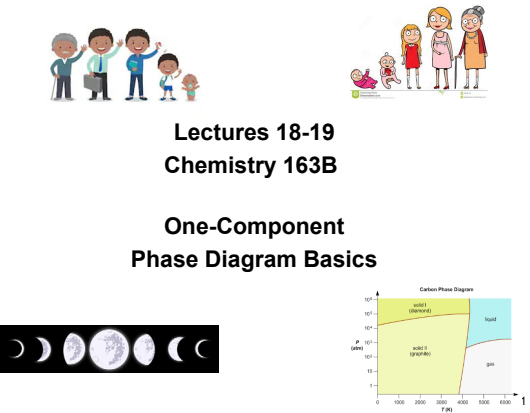


Chemistry 163B, Winter 2020
Lectures 18-19 Introduction to Phase Diagrams



Lectures 18-19
Chemistry 163B

One-Component
Phase Diagram Basics

qualitative factors in phase changes

melting
solid \rightleftharpoons liquid

freezing/fusion

vaporization
liquid \rightleftharpoons gas ENDOTHERMIC

condensation EXOTHERMIC

sublimation
solid \rightleftharpoons gas

deposition

2

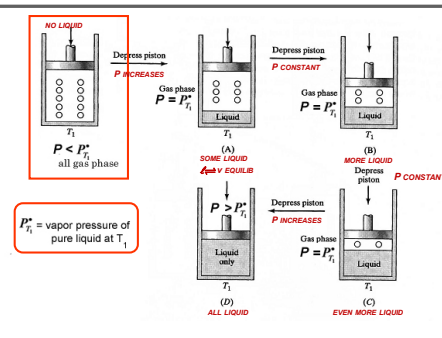
vapor pressure over **PURE** liquid (notation)

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

Gene (many others) E&R Raff

3

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



NO LIQUID
 $P < P^*_T$
all gas phase

Depress piston
 P INCREASES

Gas phase
 $P = P^*_T$

Depress piston
 P CONSTANT

Gas phase
 $P = P^*_T$

Liquid

(A) SOME LIQUID
 \rightleftharpoons V. EQUILIB

(B) MORE LIQUID

Depress piston
 P CONSTANT

Depress piston
 P INCREASES

Gas phase
 $P = P^*_T$

Liquid

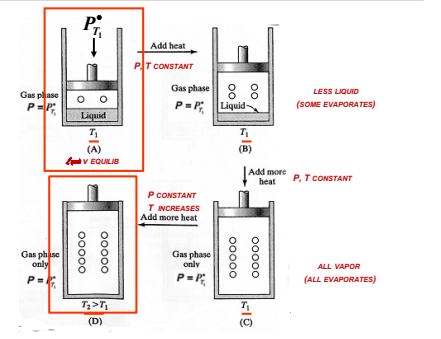
(D) ALL LIQUID

(C) EVEN MORE LIQUID

P^*_T = vapor pressure of pure liquid at T_1

4

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



Gas phase
 $P = P^*_T$

Liquid

(A)

Add heat
 T INCREASES
 P , T CONSTANT

Gas phase
 $P = P^*_T$

Liquid

(B) LESS LIQUID (SOME EVAPORATES)

\rightleftharpoons V. EQUILIB

Add more heat
 P , T CONSTANT

Gas phase only
 $P = P^*_T$

(C)

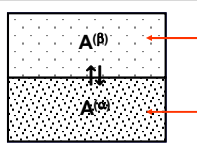
Add more heat
 P CONSTANT
 T INCREASES

Gas phase only
 $P = P^*_T$

(D) ALL VAPOR (ALL EVAPORATES)

5

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

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

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

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

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

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

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

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

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

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

$\mu_A^{(\alpha)} > \mu_A^{(\beta)} \Rightarrow dn_A^{(\alpha)} < 0$ 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

7

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

➔

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

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

8

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

A(α) \rightleftharpoons 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

$\downarrow d\mu^{(\alpha)}$

$\downarrow d\mu^{(\beta)}$

T and P covary

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

$\xrightarrow{dT, dP}$

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

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

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

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

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

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

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phase equilibrium (one-component)

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

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

$\phi = \text{phase change}$

eqn. 8.13 E&R_{4th}

since phase change is an equilibrium (reversible) process

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

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

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

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

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

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

$$\left(\frac{dP}{dT}\right)_{\text{equilibrium}} = \frac{\Delta\bar{H}_\phi}{T\left(\frac{RT}{P}\right)} = \frac{P\Delta\bar{H}_\phi}{RT^2}$$

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

Clausius-Clapeyron
≈ eqn. 8.19 E&R_{4th}

So just like before

for s or l ⇌ gas $K_p = (a_{\text{gas}}/a_{s,l}) \equiv (P_{\text{gas}}/1)$

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

midterm 2

13

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

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

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

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

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

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

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

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

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

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

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

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

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

15

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

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

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

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

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

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

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

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Denver vs Death Valley

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

$$\left[\frac{T_{\text{bp}}}{373}\right] = \frac{1}{1 - \frac{(8.3245 \text{ J K}^{-1} \text{ mol}^{-1})(373 \text{ K})}{40.65 \times 10^3 \text{ J mol}^{-1}} \ln\left(\frac{P_{\text{atm}}}{1 \text{ atm}}\right)} = \frac{1}{1 - 0.0763 \ln\left(\frac{P_{\text{atm}}}{1 \text{ atm}}\right)}$$

Denver: elev 1610m $P=0.822 \text{ atm}$ $T_{\text{bp}}=367.5 \text{ K}$
 Sea level: elev 0m $P=1.00 \text{ atm}$ $T_{\text{bp}}=373 \text{ K}$
 Death Valley: elev -82.5m $P=1.01 \text{ atm}$ $T_{\text{bp}}=373.28 \text{ K}$

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II. application to solid ⇌ 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

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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: $\mu^{(a)} = \mu^{(b)} = \mu^{(c)} = \dots$

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

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

45. E8.16a, PB.1
Within what range can you restrict the values of P and T if the following information is known about CO₂? Use Figure 8.12 to answer the question.
Note: The critical point is at 31°C, 73 atm, and P_{tr} is 5.1 atm.

- As the temperature is increased, the solid is first converted to the liquid and subsequently to the gaseous state.
- As the pressure on a cylinder containing pure CO₂ is increased from 8 to 80 atm, no interface separating liquid and gaseous phases is observed. (over the 8 atm range others than E8.16a, CO₂ TRIPS STALKE, it makes more sense)
- Solid, liquid, and gas phases coexist at equilibrium.
- An increase in pressure from 10 to 50 atm converts the liquid to the solid.
- An increase in temperature from -40 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

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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

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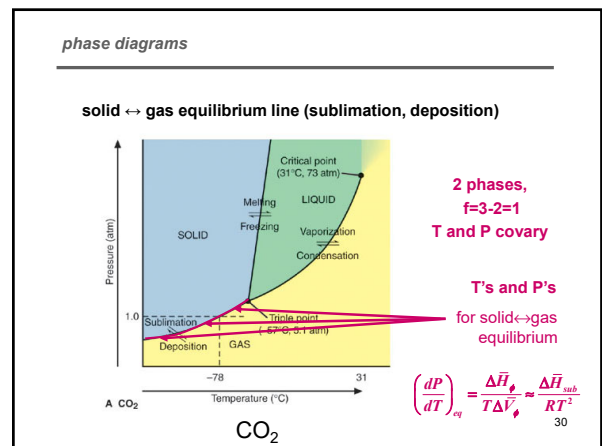
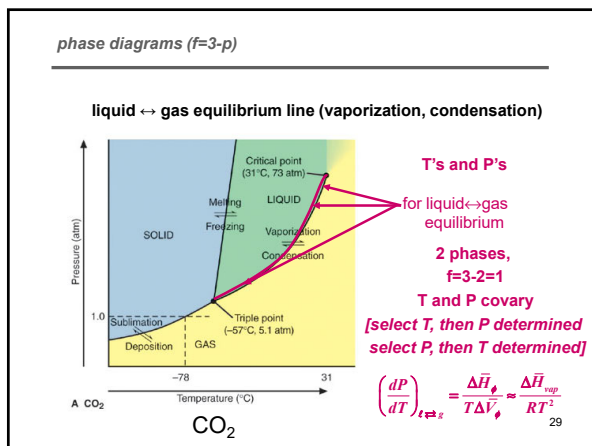
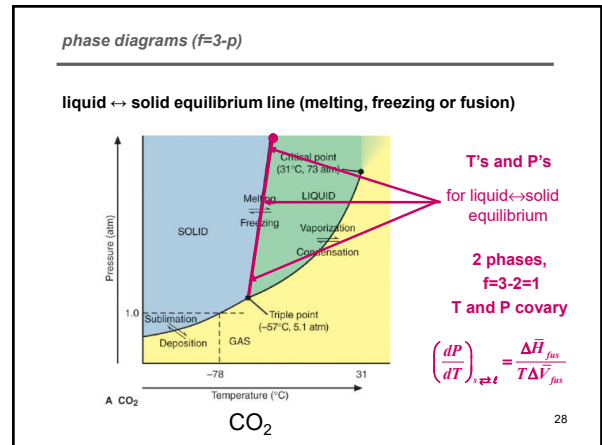
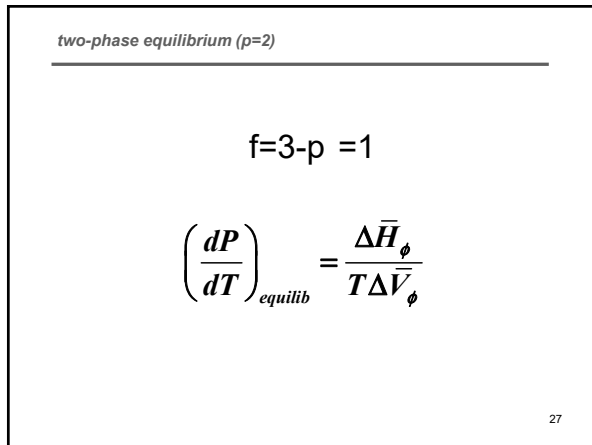
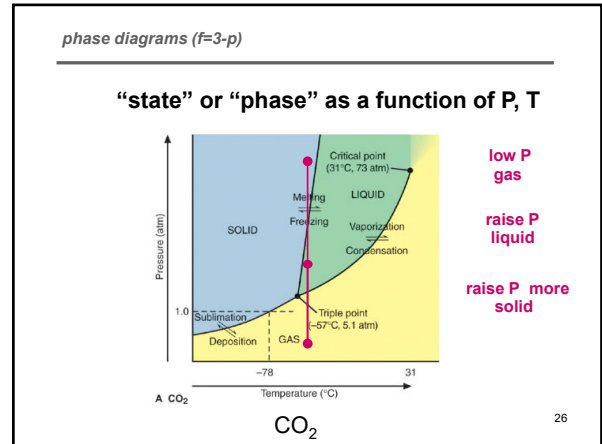
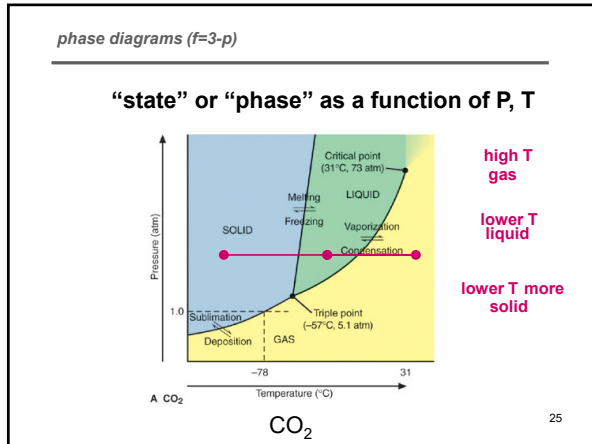
phase diagrams ($f=3-p$)

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

lower T more
solid

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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/ccca/samples/ccca2benzene.html

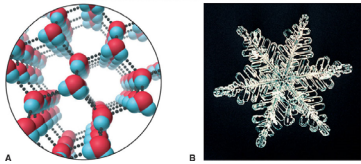
http://www.youtube.com/watch?v=79H2_OVBMGA



31


why does ice float ?

- H₂O is polar and can form hydrogen bonds (macho intermolecular forces)
- High surface tension and capillarity
- Hydrogen bonds form very open structure in solid H₂O (ice) giving ice a lower density than H₂O liquid. ICE FLOATS!!



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ice bomb !!!!

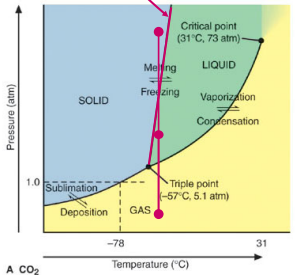


Originally at <http://www.jce.divched.org/JCESoft/CCA/irell/pages/cca2icebomb.html>

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remember for CO₂ : P increases gas → liquid → solid

CO₂(s) ⇌ CO₂(l)

$$\left(\frac{dP}{dT}\right)_{\text{gas}} = \frac{\Delta\bar{H}_{\text{melt}}}{T\Delta\bar{V}_{\text{melt}}}; \Delta\bar{H}_{\text{melt}} > 0; V_l > V_s; \Delta\bar{V} > 0 \Rightarrow \left(\frac{dP}{dT}\right)_{\text{gas}} > 0$$


low P gas

raise P liquid (more dense)

raise P more solid (most dense)

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phase diagram for water

remember for CO₂; P increases gas → liquid → solid

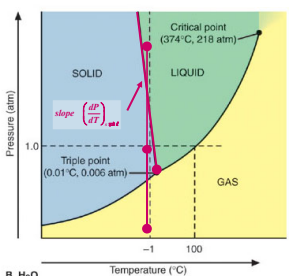
but for H₂O as P increases:

gas ↓

solid ↓

liquid

WHY? $\left(\frac{dP}{dT}\right)_{\text{gas}} < 0$ for ice ⇌ water



$$\left(\frac{dP}{dT}\right)_{\text{gas}} = \frac{\Delta\bar{H}_{\text{melt}}}{T\Delta\bar{V}_{\text{melt}}}; \Delta\bar{H}_{\text{melt}} > 0; V_s > V_l; \Delta\bar{V}_{\text{melt}} < 0 \Rightarrow \left(\frac{dP}{dT}\right)_{\text{gas}} < 0$$


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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?

$$\ln \frac{T_{\text{melt}}}{T_{\text{1 atm}}} = \frac{(\bar{V}_l - \bar{V}_s)(P - 1 \text{ atm})}{\Delta\bar{H}_{\text{fusion}}}$$

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



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

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

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

pure H₂O at 298K
P*_{H₂O} = 0.0316 bar

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

↓

$\mu_{\text{H}_2\text{O}}^{\text{liq}}$ increases at P_{total} increase

↓

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

↓

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

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

'normal' H₂O in P_{total}=1 bar
[H₂O (g) + N₂(g) + O₂(g)] at 298K
P_{H₂O} = 0.031622 bar

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

Temperature = T

H₂O at 300 K
P*_{H₂O} = 0.328 atm

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

new P_{H₂O} = 0.32832 atm
(P/P*)_{H₂O} = 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

fluid

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