

## Chem 201 Lecture 2b

Finish Statistics  
Review of equilibria

## Last time

We went over all lab experiments.  
We discussed chapter 4:  
a) Gaussian distribution  
b) Confidence intervals  
c) 3 cases: comparisons using t-test  
TODAY :  
Q-test  
Review Equilibria -  $K_{sp}$  and  $K_f$

## Today

Dixon's Q-test  
Gravimetry  
Review Equilibria and Thermodynamics  
Types of equilibria:  $K_{sp}$  and  $K_f$

## Q-test : for outliers

$$Q = \frac{2.79 - 2.34}{2.79 - 2.31} = .94 > .64$$

2.79-2.31 discard

Outliers= data numerically distant from the rest of the data

Example:

2.31, 2.34, 2.34, 2.34, 2.79

$$Q_{\text{calc}} = \frac{\text{gap}}{\text{range}}$$

If  $Q_{\text{calc}} > Q_{\text{table}}$ , discard

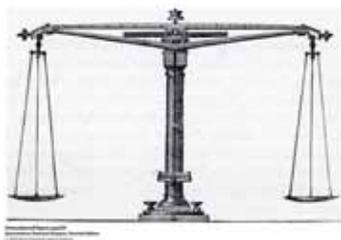
Table 4-5 Values of Q for rejection of data

Q (90% confidence)*	Number of observations
0.76	4
0.64	5
0.56	6
0.51	7
0.47	8
0.44	9
0.41	10

\*  $Q = \frac{\text{gap}}{\text{range}}$ . If  $Q_{\text{calc}} > Q_{\text{table}}$ , the value in question can be rejected with 90% confidence.

SOURCE: R. A. Dixon and W. J. Dixon, *Anal. Chem.*, **1971**, *43*, 1706; see also D. A. Brinkman, *Anal. Chem.*, **1974**, *46*, 173.

## Gravimetric Methods (Chapt 27)



## Gravimetric methods

Time-honored analytical methods of weighing accurately.

2 types to be discussed: Precipitation, & Combustion

Precipitation - selective precipitation to determine the %composition of analyte or mixture.

Combustion analysis - uses changes in mass due to thermal decomposition to determine %composition.

## Refer to Table 27-1

You are accountable for the precipitation of:  
 $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Ba^{2+}$ ,  $Mn^{2+}$ ,  $Ni^{2+}$ ,  $Ag^+$ ,  $PO_4^{3-}$ ,  $SO_4^{2-}$

Know the precipitated form and the weighed forms.

Necessary for solving problems.

## Refer to Table 27-1

Know the structure and use of  
dimethylglyoxime

## Figure of $Ni(DMG)_2$

Refer to the figure in page 635 (7<sup>th</sup> edition)  
Go over the corresponding example problem  
And the the example problem that follows (the one with  
2 components)

## Precipitation: Some criteria

**Criteria** for ideal product in precipitation gravimetry:

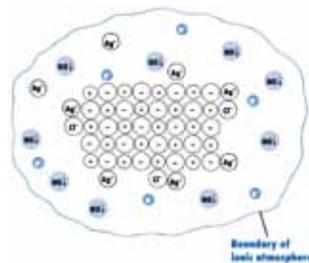
- 1) very insoluble
- 2) filterable
- 3) very pure
- 4) of known and constant composition  
(consider each of the above)

## Solubility factors

**Solubility** in turn is a function of

- a) temperature
- b) polarity of solvent (e.g. alcoholic DMG)
- c) chemical environment

## Ionic atmosphere



## Relative saturation

solubility: g solute/100 mL solution or g of solvent

example: solubility of NaCl is 36g/100g H<sub>2</sub>O @ 20°C

Relative saturation = (Q-S)/S

When rel saturation > 0, crystals can form.

**Process of Crystallization: 2 processes occur:**

- nucleation (slow) - rate dependent on relative saturation
- particle growth (fast).

## Precipitation Technique

Gravimetric technique calls for filtration. (think Ni Expt)

Larger crystals are preferred. So lower supersat'n preferred:

- raise T to keep crystal formation "dynamic" ("digestion")
- add precipitant slowly with vigorous stirring (homogeneous) (in Ni expt, precipitant is DMG)
- keep volume of solution large. (keep ionic concs rel. const)

## Thermogravimetry: combustion analysis for C & H

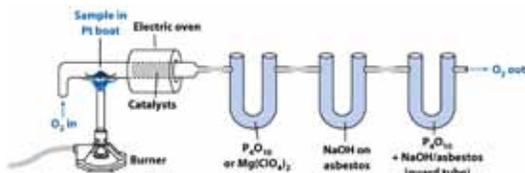


Figure 27-4  
Quantitative Chemical Analysis, Seventh Edition  
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## Modern combustion analysis

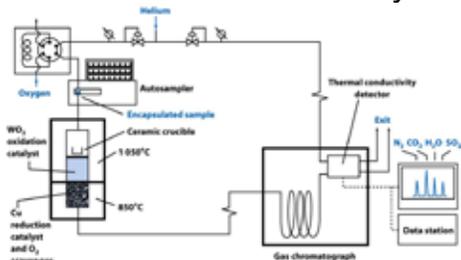


Figure 27-5  
Quantitative Chemical Analysis, Seventh Edition  
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## Thermal decomposition example

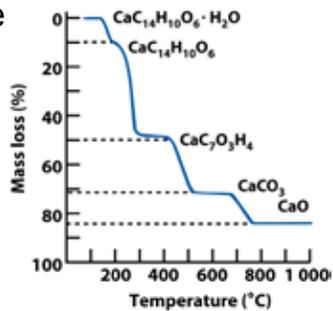


Figure 27-3  
Quantitative Chemical Analysis, Seventh Edition  
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## Some terms to know

Read up on terms: at the end of chapter 27

- absorption - penetrating surface
- adsorption - attachment to surface
- inclusions - impurities absorbed (random)
- occlusions - pockets of impurities adsorbed
- coprecipitation - impurities included in crystallized ppt (eg DMG crystals)
- gathering - gathering agent (ppt used to collect a trace)
- masking agent - used to prevent co-precipit'n of impurities (eg tartaric acid)
- peptization - break up of crystals during washing
- washing - "rinsing", washing to remove the impurities, very important.
- igniting (in thermogravimetric analysis) - heat strongly to change composition.
- hygroscopic - picks up water from the surrounding air

### Example problem #1

A 1.550 g mixture of NaCl and NaNO<sub>3</sub> is dissolved in a 100.0 mL solution. Excess AgNO<sub>3</sub> is added and a precipitate with a final dry weight of 1.100 g is produced.

What is %Cl in original mixture?

(n.b.: Cl<sup>-</sup> precipitated with Ag<sup>+</sup>; g/mol: Cl = 35.453; AgCl = 143.32)

answer: 27.21% (make sure correct # sig figs!)

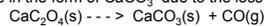
### Example problem #2

A 1.500 g dried sample contains only NaI and NaBr. It is precipitated with excess AgNO<sub>3</sub>. The dried ppt weighs 2.4782 g. What is the % NaI in the original sample? (note that AgBr and AgI are the precipitates; g/mols: AgBr = 187.772, AgI = 234.772, NaI = 149.904, NaBr = 102.904)

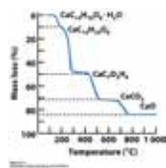
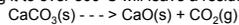
answer: 27.21% (make sure correct # sig figs!)

### Example problem #3

CaC<sub>2</sub>O<sub>4</sub> can be made to decompose thermally. For example, if heated to 600°C, it will be in the form of CaCO<sub>3</sub> due to the loss of CO:



Heating it to over 800°C will leave a residue of CaO due to loss of CO<sub>2</sub>:



### Example problem #3

After a 0.5000 g ore containing only CaC<sub>2</sub>O<sub>4</sub> and a thermally inert substances is heated to 600°C, the weight of the ore drops to 0.4781. What is the % CaC<sub>2</sub>O<sub>4</sub> in the original ore? (note: CaCO<sub>3</sub> remains; g/mol: CaC<sub>2</sub>O<sub>4</sub> = 128.1; CaCO<sub>3</sub> = 100.1, CO = 28.0 g.

Answer: 20.0%

### Review Equilibria, K expression

For  $aA + bB \rightleftharpoons cC + dD$

$$K_{\text{eq}} = \frac{[\text{products}]}{[\text{reactants}]}$$

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Note: for solids and liquids, use 1

For solutions, use M

For gases, use partial pressures (in Bar)

### Manipulating K's

If  $A \rightleftharpoons B$   $K = K_1$ ;  $B \rightleftharpoons C$   $K = K_2$

1) What is K' for  $B \rightleftharpoons A$ ?  $K' = ?$

$$K' = 1/K_1$$

2) What's K'' for  $2A \rightleftharpoons 2B$ ?

$$K'' = K_1^2$$

3) What's K''' for  $A \rightleftharpoons C$ ?

$$K''' = K_1 K_2$$

## Review Thermodynamics

$\Delta G$  = free energy change  
 $\Delta H$  = enthalpy change ( $\Delta H < 0$  exothermic)  
 $\Delta S$  = entropy change  
 $\Delta G = \Delta H - T\Delta S$   
Favored rxn:  $\Delta G < 0$     unfavored:  $\Delta G > 0$   
If  $\Delta G = 0$ , system is at equilibrium

## Le Chatelier's Principle

A system initially at equilibrium, subjected to a "stress" will respond to minimize that "stress".



Examples:

[B] increase : product is favored (forward is favored)

[A] decrease: reactant is favored (reverse favored)

$P_C$  increased: reactant is favored (reverse favored)

A or D are added or subtracted: neither favored

Temp is increased: forward is favored

## Relation of $\Delta G$ , K and Q:

$\Delta G = \Delta G^\circ + RT \ln Q$  (Q=reaction quotient)

If  $Q = K_{eq}$ ,  $\Delta G = 0$  and we have:

$\Delta G^\circ = -RT \ln K_{eq}$  or  $K_{eq} = 10^{-\Delta G^\circ / RT}$

From Q, we can predict favored direction:

$Q > K_{eq}$ , reverse favored

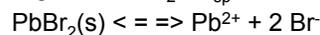
Since  $\Delta G = \Delta G^\circ + RT \ln Q > \Delta G^\circ + RT \ln K = 0$

Similarly:  $Q < K_{eq}$ , forward is favored

## Types of equilibria: solubility product, $K_{sp}$

$K_{sp}$  -used for sparingly soluble ionic substances.

E.g.  $PbBr_2$ ,  $K_{sp} = 7.9 \times 10^{-6}$



1                      s                      2s

$$(s)(2s)^2/1 = 7.9 \times 10^{-6} \Rightarrow s = (1.98 \times 10^{-6})^{1/3}$$

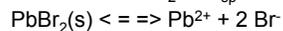
$s = 1.3 \times 10^{-2} M$  (s = molar solubility, saturated)

If  $Q = K$ ; saturated, if  $Q > K$ , supersaturated

## Common ion effect

If add  $PbBr_2$  to 0.10M NaBr, what is solubility?

Recall:  $PbBr_2$ ,  $K_{sp} = 7.9 \times 10^{-6}$



1                      s                      0.10M + 2s

$(s)(.10+2s)^2/1 = 7.9 \times 10^{-6}$ ; using 5% rule we get:

$$\Rightarrow s \approx (7.9 \times 10^{-6}) / (0.10)^2 = 7.9 \times 10^{-4}$$

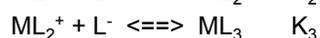
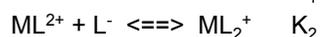
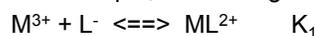
Note:  $(100\%)(7.9 \times 10^{-4}) / (0.10) = 0.79\% < 5\%$

Note: presence of *common ion* lowers solub.

## Types of equilibria: $K_f$

$K_f$  = complex ion formation constant

for example,  $M^{3+}$  and ligands  $L^-$ :

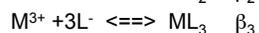
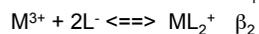
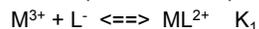


Note that  $K_1$ ,  $K_2$  and  $K_3$  are "step-wise formation constants".

## Types of equilibria: $K_f$

$K_f$  = complex ion formation constant

For the previous example,  $M^{3+}$  and ligands  $L^-$ :



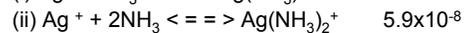
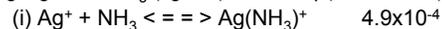
Note that  $\beta_2$  and  $\beta_3$  are "cumulative formation constants".

Note:  $\beta_n = K_1 K_2 \dots K_n$

## $K_f$ example: $Ag(NH_3)_2^+$

$K_f$  = complex ion formation constant

Eg  $Ag^+$  and  $NH_3$  (ligand)  $\beta$ (cumulative):



$K_2 = ?$  for:  $Ag(NH_3)^+ + NH_3 \rightleftharpoons Ag(NH_3)_2^+$

Do (ii)-(i):  $K_2 = K_{ii}/K_i = (5.9 \times 10^{-8}) / (4.9 \times 10^{-4}) = 1.2 \times 10^{-4}$

$K_2$  is a "step-wise formation constant".

(another way:  $\beta_2 = K_1 K_2$  so  $K_2 = \beta_2 / K_1$

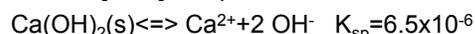
$= (5.9 \times 10^{-8}) / (4.9 \times 10^{-4}) = 1.2 \times 10^{-4}$ )

## Consider $Ca(OH)_2$

$K_{sp}$  for  $Ca(OH)_2$  is  $6.5 \times 10^{-6}$

$K_f$  for  $Ca(OH)^+$  is  $10^{-1.3}$

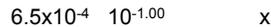
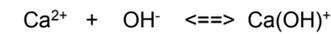
What is  $[Ca^{2+}]$  in a pH 13.00 buffer?



$$s \approx (6.5 \times 10^{-6}) / (10^{-1.00})^2 = 6.5 \times 10^{-4}$$

$[Ca(OH)^+] = ?$  Use  $K_f$  equilibrium

## $K_f$ equilibrium calculation



$$K_f = [Ca(OH)^+] / [Ca^{2+}][OH^-]$$

$$10^{-1.3} = x / (6.5 \times 10^{-4})(10^{-1.00}); \quad x = 3.3 \times 10^{-6}$$

(n.b. both equilibria satisfied at same time)

As  $[OH^-]$  increases, dissolved  $Ca^{2+}$  increases due to complex formation

Total dissolved Ca =  $[Ca^{2+}] + [Ca(OH)^+]$

## Next time: Protic Acids

Bronsted-Lowry definition

Salts can be acidic or basic

Conjugate acids and bases

Self-ionization of water

pH =  $-\log[H^+]$  (approx)

Strengths of acids and bases