Chemistry 163B

One-Component

Phase Diagram Basics

1

qualitative factors in phase changes

melting

solid ⇄ liquid

freezing/fusion

vaporization

liquid ⇄ gas

condensation

sublimation

solid ⇄ gas

deposition

ENDOTHERMIC

⇄

EXOTHERMIC

2

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

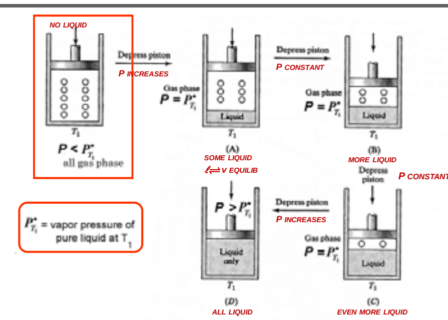
☑

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

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

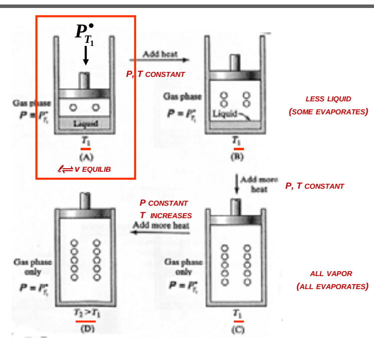
3

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



4

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



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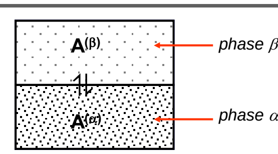
dG for phase change at constant T,P



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***

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

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

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

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Chemistry 163B, Winter 2014

Lectures 18-19 Introduction to Phase Diagrams

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 $dG_{T,P} < 0$

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

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

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

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

high $\mu \longrightarrow$ low μ

hyper $\longrightarrow$ mellow

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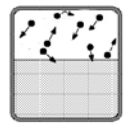
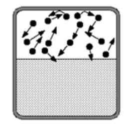
Question:

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





T=298 K
P =0.032 bar

T=473 K
P =15.5 bar

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

$$A(\alpha) \rightleftarrows A(\beta)$$

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

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

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

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

before **after**

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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

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

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

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

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

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phase equilibrium (one-component)

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

$\left(\frac{\partial T}{\partial P}\right)_{\Delta G=0} = \frac{\Delta V}{\Delta S}$ (midterm #2 prob 4b)

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

ϕ = phase change

eqn. 8.13 E&R

since phase change is an equilibrium (reversible) process

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

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

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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 $\Delta\bar{V}_\phi = \bar{V}_{vapor} = \frac{RT}{P}$

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

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

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Chemistry 163B, Winter 2014
Lectures 18-19 Introduction to Phase Diagrams

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

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

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

Clausius-Clapeyron ≈ eqn. 8.19 E&R

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

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

for s or ℓ ⇄ gas $K_P = P_{gas}$

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

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

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

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 $T^o_{boiling}$ and ΔH_{vap} :

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

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

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

application to problems:

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

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

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

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

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

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

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

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

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

Denver: elev=1610m P=0.822 atm

$$P < 1atm \quad \Rightarrow \quad \left[\frac{T_{bp}}{T^\circ_{bp}}\right] < 1 \quad \Rightarrow \quad T_{bp} < T^\circ_{bp}$$

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

$$P > 1atm \quad \Rightarrow \quad \left[\frac{T_{bp}}{T^\circ_{bp}}\right] > 1 \quad \Rightarrow \quad T_{bp} > T^\circ_{bp}$$

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= degrees of freedom
p=phases simultaneously present

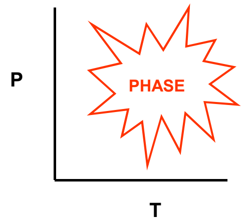
2 variables : T, P (same for each phase)
p-1 restrictions: $\mu^{(\alpha)} = \mu^{(\beta)} = \mu^{(\gamma)} = \ldots$

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

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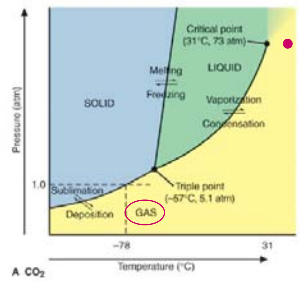
phase diagrams (f=3-p)

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



high T

gas

1 phase, f=2
vary both T,P

CO_2

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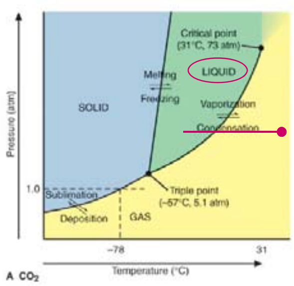
phase diagrams (f=3-p)

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



lower T

liquid

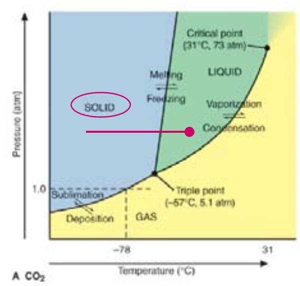
1 phase, f=2
vary both T,P

CO_2

21

phase diagrams (f=3-p)

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



lower T more

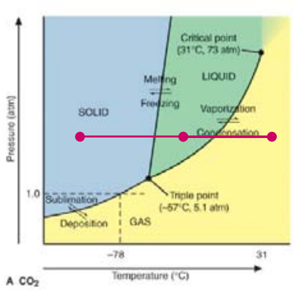
solid

CO_2

22

phase diagrams (f=3-p)

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



high T
gas

lower T
liquid

lower T more
solid

CO_2

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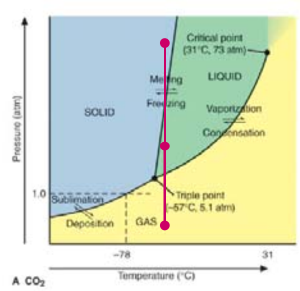
phase diagrams (f=3-p)

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



low P
gas

raise P
liquid

raise P more
solid

CO_2

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two-phase equilibrium (p=2)

f=3-p =1

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

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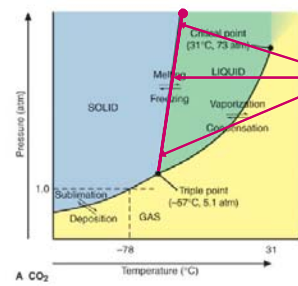
phase diagrams (f=3-p)

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

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

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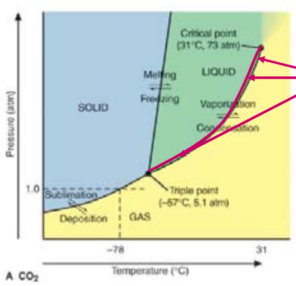
phase diagrams (f=3-p)

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]

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

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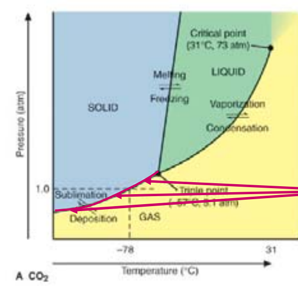
phase diagrams

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

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

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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

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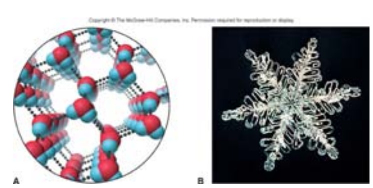
why does ice float ?

- H_20 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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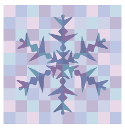
ice bomb !!!!



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

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remember for CO_2 : P increases gas → liquid → solid

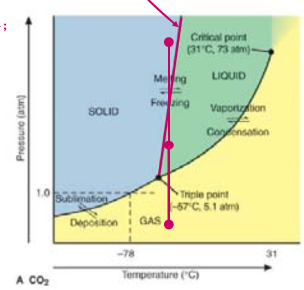
$CO_2(s) \rightarrow CO_2(\ell)$

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

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

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

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



CO_2

low P
gas

raise P
liquid
(more dense)

raise P more
solid
(most dense)

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phase diagram for water

remember for CO_2 : P increases gas → liquid → solid

but for H_2O as P increases:

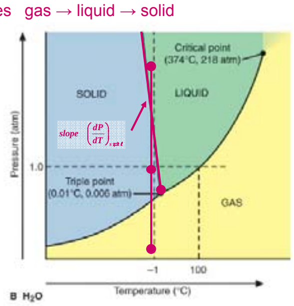
gas
↓
solid
↓
liquid

WHY?

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

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

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



H_2O

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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≈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.

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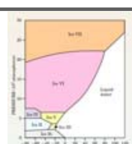
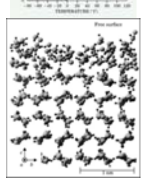
Rosenberg, Robert (December 2005). "Why is ice slippery?". Physics Today: 50–54.

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.

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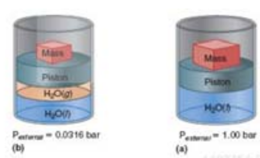
effects of inert gas (increased total pressure) on vapor pressure E&R sec. 8.7



pure H_2O at 298K

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

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

⇓

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

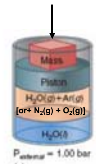
⇓

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

⇓

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

P=1 bar



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

P_{H20}= 0.031622 bar

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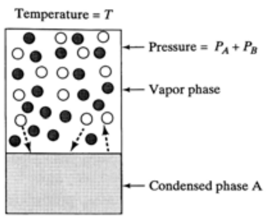
E&R section 8.7 (effect of inert gas on vapor pressure)



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

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End of Lecture

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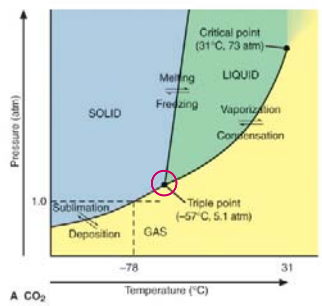
triple point

triple point: simultaneous equilibrium of gas, liquid solid



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

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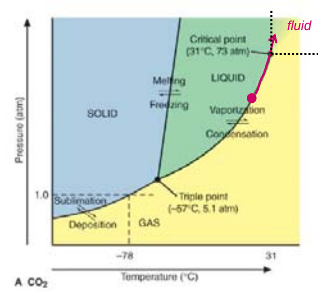
vary T and P through critical point



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