Slide 1

Lectures 18-19
Chemistry 163B

One-Component
Phase Diagram Basics

Slide 2

qualitative factors in phase changes

solid ⇌ liquid — *melting* / *freezing/fusion*

liquid ⇌ gas — *vaporization* / *condensation*   **ENDOTHERMIC** / **EXOTHERMIC**

solid ⇌ gas — *sublimation* / *deposition*

Slide 3
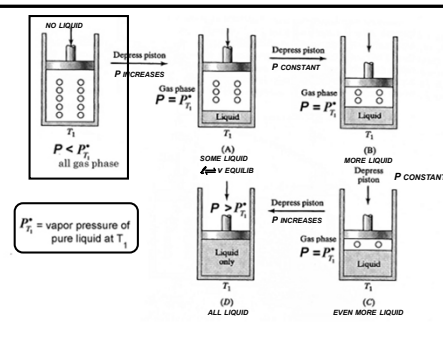
vapor pressure over PURE liquid (notation)

☑

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

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

Slide 4
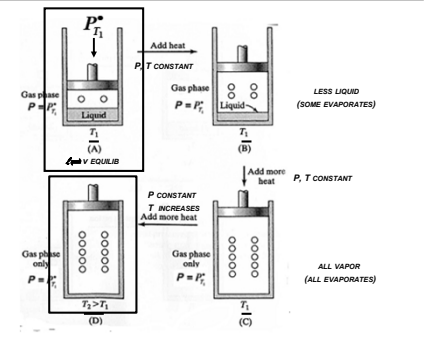
gas ⇌ liquid as pressure increases (vary P, const T)

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

Slide 5
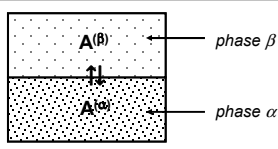
liquid ⇌ vapor as heat added   (vary T, const P)

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

phase β

phase α

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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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**

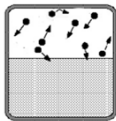$\mu_A^{(\beta)} > \mu_A^{(\alpha)} \;\Rightarrow\; dn_A^{(\alpha)} > 0$ **molecules gained by phase α**

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

high $\mu \rightarrow$ low μ
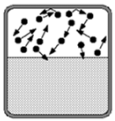
hyper $\rightarrow$ mellow

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Slide 8

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(α) $\rightleftarrows$ A(β)

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

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

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

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

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)

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

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

$\phi = $ *phase change*

eqn. 8.13 E&R$_{4th}$

since phase change is an equilibrium (reversible) process

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

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

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

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

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

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

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

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

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

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

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

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

Clausius-Clapeyron
≈ eqn. 8.19 E&R$_{4th}$

So just like 'before'

$$for \ s \ or \ l \rightleftarrows gas \quad K_P = \left(a_{gas}/a_{s,l}\right) \cong \left(P_{gas}/1\right)$$
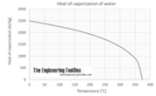
$$\left(\frac{d(\ln K_P)}{dT}\right)_{equilibrium} = \frac{\Delta \bar{H}_{vapor \ or \ sub}}{RT^2}$$

midterm 2

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

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

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

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

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°$_{boiling}$ and ΔH$_{vap}$:

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

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

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

application to problems:
to get T$_{boiling}$ when P$_{atm}$≠ 1atm :

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

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

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

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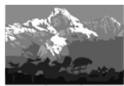
$$\left[\frac{T_{bp}}{T_{bp}^{\circ}}\right] = \frac{1}{\left[1 - \frac{RT_{bp}^{\circ}}{\Delta \bar{H}_{vap}}\ln\left(\frac{P_{atm}}{1 \ atm}\right)\right]}$$

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

application to problems: to get T$_{boiling}$ when P$_{atm}$≠ 1atm :

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

Denver: elev=1610 m P=0.822 atm

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

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

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

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Denver vs Death Valley

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

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

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

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II. application to solid ⇄ liquid

$$\left(\frac{dP}{dT}\right)_{phase \ equilibrium} = \frac{\Delta \bar{H}_{\phi}}{T\Delta \bar{V}_{\phi}} \quad \begin{array}{l} T_{melting}^{\circ} \ for \ phase \ equilibrium \ at \ P = 1 \ atm \\ what \ is \ T_{melting} \ at \ other \ pressures? \end{array}$$

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

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

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*

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

f   f= degrees of freedom
     p=phases simultaneously present

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

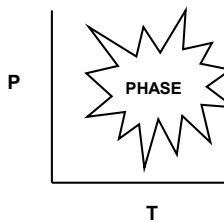f: degrees of freedom = (variables-restrictions)
$$f = 2-(p-1) = 3-p$$

$\boxed{f = 3-p}$

1 phase: T,P vary independently
2 phases present: T and P covary
3 phases present: fixed T and P

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

P   PHASE

T

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

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

45. E&Res. 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 8 to 80 .atm, no interface delineating liquid and gaseous phases is observed. *(note the 5 atm here differs from E&Rees 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.
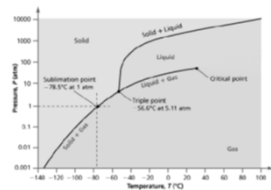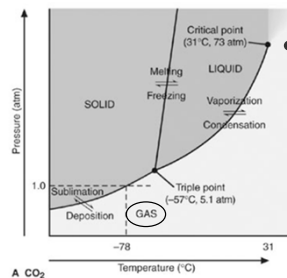e. An increase in temperature from -80 ° to 20 °C converts a solid to a gas with no intermediate liquid phase.

Figure 8.12 The P–T phase diagram for CO2

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phase diagrams (f=3-p)
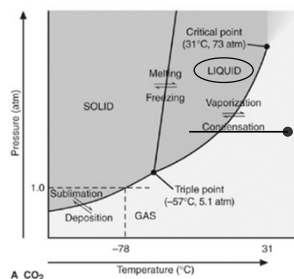
"state" or "phase" as a function of P, T

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
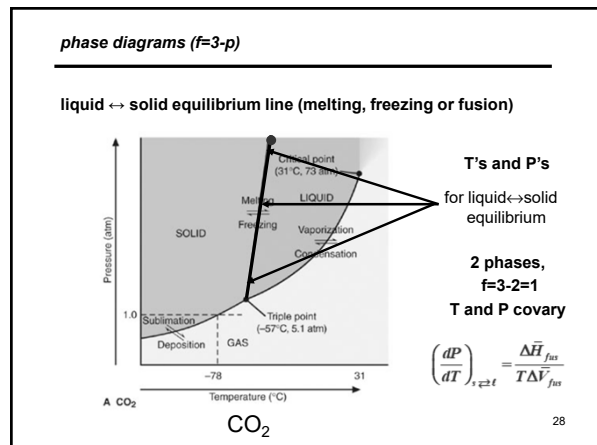
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phase diagrams (f=3-p)

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

lower T more
solid

CO_2

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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 25

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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 26

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two-phase equilibrium (p=2)

f=   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)

T's and P's

for liquid↔solid
equilibrium

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

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

CO_2 28

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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]*

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

CO_2 29

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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

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

CO_2 30

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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 <u>A</u>   <u>B</u>
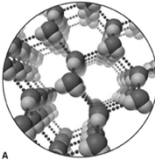
originally from: *jchemed.chem.wisc.edu/jcesoft/cca/samples/cca2benzene.html*

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

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why does ice float ?

- H_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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ice bomb !!!!

Originally at
http://www.jce.divched.org/JCESoft/CCA/pirelli/pages/cca2icebomb.html
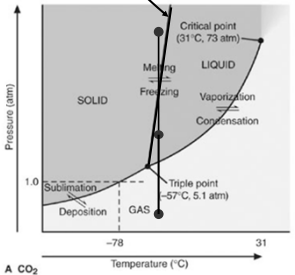
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remember for CO_2 : P increases   gas → liquid → solid

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

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

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

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

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

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

Critical point (31°C, 73 atm)

Melting / Freezing

LIQUID

SOLID

Vaporization

Condensation

Sublimation / Deposition

GAS

Triple point −57°C, 5.1 atm

−78   31

Temperature (°C)

A CO_2

low P
gas

raise P
liquid
(more dense)

raise P more
solid
(most dense)

CO_2

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phase diagram for water

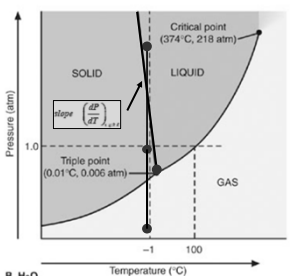remember for CO_2 : P increases   gas → liquid → solid

but for H_2O
as P increases:

gas
↓
solid
↓
liquid
WHY? $\left(\dfrac{dP}{dT}\right)_{s \rightleftarrows \ell} < 0$

for ice $\rightleftarrows$ water

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

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

Critical point (374°C, 218 atm)

SOLID   LIQUID

$slope \left(\dfrac{dP}{dT}\right)$

Triple point (0.01°C, 0.006 atm)

GAS

−1   100

Temperature (°C)

B H_2O

H_2O

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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?

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

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

E&R(4ᵗʰ) Problem P8.3
508 bar for ΔT=-3.5°
'thin blade'; 78kg≈172lb;
$P_{thin\,blade}$=243 bar; ΔT= -1.67°

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$_{4th}$ sec. 8.7

pure H_2O at 298K

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

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

⇓

$\mu^{(l)}_{H_2O}$ increases at P_{ext} increase

⇓

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

⇓

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

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$_{4th}$ section 8.7 (effect of inert gas on vapor pressure)

Temperature = T

← Pressure = $P_A + P_B$

← Vapor phase

← Condensed phase A

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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