

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

**Chemistry 163B**  
**One-Component**  
**Phase Diagram Basics**

1

**qualitative factors in phase changes**

---

*melting*  
 solid  $\rightleftharpoons$  liquid  
*freezing/fusion*

*vaporization* **ENDOTHERMIC**  
 liquid  $\rightleftharpoons$  gas  $\rightleftharpoons$   
*condensation* **EXOTHERMIC**

*sublimation*  
 solid  $\rightleftharpoons$  gas  
*deposition*

2

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

---

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

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

3

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

---

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

4

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

---

5

**$dG$  for phase change at constant  $T, P$**

---

same  $T, P$  for each phase  
 $dG = -SdT + VdP + \sum \mu_A d n_A$   
**one component 'A' in phases  $\alpha$  and  $\beta$  constant  $T, P$**   
 $dG_{T,P} = \mu_A^{(\alpha)} d n_A^{(\alpha)} + \mu_A^{(\beta)} d n_A^{(\beta)}$   
 $d n_A^{(\beta)} = -d n_A^{(\alpha)}$   
 $dG_{T,P} = (\mu_A^{(\alpha)} - \mu_A^{(\beta)}) d n_A^{(\alpha)}$

6

# Chemistry 163B, Winter 2014

## Lectures 18-19 Introduction to Phase Diagrams

**at equilibrium  $\mu^{(\alpha)} = \mu^{(\beta)}$ ;  $\mu$  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  $\alpha$**

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

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

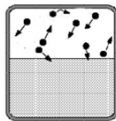
high  $\mu \rightarrow$  low  $\mu$   
hyper  $\rightarrow$  mellow

7

**Question:**

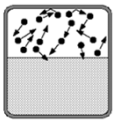
---

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



T=298 K  
P = 0.032 bar

➡



T=473 K  
P = 15.5 bar

8

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

---

**A( $\alpha$ )  $\rightleftharpoons$  A( $\beta$ )**

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

How can P and T covary to maintain equilibrium?

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

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

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

9

**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

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

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

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

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

10

**phase equilibrium (one-component)**

---

$$\left(\frac{\partial T}{\partial P}\right)_{\infty} = \frac{\Delta P}{\Delta \bar{S}}$$

[mkterm #2, prob 4b]

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

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

eqn. 8.13 E&R

since phase change is an equilibrium (reversible) process

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

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

11

**1. 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

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

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

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

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

12

# Chemistry 163B, Winter 2014

## Lectures 18-19 Introduction to Phase Diagrams

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

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

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

**Clausius-Clapeyron**  
 $\approx$  eqn. 8.19 E&R

13

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

$$\left(\frac{d \ln P}{dT}\right)_{\text{equilibrium}} = \frac{\Delta\bar{H}_{\text{vap or sub}}}{RT^2} \quad \text{for s or l} \rightleftharpoons \text{gas} \quad E_p = P_{\text{ext}} = P_{\text{ext}} = P_{\text{ext}}$$

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

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta\bar{H}_\phi}{R} \left[\frac{1}{T_2} - \frac{1}{T_1}\right] \quad \text{E\&R eqn 8.20 where } \phi \text{ is vaporization similar for sublimation}$$

**application to problems:** normal b.p. (1 atm), standard b.p. (1 bar)

to get vapor pressure given  $T_{\text{boiling}}^\circ$  and  $\Delta H_{\text{vap}}$ :

at  $T_1 = T_{\text{boiling}}^\circ$   $P_1 = P_{\text{vap}} = 1 \text{ atm}$

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

14

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

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

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

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

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

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

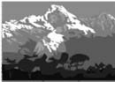
$$\left[\frac{T_{\text{bp}}}{T_{\text{bp}}^\circ}\right] = \frac{1}{1 - \frac{RT_{\text{bp}}^\circ}{\Delta\bar{H}_{\text{vap}}} \ln\left(\frac{P_{\text{atm}}}{1 \text{ atm}}\right)}$$

15

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


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

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




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

$P < 1 \text{ atm} \Rightarrow \left[\frac{T_{\text{bp}}}{T_{\text{bp}}^\circ}\right] < 1 \Rightarrow T_{\text{bp}} < T_{\text{bp}}^\circ$



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

$P > 1 \text{ atm} \Rightarrow \left[\frac{T_{\text{bp}}}{T_{\text{bp}}^\circ}\right] > 1 \Rightarrow T_{\text{bp}} > T_{\text{bp}}^\circ$



ouch

16

**II. application to solid  $\rightleftharpoons$  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  $T_{\text{melting}}$  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  $T_{\text{melting}}$  ?

$\Delta H_{\text{melting}} > 0$

(usual)  $\bar{V}_{\text{liquid}} > \bar{V}_{\text{solid}} \quad T_{\text{melting}} \text{ increases}$

(when??)  $\bar{V}_{\text{liquid}} < \bar{V}_{\text{solid}} \quad T_{\text{melting}} \text{ decreases}$

17

**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:  $\mu^{(\alpha)} = \mu^{(\beta)} = \mu^{(\gamma)} = \dots$

$f$ : 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  $P$

18

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

**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**

19

**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<sub>2</sub>

20

**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<sub>2</sub>

21

**phase diagrams (f=3-p)**

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

lower T more solid

CO<sub>2</sub>

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<sub>2</sub>

23

**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<sub>2</sub>

24

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

**two-phase equilibrium (p=2)**

---

f =  $f=3-p=1$

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

25

**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**

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

26

**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]**

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

27

**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

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

28

**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://jchemed.chem.wisc.edu/jcesoft/ccca/samples/ccca2benzene.html)

[http://www.youtube.com/watch?v=79H2\\_QVBMGA](http://www.youtube.com/watch?v=79H2_QVBMGA)

29

**why does ice float ?**

- H<sub>2</sub>O is polar and can form hydrogen bonds (macho intermolecular forces)
- High surface tension and capillarity
- Hydrogen bonds form very open structure in solid H<sub>2</sub>O (ice) giving ice a lower density than H<sub>2</sub>O liquid. ICE FLOATS!!

30

# Chemistry 163B, Winter 2014

## Lectures 18-19 Introduction to Phase Diagrams

**ice bomb !!!!**

<http://www.ice.dvvhed.org/UCI/Soft/CCA/jrrell/papers/cca2icebomb.html>

31

**remember for CO<sub>2</sub> : P increases gas → liquid → solid**

**CO<sub>2</sub>(s) → CO<sub>2</sub>(l)**

$$\left(\frac{dP}{dT}\right)_{i,cr,t} = \frac{\Delta\bar{H}_{i,cr,t}}{T\Delta\bar{V}_{i,cr,t}}$$

$$\Delta\bar{H}_{i,cr,t} > 0;$$

$$V_g > V_l \Rightarrow \Delta\bar{V} > 0$$

$$\Rightarrow \left(\frac{dP}{dT}\right)_{i,cr,t} > 0$$

low P  
gas

raise P  
liquid  
(more dense)

raise P more  
solid  
(most dense)

A CO<sub>2</sub> CO<sub>2</sub>

32

**phase diagram for water**

remember for CO<sub>2</sub>: P increases gas → liquid → solid

**but for H<sub>2</sub>O**  
**as P increases:**

gas  
↓  
solid  
↓  
liquid

**WHY?**

$$\left(\frac{dP}{dT}\right)_{i,cr,t} < 0$$

for ice ⇌ water

$$\left(\frac{dP}{dT}\right)_{i,cr,t} = \frac{\Delta\bar{H}_{i,cr,t}}{T\Delta\bar{V}_{i,cr,t}}; \Delta\bar{H}_{i,cr,t} > 0$$

$$V_s > V_l \Rightarrow \Delta\bar{V}_{i,cr,t} < 0 \Rightarrow \left(\frac{dP}{dT}\right)_{i,cr,t} < 0$$

B H<sub>2</sub>O

33

**ice skater myth**

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

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

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

E&R(3<sup>rd</sup>) 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.

34

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.

35

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

pure H<sub>2</sub>O at 298K

P<sub>H<sub>2</sub>O</sub> = 0.0316 bar

P<sub>external</sub> = 0.0316 bar (b)

P<sub>external</sub> = 1.00 bar (a)

P = 1 bar

'normal' H<sub>2</sub>O in P<sub>total</sub> = 1 bar  
[H<sub>2</sub>O(g) + N<sub>2</sub>(g) + O<sub>2</sub>(g)] at 298K

P<sub>H<sub>2</sub>O</sub> = 0.031622 bar

36

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

**E&R 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  
 $P_{H_2O} = 0.328 \text{ atm}$

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

new  $P_{H_2O} = 0.32832 \text{ atm}$   
 $(P/P)_{H_2O} = 1.00071$

37

*End of Lecture*

38

**triple point**

triple point: simultaneous equilibrium of gas, liquid solid

Pressure (atm)

Temperature ( $^{\circ}C$ )

SOLID

LIQUID

GAS

Melting

Freezing

Vaporization

Condensation

Sublimation

Deposition

Critical point (31  $^{\circ}C$ , 73 atm)

Triple point (-57  $^{\circ}C$ , 5.1 atm)

1.0

-78

31

A  $CO_2$

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

39

**vary T and P through critical point**

Pressure (atm)

Temperature ( $^{\circ}C$ )

SOLID

LIQUID

GAS

Melting

Freezing

Vaporization

Condensation

Sublimation

Deposition

Critical point (31  $^{\circ}C$ , 73 atm)

Triple point (-57  $^{\circ}C$ , 5.1 atm)

1.0

-78

31

A  $CO_2$

fluid

40