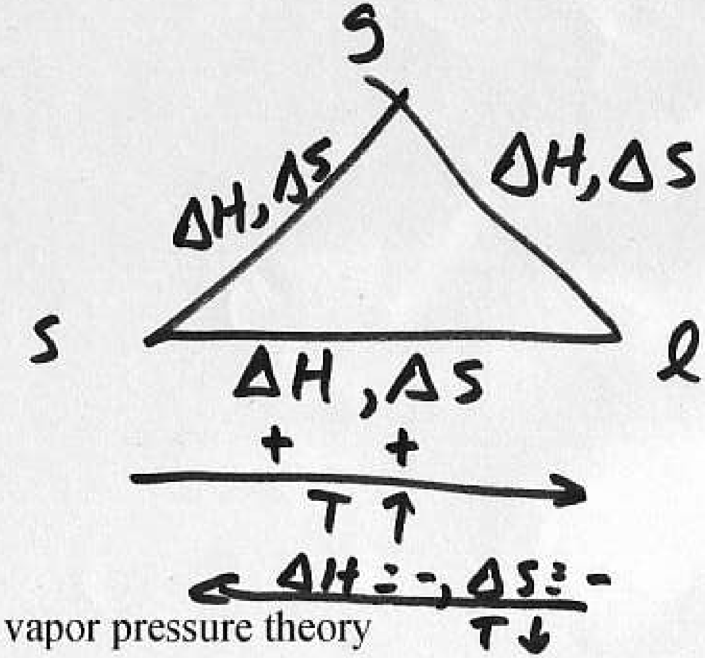
## Physical Equilibria

1 temperature dependence of phase changes



be able to understand this across all phase transitions

2 vapor pressure theory

- closed system, at equilibrium $G_l = G_v$
- surface phenomenon, the more spots on surface the greater the vapor pressure

$$P = P^\circ X$$

- the magnitude of v.p. is related to the strength of IMF which is proportional to $\Delta H_{vap}$
- ∴ Clausius Clapeyron $\ln \frac{P_2}{P_1} = \frac{\Delta H_v}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

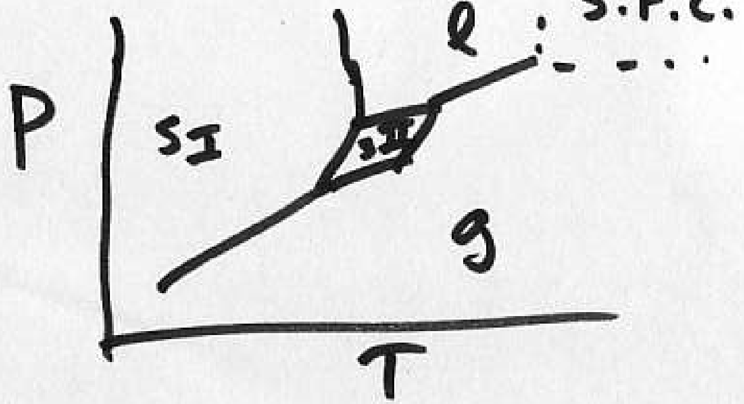
## 3 salt dissociation in water

first example of mixing + equilibrium

- salts form ions, ions are polarized ∴ ions love water which is polar
- There are competing forces in dissolving salt in water $\Delta H_{soln} = \Delta H_L + \Delta H_{Hyd}$
- $\Delta H_L$ is always ⊕ $\Delta H_{Hyd}$ is always ⊖, added together they equal ~ 0 for $\Delta H_{soln}$.
- The magnitude of $\Delta H_L$, + $\Delta H_{Hyd}$ are related to charge density.

## 4 phase diagram interpretation

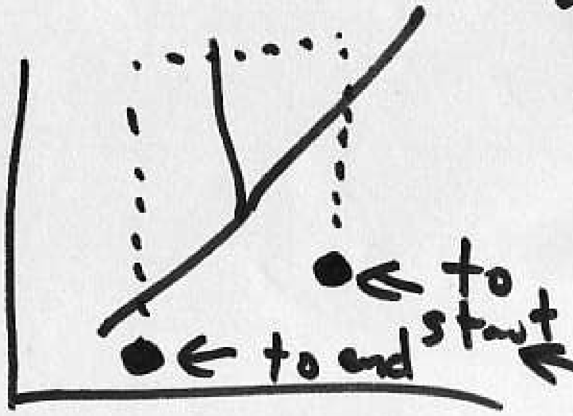
I will provide a phase diagram. Be able to explain features of the diagram.



note the

- 2 triple points
- SFC region
- 2 solid crystal region
- the multiple equil lines at phase transitions.

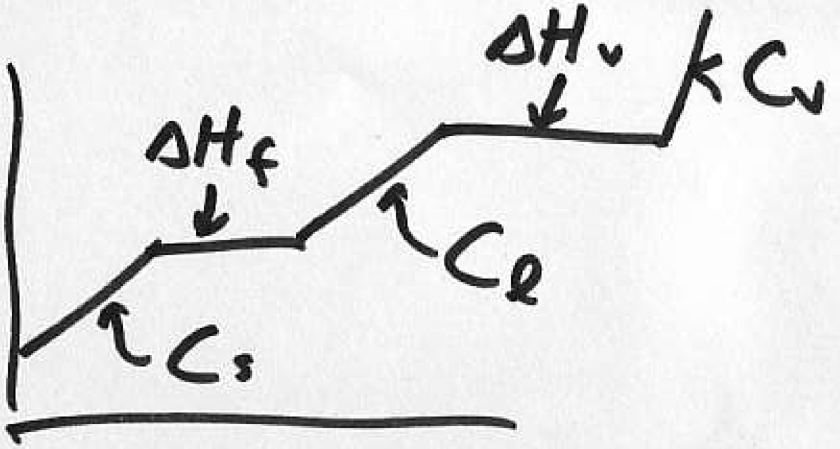
## 5 phase diagram navigation



you will be given a phase diagram and a starting P + T, and asked to go to a new P + T and tell what happened along the way.

in this example, nothing happened since gas became a gas although it went through $g \to l \to s \to g$

## 6 calculating ΔH across phases transitions



$$\Delta H = mC\Delta T$$
$$\Delta H = mC$$

you will be given starting and ending T values and asked to determine heat needed to change temperature

7 gas solubility in liquids

Some important things to know

- some gases are soluble because of reaction
- some gases are soluble because of polarity
- some gases (inert) are moderately soluble because of size

1. remember that Henry's Law explains gas solubility
2. dissolving most gases is exothermic so according to Le Chatelier, as T ↑, solubility ↓

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8 ranking miscibility of liquids

employs the idea that like dissolves like.

So I will give you either

- a nonpolar liquid or
- a polar liquid

and you have to look at a series of chemicals and rank their polarity knowing that like dissolves like.

Example : hexane solvent is ← nonpolar, so the ranking would be most polar < < < most nonpolar

## 9 Clausius Clapeyron equation

The quantitative measure of vapor pressure.

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

I might ask a crank it out problem but more likely I will ask for an understanding of how to set up the solution algebraically. (like on quiz)

## 10 Van't Hoff factor and colligative properties

All colligative properties count the number of particles in solution. But the # of particles in solution depends on solubility and extent of dissociation.

Example

NaCl
assume $i=2$
because dissolves
completely + dissociates into 2

CaO
assume $i \sim 0$
because doesn't
dissolve

## 11 colligative property application

I have told some cool stories about the relevance of colligative properties. Know them.

- car radiators don't overheat or freeze
- fish explode (+ cells)
- Ice melts when salt added
- water boils at higher temperature

} know theory + concept

## 12 colligative property calculation

There are two of these. They will be applied to following equations

$$P = iP_0X$$

$$\Delta T_f = iK_f m$$

$$\Delta T_b = iK_b m$$

$$\Pi = iMRT$$

} Note the general form. I bet that at least one will be a plug + chug with $i \neq 1$

13 colligative property calculation

And a second will ask you to mess with m, X, M to look at # of g or MW.

Example, what is the MW of a polymer which creates an osmotic pressure of 3 atm when 6 g of polymer is added to ..... . . . . . . .

$\pi = MRT \Rightarrow \pi = \frac{\text{moles}}{V} RT \Rightarrow \pi = \frac{g/MW}{V} RT$

## Chemical Equilibria

14 setting up K from equilibrium expression

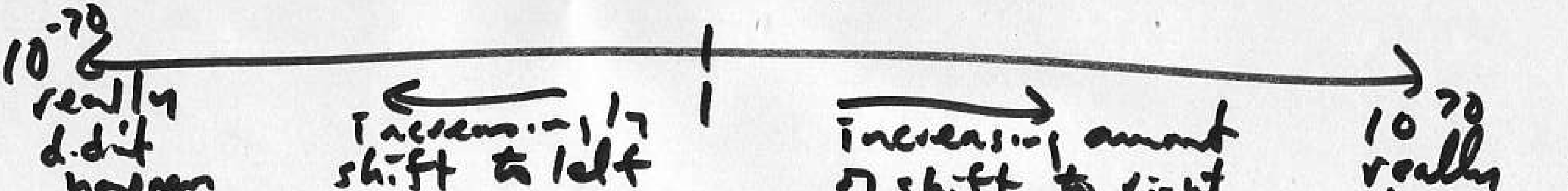
Mind numbingly simple problem in which I give you a chemical reaction and you set up the mass action relationship.

But!! remember that solids + pure liquids have activity = 1

$H_2O(l) \rightleftharpoons H^+ + OH^-$ $K_w = [H^+][OH^-] \xleftarrow{\text{no}}_{H_2O}$

## 15 appreciating the magnitudes of K

If you are told about a reaction and its extent (did happen, didn't happen, went to completion, etc.) you should know something about K and its magnitude



## 16 calculating equilibrium concentrations from K

classic RICE expression problem. I will give you K + [illegible] a reaction and starting materials. you will give me the equil. amount of something.

$A + B \rightarrow 2C$

| | | |
|---|---|---|
| 3 | 2 | 0 |
| -x | -x | +2x |
| 3-x | 2-x | 2x |

$$K = \frac{[C]^2}{[A][B]} = 11.3$$

$$K = \frac{(2x)^2}{(3-x)(2-x)} = 11.3$$

solve for x

17 determining reaction direction from Q and K

I will give you a K value (or let you calculate it from equil. conc.) and I will give you starting values. you will determine Q and

- if $Q < K$ rxn shifts right
- if $Q = K$ rxn equil.
- if $Q > K$ rxn shifts left

18 LeChatelier and reaction direction

All LeChatelier done the same.

1. Determine external stress
   T ↑ or T ↓
   P ↑ (V ↓) or P ↓ (V ↑)
   [ ] ↑ or [ ] ↓
   } The surroundings
2. Make the system do the opposite
   ie. If P external ↑ and P in system ↓

## 19 LeChatelier and reaction direction

cont. from 18

∴ a reaction will shift either left or right.

Some hints.

- It is impossible one of the questions won't be a T change

- Oldest trick in the book, if $\Delta n_{gas} = 0$ then system can't shift.

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

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

you can almost bet it will be one that gives you $K_2, T_2$ vs $K_1, T_1$ and expects you to understand what this must mean about $\Delta H$ and reaction direction

### 21 relationship of $\Delta G$ to K

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

most likely need to understand the relationships (and magnitudes) for K vs. $\Delta G$. Have some idea, give a $\Delta G$, what the K should be.

## Introduction to Water Equilbria

### 22 theory of auto-protolysis of water

Water does this by itself

$$H_2O \rightleftharpoons H^+ + OH^-$$

but only in very small amounts

at 300K $[H_2O] \sim 55M$, $H^+ = OH^- = 10^{-7}$

Things to know.

- $K_w \sim 10^{-14}$ at 300K
- "neutrality" is defined [illegible] as $H^+ = OH^-$ or $pH = pOH$

## 23. temperature dependence of Kw

$H_2O \rightleftarrows H^+ + OH^-$  $K_w = [H^+][OH^-] = 10^{-14}$ at 300K.

but the process is endothermic so $\Delta H$ is ⊕. This means that

T ↑ , reaction shifts right

T ↓ , reaction shifts left.

∴ Kw changes. at 0° ~ $10^{-16}$, pH ~ 8 // 100° ~ $10^{-12}$ pH ~ 6

both neutral because $H^+ = OH^-$

## 24. molar solubility calculation

salts dissociate to make cations + anions.

There are only a few forms to salts

$AB \rightleftarrows A^+ + B^-$  so can write $K_{sp} = [A^+][B^-]$ ← no denominator.

$AB_2$
$A_2B$
$A_3B$ etc.

$AB_3 \rightarrow A^{+++} + 3B^-$ or $K_{sp} = [A^{+3}][B^-]^3$

$A_2B_3$

so simple to find molar solubility based on

$AB = \sqrt{K_{sp}}$

$AB_2 = \sqrt[3]{K_{sp}/4}$

### 25. ranking solubilities based on Ksp values

most salts are sparingly soluble. So see values like $10^{-10} \sim 10^{-37}$. Obviously the smaller the Ksp the less soluble.

**BUT** since the number of ions in solution depends on type of salt you must take this into account

AB ← 2 ions $AB_2$ ← 3 ions.

so $K_{sp} = 1\times10^{-10}$ $AB \approx [10^{-5}]$

$K_{sp} = 1\times10^{-12}$ $AB_2 \cong [10^{-4}]$

so $AB_2$ salt is more soluble even though Ksp is smaller.

~~**~~ this is on test **

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

because

$K_w = [H^+][OH^-] = 10^{-14}$

I can find $H^+$ if given $OH^-$ and vice versa.

But $pK_w = pH + pOH = 14$

so I can also find $pH, pOH, H^+, OH^-$ given any one to start.

Example.

$H^+ = 10^{-5}$.

$\therefore OH^- = 10^{-9}$

and $pH = 5$

and $pOH = 9$

27. ranking acidity and basicity from Ka and Kb ⟸ the most missed question on exam.

Ka and Kb values of weak acids + bases are small, like $10^{-3} \rightarrow 10^{-15}$

this is related directly to strength of acid or base.

The smaller the Ka, the weaker the acid
The larger the Ka, the stronger the acid
The smaller the Kb, the weaker the base
The larger the Kb the stronger the base.

28. strong acid or base calculation

Know the strong acids + bases

$HCl$, $HI$, $HBr$ alk. metal or earth $(OH)$
$HClO_4$, $HClO_3$
$HNO_3$, $H_2SO_4$

what you start with

Then. $[H^+] = C_a$ $[OH^-] = C_b$

Example. what is pH of 0.1 M NaOH
$\therefore$ $C_b = .1\,M$ $OH^- = .1\,M$ $pOH = 1 \Rightarrow pH = 13$

29. weak acid or base calculation

This is plug + chugging

$$H^+ = (K_a C_a)^{1/2} \text{ or } OH^- = (K_b C_b)^{1/2}$$

you need to see you have a weak acid or base. Find $C_a$ or $C_b$ Find $K_a$ or $K_b$

Then crank it out.

an acid ⇒ • what is pH of a $10^{-3}$ M solution of a weak acid with $K_a = 10^{-5}$?

30. weak acid or base calculation

$$H^+ = [(10^{-3})(10^{-5})]^{1/2} = 10^{-4}$$

$$pH = 4$$

a weak base ⇒ • what is pH of a $10^{-2}$ M solution of a weak base if $K_b = 10^{-6}$?

$$OH^- = (K_b C_b)^{1/2} = [(10^{-2})(10^{-6})]^{1/2} = 10^{-4} \quad pOH = 4 \quad pH = 10$$