

## CHAPTER 7

# CHEMICAL EQUILIBRIUM

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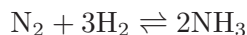
Chemical equilibrium is the single most important topic on the AP exam. It gets the most ink from the question writers. As a result, it should get the most “ink” back from students. Our best advice: you should spend any available free time improving your understanding of chemical equilibrium!

### WHAT IS CHEMICAL EQUILIBRIUM?

#### Recognizing and explaining chemical equilibrium

In Chapter 5, we discussed reactions that go to completion; that is, reactions in which the limiting reactant is consumed and a maximum quantity of product is formed. However, in actual practice, many reaction systems reach a condition in which some quantity of each reactant remains in contact with some quantity of each product and that no further change appears to occur. The system has achieved a steady state, called equilibrium, with no apparent further change in its properties including color, mass, density and pH. Any system at equilibrium is always a closed system.

Equilibrium is recognized by constant macroscopic properties explained in terms of dynamic molecular behavior. This equilibrium condition occurs as the result of two opposing reactions that are occurring at the same rate. The rate of the forward reaction is equal to the rate of the reverse reaction. The concept of molecular collisions as the basis for chemical reaction helps explain why equilibrium exists. In the very familiar Haber process



equilibrium is achieved when the rate of formation of ammonia is equal to the rate of consumption of ammonia.

**The Reaction Quotient** Experiments have shown that there is a reaction quotient (mass action expression) that describes quantitatively the contents of a reaction system which has reached equilibrium.

$$Q = \frac{[\text{Products}]}{[\text{Reactants}]}$$

For the generalized reaction system at equilibrium  $aA + bB \rightleftharpoons cC + dD$ .

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

The numerical value is known as the equilibrium constant,  $K_{eq}$ . There is a specific  $K_{eq}$  for any equilibrium system. The value of  $K_{eq}$  varies with temperature.

## FACTORS AFFECTING CHEMICAL EQUILIBRIUM

Equilibrium can be disturbed when one or more of its characteristics is subjected to change.

Among the factors affecting equilibrium are

- concentration for solution systems
- volumes, concentrations or partial pressures for gas phase systems
- temperature for any system in general.

**Le Chatelier's Principle** By the end of the 19th Century, study of equilibrium systems was sufficiently advanced to allow the establishment of Le Chatelier's Principle, a basis for the prediction of the effects of changes in systems at equilibrium.

**When a system at equilibrium is subjected to a stress, the system will shift so as to relieve the stress.**

AP exam questions are often presented so that students are expected to discuss equilibrium systems and changes in those systems from one or more of three perspectives:

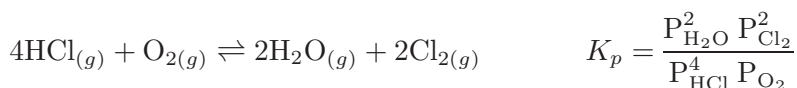
- rates of opposing reactions (the forward and reverse reactions)
- the equilibrium constant (or reaction quotient)
- Le Chatelier's principle

## SOLVING EQUILIBRIUM PROBLEMS

### Quantitative equilibrium problems

Some questions call for calculations about systems that have achieved equilibrium and systems that are moving to an equilibrium position. These questions require use of  $K_{eq}$  in a wide variety of calculations. Some commonly encountered types of equilibrium systems with examples are listed below.

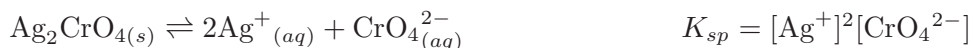
Gas Phase (homogeneous) Equilibrium System



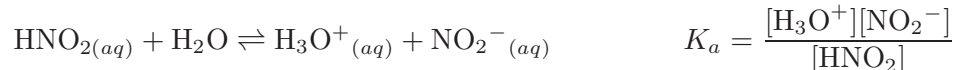
Gas/Solid Phases (heterogeneous) Equilibrium System - Dissociation of a Solid



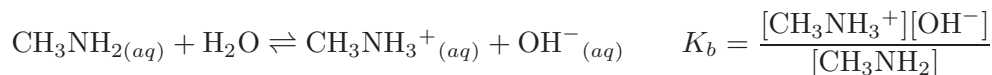
Solid/solution phases (heterogeneous) - Solubility Equilibrium



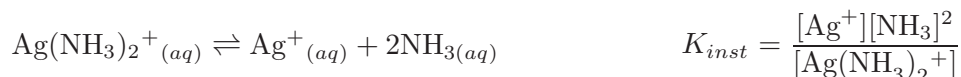
Solution phase (homogeneous) equilibrium - Ionization of a Weak Acid



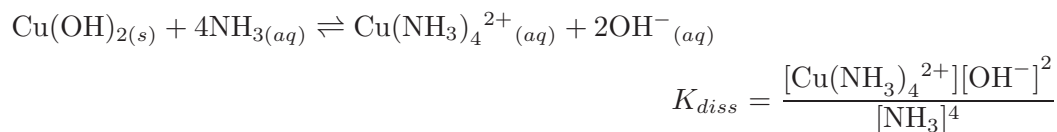
Ionization of a Weak Base



Instability (Dissociation of a Complex Ion)



Dissolving/Complex Ion Formation (Complexation)



Gas/Liquid heterogeneous equilibrium (Vapor Pressure)



Equilibrium constant expressions include only those terms whose concentrations can change such as pressures or concentrations of gases and concentrations of ions in solution.

## Systems at equilibrium

For systems at equilibrium, the chemical equation is generally known, as well as enough components of the reaction quotient to permit calculation of other quantities. Solution of these problems calls for writing the equilibrium constant expression (reaction quotient or mass action expression), substituting the known quantities, then solving for the other values.

## Systems moving to equilibrium

Some systems move from a previous non-equilibrium condition to a new equilibrium condition. Solution of such a problem calls for application of the principles of reaction stoichiometry to solve for concentrations at equilibrium, then further calculations using the equilibrium concentrations as determined.

One strategy commonly presented in textbooks recommends the use of a table such as that in Figure 7.1 to summarize the behavior of the system as it moves to equilibrium. Sometimes these are called “Rice”, “Ice” or “Nice” tables. Especially helpful is the explicit statement of changes in quantities,  $\Delta n$ , or  $\Delta mol$  due to rxn, as the reaction proceeds. You should express all amounts in moles rather than moles per liter in order to avoid losing track of volume effects.

**Figure 7.1 A Problem Solving Format for Equilibrium Problems**  
 using  $n_{av}$ ,  $\Delta n_{rxn}$ ,  $n_{av}$ ,  $n_{eq}$ ,  $[ ]_{eq}$ : an improvement on "RICE" or "ICE"

<ul style="list-style-type: none"> <li>Use this format when a reaction occurs in a system (apply principles of stoichiometry)</li> </ul>				
AND				
<ul style="list-style-type: none"> <li>that system establishes a new equilibrium (apply principles of equilibrium).</li> </ul>				
<b>Substance</b>	<b>A</b>	<b>B</b>	<b>C</b>	<b>D</b>
$n_{av}$ , mol available				
$\Delta n$ , $\Delta n_{rxn}$ , $\Delta$ mol due to rxn				
$n_{eq}$ , mol at equilibrium				
$[ ]_{eq}$ , conc. at equilb.				

The Students Solution Manual has many illustrations of the use of a RICE table.

### Solubility equilibrium

Solubility equilibrium can be established by dissolving the solid, usually an ionic solid, into the solvent, usually water. This is generally regarded as the forward reaction. Solubility equilibrium can also be established by mixing solutions of ions that form a precipitate, in the reverse reaction. Refer to the  $\text{Ag}_2\text{CrO}_4$  solubility equilibrium equation above. In a typical problem, the information could be provided as mass (or moles) of the specified solute dissolved per unit volume of solvent (or solution) with directions to calculate the value for  $K_{sp}$ . Alternatively, the given information may include the  $K_{sp}$ , with the molar or mass solubility as the value to be calculated.

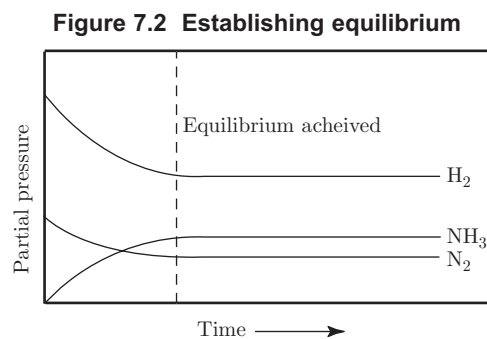
### Acid Base equilibrium

In Chapter 9, more attention will be given to the implications of chemical equilibrium for acid/base systems that include

- proton transfer (donation/acceptance);  $K_a$  and  $K_b$
- self-ionization of water;  $K_w$
- ionization of weak acids and bases;  $K_a$  and  $K_b$
- ionization of polyprotic acids;  $K_I$ ,  $K_{II}$  and  $K_{III}$
- hydrolysis of salts;  $K_h$
- buffer solutions
- titrations/pH curves

**Graphic representations**

Figure 7.2 shows a plot of concentration *vs* time (progress of the reaction) as a system moves from some starting conditions and achieves equilibrium after some reactants have been consumed and some products formed. Note that an unchanging horizontal line indicates the steady state characteristic of equilibrium. An abrupt vertical shift indicates a “stress” in the form of addition or removal of some portion of one or more of the reactants or products as shown in questions 21-24 below.



from the TOPIC OUTLINE (website: [apcentral.collegeboard.com](http://apcentral.collegeboard.com))

### III. Reactions

#### C. Equilibrium

1. Concept of dynamic equilibrium, physical and chemical; Le Chatelier's Principle; equilibrium constants
2. Quantitative treatment
  - a. Equilibrium constants for gaseous reactions:  $K_p$ ,  $K_c$
  - b. Equilibrium constants for reactions in solution
    - (1) Constants for acids and bases; pK; pH
    - (2) Solubility product constants and their application to precipitation and the dissolution of slightly soluble compounds
    - (3) Common ion effect; buffers; hydrolysis



### from the list of CHEMICAL CALCULATIONS

8. Equilibrium constants and their applications, including their use for simultaneous equilibria



### from the list of EQUATIONS & CONSTANTS

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \text{ where } aA + bB \rightarrow cC + dD$$

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

$$K_b = \frac{[OH^-][HB^+]}{[B]}$$

$$K_w = [OH^+][H^+] = 10^{-14} \text{ @ } 25^\circ\text{C}$$

$$= K_a \times K_b$$

$$\text{pH} = -\log[H^+], \text{ pOH} = -\log[OH^-]$$

$$14 = \text{pH} + \text{pOH}$$

$$\text{pH} = \text{p}K_a + \log \frac{[A^-]}{[HA]}$$

$$\text{pOH} = \text{p}K_b + \log \frac{[HB^+]}{[B]}$$

$$\text{p}K_a = -\log K_a, \text{ p}K_b = -\log K_b$$

$$K_p = K_c(RT)^{\Delta n}, \text{ where } \Delta n = \text{moles product gas} - \text{moles reactant gas}$$



### from the list of RECOMMENDED EXPERIMENTS

10. Determination of the equilibrium constant for a chemical reaction

The experiment calls for measuring the changes in concentration of a colored ion in water solution using a spectrophotometer. Using Beer's Law, absorbance can be measured and corresponding concentration calculated. This is especially useful in determining the concentration of colored ions such as  $\text{Cu}^{2+}$  and  $\text{Co}^{3+}$  where those ions are precipitated from water solution to establish solubility equilibrium. The concentration of such ions can also be estimated using the unaided eye by comparing color intensity of solutions of known concentration to the color of solutions of unknown concentrations.