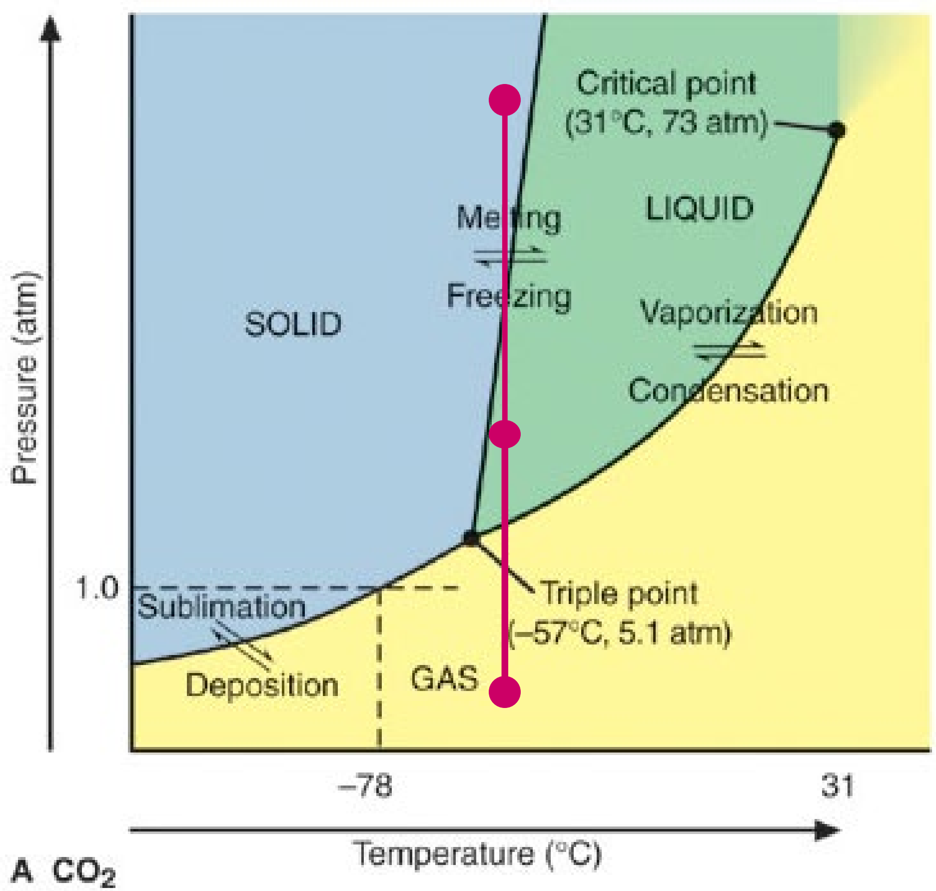
high T
gas

lower T
liquid

lower T more
solid

CO_2

"state" or "phase" as a function of P, T



low P gas

raise P liquid

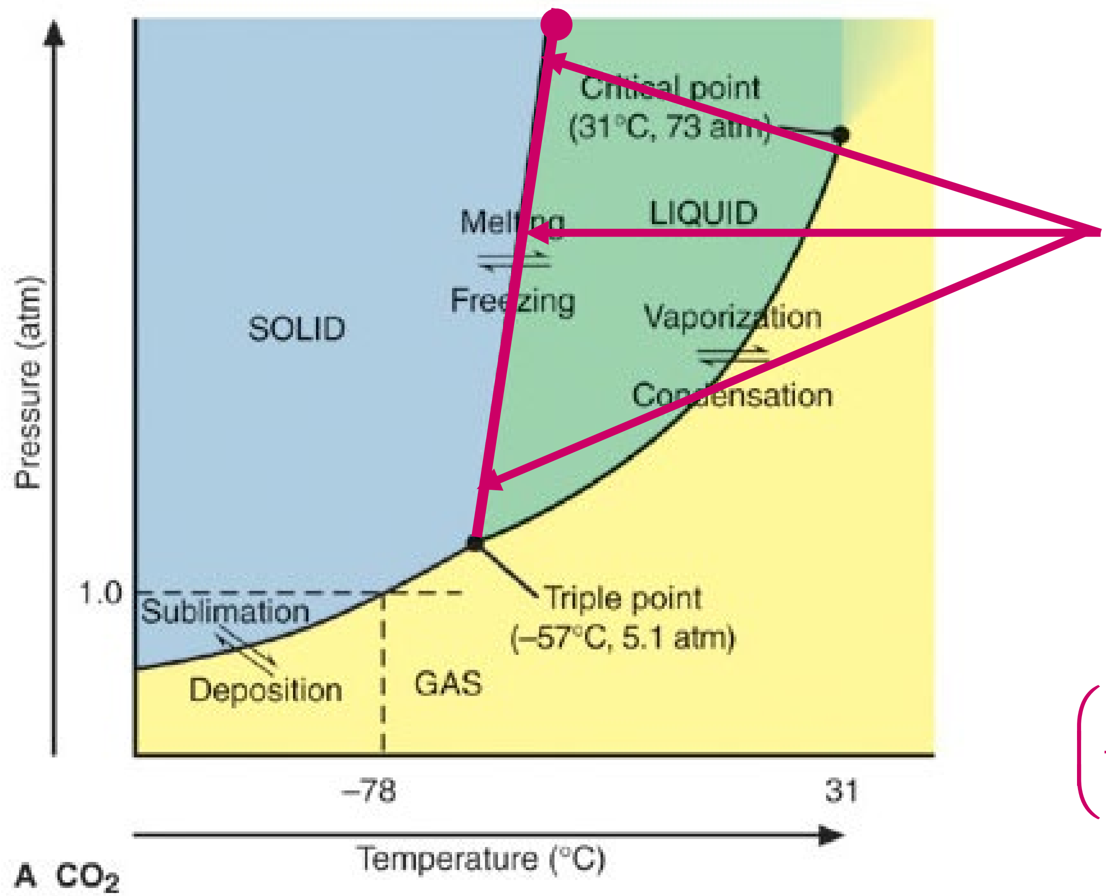
raise P more solid

CO_2

f=3-p =1

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

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



CO_2

T's and P's

for liquid↔solid equilibrium

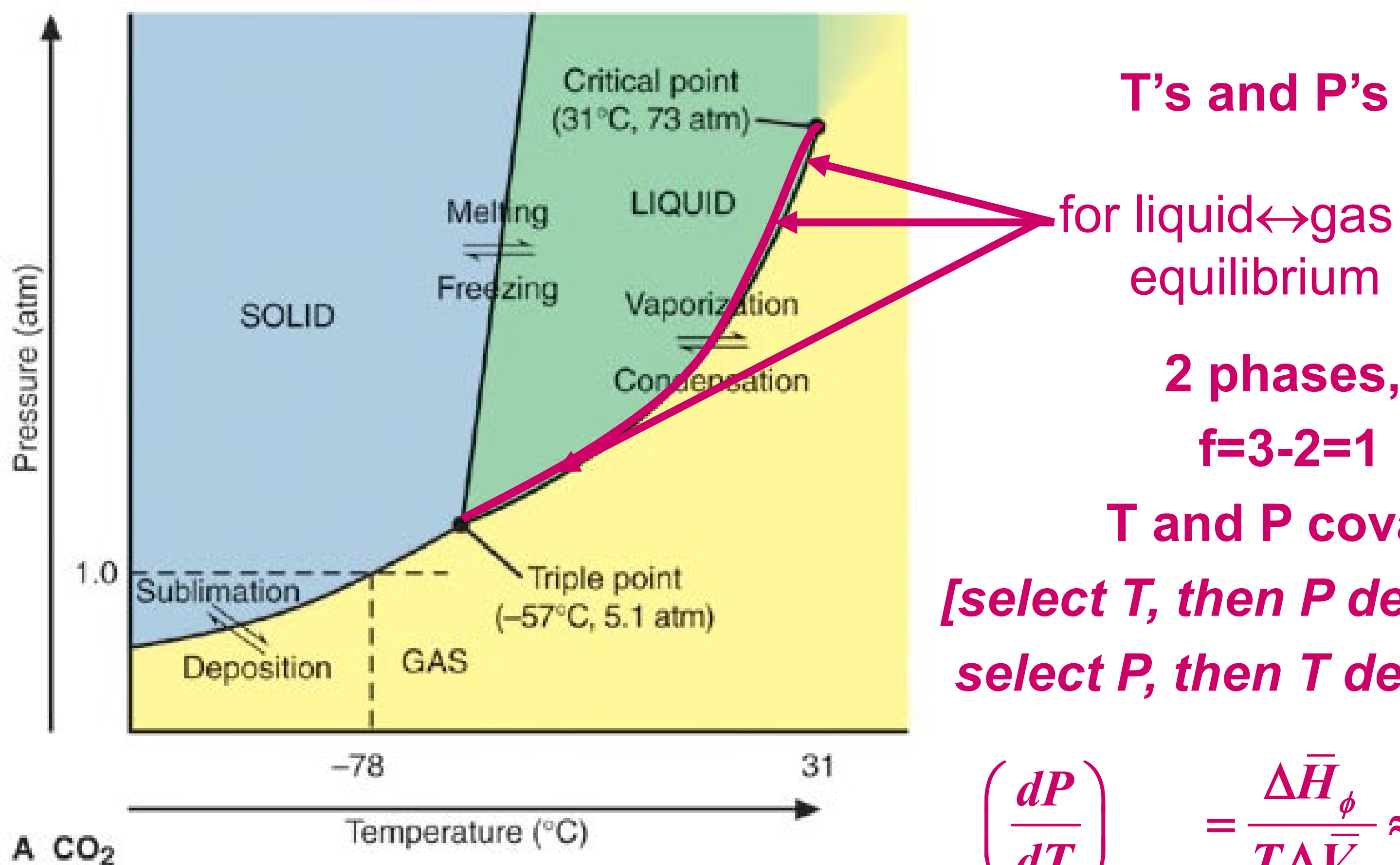
2 phases,

f=3-2=1

T and P covary

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

liquid ↔ gas equilibrium line (vaporization, condensation)



CO_2

T's and P's

for liquid↔gas equilibrium

2 phases,

f=3-2=1

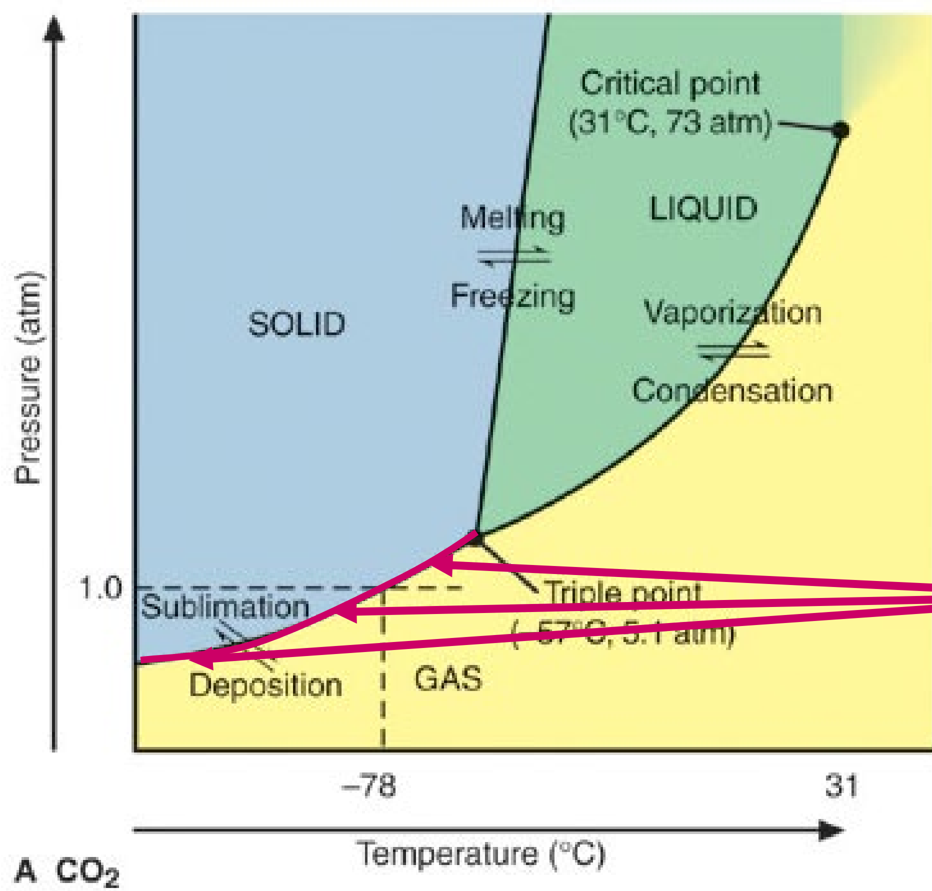
T and P covary

[select T, then P determined

select P, then T determined]

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

solid ↔ gas equilibrium line (sublimation, deposition)



CO_2

2 phases,

f=3-2=1

T and P covary

T's and P's

for solid↔gas equilibrium

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

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)

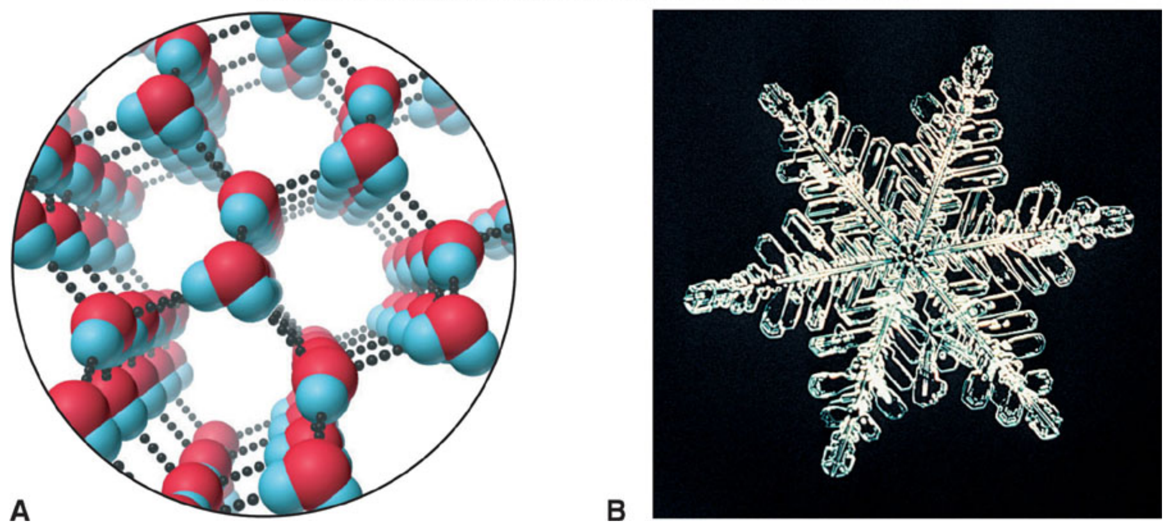
movie: benzene critical point A B

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

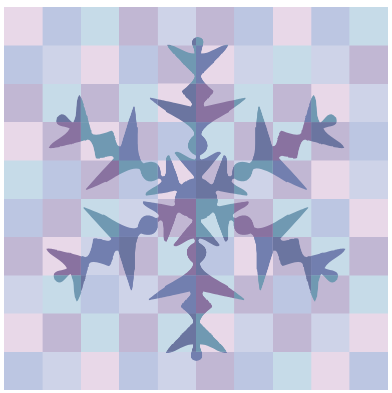
http://www.youtube.com/watch?v=79H2_QVBMGA

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!!



ice bomb !!!!



Originally at
http://www.jce.divched.org/JCESoft/CCA/pirelli/pages/cca2icebomb.html

remember for CO_2 : P increases gas → liquid → solid

$CO_2(s) \rightleftarrows CO_2(\ell)$

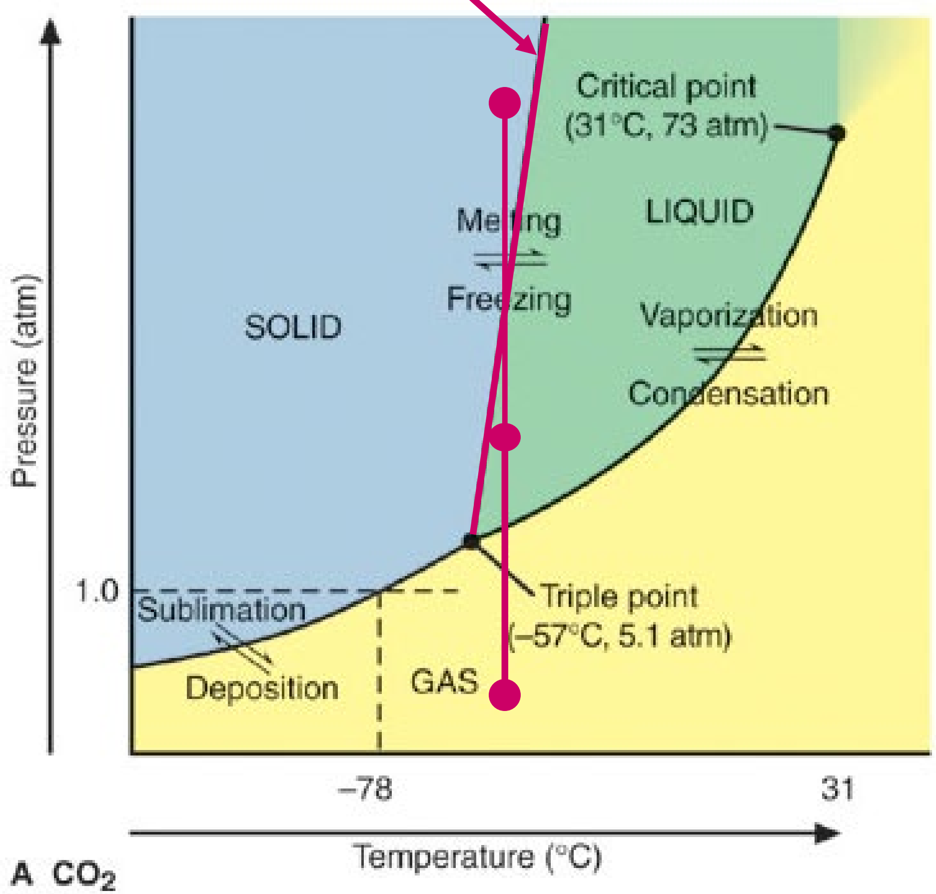
$$\left(\frac{dP}{dT}\right)_{s\rightleftarrows\ell} = \frac{\Delta\bar{H}_{melt}}{T\Delta\bar{V}_{melt}};$$

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

$$V_\ell > V_s \quad \Delta V > 0$$

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

slope $\left(\frac{dP}{dT}\right)_{s\rightleftarrows\ell}$



low P gas

raise P liquid (more dense)

raise P more solid (most dense)

CO_2

phase diagram for water

remember for CO_{2} : P increases gas → liquid → solid

but for H_2O

as P increases:

gas

↓

solid

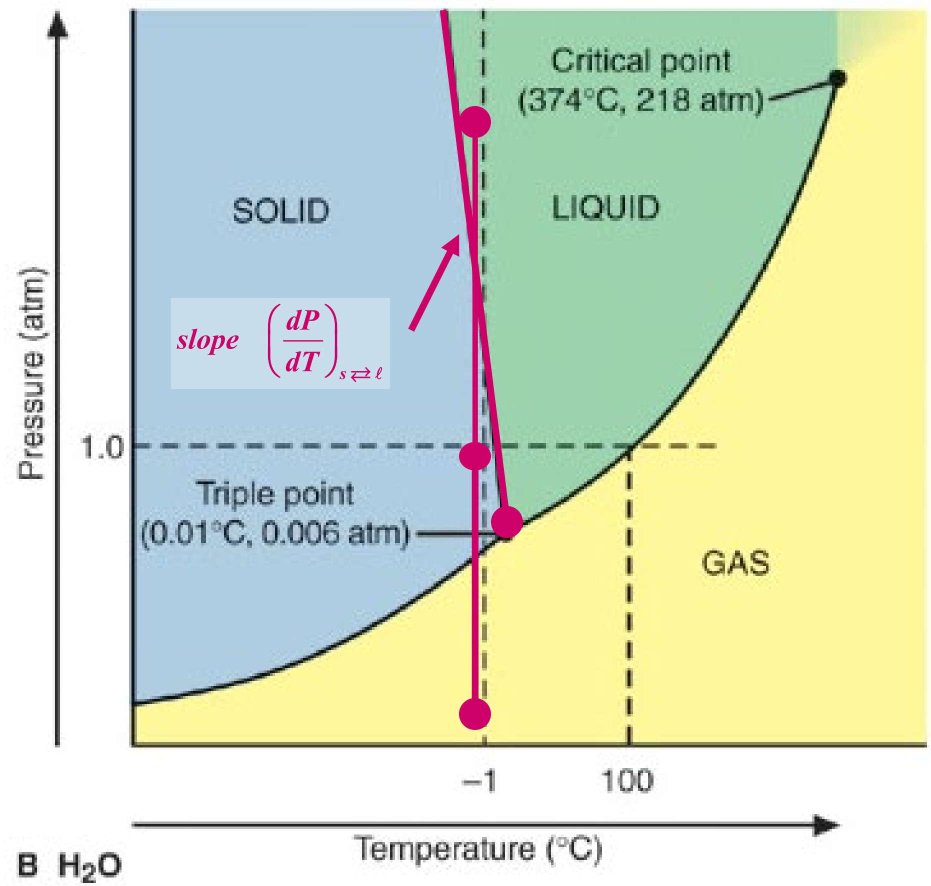
↓

liquid

WHY?

$$\left(\frac{dP}{dT}\right)_{s \rightleftarrows \ell} < 0$$

for ice ⇌ water



H_2O

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

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

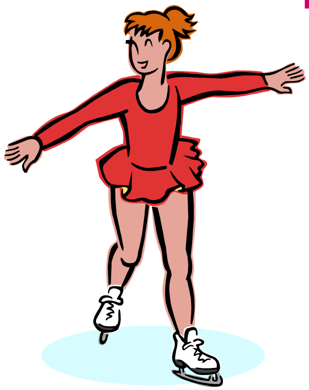
ice skater myth

(ice skater real; Kristi Yamaguchi)

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

$$\ln \frac{T_{melt}}{T_{1atm}} = \frac{\left(\bar{V}_\ell - \bar{V}_s\right)}{\Delta \bar{H}_{fusion}} \left(P - 1\,atm\right)$$

$$\left(\bar{V}_\ell - \bar{V}_s\right) < 0 \Rightarrow pressure\ 'melts'\ ice$$



E&R$_{(4^{th})}$ Problem P8.3

508 bar for ΔT=-3.5º

'thin blade'; 78kg≈172lb;

$P_{thin\ blade}$=243 bar; ΔT= -1.67º

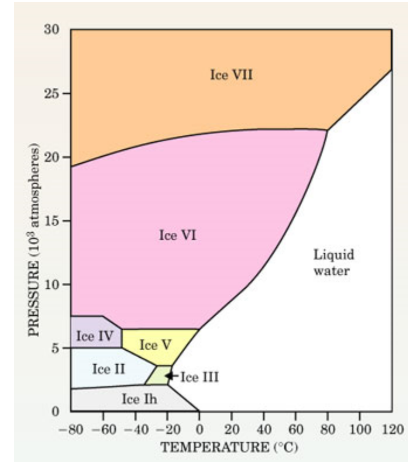
NO, not even if they are quite 'weighty' !

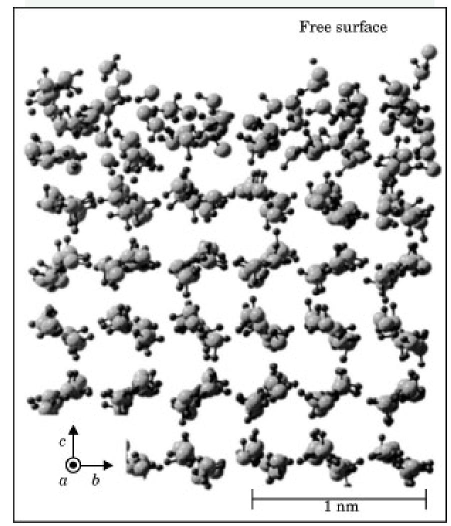
(not enough pressure and further details of water-ice phase diagram)

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

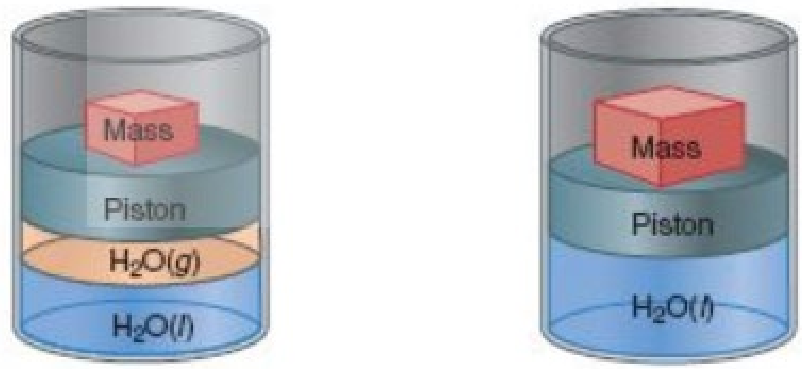
Rosenberg, Robert (December 2005). "Why is ice slippery?". Physics Today: 50–54.

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.



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

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

pure H_2O
at 298K

$P^\bullet_{H20}$= 0.0316 bar

$$\left(\frac{\partial \mu^{(\ell)}_{H_2O}}{\partial P}\right)_T = \overline{V}^{(\ell)}_{H_2O}$$

$$\Downarrow$$

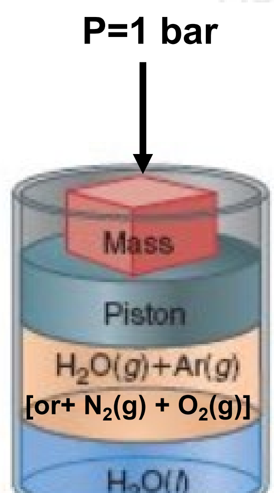
$\mu^{(\ell)}_{H_2O}$ increases at P_{total} increase

$$\Downarrow$$

$P_{H_2O(g)}$ must increase to restore $\mu^{(\ell)} = \mu^{(g)}$

$$\Downarrow$$

$$RT\ln\left(\frac{P^{(g)}}{P^\bullet}\right) = \int_{P^\bullet}^{P_{total}} \overline{V}^{(\ell)}_{H_2O}\, dP$$

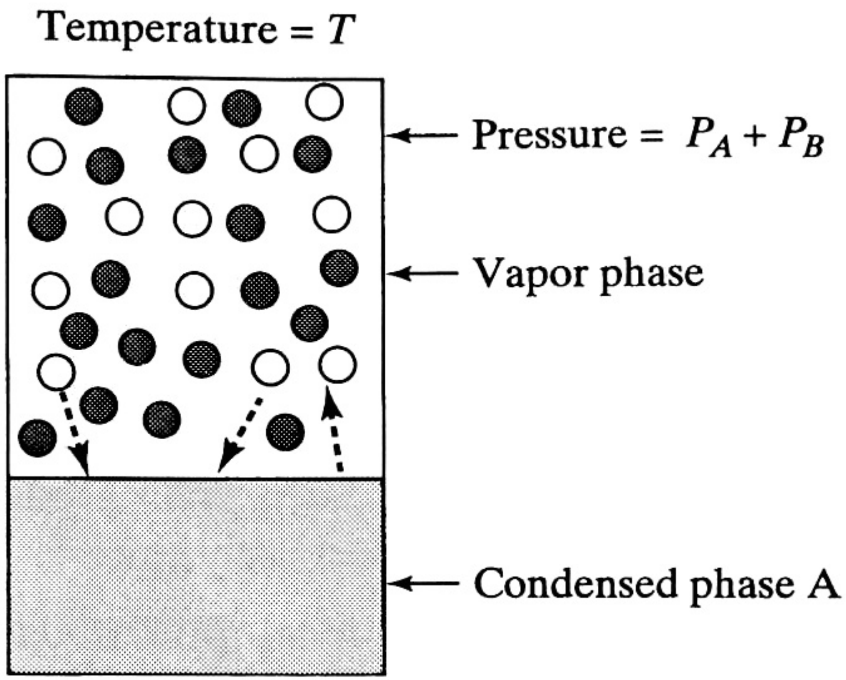


$P_{external}$ = 1.00 bar
(c)

'normal' H_2O in P_{total}=1 bar
[H_2O (g) + N_2(g) + O_2(g)]
at 298K

P_{H20}= 0.031622 bar

$E\&R_{4th}$ section 8.7 (effect of inert gas on vapor pressure)



H_2O at 300 K

$P^{\bullet}{}_{H20}$= 0.328 atm

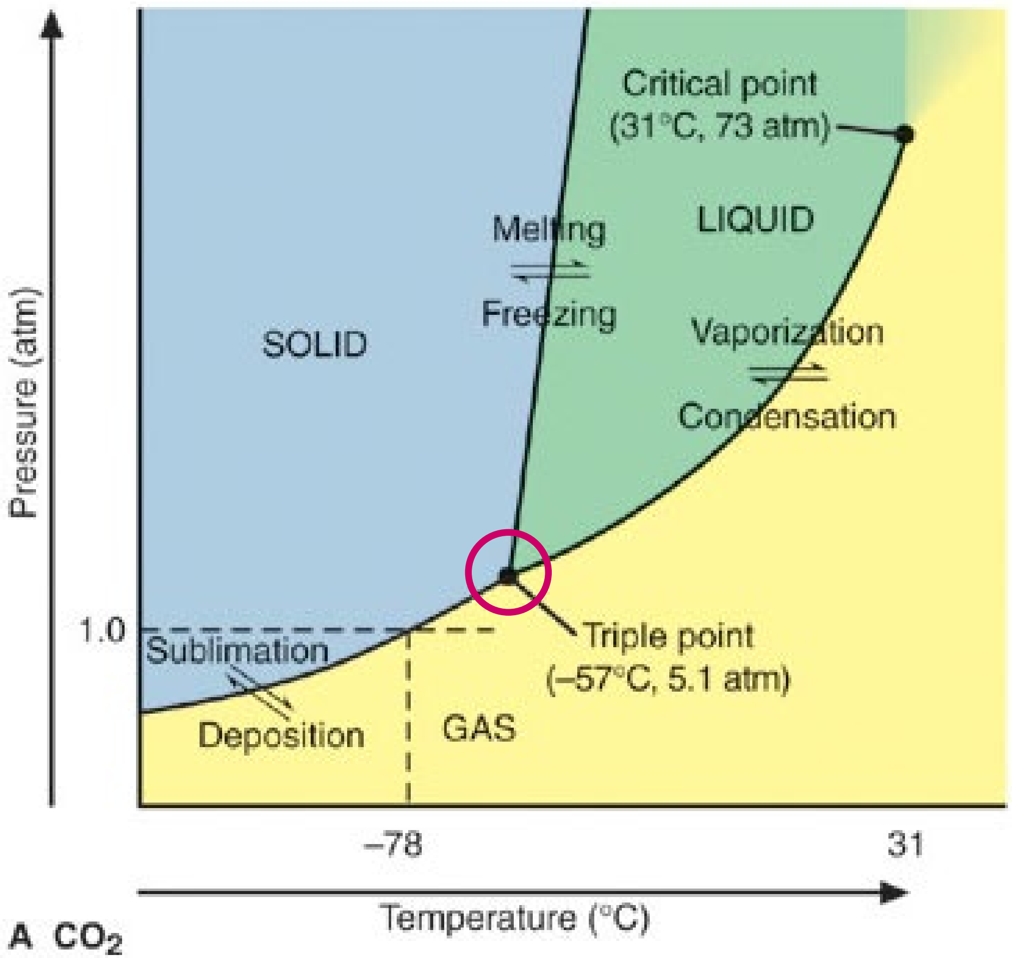
add air (inert N_2 + O_2)
to raise P_{total}=1 atm

new P_{H20}= 0.32832 atm

$(P/P^{\bullet})_{H20}$=1.00071

End of Lecture

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