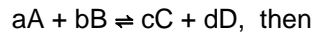


## Chemical Equilibrium...Review?

Most chemical systems are governed by equilibria such that if:



$$\frac{(a_C)^c (a_D)^d}{(a_A)^a (a_B)^b} = K$$

where K is the equilibrium constant, and  $a_X$  is the *activity* of X and described by the activity coefficient  $\gamma_X$  and [X]:

$$a_X = \gamma_X [X]$$

In dilute solutions, the activity coefficient approaches unity. Often, experimental conditions allow us to assume activity coefficients of one so that concentrations can be substituted for activities.

(This assumption isn't always good!)

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

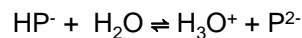
1

## Chemical Equilibrium

So, knowledge of reaction stoichiometry and the equilibrium constant allows us to make some predictions about the system.

If K is very large, that the equilibrium lies far to the right (or towards products). If K is small, the reaction lies towards reactants.

*For example*, the KHP we are using in lab is a monoprotic acid that undergoes the following equilibrium:



$$K = \frac{[H_3O^+][P^{2-}]}{[HP^-]} = 3.9 \times 10^{-6}$$

From the small magnitude of K, the equilibrium must lie to the left, which makes sense, since KHP is a *weak* acid.

2

## Manipulating Equilibria

It is possible to drive a reaction towards reactions or products by applying an appropriate stress to the system.

- **Le Chatlier's Principle**
- In the KHP titration, the *stress* is the loss of hydronium ion via neutralization with NaOH
  - What happens when we add NaOH?

3

## Quantitative Predictions

Assume we are at a point in the titration where  $[HP^-] = 0.095M$ ,  $[P^{2-}] = 0.00013M$ , and  $[H_3O^+] = 0.00029M$ .

$$K = \frac{0.00029 \times 0.00013}{0.095} = 3.9 \times 10^{-6}$$

Now lets add enough NaOH to drop the  $[H_3O^+]$  to  $=0.00014M$ , what does the reaction have to do to regain equilibrium?

Calculate a reaction quotient  $Q$ , (the equilibrium constant expression with non-equilibrium concentrations plugged in).

- If  $Q > K$ , the reaction must proceed to the left
- If  $Q < K$ , the reaction must proceed to the right
- If  $Q = K$  the reaction is at equilibrium

In our case,

$$Q = \frac{0.00014 \times 0.00013}{0.095} = 1.9 \times 10^{-7}$$

$Q < K$  so the reaction must proceed to the right!

4

### Important items to remember regarding equilibrium constant expressions

1. Take care when assuming unit activity coefficients!
2. All solute concentrations should be in moles per liter
3. All gas concentrations should be in atmospheres
4. By convention, all  $K$ 's are calculated relative to 1 M solutions or 1 atm gas, so the resulting constants are dimensionless
5. Concentrations of pure solids, pure liquids and solvents are omitted from the equilibrium constant expression.

5

### Equilibrium and Thermodynamics

***ALWAYS REMEMBER: Equilibrium constant expressions are thermodynamic relations.***

So, they can provide information related to the \_\_\_\_\_  
of a reaction to proceed, but say nothing about the \_\_\_\_\_.

Relating equilibrium constants and thermodynamic properties:

- Enthalpy
- Entropy
- Free Energy

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## Thermodynamic Parameters

### Enthalpy, $\Delta H$ :

“Heat” of reaction

If  $\Delta H$  is positive, heat is absorbed (acts as a reactant), reaction is *endothermic*

If  $\Delta H$  is negative, heat is released (acts as a product), reaction is *exothermic*

### Entropy, $\Delta S$ :

“Disorder” of reaction

If  $\Delta S$  is positive, products have greater entropy than reactants

If  $\Delta S$  is negative, reactants have greater entropy than products

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## Thermodynamic Parameters

The combination of entropy and enthalpy in a given reaction determine whether the reaction is spontaneous, or *thermodynamically favorable*.

This combination is the **Gibbs free energy** change in the system.

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

If  $\Delta G$  is positive, the reaction is

If  $\Delta G$  is negative, the reaction is

*How do these situations occur?*

8

## Free Energy and Equilibrium

$\Delta G^\circ = -RT \ln(K)$ , or

$$K = e^{-\Delta G^\circ / RT}$$

If  $K$  is large ( $>1$ ),  $\ln(K)$  is positive, and  $\Delta G^\circ$  is negative  $\Rightarrow$  the reaction lies towards products.

If  $K < 1$  (small),  $\ln(K)$  is negative,  $\Delta G^\circ$  is now positive, and the reaction lies to the left.

For KHP at 25°C,

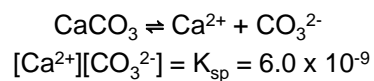
$$\Delta G^\circ = -RT \ln(3.9 \times 10^{-6}) = -8.3144 \text{ J/molK} \times 298 \text{ K} \times -12.4545$$

$$\Delta G^\circ = -(-30858.5 \text{ J/mol}) = 30.9 \text{ kJ/mol}$$

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## Solubility Equilibria

The *solubility product* describes the concentrations of species present when ions are in equilibrium with undissolved salt.



What is the concentration of calcium ion in a saturated solution of calcium carbonate?

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## Solubility Equilibria

How does this concentration change if the solution originally contained 0.010 F  $\text{Li}_2\text{CO}_3$ ?

This presence of carbonate results in a *common ion effect*.

- What does Le Chatlier's principle say should happen?
- How do we verify this quantitatively?

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## Rules of Thumb Regarding Approximations

What does " $\ll$ " mean? Why make the approximation?

- It depends on the accuracy needed in the calculation.
- For example, if  $1000x = y$ , then  $x$  is  $(1/1000)*100\% = 0.1\%$  of  $y$ , so if 99.9% accuracy is acceptable,  $x$  must be 1000 times less than  $y$  for " $x \ll y$ "
- If 99% is acceptable,  $x \ll y$  if  $x$  is 100 times less than  $y$ .
- Always document your approximations!
- Always check your approximations
  - Be sure  $x$  really is  $\ll y$ !

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## Separation by Precipitation

- It is possible to quantitatively separate two or more species based on their solubility.
  - Ability to do so is related to the magnitudes of the  $K_{sp}$  for each ion.

**Example:** Is it *feasible* to perform a 99% complete separation of 0.010M  $\text{Ca}^{2+}$  from 0.010M  $\text{Ce}^{3+}$  by precipitation with oxalate ( $\text{C}_2\text{O}_4^{2-}$ )?



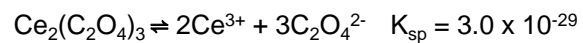
Questions to ask:

1. What ion will precipitate first?

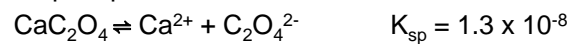
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## Separation by Precipitation

2. What concentration of oxalate is needed to reduce the  $\text{Ce}^{3+}$  concentration to 1% of its initial value?



3. Will calcium precipitate at this oxalate concentration?



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## Acids, Bases and Equilibria

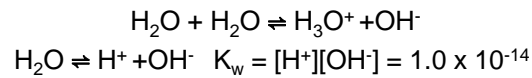
**Definitions (several):**

1. Lewis - Electrons
2. Bronsted - Protons

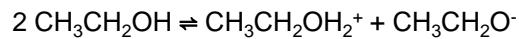
**Conjugate Acid-Base Pairs and Neutralization Reactions**

**Solvent Autoprotolysis or self-ionization**

- Water is the most common:



- Also occurs in all *protic* solvents.



**pH**

$$\text{pH} = -\log [\text{H}^+] \text{ (really activity of H}^+)$$

$$\text{pH} + \text{pOH} = \text{p}K_w = 14.00 \text{ at } 25^\circ\text{C}$$

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## Acid and Base Strength

Based on percent dissociation in solution

- **Strong acids/bases** dissociate essentially completely in water
- **Weak acids/bases** only partially dissociate, results in equilibrium concentrations of both the acid and its conjugate base

Fraction of Dissociation:

Know the strong acids and bases in Table 6-2

**TABLE 6-2** Common strong acids and bases

Formula	Name
<i>Acids</i>	
HCl	Hydrochloric acid (hydrogen chloride)
HBr	Hydrogen bromide
HI	Hydrogen iodide
H <sub>2</sub> SO <sub>4</sub> <sup>a</sup>	Sulfuric acid
HNO <sub>3</sub>	Nitric acid
HClO <sub>4</sub>	Perchloric acid
<i>Bases</i>	
LiOH	Lithium hydroxide
NaOH	Sodium hydroxide
KOH	Potassium hydroxide
RbOH	Rubidium hydroxide
CsOH	Cesium hydroxide
R <sub>4</sub> N <sup>b</sup> OH <sup>b</sup>	Quaternary ammonium hydroxide

<sup>a</sup> For H<sub>2</sub>SO<sub>4</sub>, only the first proton ionization is complete. Dissociation of the second proton has an equilibrium constant of  $1.0 \times 10^{-2}$ .

<sup>b</sup> This is a general formula for any hydroxide salt of an ammonium cation resulting from organic groups. An example is tetraethylammonium hydroxide: (C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N<sup>+</sup>OH<sup>-</sup>.

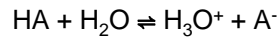
Harris, Quantitative Chemical Analysis, 8e  
© 2011 W. H. Freeman

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## Weak Acid/Base Equilibria

### Weak Acid



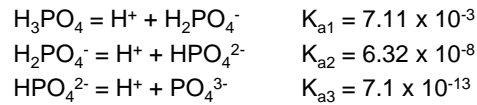
$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

Examples:

Relationship between  $K_a$  and  $K_b$  for conjugate acid/base pairs:

$$K_a \times K_b = K_w$$

Polyprotic acids/Polybasic bases ( $K_{a1}$ ,  $K_{a2}$  ...)



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## Complexation Equilibria

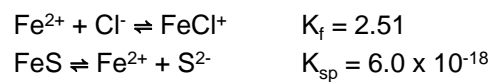
Formation of coordinate bonds between Lewis Acids/Bases

Can be described by **step-wise** or **cumulative** formation constants



Influence on solubility:

**Example:** How many grams of Iron (II) Sulfide can be dissolved in 100.0 mL of 0.10 F KCl?



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### Tune-up Problems

What are the pH, pOH of a 0.015 F solution of benzoic acid?

What is the pH of a solution prepared by mixing 100 mL of 0.010 F acetic acid with 25 mL 0.010 F sodium hydroxide?