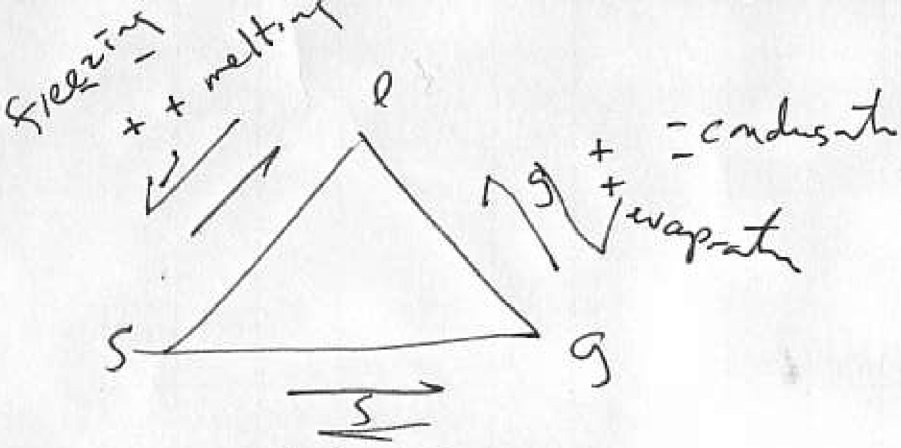
**Physical Equilibria**

1 temperature dependence of phase changes



$\Delta G = 0 = \Delta H - T\Delta S$

$\Delta H, \Delta S$
+ + sublimation
− − deposition

2 vapor pressure theory

fun facts about v.p.

1. physical equilibrium $l \rightleftarrows g$ where rate is equal and opposite
2. surface phenomenon $\Delta H_{vap} \approx$ I.M.F
   as IMF ↑ $\Delta H_{vap}$ ↑
   IMF ↓ $\Delta H_{vap}$ ↓
3. T dependent
   as T ↑ v.p. ↑ exponentially
4. into Clausius Clapeyron equation to calc. v.p. at any T.
5. Know how to compare two compounds
   $H_2O$ has very low v.p. $CH_4$ is very high v.p.

## 3 salt dissociation in water

A salt dissolves if $\Delta G$ is ⊖

but $\Delta G = \Delta H - T\Delta S$ and $T\Delta S$ is always ⊕ because of mixing

so $\Delta H$ defines whether dissolving occurs

$$\Delta H_{soln} = \underset{\substack{\text{very large} \\ \text{and } \oplus}}{\underset{\Uparrow}{\Delta H_{c.L.}}} + \underset{\substack{\text{very large} \\ \text{and neg}}}{\underset{\Uparrow}{\Delta H_{hyd\ (solvation)}}}$$

added together, they ~ cancel making $\Delta H_{soln}$ relatively small and ±

Hint. be able to use the $\Delta H_{soln}$ calculation.

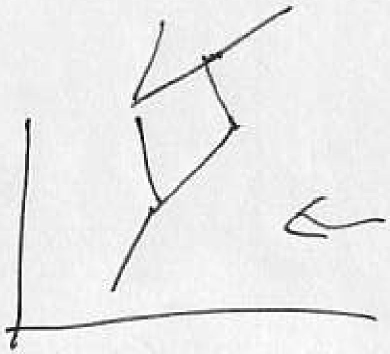
## 4 phase diagram interpretation

KNow ~~All~~ All the important defining features of a phase diagram.

equilibrium lines where $\Delta G = 0$ at transition

critical point where beyond it a supercritical fluid is formed

triple point where all 3 phases exist.



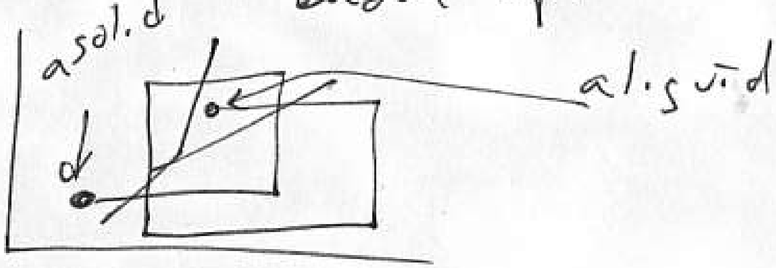
← be able to label all the parts of this.

be aware that more than one triple point might exist.

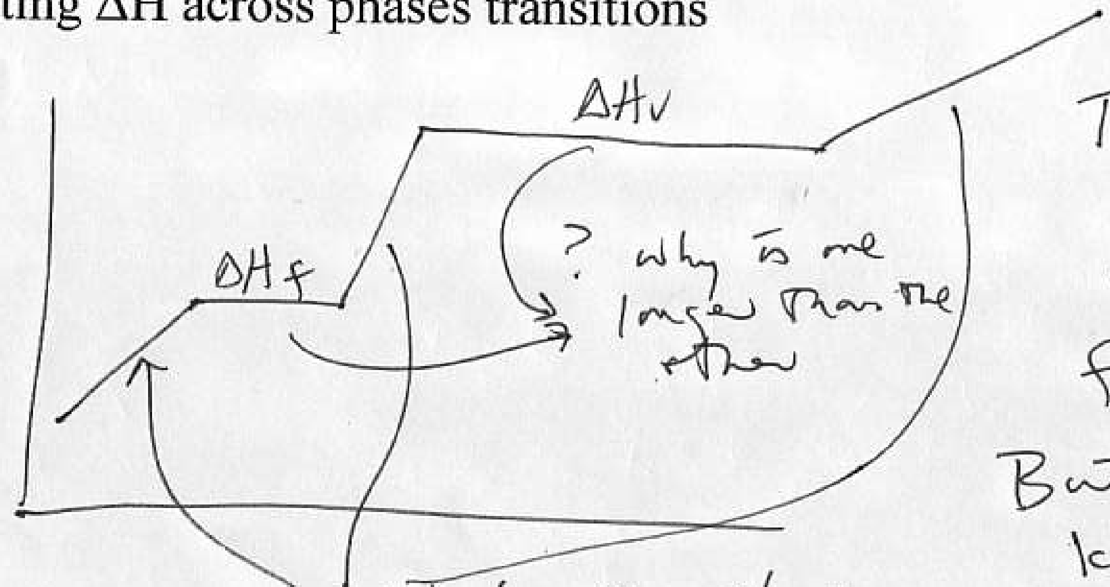
be aware that $H_2O$ has a ⊖ slope for the $s \leftrightarrow l$ line

## 5 phase diagram navigation

I will provide you with a starting point on a graph of P vs T. Then give you direction. Go 20°C east, 15 atm north. Then you tell me what happened and where you ended up.



## 6 calculating ΔH across phases transitions



? why is one larger than the other

What does the slope mean? The smaller the C the larger the slope.

This is a problem where you calculate ΔH from one T to another. But, no calc. so, know the diagram features well.

## 7 gas solubility in liquids

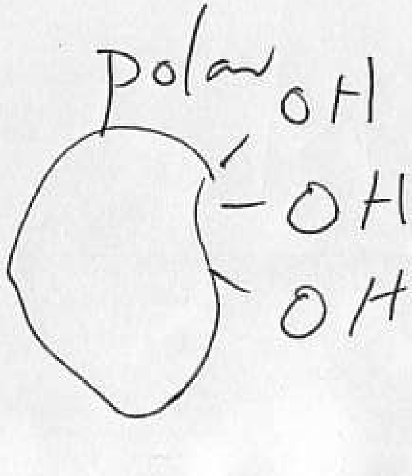
Know the following facts.

- like dissolves like explains why polar → polar and N.P. → N.P.
- reactivity explains $CO_2 \rightarrow H_2O$
- entropy explains nonpolar small molecules → $H_2O$.
- $O_2$, $N_2$, $H_2$ dissolve exothermically. This is why as T ↑ the solubility goes down (Le Chatelier)
- explains dead fish in ocean.

## 8 ranking miscibility of liquids

classic like dissolve like example

polar



⇓

in the middle is soap

nonpolar hydrocarbon

be able to rank the relative amounts of OH vs hydrocarbon

example sugar > $CH_3OH$ > $CH_3\overset{\overset{O}{\|}}{C}CH_3$ > $CH_4$ in $H_2O$

## 9 Clausius Clapeyron equation

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_v}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Know the functional relationships and how this relates to theory in ②

① see that IMF ↑, $\Delta H_{vap}$ ↑ and P ↓ (exponentially)

② see that T ↑ the P ↑ exponentially

Hint the problem type is very similar to the quiz

## 10 Van't Hoff factor and colligative properties

Colligative properties are ∝ to amount.

But some solutes do not dissolve 1:1 with amount added to solution

$i$ is the correction factor.

salts that dissolve fully

NaCl $i = 2$

$CaCl_2$ $i = 3$

non [illegible] molecules

sugar

urea

$i = 1$

rocks

CaO

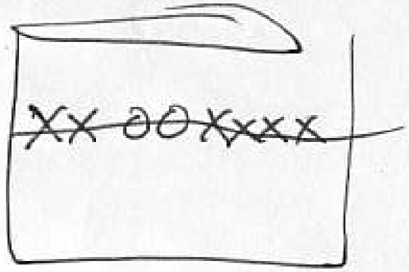
$Al_2O_3$

$i = 0$

## 11 binary mixture and Raoult's Law

This will be a simple hand calculation

× step 1. calculate $P = P_o X$ for first compound.
○ step 2. calculate $P = P_o X$ for second compound
step 3. total $P = P_x + P_o$



## 12 colligative property calculation

b.p. or f.p. calc.

$\Delta T_f = i K_f m$

$\Delta T_b = i K_b m$

Hint. remember. $\Delta T$ is
the change but it (subtracted)
needs to be added (or) to
$T_b$ or $T_f$ to get the
new b.p. or f.p.

one of these ⑫ or ⑬
will be a simple
hand calculated
plug + chug.
The other will
be a simple
prediction based
on function.

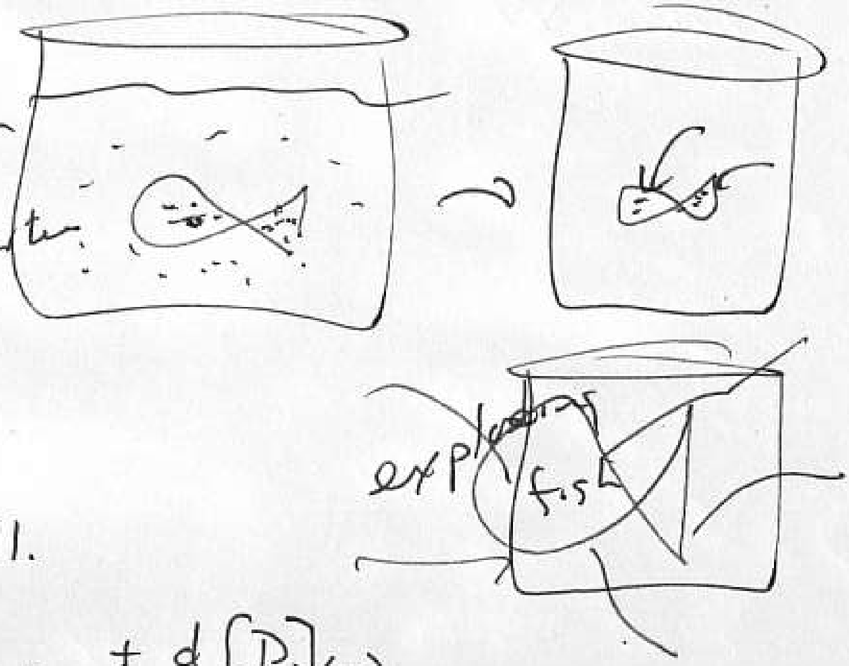
13 colligative property calculation

osmotic pressure calc.

$\Pi = \underbrace{M}_{\text{is really large}} RT$

This is the dead fish case for differences in osmotic pressure from clean water.

so osmotic pressure differences are much larger than v.P. or $\Delta T_{f,b}$ collig. properties



**Chemical Equilibria**

14 setting up K from equilibrium expression

I will give you an equil.

$$\underbrace{aA_{(s)} + bB_{(l)}}_{\text{activity}=1 \text{ so ignore}} \rightleftharpoons \underbrace{cC_{(g)} + d[D]_{(aq)}}_{P + [\,]\text{ can change so include}}$$

$$K = [C]^c[D]^d$$

## 15 calculating equilibrium concentrations from K

This is RICE

I give you an equil. expression. you set up K and RICE.

$2AB \rightleftharpoons A_2 + B_2$

| | | |
|---|---|---|
| $C_{AO}$ | 0 | 0 |
| $-2x$ | $+x$ | $+x$ |
| $C-2x$ | $x$ | $x$ |

← use Q vs K for signs

I then give you starting amounts. You solve in terms of a value x

plug these into $K = \frac{x^2}{C-2x}$. Then solve.

## 16 calculating equilibrium concentrations from K

This is RICE

Hint. I have to make these easy because you don't get a calculator.

possible ways to solve.

- you find answer in terms of x

or
- The x you solve is in a first order expression

## 17 determining reaction direction from Q and K

This is a subset of 15 + 16.

I give you a K. You then stick starting values of materials in to find Q from mass action quotient.

If Q < K shift R
Q > K shift L

## 18 LeChatelier and reaction direction

most certainly a P or [ ]

These are easy.

① what is the external stress P↓↑? [ ]↑↓ T↑↓

② make the system do the opposite by shifting L or R.

$3A_{(g)} \rightleftarrows 2B_{(g)}$ then if ① P↑ then ② P↓ shifting R
if ① A↑ then ② A↓ shifting R

## 19 LeChatelier and reaction direction

most certainly a T

Same idea as (18) but there is a $\Delta H$ ⊕ or ⊖ involved.

to make it easy, stick "heat" on side of reaction it should go. On left if $\Delta H$ ⊕ on right if $\Delta H$ ⊖

$$\left.\begin{array}{l} 3A \rightarrow 2B + \text{heat} \\ \text{or heat} + 3A \rightarrow 2B \end{array}\right\}$$

Then apply idea in (18).

Example ① T ↑ so ② T ↓ the shift L in top example, shifts R in bottom example.

## 20 Van't Hoff equation and T dependence of K

Expect a problem very similar to

$$\ln \frac{K_2}{K_1} = \frac{\Delta H_r}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

have understand that $\Delta H$ being exo or endo drives whether the K increase (rxn shifts R) or K decrease (rxn shifts) left.

Hint use LeChatelier to solve. (19) This type was on the quiz

21 relationship of ΔG to K

$$\Delta G = -RT \ln K$$

understand the functional relationship of ΔG to K

that ΔG ⊖ means $K > 1$ (happens)

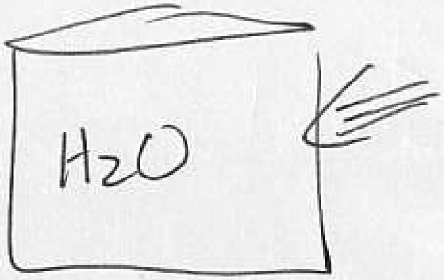
ΔG ⊕ means $K < 1$ (doesn't happen)

understand that there is an exponential relationship.

a large ΔG "explodes" the magnitude of K

**Introduction to Water Equilbria**

22 theory of auto-protolysis of water



pure $H_2O$ dissociates

$H_2O \rightleftarrows H^+ + OH^-$ $K_W = [H^+][OH^-]$

$\Uparrow$

no $[H_2O]$ term

note this reaction "doesn't happen" because K is very small

understand neutrality means $[H^+] = [OH^-]$ because 1:1 $H^+$ to $OH^-$

pH = pOH

## 23. temperature dependence of Kw

adding T (energy) to water makes more dissociation $H_2O \rightarrow H^+ + OH^-$ in > amounts

so $K_w > 10^{-14}$

removing T (energy) from $H_2O$ makes less $H^+ + OH^-$

$K_w < 10^{-14}$

i.e. since $H^+ = OH^- = \sqrt{K_w}$ Then pH > 7 for low T 0° ≈ 7.5

pH < 7 for high T 100° ≈ 6

## 24. molar solubility calculation

This is dissociation of salts in water to find [ ] of a dissolved ion.

$$AB_{(s)} \rightleftharpoons \cancel{[}A^+\cancel{]} + B^- \qquad K_{sp} = [\overset{x}{A^+}][\overset{x}{\cancel{B}^-}]$$

$$x^2 = K_{sp} \qquad x = \sqrt{K_{sp}}$$

But not all salts are 1:1 of cation to anion

| AB | $AB_2$ + $A_2B$ | $AB_3$ $A_3B$ |
|---|---|---|
| $\sqrt{K_{sp}}$ | $\sqrt[3]{\frac{K_{sp}}{4}}$ | $\sqrt[4]{\frac{K_{sp}}{27}}$ |

this will be a very easy exp. math calc.

25. ranking solubilities based on Ksp values

note from ② That as Ksp increases the [ ] increases. But, need to account for # of ions going into solution.

AB $K_{sp} = 10^{-12} \longrightarrow \sim \sqrt[2]{\ } = 10^{-6}$ ← least soluble

$AB_2$ $K_{sp} = 10^{-12} \longrightarrow \sim \sqrt[3]{\ } = 10^{-4}$

$AB_3$ $K_{sp} = 10^{-18} \sim \sqrt[4]{\ } \approx 10^{-4.5}$

$A_2B_3$ $K_{sp} = 10^{-20} \sim \sqrt[5]{\ } \approx 10^{-4}$

26. converting between pH, pOH, [H+] and [OH-]

$$[H^+][OH^-] = \overset{10^{-14}}{K_w} = K_a K_b$$

and $$pH + pOH = p\overset{14}{K_w} = pK_a + pK_b$$

a very simple plug and chug

27. ranking acidity and basicity from Ka and Kb

because there is a 1:1 of $H^+$ to $A^-$

this is easier than ㉕

$HA \rightleftharpoons H^+ + A^-$ $B \rightleftharpoons BH^+ + OH^-$

∴ as Ka increases, acidity increase

as Ka decrease, acidity decrease

as Kb increase, basicity increase

as Kb decreases, basicity decrease.

28. strong acid or base calculation Example ① $Ka = 10^{-5}$ ② $Ka = 10^{-7}$ ③ $Ka = 10^{-8}$

$\Uparrow$ most acidic $\Uparrow$ least acidic

Know the strong acids + strong bases

$HCl$, $HBr$, $HI$

$HNO_3$ $HClO_4$ $HClO_3$ $H_2SO_4$

$NaOH$ · $Ca(OH)_2$

$LiOH$ $Ba(OH)_2$

$KOH$ $Sr(OH_2)$

$RbOH$

① remove the spectator ( either $Cl^-$, $F^-$, $Br^-$, $NO_3^-$, $SO_4^=$, $ClO_4^-$, $ClO_3^-$) or $Na^+$, $K^+$, $Li^+$ ... )

② what is left. either $H^+$ or $OH^-$: That is the answer.

$H^+ = Ca$ $OH^- = Cb$

29. weak acid or base calculation

weak acid

$H^+ = (K_a C_a)^{1/2}$

simple exponent math is used. The pH ↔ pOH

Ka ↔ Kb

will be needed to be in correct Acid or base environment.

what is the pH

of $10^{-5}$ M acetic acid

if it is 0.1M in soln?

$H^+ = [(10^{-5})(.1)]^{1/2} = 10^{-3}$ ∴ pH = 3

30. weak acid or base calculation

weak base

$OH^- = (K_b C_b)^{1/2}$

What is pH of

0.1 M sodium acetate

if Ka of acid is $10^{-5}$?

$OH^- = (\overset{10^{-9} \leftarrow \text{convert}}{K_b}\ .1)^{1/2} = \sqrt{10^{-10}} = 10^{-5}$

but that is $OH^-$

pOH = 5

so pH = 9

use ㉖ to get to pH