

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

The slide features two illustrations at the top: on the left, a group of diverse people including an elderly man, a businesswoman, a teacher, a student, and a child; on the right, a family including a pregnant woman, a young girl, a baby, and an older woman. Below these is the title text. A small image of the Moon's phases is shown. To the right is a 'Carbon Phase Diagram' plot of Pressure (P) in atm versus Temperature (T) in K.

Lectures 18-19
Chemistry 163B

One-Component
Phase Diagram Basics

Carbon Phase Diagram

P (atm)

T (K)

solid I (diamond)
solid II (graphite)
liquid
gas

qualitative factors in phase changes

melting

solid \rightleftharpoons liquid

freezing/fusion

vaporization

liquid \rightleftharpoons gas

condensation

sublimation

solid \rightleftharpoons gas

deposition

ENDOTHERMIC

EXOTHERMIC

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



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

Gene

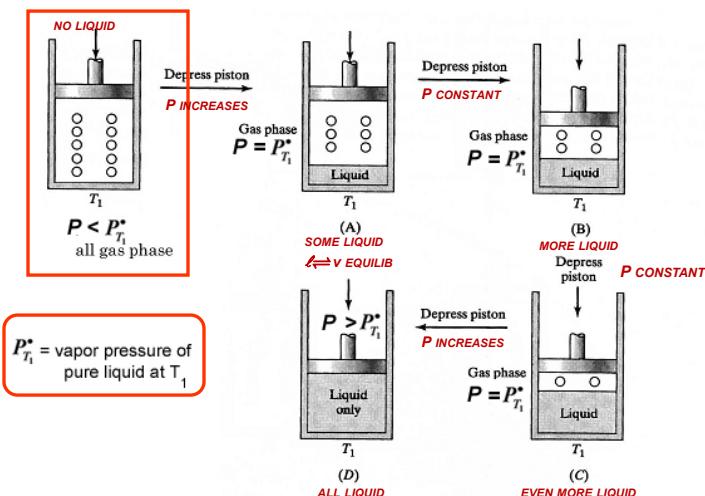
E&R

Raff

(many others)

3

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

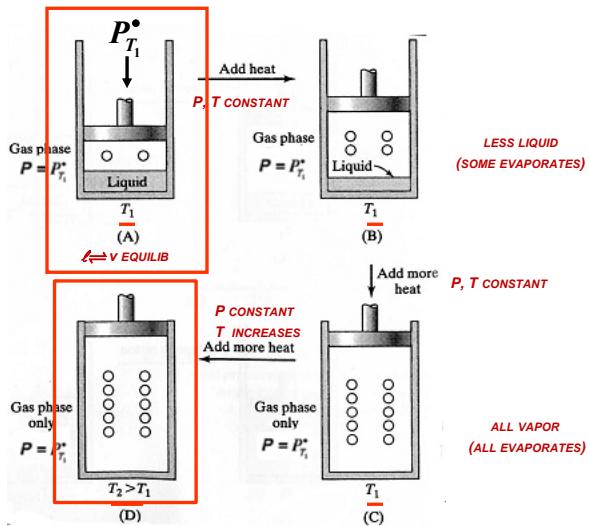


4

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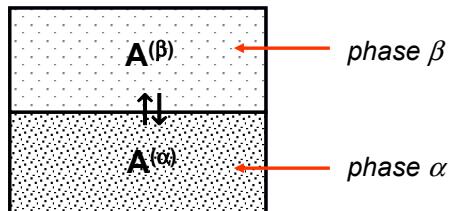
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liquid ⇌ vapor as heat added (vary T, const P)



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



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

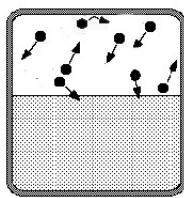
high $\mu \rightarrow$ low μ

hyper \rightarrow mellow

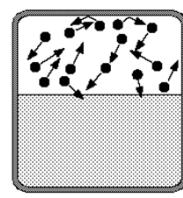
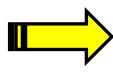
7

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

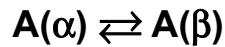
https://www.engineeringtoolbox.com/water-vapor-saturation-pressure-d_599.html

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

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



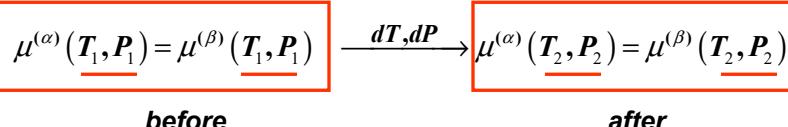
$$\text{at equilibrium} \quad \Delta\mu = 0 \quad \Rightarrow \mu_A^{(\alpha)} = \mu_A^{(\beta)}$$

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

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



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

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

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

with

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

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

$$-\bar{\mathbf{S}}^{(\alpha)}d\mathbf{T} + \bar{\mathbf{V}}^{(\alpha)}d\mathbf{P} = -\bar{\mathbf{S}}^{(\beta)}d\mathbf{T} + \bar{\mathbf{V}}^{(\beta)}d\mathbf{P}$$

$$\left(\bar{\mathbf{S}}^{(\beta)} - \bar{\mathbf{S}}^{(\alpha)} \right) d\mathbf{T} = \left(\bar{\mathbf{V}}^{(\beta)} - \bar{\mathbf{V}}^{(\alpha)} \right) d\mathbf{P}$$

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phase equilibrium (one-component)

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

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

$\phi = \text{phase change}$

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

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

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

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

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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_{4th}

So just like
'before'

$$\text{for } s \text{ or } \ell \rightleftharpoons \text{gas} \quad K_p = (a_{\text{gas}}/a_{s,\ell}) \equiv (P_{\text{gas}}/1)$$

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



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

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

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

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

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} :

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

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

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

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

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

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

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

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

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

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

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

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



Denver: elev=1610 m P=0.822 atm

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



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

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

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Denver vs Death Valley

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

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

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

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

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_{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 = 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)

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

$$f = 3-p$$

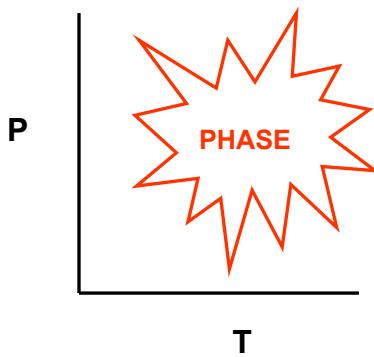
1 phase: T,P vary independently

2 phases present: T and P covary

3 phases present: fixed T and P

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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. E&R#8.1
 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 this question.
 NOTE: The critical point is at T=31.1°C and P=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 CO₂ is increased from 5 to 80. atm, no interface delineating liquid and gaseous phases is observed. (*note the 5 atm zero differs from the 50 atm value, makes more sense*)
 c. Solid 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.

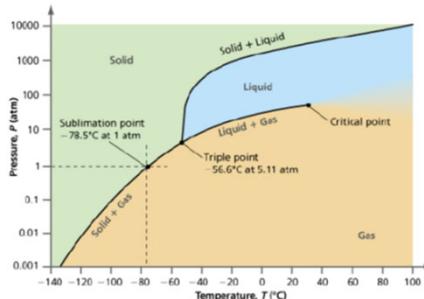
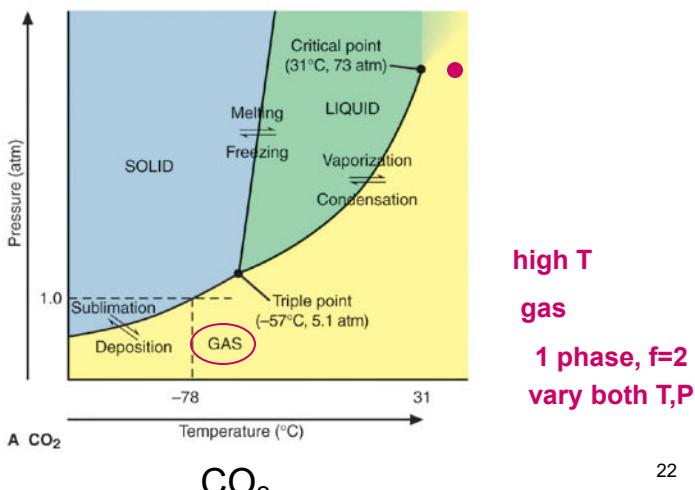


Figure 8.12 The P-T phase diagram for CO₂

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phase diagrams (f=3-p)

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

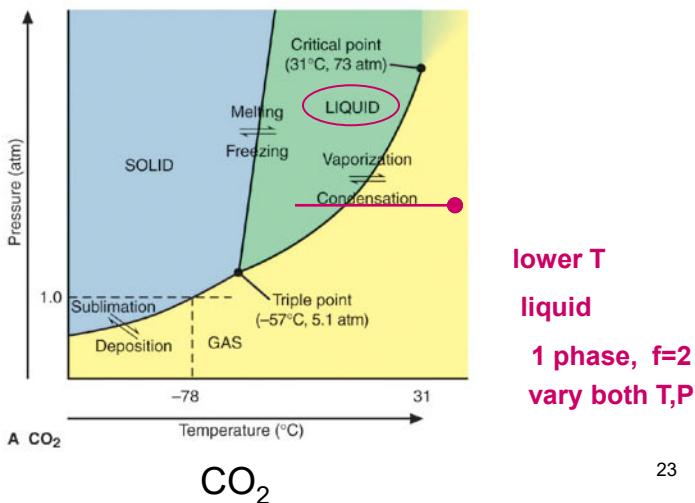


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phase diagrams ($f=3-p$)

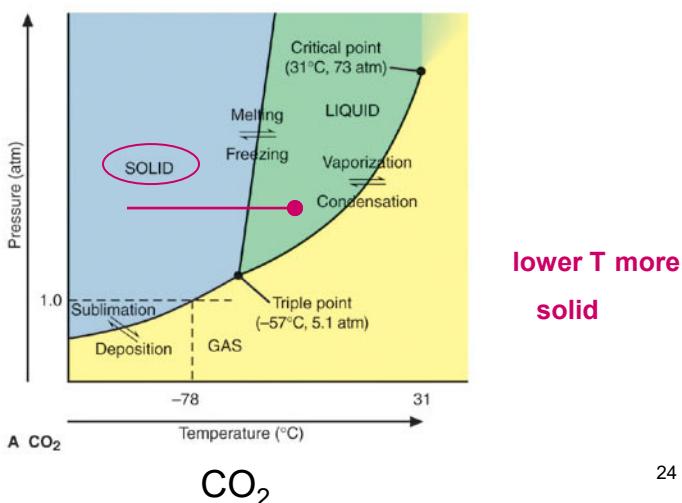
“state” or “phase” as a function of P, T



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phase diagrams ($f=3-p$)

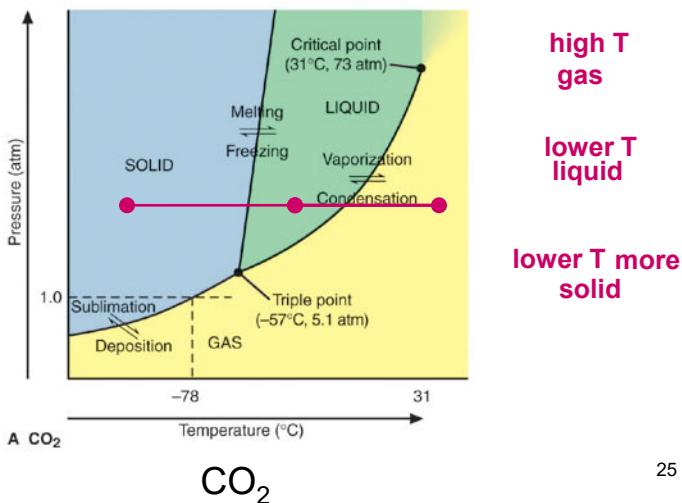
“state” or “phase” as a function of P, T



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phase diagrams ($f=3-p$)

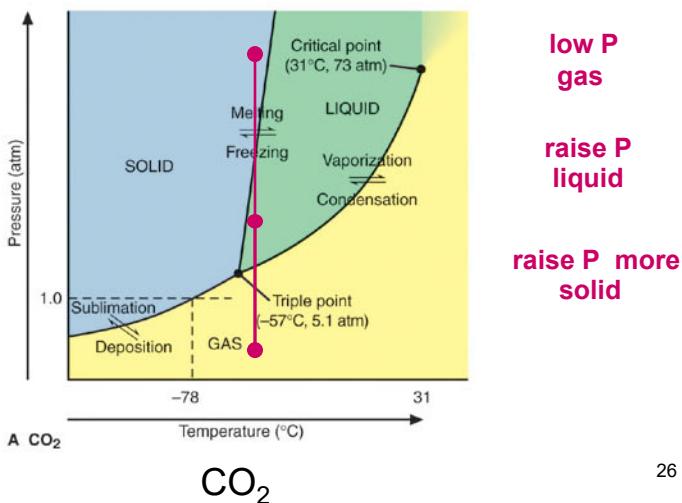
“state” or “phase” as a function of P , T



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phase diagrams ($f=3-p$)

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



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two-phase equilibrium (p=2)

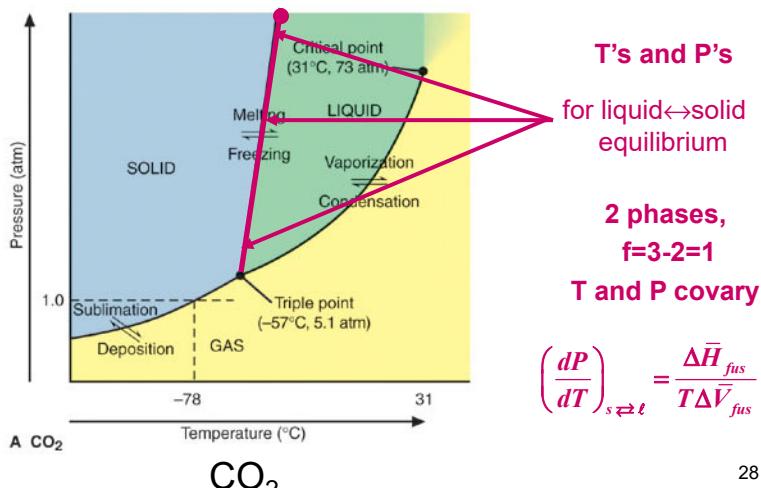
$$f = 3 - p = 1$$

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

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phase diagrams (f=3-p)

liquid \leftrightarrow solid equilibrium line (melting, freezing or fusion)



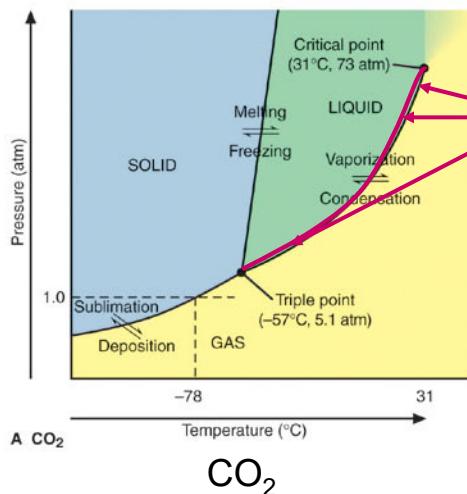
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phase diagrams (f=3-p)

liquid \leftrightarrow gas equilibrium line (vaporization, condensation)



T's and P's

for liquid \leftrightarrow gas equilibrium

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

T and P covary

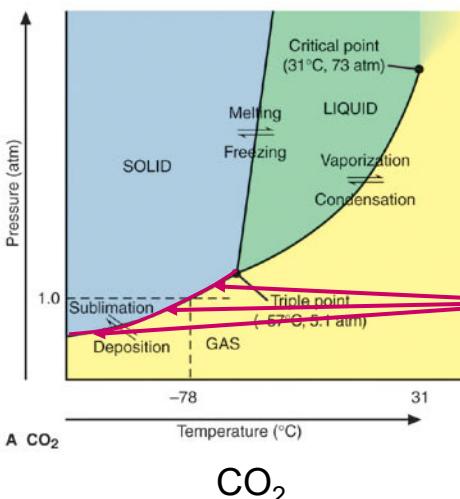
[select T, then P determined
 select P, then T determined]

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

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phase diagrams

solid \leftrightarrow gas equilibrium line (sublimation, deposition)



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

T and P covary

T's and P's

for solid \leftrightarrow 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

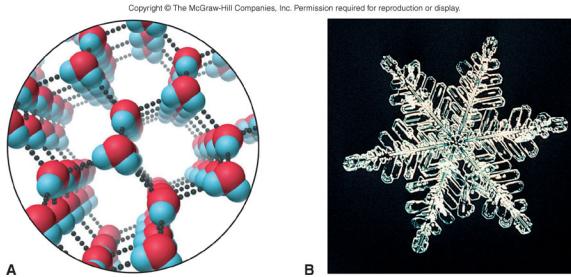
http://www.youtube.com/watch?v=79H2_QVBMGA



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why does ice float ?

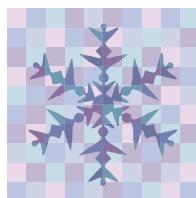
- H₂O is polar and can form hydrogen bonds
(macho intermolecular forces)
 - High surface tension and capillarity
 - Hydrogen bonds form very open structure in solid H₂O (ice)
giving ice a lower density than H₂O liquid. ICE FLOATS!!



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ice bomb !!!!



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

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remember for CO_2 : P increases gas \rightarrow liquid \rightarrow solid

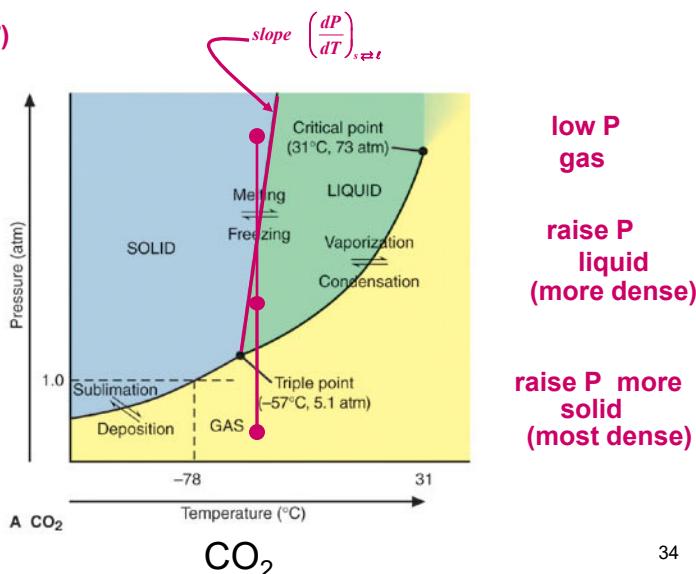


$$\left(\frac{dP}{dT} \right)_{\text{ext}} = \frac{\Delta \bar{H}_{\text{melt}}}{T \Delta \bar{V}_{\text{melt}}};$$

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

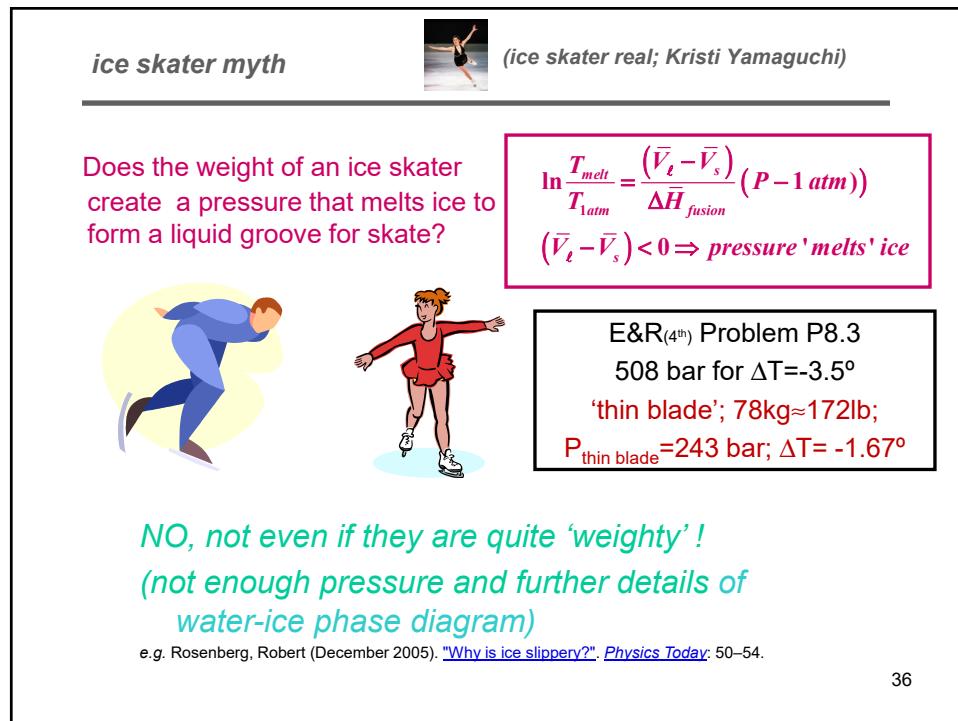
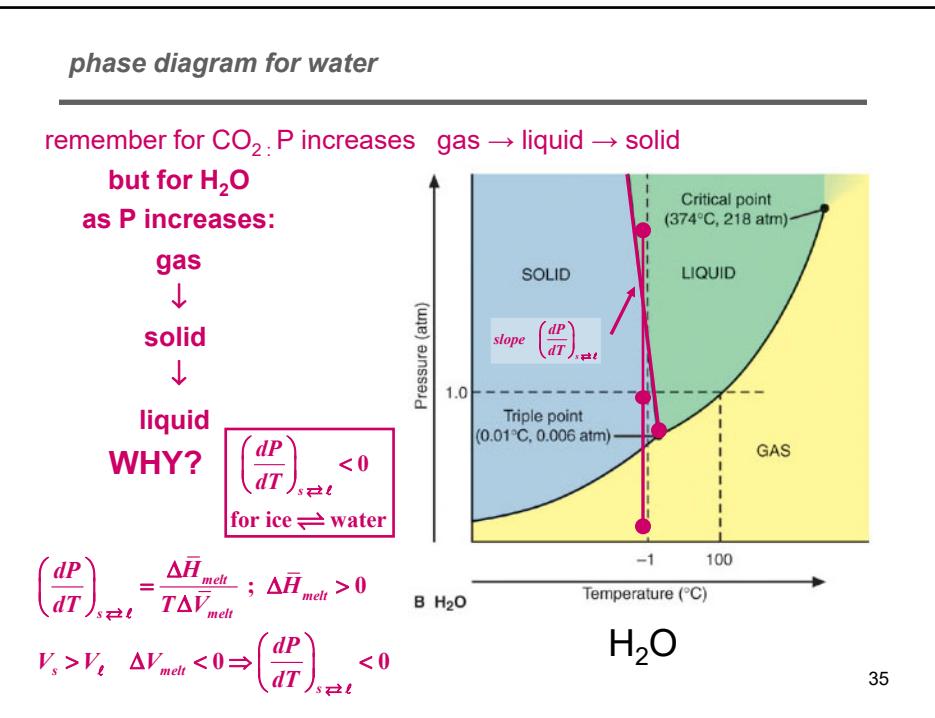
$$V_{\ell} > V_s \quad \Delta V > 0$$

$$\Rightarrow \left(\frac{dP}{dT} \right)_{\text{ext}} > 0$$



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

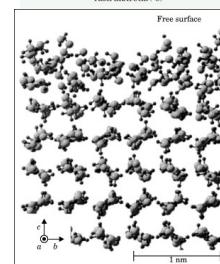
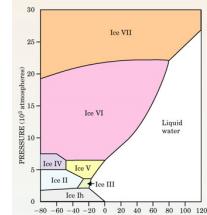


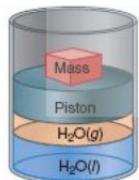
Figure 1. An **ice skater** exerts pressures on the order of a few hundred atmospheres on the ice surface, enough to reduce the melting temperature by only a few **degrees**.

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



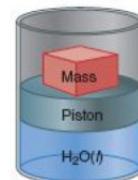
$$P_{\text{external}} = 0.0316 \text{ bar}$$

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

$\mu_{H_2O}^{(t)}$ increases at P_{total} increase

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

$$RT \ln \left(\frac{P^{(g)}}{P^*} \right) = \int_{P^*}^{P_{\text{total}}} \bar{V}_{H_2O}^{(t)} dP$$

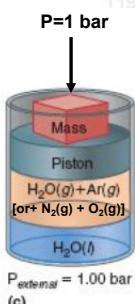


$$P_{\text{external}} = 1.00 \text{ bar}$$

pure H₂O
at 298K

$$P^*_{H_2O} = 0.0316 \text{ bar}$$

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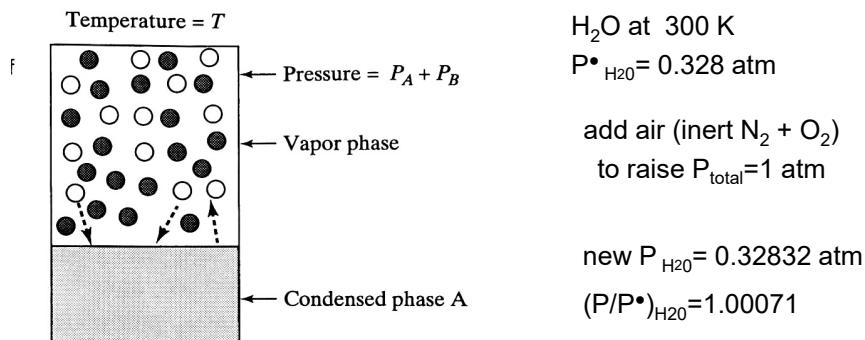
‘normal’ H₂O in $P_{\text{total}}=1 \text{ bar}$
[H₂O(g) + N₂(g) + O₂(g)]
at 298K

$$P_{H_2O} = 0.031622 \text{ bar}$$

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

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



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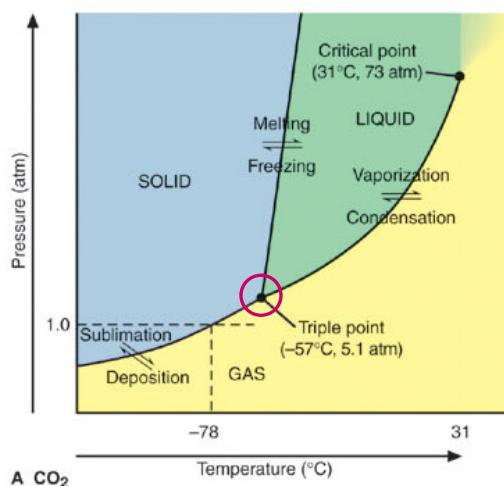
End of Lecture

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

triple point

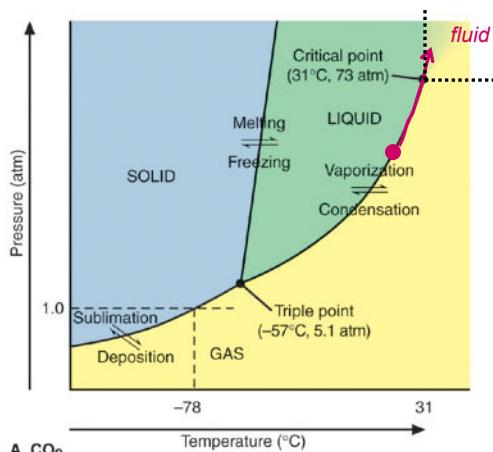
triple point: simultaneous equilibrium of gas, liquid solid



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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