

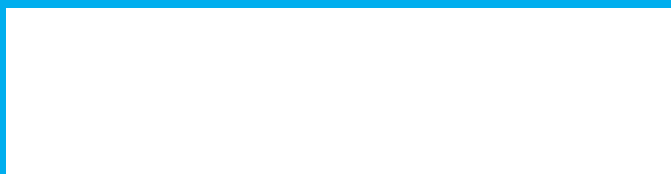


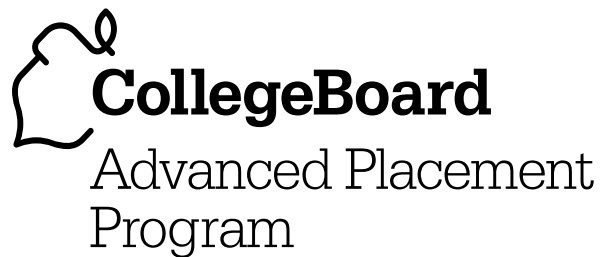
# AP<sup>®</sup> Chemistry

2006–2007  
Professional Development  
Workshop Materials

**Special Focus:**  
**Chemical Equilibrium**

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**Special Focus on AP Chemistry: Chemical Equilibrium**

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**Important Note:** The following set of materials is organized around a particular theme, or “special focus,” that reflects important topics in the AP Chemistry course. The materials are intended to provide teachers with resources and classroom ideas relating to these topics. The special focus, as well as the specific content of the materials, cannot and should not be taken as an indication that a particular topic will appear on the AP Exam.

## **Resource Materials for Dynamic Equilibrium: Introduction from the Editors**

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When asked to produce a series of resource materials addressing concepts in AP Chemistry, we faced a difficult decision. Considering a curriculum as vast as ours, where would we begin? Upon reflection, we agreed dynamic equilibrium should be our first topic for a variety of reasons. Equilibrium connects to many other topics in the AP Chemistry course including kinetics, thermodynamics, and electrochemistry. In addition, it is central to the required calculation in every AP Chemistry Examination. Even though understanding equilibrium is essential to the mastery of chemistry, students and teachers continue to have many misconceptions regarding the concept.

The following material consists of a series of chapters dealing with specific topics in equilibrium. Each chapter contains important teaching points and strategies, ideas for laboratory activities, demonstrations, and a sampling of questions and solutions from previous AP Chemistry Examinations. We have included icons to draw teachers' attention to each of these resources.

The contributing authors are all experienced AP teachers and university professors with years of experience. Each has spent several years at the AP Reading, some as Table Leaders, Questions Leaders, or Chief Readers. To ensure consistency of content with the current AP Chemistry curriculum, the chapters were reviewed by an exceptional group of advisors, each of whom has served on the AP Chemistry Development Committee at one time or another. Head advisor George Miller provided invaluable assistance to us in the preparation of this document. In addition to these fine educators, Jim Spencer, current Development Committee Chair, and John Gelder, current Chief Reader of the AP Chemistry Exam, have contributed comments to the material.

We gratefully acknowledge the assistance of each one of the dedicated and talented individuals involved in the production of this first installment in a series of AP Chemistry resources. It is our sincere hope that new and experienced teachers will find these materials useful for the instruction of AP Chemistry.

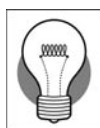
## Special Focus: Chemical Equilibrium

### Guide to Icons

The icons that appear in the following theme materials are designed to help teachers find material quickly in each of the chapters.



The “Lab/Demo” icon marks ideas for laboratories and demonstrations.



The “Teaching Strategy” icon indicates methods that teachers might employ in the classroom to convey a concept or idea effectively.



The “Points to Emphasize” icon marks critical concepts that teachers should emphasize to ensure that their students fully comprehend a topic.



The “Q&A” icon indicates questions and answers taken from past AP Chemistry Exams.

### Chemical Equilibrium: Introduction and Overview

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AP Chemistry, like the college chemistry courses it emulates, places a strong emphasis on understanding the concept and applications of equilibrium in chemistry. The mandatory first question in every AP free-response section concerns itself with some application of equilibrium. Several multiple-choice questions address various aspects of chemical equilibrium. AP Chemistry students need to learn how to address systems at (or not at) equilibrium in both qualitative and quantitative ways.

Generally, people think of “equilibrium” in connection with something that is “balanced”—a condition that suggests a description of something that is expected to change but is not changing. In scientific terms, the “something” is a “system,” carefully defined and separated (at least in mind) from its surroundings, that we can anticipate might change given a change in circumstances.

An obvious example in the physical world is a rock balanced on the edge of a cliff—it looks as if a slight change in its circumstances would send it hurling down the cliff. A more common example that might not be thought of instantly as equilibrium is a book resting on a table. Physics principles tell us that if an object with mass is not moving, then it must be subject to a balance of forces, so that no net force exists in any direction. Such situations are usually identified as “static equilibria,” though in some cases, such as when you hold a book up in your hand, the distinction may be subtle. In this case, lots of small muscle cell movements do occur to maintain the equilibrium, and that is why work is clearly felt to be done, since your arm gets tired!

Chemical equilibrium is a dynamic state of a chemical reaction where the rate of the forward reaction equals the rate of the reverse reaction in a closed system, but *no net effect is observable*. It is recognized when there is no change in macroscopic properties such as pressure, color of solution, or concentration of solution at a constant temperature. However, at the atomic level, atoms, ions, and/or molecules are in constant reaction, hence the term “dynamic equilibrium.” It is the rates of the forward and reverse reactions that are equal, not the concentrations of reactants and products. The observable balance is that the quantities of reactants and products present in a system at equilibrium are measurably unchanged over time. Since a system in chemistry is often a solution or gas reaction vessel, concentrations or partial pressures are used to represent the amounts of substances present in the equilibrium condition.



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An important feature of the chemical equilibrium state is that it can usually be reached from either direction; the same end state results whether the “reactants” are the initial reactants or the “products” are the initial reactants. To make sense of numerical values, chemists have developed a specific protocol for writing equilibrium constant expressions that must be followed in terms of defining which are *initial* reactants and *initial* products.

However, it must be established that, over time, matter does not enter or leave the “system” and that opportunity for individual reactions *must* not be affected. This is often modeled for students by establishing a situation where macroscopic change can be observed, while no net effect is seen. Texts have pictures showing two people throwing apples over a fence, so the number of apples on each side of the fence remains unchanged, while the individual apples change sides. The total number of apples in the picture must remain fixed. Others picture small fish swimming backward and forward through a wide tube connecting two fish tanks. The number of fish in each tank stays constant, while individual fish change tanks.

When a system contains only reactant species, a chemical reaction will proceed at a rate dependent on the concentrations, and product species will start to form. For most chemical systems, products then begin to react to reform the original reactants. Such a reaction system may be termed to be *reversible*. The rate of the reverse reaction will increase as the concentrations of products increase until the rate of reverse reaction equals the rate of the forward reaction and the system is at equilibrium. The net concentrations of reactants and products will remain unchanged, but will *not* usually be equal.

The *equilibrium constant expression* was devised to provide a mathematical expression of the equilibrium condition and results in a quantitative value for an equilibrium constant under specified conditions of the reacting system. While a more recent understanding of chemical equilibrium is based on the chemical kinetics view of equilibrium expressed above (forward rate = reverse rate), the earlier formulation of the equilibrium constant expression was based on the law of mass action. In this, the equilibrium constant ( $K_{eq}$ ) is computed as the ratio of the mathematical product of the concentrations of the products to the mathematical product of the concentrations of reactants. If molarities ( $[X]$ ) are used, the constant is usually termed  $K_c$ . If partial gas pressures ( $p_x$ ) are used in place of concentrations for a gas phase equilibrium, the constant is termed  $K_p$ .

A vexing issue for many beginning students, who have learned to use units carefully in other areas of chemistry, is why equilibrium constant values have no units. Some discussion of this issue is presented in an appendix. Suffice that in one problem, students

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must consistently use the *same units* for concentrations or pressures throughout the problem to obtain correct values, but it is incorrect to add units to equilibrium constant values in any circumstance.

A second “trap,” discussed in several chapters, is that pure solids and pure liquids are conventionally excluded from appearing in equilibrium constant expressions, on the justification that their “activities” are unity. (See the appendix for further discussion of this issue.)

A balanced chemical equation must provide the basis for the protocol in performing these computations. The reaction must be reversible. Reactants are those substances on the left side of the equation, and products are to the right. The stoichiometric coefficients in the balanced equation become exponents for the concentration or pressure values. For example, consider the reaction:  $aA(aq) + bB(aq) \rightleftharpoons cC(aq) + dD(aq)$ .

$K_c$  is computed by using the following (mass action):  $K_c = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}$

If the reaction was stated as:  $aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$ , then

$K_p$  is computed by using the following (mass action):  $K_p = \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b}$ .

Equilibrium constant values are thus established for a *specific* reaction in a *specific* system and will be unchanging (constant) in that system, providing the temperatures does not change. Chemical kinetic theory explains why changing the system temperature affects the forward and reverse reactions by different amounts, thus changing the ratio of concentrations at equilibrium and thus the value of the equilibrium constant. Tables of equilibrium constants for specific reactions can be compiled but must specify a temperature for the values to be meaningful. Students may fail to appreciate that neither the reaction itself nor the system in which it is occurring can change, or the value of the equilibrium constant will not be valid.

In tables, because many values of interest are very large or very small, negative logarithmic values, termed  $pK_{eq}$  by analogy with pH terminology, are listed. Care must be exercised in using such values, as sometimes reactions are written in reverse from normal assumptions. For instance, formation equilibrium constants (sometimes referred to as stability constants) for complex ions may be derived from experiments measuring their dissociation equilibria, but they are listed as positive  $pK_{eq}$  values because they refer to stability of formation.

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### General Manipulations Involving Equilibrium Expressions

#### Names and Symbols for Equilibrium Constants

Special names and symbols are used for different types of chemical reactions. While some involve special protocol considerations, students should realize that these are all equilibrium constants following the same general principles.

- $K_c$  is the most used general form with molar concentrations.
- $K_p$  can be used with partial pressures when working with a gas phase reaction.
- $K_a$  is used for the dissociation of weak acids in water.
- $K_b$  is used for the dissociation of weak bases in water.
- $K_w$  is the equilibrium expression for the dissociation of water into its ions.
- $K_{sp}$  is used for the dissociation into ions of sparingly soluble solids in water.

#### $K_p$ vs. $K_c$

There is a mathematical relationship between  $K_p$  and  $K_c$  for gas phase reactions where either molar concentrations or partial pressures can be used for input data:

$$K_p = K_c (RT)^{\Delta n_{(gas)}}$$

Where  $R$  is the gas law constant (0.0821 liter atm/mole K),  $T$  is the temperature in Kelvin, and  $\Delta n_{(gas)}$  is the difference in total moles of gaseous products and moles of gaseous reactants in the stoichiometric reaction equation.

#### Size of $K_{eq}$

If  $K_{eq}$  is greater than 10, the reaction goes nearly to completion, and the concentrations of the products are much greater than the reactants. If  $K_{eq}$  is less than 0.1, the reaction doesn't go very far to completion at all, and the concentrations of the reactants are much greater than the products. Often this simplifies calculations.

If  $K_{eq}$  equals 1, then there are substantial amounts of both product and reactant present in the system, and no approximations may be made.



### Related Reactions and Related $K_{eq}$ Expressions

The “no units” protocol mentioned above means that changes in units do not need to be taken into account in manipulations described in this section. Also, since these relationships apply to *all* equilibrium constants, no subscript is included for  $K$  in this section.

1. **Coefficient rule:** If the coefficients of the reaction are increased or decreased by a factor of  $n$ , then the  $K$  is raised to that power. For example, if a reaction is represented by equation (I):  $2A(aq) + B(aq) \rightleftharpoons 4C(aq)$ , it follows that:

$$K^I = \frac{[C]^4}{[A]^2[B]}$$

Changing the equation to (II):  $A(aq) + 1/2B(aq) \rightleftharpoons 2C(aq)$  results in:

$$K^{II} = \frac{[C]^2}{[A][B]^{1/2}}$$

so that  $K^{II} = (K^I)^{1/2}$ .

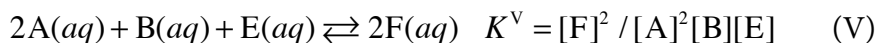
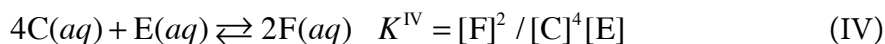
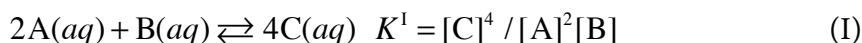
2. **Reciprocal rule:** If you reverse a reaction, you reciprocate (invert) the  $K$ , so if reaction (III) is represented by  $4C(aq) \rightleftharpoons 2A(aq) + B(aq)$ , then it follows that:

$$K^{III} = \frac{[A]^2[B]}{[C]^4}$$

so that  $K^{III} = 1 / K^I$ .

3. **Multiple equilibria rule:** When two or more reaction equations are added together, the equilibrium constant for the sum reaction is the product of the equilibrium constants of the added reactions.

For example:



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The proof is easy to see:

$$\frac{[C]^4}{[A]^2[B]} \times \frac{[F]^2}{[C]^4[E]} = \frac{[F]^2}{[A]^2[B][E]} \text{ so } K^V = K^I \times K^{IV}$$



### $K_{eq}$ Relationships to Thermodynamic Values

1. There is a relationship between  $K_{eq}$  and the standard free-energy change of a system that can be used to determine values if one or the other is known:

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

2. There is a relationship between  $K_{eq}$  and the standard cell potential of a voltaic cell,  $E^\circ$ , that can be used to determine values if one or the other is known:

$$E^\circ = \frac{(0.0257)}{n} \ln K_{eq}$$



### Steps in Addressing Some Typical Equilibrium Problems, the Use of the Q Concept

1. The major first step is to always write and balance a reaction equation.
2. To determine the value of an equilibrium constant given equilibrium concentrations or partial pressures (see example Sample AP Question 1995: Free Response 1 (b) and (c) on page 31 in chapter 3):
  - (a) Use the balanced equation, and underneath each species list each concentration given.
  - (b) Write the equilibrium expression, using the appropriate coefficients as exponents.
  - (c) Substitute the values given for each reactant and product into the expression.
  - (d) Perform the computations and convert between  $K_c$  and  $K_p$  (if necessary).

3. To determine equilibrium concentrations given the  $K$  and an initial set of concentrations (see Sample AP Question 1995: Free Response 1 (e) on page 32):

- (a) In this type of equilibrium problem, the first two steps are the same as steps 2(a) and 2(b) above.
- (b) Next, we must express the reactant and product equilibrium concentrations in terms of their initial concentrations and their changes. To determine how a reactant's and product's concentrations change,  $Q$  (the reaction quotient) must be determined.  $Q$  is calculated by substituting the initial concentrations into the equilibrium expression. Once  $Q$  is calculated, then the following is applied:
- If  $Q$  is less than  $K$ , the reaction goes in the forward direction, and the initial concentration of each reactant is reduced by a value of  $x$ :  $[R]_{eq} = [R]_{init} - x$ . The initial concentration of each product is increased by  $x$ :  $[P]_{eq} = [P]_{init} + x$ .  
**Note:** The amount we have assigned as  $x$  may need to be modified depending on the stoichiometry of the balanced chemical equation.
  - If  $Q$  is greater than  $K$ , the reaction goes in the reverse direction, and the initial concentrations of each product lose a value of  $x$ .  
 $[P]_{eq} = [P]_{init} - x$  and  $[R]_{eq} = [R]_{init} + x$ .
  - If  $Q$  equals  $K$ , then the reaction is at equilibrium.

Now substitute the equilibrium concentrations in terms of their initial concentrations and  $x$  into the equilibrium expression.

- (c) In the last step, we must solve for  $x$  so the equilibrium concentrations of each reactant and product can be determined. Depending on the relative magnitude of  $K$  and the initial concentration, an assumption can sometimes be made to simplify the determination of  $x$ .

4. To determine the equilibrium constant,  $K$ , given the initial concentrations of all reactants and products and the equilibrium concentration of one of the species (see Sample AP Question 1995: Free Response 1 (d) on page 32):

- (a) In this type of equilibrium problem, the first two steps are again the same as steps 2(a) and 2(b) above.

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- (b) The given equilibrium concentration of one species must be considered along with its initial concentration to determine the change in concentration that has occurred. This change may then be considered along with the stoichiometry of the balanced equation to determine the concentration changes and subsequently the equilibrium concentrations of all other species in the reaction.
- (c) Once all equilibrium concentrations have been determined, they may be substituted back into the expression to determine the value of  $K$ .

The process described above is often referred to as the *ICE process*:

**I** = Initial concentration

**C** = Change

**E** = concentration at Equilibrium

Other equilibrium problems can be addressed by using minor variations of the above steps.

Subsequent text in this document provides more detailed discussions of these principles and examples drawn from past AP Chemistry Examinations.

### **Caveat: Idealistic Nature of Equilibrium Calculations in AP**

In the AP Chemistry course and examination, it is assumed that all substances and solutions are ideal. Solutions approach ideality as they become infinitely dilute. Gases approach ideality at low pressures and high temperatures. In real chemical situations, this is often far from correct. Technically speaking, therefore, most literature  $K_{eq}$  values are considered to be “limiting,” either at infinite dilution or infinitely low pressure.

As an example, consider the familiar ion-product “constant” for water, usually quoted (at 298 K) as  $1.0 \times 10^{-14}$ . If 0.1 M NaCl is added, the value for the product is measured to be  $1.65 \times 10^{-14}$ , a change of over 60 percent.

Thus, in the laboratory, calculations done according to ideal assumptions are seldom reproduced. Discussion of the corrections that can be applied are considered beyond the scope of AP Chemistry. However, to introduce teachers and students to the idea that the systems considered are simplified, a brief discussion section entitled “Beyond AP” is included as an appendix.

## Le Chatelier's Principle

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A very useful principle for thinking about equilibrium systems in a qualitative way was first announced by Le Chatelier in 1884, followed by a simplified statement in 1888. Textbooks have different ways of expressing this principle, so it should not be taught as a “law” to be quoted verbatim without understanding but rather presented in a way that a student can understand and use it. One short statement of Le Chatelier's principle is:

If a closed system at equilibrium is subjected to a stress, a shift will occur to counteract the stress and establish a new equilibrium.

Equilibrium systems may be subjected to a variety of different *external* stresses. No closed equilibrium system can “stress itself.” The most common external stresses are changes in temperature, concentration (partial pressure), or volume. Addition of a catalyst or an inert gas to an equilibrium system might be considered to be a stress, but these changes do not result in equilibrium shifts (in ideal systems). Note that the stress *initially* results in a *nonequilibrium* condition. A new equilibrium is then established over time. It is important for students to understand whether the question is asking about *initial* change in response to stress or the *final* “new equilibrium” condition. While it is not necessary to use the equilibrium constant expression in applying Le Chatelier's principle, it is often useful to have it present. While the principle is useful, it is often overapplied in nonequilibrium situations. In addition, it is important to realize that in order to be certain of the direction of a shift due to a stress, all conditions, particularly pressure and volume, need to be considered. In some cases, the prediction cannot be made without a calculation.

Students will need to learn how to distinguish between stresses that result in a change of the value of the actual equilibrium constant and those changes that affect the amounts of substances present, but leave the ratio as calculated in the equilibrium constant expression unchanged.



### Temperature Stresses

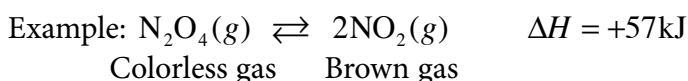
Increasing the temperature of an equilibrium system provides more available energy for the reaction (a larger fraction of molecules will collide with at least the required



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activation energy) increasing the rate of both the forward and reverse reactions. Activation energies ( $E_a$ ) for reversible reactions differ in value for forward direction versus reverse direction by the enthalpy change for the reaction  $\Delta H$ .

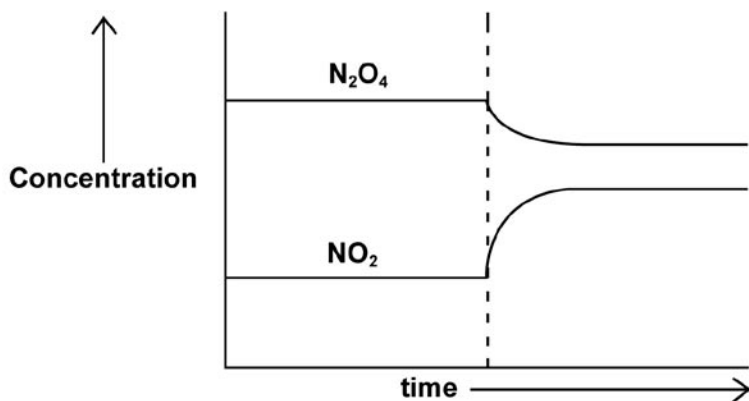
If the reaction is *endothermic* ( $\Delta H$  positive), the forward rate will be increased more than the reverse, resulting in a net shift of the reaction toward the products. If the reaction is *exothermic* ( $\Delta H$  negative), the reverse rate will be increased more than the forward, resulting in a net shift of the reaction toward the reactants. The net change in the position of an equilibrium due to a temperature change will result in a new value for the equilibrium constant,  $K_{eq}$ , for the reaction. **It should be emphasized to students that temperature change is the only thing that will affect the value of an equilibrium constant for an ideal closed system.**



The equilibrium constant expression for the reaction is written as

$$K_{eq} = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

If a closed system containing the above gases at equilibrium is heated, the equilibrium will shift right, resulting in a darker brown color. (Cooling of this system will cause a left shift, lightening the color.) The net change in  $\text{NO}_2$  concentration is double that of the  $\text{N}_2\text{O}_4$  due to the mole ratio. The increased temperature stress and resulting shift may be represented graphically as follows:



**At the new equilibrium, the values of the concentrations in the  $K_{eq}$  expression will clearly lead to a new value for  $K_{eq}$ .**

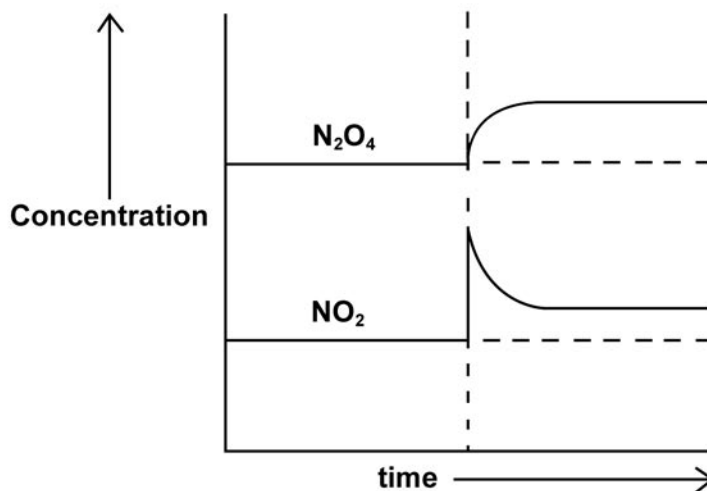


### Concentration or Partial Pressure Stresses

Increasing the concentration, or the partial pressure, of a reactant in an equilibrium system will result in an increase in the rate of the forward reaction, assuming that the reactant appears in the rate law (which is usual). The system will no longer be at equilibrium. However, in these cases, it is vital to stress to students that the **equilibrium constant has not changed**. Note that this is *not* a closed system.

**Initially** as products are produced more quickly, the reverse reaction rate will increase as well, but to a lesser extent. The net result is that **the addition of a reactant in an equilibrium system will produce a shift toward the products**. By the same token, **addition of a product will produce a shift toward the reactants**. However, eventually, the reverse and forward reactions will again be at the same rates, and equilibrium will be reestablished.

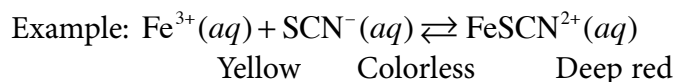
**Example:** For the equilibrium system in the previously discussed example, an injection of  $\text{NO}_2$  gas (which would increase the concentration and the partial pressure of the  $\text{NO}_2$ ) would result in a left shift. Interestingly enough, this shift is not accompanied by a dramatic decrease in the intensity of the brown color, since the added  $\text{NO}_2$  will cause its own concentration to rise as well. The graphic representation of this shift is as follows:



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Removal of reactants will result in less frequent particle collisions and hence a decrease in the rate of the forward reaction. The accompanied decrease in product production will lead to a decrease in the rate of the reverse reaction as well, but to a lesser extent. The net result is that **the removal of a reactant in an equilibrium will cause a shift toward the reactants**. Similarly, **removal of a product will produce a shift in the forward direction**. There are three common means of removing species from equilibrium systems:

1. Neutralization—The addition of a strong acid to an equilibrium containing a base or the addition of a strong base to an equilibrium containing an acid
2. Precipitation—The addition of an ion having low solubility with an ion present in an equilibrium system
3. Complex ion formation—The addition of a ligand that may bind some ion present in an equilibrium system



The addition of a few drops of  $\text{Fe}(\text{NO}_3)_3(\text{aq})$  to the above equilibrium will cause a right shift, resulting in a deepening of the red color. Adding NaOH, on the other hand, would remove the  $\text{Fe}^{3+}$  ion as a precipitate of  $\text{Fe}(\text{OH})_3(\text{s})$ . The result would be a lightening of the red color with yellow precipitate becoming evident.

It is vital that students recognize that changing the position of an equilibrium by adding a reactant or removing a product **does not change the value of the equilibrium constant,  $K_{eq}$** . For the example above, it might be pointed out that increasing the concentration of  $\text{Fe}^{3+}$  causes a right shift and hence increases the numerator of the  $K_{eq}$  expression; however, the denominator also increases because of the added  $\text{Fe}^{3+}$  ion. As a result, the ratio in the expression returns to the same constant when equilibrium is reestablished.

Again it is important to note that all of the above are *open* systems.



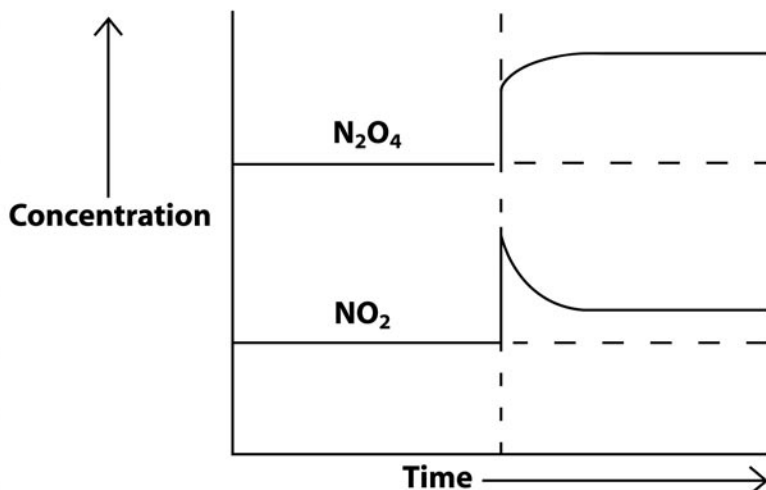
### Volume Change Stresses

Altering the volume of a closed ideal gaseous system at equilibrium will result in a reciprocal change in the overall pressure of the system according to Boyle's law. If the volume is decreased, the overall pressure will increase. All gas particles will be closer together and hence will collide more frequently. The result is an increase in the rate of both forward and reverse reactions.

Whether the forward or reverse reaction rate will be increased more than the other depends upon the **stoichiometry of the chemical reaction**—the number of moles of gaseous reactants versus products. If reactants and products have an **equal number of gas moles**, then changing the volume will have **no effect** on the equilibrium.

However, if the volume is **decreased**, causing an overall pressure increase, **the system will attempt to decrease the pressure by shifting to the side with the fewest moles of gas**. On the other hand, if the volume is **increased**, causing an overall pressure decrease, **the system will shift to the side with more moles of gas**. It is important to stress that only the gas moles are considered in such applications. If liquid or solid phases are present, these are ignored in the arguments.

**Example:** In our previous example,  $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$ , a decrease in the volume of the container would cause an increase in the overall pressure. The system would shift to the left to attempt to decrease the pressure. Interestingly enough, there would be an increase in the intensity of brown color despite the fact that the shift is away from the brown  $\text{NO}_2$  gas. This is due to the increased concentration of both gases caused by the volume decrease. The graphic representation of this change is as follows:



## Special Focus: Chemical Equilibrium

Once again, it is important for students to recognize that changing the position of an equilibrium due to a volume change **does not affect the value of  $K_{eq}$** . Despite the left shift in the example above, both the  $N_2O_4$  and the  $NO_2$  concentrations are increased due to the decrease in volume (notice this point on the graph). As both numerator and denominator increase together, once again, the ratio in the expression remains constant. Students should be reminded repeatedly that only a change in temperature will result in a change in the  $K_{eq}$  value.



### Stresses That Cause No Shift

The addition of a catalyst will cause an equal increase in the forward and reverse rates of reaction. Consequently, **the addition of a catalyst to a closed system at equilibrium will not cause any net change in the position of the equilibrium.**

Occasionally, inert gases, such as helium, are added to closed, ideal-gas reacting systems at equilibrium. Students may recognize that such a change causes an increase in the overall pressure of the system, and hence they might expect a shift to the side of the equilibrium with fewer moles of gas. Because the inert gas affects collisions between all reacting particles and thus forward and reverse reaction rates in the same manner, **adding an inert gas to an equilibrium system will not cause any shift in the equilibrium position.**

Occasionally an equilibrium system may contain a solid or liquid species. It is important for students to understand that the concentrations of pure liquids and solids are fixed. For example, an 18 mL sample of water contains 1 mole (since the density of water is 1 g/mL). Hence the concentration of water is 1 mole/0.018 L, or 56 mol/L. If a 36 mL sample of water is considered, the concentration would be 2 moles/0.036 L, which is still 56 mol/L. A similar explanation shows that solids have a fixed concentration. Increasing or decreasing the number of moles of a solid or liquid does *not* change its concentration. Consequently, **adding a pure liquid or solid to an equilibrium system will not cause a shift in the equilibrium position.** Clearly it is important to distinguish this case from the one in which a solution concentration is changed (for example, by adding more concentrated  $HCl(aq)$  to a dilute solution of  $HCl(aq)$  in an acid-base reacting mixture).

### Examples from Previous AP Exams



**Sample AP Question: 1977 Question 6**

For the system  $2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)$ ,  $\Delta H$  is negative for the production of  $\text{SO}_3$ . Assume that one has an equilibrium mixture of these substances. Predict the effect of each of the following changes on the value of the equilibrium constant and on the number of moles of  $\text{SO}_3$  present in the mixture at equilibrium. Briefly account for each of your predictions. (Assume that in each case all other factors remain constant.)

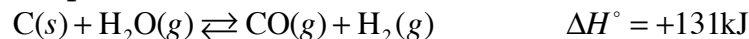
- (a) Decreasing the volume of the system.
- (b) Adding oxygen to the equilibrium mixture.
- (c) Raising the temperature of the system.

**Solution**

- (a) As volume decreases, pressure increases, and the reaction shifts in the direction of fewer molecules of gas to relieve the stress. More moles of  $\text{SO}_3$  are formed. The value of  $K_{eq}$  does not change.
- (b) Additional  $\text{O}_2$  disturbs the equilibrium, and  $\text{SO}_3$  is formed to relieve the stress. The value of  $K_{eq}$  does not change.
- (c) An increase in temperature shifts the reaction to the left to “use up” some of the added heat. Less  $\text{SO}_3$  remains. The value of  $K_{eq}$  decreases due to the relative greater increase in the rate of the endothermic reaction.



**Sample AP Question: 1988 Question 6**



A rigid container holds a mixture of graphite ( $\text{C}(s)$ ) pellets,  $\text{H}_2\text{O}(g)$ ,  $\text{CO}(g)$ , and  $\text{H}_2(g)$  at equilibrium. State whether the number of moles of  $\text{CO}(g)$  in the container will *increase*, *decrease*, or *remain the same* after each of the following disturbances is applied to the original mixture. For each case, assume that all other variables remain constant except for the given disturbance. Explain each answer with a short statement.

- (a) Additional  $\text{H}_2(g)$  is added to the equilibrium mixture at constant volume.
- (b) The temperature of the equilibrium mixture is increased at constant volume.

## Special Focus: Chemical Equilibrium

- (c) The volume of the container is decreased at constant temperature.
- (d) The graphite pellets are pulverized.

### Solution

- (a) CO will decrease. An increase of hydrogen gas molecules will increase the rate of the reverse reaction that consumes CO. This is a Le Chatelier's principle shift to the left.
- (b) CO will increase. Since the forward reaction is endothermic ( $\Delta H > 0$ ), an increase in temperature will cause the forward reaction to increase its rate and produce more CO. This is a Le Chatelier's principle shift to the right.
- (c) CO will decrease. A decrease in volume will result in an increase in pressure, and the equilibrium will shift to the side with fewer gas molecules to decrease the pressure, therefore causing a shift to the left.
- (d) CO will remain the same. Once at equilibrium, the size of the solid will not affect the position of the equilibrium.



Most college lab manuals contain a lab devoted to Le Chatelier's principle. Many of the procedures may be adapted to microscale and may be performed in "spot plates" or "microwells" quickly and easily to minimize cost and waste.

An excellent lab designed for a standard one-hour or 90-minute period (including pre- and postlab discussion) is Experiment 12A from *Essential Experiments for Chemistry* by Morrison and Scodellaro (2005). Information on this manual, along with a correlation guide for all suggested AP Chemistry labs, may be found at [www.smglabbooks.com](http://www.smglabbooks.com).

Demonstrations are useful when laboratory time and equipment are restricted. The four-volume *Chemical Demonstrations* series by Shakhashiri (University of Wisconsin Press, 1983-90) and *Chemical Demonstrations: A Sourcebook for Teachers* by Summerlin and Ealy (ACS, 1985) contain many excellent demonstrations of equilibria that can be used to exemplify the use of Le Chatelier's principle.

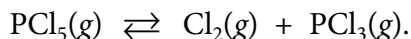
## **$K_c$ and $K_p$ Problems with Reference to Experimental Data**

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In a chemical reaction, conversion of reactants to products is often incomplete, no matter how long the reaction is allowed to continue. When a reaction begins, reactants are present in some definite concentration. As the reaction proceeds, these concentrations decrease. In addition, when the reaction starts, the products are not present at all. As the reaction proceeds, the concentration of the products increases. Sooner or later both concentrations level off and become constant. A state in which the concentrations no longer change with time becomes established. This state, which exists as long as there are no external perturbations, is known as the state of chemical equilibrium. Each state at a given temperature will have its own equilibrium constant,  $K_{eq}$ . If measured using molar concentrations, the constant is referred to as  $K_c$ ; if measured in gas partial pressures, the term  $K_p$  is used.

### **Determining $K_c$**

Every particular reaction has its own specific equilibrium state at a given temperature, characterized by a definite relation between the concentrations of the reactants and products known as the equilibrium expression. To illustrate this relation, we consider the equilibrium involving  $\text{PCl}_3(g)$ ,  $\text{Cl}_2(g)$ , and  $\text{PCl}_5(g)$ .  $\text{PCl}_5$  is thermally unstable, so it decomposes to  $\text{PCl}_3$  and  $\text{Cl}_2$ :



Let us consider a series of three experiments, all done at the same temperature but differing in starting concentration of materials. The initial and final conditions for each are summarized in Table 1.

**Experiment 1:** 1 mol of  $\text{PCl}_5$  is placed into a previously empty 1-liter flask at 546 K. When the system has reached equilibrium, the concentrations found are

$$\text{PCl}_5 = 0.764 \text{ M}, \text{PCl}_3 = 0.236 \text{ M}, \text{ and } \text{Cl}_2 = 0.236 \text{ M}.$$



## Special Focus: Chemical Equilibrium

**Experiment 2:** 1 mol of  $\text{PCl}_3$  and 1 mol of  $\text{Cl}_2$  are placed in a different 1-liter flask. At equilibrium, the concentrations are found to be the same as for Experiment 1:

$$\text{PCl}_5 = 0.764 \text{ M}, \text{PCl}_3 = 0.236 \text{ M}, \text{ and } \text{Cl}_2 = 0.236 \text{ M}.$$

It makes no difference whether we start with 1 mole of  $\text{PCl}_5$  and let it decompose or with 1 mole of  $\text{PCl}_3$  and with 1 mole of  $\text{Cl}_2$  and let them react—the two starting systems lead to the same equilibrium state.

**Experiment 3:** 1 mole of  $\text{PCl}_5$ , 2 moles of  $\text{PCl}_3$ , and 3 moles of  $\text{Cl}_2$  are placed in a third 1-liter flask. At equilibrium, the concentrations are found to be

$$\text{PCl}_5 = 2.82 \text{ M}, \text{PCl}_3 = 0.175 \text{ M}, \text{ and } \text{Cl}_2 = 1.175 \text{ M}.$$

This time, the concentrations are not the same. How are they related, and why?

**Table 1**

		$\text{PCl}_3$ (moles liter <sup>-1</sup> )	$\text{Cl}_2$ (moles liter <sup>-1</sup> )	$\text{PCl}_5$ (moles liter <sup>-1</sup> )	$K_c$
<b>Experiment 1</b>	Start	0	0	1.000	
	Change	+0.236	+0.236	-0.236	
	Equilibrium	0.236	0.236	0.764	13.7
<b>Experiment 2</b>	Start	1.000	1.000	0	
	Change	-0.764	-0.764	+0.764	
	Equilibrium	0.236	0.236	0.764	13.7
<b>Experiment 3</b>	Start	2.00	3.00	1.00	
	Change	-1.875	-1.825	+1.82	
	Equilibrium	0.175	1.175	2.82	13.7

For the reaction equation:  $\text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{PCl}_5(\text{g})$ .

The equilibrium constant,  $K_c$ , is obtained by the following expression:

$$K_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]}$$

## Special Focus: Chemical Equilibrium

The value of this expression at the temperature of all three experiments is the same (13.7). Note that no units are given for  $K$  values (see the appendix for an explanation of this issue). In other words, if the system is at equilibrium at 546 K, the value of the constant will always be 13.7, and this value can be used to describe any equilibrium system at 546 K involving  $\text{PCl}_5$ ,  $\text{PCl}_3$ , and  $\text{Cl}_2$ .

A useful derivation for use in Experiment 2 is to recognize the relationship between the equilibrium constant expressions written for the forward and reverse reaction directions.

For the reaction equation:  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ .

$$K'_c \text{ would be written} = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$$

and have a value on substitution of concentrations = 0.0730.

The relationship mathematically is obviously  $K'_c = 1/K_c = 1/13.7 = 0.0730$ .

Other relationships exist between equilibrium constants written for the same reaction using different stoichiometric coefficients, as shown in Table 2. The important message for students is that establishing a properly balanced equation for a reaction is vital for writing equilibrium constant expressions.

**Table 2**

	Reaction	$K_c$
<b>Reaction 1</b>	$2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$	$4.20 \times 10^2$
<b>Reaction 2</b>	$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$	$2.38 \times 10^{-3}$
<b>Reaction 3</b>	$\text{NH}_3(\text{g}) \rightleftharpoons 1/2\text{N}_2(\text{g}) + 3/2\text{H}_2(\text{g})$	20.5

- The value of  $K_c$  of reaction 2 =  $2.38 \times 10^{-3}$  because reaction 2 is the inverse of reaction 1; therefore  $K_2 = K_1^{-1}$ .
- The value of  $K_c$  of reaction 3 = 20.5. Why? The ratio for reaction 1 is  $[\text{N}_2][\text{H}_2]^3/[\text{NH}_3]^2$ . The ratio for reaction 3 is  $[\text{N}_2]^{1/2}[\text{H}_2]^{3/2}/[\text{NH}_3]$ . This ratio is the same as  $([\text{N}_2][\text{H}_2]^3/[\text{NH}_3]^2)^{1/2}$ . The reaction 3  $K_c$  expression is the square root of the reaction 1 expression; therefore  $K_3 = K_1^{1/2}$ .

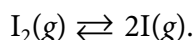
## Special Focus: Chemical Equilibrium



### Percent Decomposition in Determining $K_c$

A frequent feature of equilibrium problems is to express amounts of reactants or products in less-familiar units. It is important to understand how to convert these to *molar concentrations*, since these are the values needed for the equilibrium constant expression. Another common feature is that the amount of reaction is quite small, so the problem may be simplified. The following problem illustrates these points.

At high temperatures, diatomic iodine,  $I_2$ , decomposes into atomic iodine. In a typical experiment at 1,000 K, 2.74 percent of the iodine decomposes when 0.00305 mole of  $I_2$  is placed in a flask of volume 0.250 liter. Calculate  $K_c$  for the reaction



First, the starting concentration is  $0.00305 \text{ mole}/0.250 \text{ liter} = 0.0122 \text{ mole liter}^{-1}$ .

Second, since the starting concentration is  $0.0122 \text{ M}$  and 2.74 percent decomposes, the amount of  $I_2$  that reacts is  $3.34 \times 10^{-5} \text{ M}$ . This is obtained by multiplying  $0.0122 \text{ M} \times 2.74/100$ . The final concentration of  $I_2$  is 2.74 percent less than the starting concentration. This small amount (less than 5 percent) is often assumed to be negligible in equilibrium calculations.

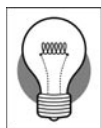
The amount of  $I(g)$  that is formed is  $2 \times 3.34 \times 10^{-5} \text{ M} = 6.68 \times 10^{-5} \text{ M}$  because the stoichiometric ratio of  $I(g)$  to  $I_2(g)$  is 2/1. The equilibrium expression will be

$$K_c = [I]^2 / [I_2].$$

Taking the equilibrium concentrations calculated above, the value of the equilibrium constant at 1,000 K is  $3.66 \times 10^{-7}$ . This is summarized in Table 3.

Table 3

	$I_2$ (mole liter <sup>-1</sup> )	I (mole liter <sup>-1</sup> )	$K_c$
Start	$1.22 \times 10^{-2}$	0.00	
Change	$-3.34 \times 10^{-5}$	$+6.68 \times 10^{-5}$	
Equilibrium	0.0122	$6.68 \times 10^{-5}$	$3.66 \times 10^{-7}$

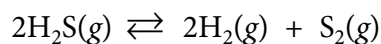


### Calculating $K_c$ from Experimental Data

Note: The order of the subquestions presented here (referred to as “scaffolding”) is designed to help students through the steps of the problem, so students should realize this order is both important and helpful. Additionally, as in all chemistry manipulations, students must be ever watchful not to confuse moles with molarity.



### Sample AP Question: 2000 Free-Response 1



When heated, hydrogen sulfide gas decomposes according to the equation above. A 3.40 g sample of  $\text{H}_2\text{S}(g)$  is introduced into an evacuated rigid 1.25 L container. The sealed container is heated to 483 K, and  $3.72 \times 10^{-2}$  mol of  $\text{S}_2(g)$  is present at equilibrium.

- (a) Write the expression for the equilibrium constant,  $K_c$ , for the decomposition reaction represented above.

#### Solution

$$K_c = [\text{H}_2]^2[\text{S}_2] / [\text{H}_2\text{S}]^2.$$

- (b) Calculate the equilibrium concentration, in  $\text{mol L}^{-1}$ , of the following gases in the container at 483 K.
- (i)  $\text{H}_2(g)$
  - (ii)  $\text{H}_2\text{S}(g)$

#### Solution

Students need to set up an ICE system to track moles and calculate molar concentrations. Initially, converting 3.40 g of  $\text{H}_2\text{S}(g)$  to moles:  $3.40 \text{ g} / 34.0 \text{ g/mol} = 0.100 \text{ mol}$ . No  $\text{S}_2(g)$  was present initially.

At equilibrium, converting  $3.72 \times 10^{-2}$  mol of  $\text{S}_2(g)$  in 1.25 L to  $M$ :

$$3.72 \times 10^{-2} \text{ mol} / 1.25 \text{ L} = 0.0298 \text{ M}.$$

Stoichiometry dictates that for *each* mole of  $\text{S}_2(g)$  produced, 2 mol of  $\text{H}_2\text{S}$  reacts, and 2 mol of  $\text{H}_2(g)$  is produced. So moles  $\text{H}_2$  produced and moles  $\text{H}_2\text{S}$  that must have reacted =  $2 \times 3.72 \times 10^{-2} \text{ mol} = 0.0744 \text{ mol}$ .

## Special Focus: Chemical Equilibrium

$\text{H}_2\text{S}(\text{g})$  remaining at equilibrium =  $0.100 - 0.0744 = 0.026$  mol (note the loss of one significant figure because of the subtraction). Converting these moles to molarities, we have

$$[\text{H}_2] = 0.0744 \text{ mol}/1.25\text{L} = 5.95 \times 10^{-2} \text{ M}, \text{ and}$$
$$[\text{H}_2\text{S}] = 0.026 \text{ mol}/1.25\text{L} = 2.0 \times 10^{-3} \text{ M}.$$

The ICE chart looks like this:

	$\text{H}_2\text{S}(\text{g}) \rightleftharpoons$	$\text{H}_2(\text{g}) +$	$\text{S}_2(\text{g})$
Initial moles	$1.00 \times 10^{-1}$	0	0
Change in moles	$-7.44 \times 10^{-2}$	$+7.44 \times 10^{-2}$	$+3.72 \times 10^{-2}$
Equilibrium moles	$2.6 \times 10^{-2}$	$7.44 \times 10^{-2}$	$3.72 \times 10^{-2}$
Equilibrium [X]	$2.0 \times 10^{-2} \text{ M}$	$5.95 \times 10^{-2} \text{ M}$	$2.98 \times 10^{-2} \text{ M}$

(c) Calculate the value of the equilibrium constant,  $K_c$ , for the decomposition reaction at 483 K.

### Solution

Substituting the values from the bottom row in the chart into the expression written in part (a) yields  $K_c = (0.0595)^2(0.0298) / (0.020)^2 = 0.25$ .

(d) Calculate the partial pressure of  $\text{S}_2(\text{g})$  in the container at equilibrium at 483 K.

### Solution

Assuming ideal gas laws apply, the partial pressure is given by  $P = nRT/V$ , where  $n/V$  is the equilibrium concentration from the chart =  $2.98 \times 10^{-2}$  mol/L. Using  $R = 0.0821$  L-atm/mol-K and  $T = 483$ ,  $P_{\text{S}_2(\text{g})} = 1.18$  atm.

(e) For the reaction  $\text{H}_2(\text{g}) + 1/2\text{S}_2(\text{g}) \rightleftharpoons \text{H}_2\text{S}(\text{g})$  at 483 K, calculate the value of the equilibrium constant,  $K_c$ .

### Solution

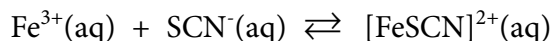
The new equation is the inverse of the first, and the coefficient is halved, so using the reciprocal and coefficient rule:

$$K_c \text{ for this reaction is equal to } 1 / \sqrt{0.25} = 2.0.$$



### Experimental Determination of $K_c$

The best way for students to understand the meaning of  $K_c$  is to determine it experimentally. A number of laboratory manuals use the following equilibrium expression to determine  $K_c$ :



The iron(III) ion in an acid solution is almost colorless, and the  $\text{SCN}^{-}$  ion is also colorless, but upon mixing the red complex ion,  $[\text{FeSCN}]^{2+}$  is formed. The equilibrium expression is  $K_c = \frac{[\text{FeSCN}]^{2+}}{[\text{Fe}^{3+}][\text{SCN}^{-}]}$ , and the value of  $K_c$  is determined.

This experiment familiarizes students with colorimetric methods, which involve constructing a standard curve, and it requires a spectrophotometer (e.g., Spec 20) or a Vernier colorimeter using a CBL, LabPro, or a computer.

In the first part of the experiment, students apply a limiting reagent method by preparing a series of iron(III) nitrate solutions with decreasing concentrations, mixed with excess KSCN. They determine the final concentration of the  $[\text{FeSCN}]^{2+}$  ion in each of the solutions by assuming  $[\text{FeSCN}^{2+}] = [\text{Fe}^{3+}]$ , and they measure the absorbance. On a graph of concentration of the  $[\text{FeSCN}]^{2+}$  versus absorbance (which should be a straight line), the slope represents the molar absorptivity constant for the ion, which is then used in the second part of the experiment.

In the second part, students carry out a series of trials where the starting concentrations of the iron(III) ion and the thiocyanate ion are varied. At this point of the experiment, neither reaction is significantly in excess. From the absorbance of each trial and using the slope determined in the first part of the experiment, they calculate the equilibrium concentration of the  $[\text{FeSCN}]^{2+}$  ion.

Since the starting concentrations of the reactants are known and the equilibrium concentration of the product is measured, stoichiometry (1:1) is used to determine the equilibrium concentration of the iron(III) ion and the thiocyanate ion. The equilibrium concentrations of both reactants are found by subtracting the change in the reactants. This is summarized in the following table for typical student data.

## Special Focus: Chemical Equilibrium

	[Fe <sup>3+</sup> ] moles/L	[SCN <sup>-</sup> ] moles/L	[[FeSCN] <sup>2+</sup> ] moles/L
I	$6.00 \times 10^{-4} M$	$4.00 \times 10^{-4} M$	0.0 M
C	$-2.88 \times 10^{-5}$	$-2.88 \times 10^{-5}$	$+2.88 \times 10^{-5} M$
E	$5.71 \times 10^{-4} M$	$3.71 \times 10^{-4} M$	$2.88 \times 10^{-5} M$

From this data,  $K_c$  is equal to  $[[\text{FeSCN}]^{2+}] / [\text{Fe}^{3+}][\text{SCN}^-] = 136$ .

Students perform this procedure for each trial and should obtain similar values for  $K_c$ . This is an excellent experiment for students to master the skills of determining an equilibrium constant, performing dilutions, and becoming familiar with colorimetric methods



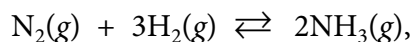
### Examples of Gas Phase Reactions and Use of $K_p$

If a reaction is occurring entirely in the gas phase, the equilibrium constant can be expressed in terms of partial pressures and be termed  $K_p$ . Assuming ideality, there is a simple relationship to be found between the two constants. Using the ideal gas law, we can derive the relationship  $P = MRT$  (where  $M = n/V$ ) for each reactant or product gas present. Substitution into a general  $K_p$  expression shows that:

$$K_p = K_c(RT)^{\Delta n}.$$

Where  $R$  is the gas constant,  $T$  is temperature, and  $\Delta n$  is the *change* in the number of moles of gas between products and reactants.

For example, for the Haber Process reaction:



$$\Delta n = 2 \text{ moles in the products} - 4 \text{ moles in the reactants} = -2,$$

$$\text{so } K_p = K_c(RT)^{-2}.$$

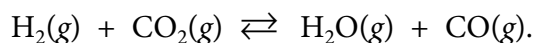
For the reaction  $\text{H}_2(\text{g}) + 2\text{Cl}_2(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g})$ ,  $\Delta n = 0$ , so in this case  $K_p = K_c$ .



**Sample AP Problem: 1995 Free-Response 1b–e**

The following parts of this question illustrate how  $K_p$  or  $K_c$  are determined and compared to each other.

Given the following reaction:



When  $\text{H}_2(\text{g})$  is mixed with  $\text{CO}_2(\text{g})$  at 2,000 K, equilibrium is achieved according to the equation above. In one experiment, the following equilibrium concentrations were measured.

$$\begin{aligned} [\text{H}_2] &= 0.20 \text{ mol/L} \\ [\text{CO}_2] &= 0.30 \text{ mol/L} \\ [\text{H}_2\text{O}] &= [\text{CO}] = 0.55 \text{ mol/L} \end{aligned}$$

- (b) Using the equilibrium concentrations given above, calculate the value of  $K_c$ , the equilibrium constant for the reaction.

**Solution**

	$[\text{H}_2]$ +	$[\text{CO}_2]$ $\rightleftharpoons$	$[\text{H}_2\text{O}]$	+ $[\text{CO}]$
<b>I</b>	Not given	Not given	Not given	Not given
<b>C</b>	Not applicable	Not applicable	Not applicable	Not applicable
<b>E</b>	0.20 M	0.30 M	0.55 M	0.55 M

$$K_c = \frac{[\text{H}_2\text{O}][\text{CO}]}{[\text{H}_2][\text{CO}_2]} = \frac{(0.55)(0.55)}{(0.20)(0.30)} = 5.0$$

- (c) Determine  $K_p$  in terms of  $K_c$ .

**Solution**

Since  $K_p = K_c (RT)^{\Delta n}$ , and recognizing that  $\Delta n = 0$  in this reaction,  $K_p = K_c = 5.0$ .



## Special Focus: Chemical Equilibrium

- (d) When the system is cooled from 2,000 K to a lower temperature, 30.0 percent of the  $\text{CO}(g)$  is converted back to  $\text{CO}_2(g)$ . Calculate the value of  $K_c$  at this lower temperature.

### Solution

A system at equilibrium is disturbed, causing changes in the concentrations. A temperature change will alter the value of the equilibrium constant. Setting up the ICE will help, and since all stoichiometric coefficients are 1, this is easy:

	$[\text{H}_2]$ +	$[\text{CO}_2]$ $\rightleftharpoons$	$[\text{H}_2\text{O}]$	+ $[\text{CO}]$
<b>I</b>	0.20 M	0.30 M	0.55 M	0.55 M
<b>C</b>	+ 0.55 $\times 0.30 =$ + 0.17 M	+ 0.17 M	- 0.17 M	-0.55 $\times 0.30 =$ - 0.17 M
<b>E</b>	0.37 M	0.47 M	0.38 M	0.38 M

Value of  $K_c$  and  $K_p$  at lower  $T = (0.38)(0.38) / (0.37)(0.47) = 0.83$ .

- (e) In a different experiment, 0.50 mole of  $\text{H}_2(g)$  is mixed with 0.50 mole of  $\text{CO}_2(g)$  in a 3.0-liter reaction vessel at 2,000 K. Calculate the equilibrium concentration, in moles per liter, of  $\text{CO}(g)$  at this temperature.

### Solution

This is a classic type of problem where the constant is given (calculated in the part (b)), and the initial concentrations of the reactants and the equilibrium concentration of one of the products is to be determined. The stoichiometry is still 1:1:1:1. Setting up ICE with algebraic notation gives the following chart:

	$[\text{H}_2]$ +	$[\text{CO}_2]$ $\rightleftharpoons$	$[\text{H}_2\text{O}]$	+ $[\text{CO}]$
<b>I</b>	$0.50/3.0 = 0.17 M$	$0.50/3.0 = 0.17 M$	0.0 M	0.0 M
<b>C</b>	- $x$	- $x$	+ $x$	+ $x$
<b>E</b>	$(0.17 - x) M$	$(0.17 - x) M$	$x M$	$x M$

Substituting in the expression, we get:

$$5.0 = \frac{[\text{H}_2\text{O}][\text{CO}]}{[\text{H}_2][\text{CO}_2]} = \frac{x^2}{(0.17 - x)^2}$$

which is easily solvable, as it is a perfect square, so  $x = 0.12 \text{ M} = [\text{CO}]$ .

(Note that  $x$  is not negligible compared to 0.17, so no approximation could be made.)



**Sample AP Question: 1981 Free-Response 1**

In this problem, the use of  $K_p$  is seen in a heterogeneous equilibrium.

Ammonium hydrogen sulfide is a crystalline solid that decomposes as follows:



- (a) Some solid  $\text{NH}_4\text{HS}$  is placed in an evacuated vessel at  $25^\circ\text{C}$ . After equilibrium is attained, the total pressure inside the vessel is found to be 0.659 atmospheres. Some solid  $\text{NH}_4\text{HS}$  remains in the vessel at equilibrium. For this decomposition, write the expression for  $K_p$  and calculate its numerical value at  $25^\circ\text{C}$ .

**Solution**

Equilibrium “rules” establish that pure solids or liquid are not to be included in equilibrium expressions (see the appendix for justification). So the equilibrium expression for this reaction, in terms of pressure units, is

$$K_p = P_{\text{NH}_3} \times P_{\text{H}_2\text{S}}$$

Since only solid was present initially, the 1:1 stoichiometry tells us that the final pressure of products must be equal and add to the total pressure of 0.659 atm, so they are each equal to 0.330 atm. The ICE chart would be very simple, so it is not included here.

Substituting, we have  $K_p = (0.330)(0.330) = 0.109$ .

- (b) Some extra  $\text{NH}_3$  gas is injected into the vessel containing the sample described in part (a). When equilibrium is reestablished at  $25^\circ\text{C}$ , the partial pressure of  $\text{NH}_3$  in the vessel is twice the partial pressure of  $\text{H}_2\text{S}$ . Calculate the numerical value of the partial pressure of  $\text{NH}_3$  and the partial pressure of  $\text{H}_2\text{S}$  in the vessel after the  $\text{NH}_3$  has been added and the equilibrium has been reestablished.

## Special Focus: Chemical Equilibrium

### Solution

This is an example of a perturbed equilibrium, but the temperature does not change, so  $K_p$  is known from part (a) = 0.109. We know only the ratio of the partial pressures, so we can state that if  $P_{\text{H}_2\text{S}} = x$ , then  $P_{\text{NH}_3} = 2x$ . Then we have

$$K_p = 0.109 = (x)(2x) = 2x^2; \text{ hence } x^2 = 0.0545 \text{ and } x = 0.233 \text{ atm,} \\ \text{so that } P_{\text{H}_2\text{S}} = 0.233 \text{ atm, and } P_{\text{NH}_3} = 0.466 \text{ atm.}$$

(Note: Where do the units of atm come from if they are not in the  $K$  value? Simply, they come from the units that were used to compute  $K$ . For instance if Pa [pascal] were used initially, then Pa would be the units of pressure computed here.)

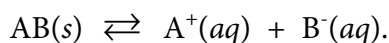
### Laboratory Manuals Where the Referenced Experiment May Be Found

- *Advanced Chemistry with Vernier Experiments for AP<sup>®</sup>, IB, and College General Chemistry*. Vernier Software and Technology ([www.vernier.com](http://www.vernier.com)).
- Wentworth, R. A. D. *Experiments in General Chemistry*. Houghton Mifflin Company. (This manual accompanies Ebbing's General Chemistry book.)

## The Solubility Product Constant: $K_{sp}$

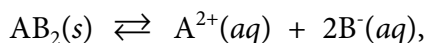
Cheri Smith  
Yale Secondary School  
Abbotsford, British Columbia

The solubility product constant,  $K_{sp}$ , is a specialized equilibrium constant that is typically applied to a saturated solution of a low solubility salt that is dissolving to form ions. Such a process might be represented by the following equation:



In this case, the equilibrium expression would appear as follows:  $K_{sp} = [A^+][B^-]$ .

In the case of a salt where two anions combine with one cation (an  $AB_2$  salt), the dissolving process would be represented by



and the equilibrium expression for this salt would be  $K_{sp} = [A^{2+}][B^-]^2$ .

The magnitude of the solubility product constant is related to the solubility of a salt. The more soluble a particular salt, the larger its  $K_{sp}$  will be. The term “solubility” in this regard only refers to the dissociative process. The fact that some undissociated salts may also “dissolve” is considered beyond AP level and will not be discussed further.

Like all equilibrium constants,  $K_{sp}$  is temperature dependent. As the dissolution of most salts (but not all) is an endothermic process,  $K_{sp}$  will generally increase with temperature.

There are several applications for the solubility product constant, including:

- Determining the solubility of a salt in a saturated solution
- Predicting whether a precipitate will form when two solutions combine
- Predicting the effect of the addition of a common ion to a solution

These will be described using examples from the free-response sections of past AP Chemistry Examinations.

## Special Focus: Chemical Equilibrium



### Determination of Solubility from $K_{sp}$ or $K_{sp}$ from Solubility

It is crucial for students to understand that according to this model, the concentrations of ions in a saturated solution of a salt in water represent the salt's molar solubility. **However, the concentration of individual ions derived from the salt will depend on the stoichiometry of the salt and its dissolving process. Thus only the concentration in a solution of an ion with a 1:1 mole ratio to its salt can be used to define the salt's "solubility."**

An easy-to-follow attack plan for this type of problem consists of four steps:

1. Write the equation for the dissolving process described.
2. Write given information, such as the concentrations below each species. (Be sure to express concentrations in moles per liter. Pay attention to the stoichiometry [mole ratios]. If a concentration is unknown, represent it with a variable.)
3. Write the equilibrium constant expression.
4. Substitute and solve the problem.

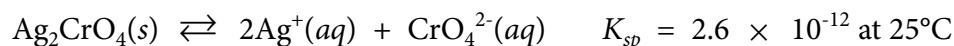
The scaffolding of the following questions will generally help lead a student through these steps.



### AP Sample Problem: 2004 1(a)–(c) and (e)–(f)

Answer the following questions relating to the solubilities of two silver compounds: silver chromate,  $\text{Ag}_2\text{CrO}_4$ , and silver phosphate,  $\text{Ag}_3\text{PO}_4$ .

Silver chromate dissociates in water according to the equation shown below:



- (a) Write the equilibrium-constant expression for the dissolving of  $\text{Ag}_2\text{CrO}_4(s)$ .

#### Solution

Step 1:  $K_{sp} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}]$  (note the application of the stoichiometric coefficients).

(b) Calculate the concentration, in mol L<sup>-1</sup>, of Ag<sup>+</sup>(aq) in a saturated solution of Ag<sub>2</sub>CrO<sub>4</sub> at 25°C.

**Solution**

Step 1: Write the equation:  $\text{Ag}_2\text{CrO}_4(s) \rightleftharpoons 2 \text{Ag}^+(aq) + \text{CrO}_4^{2-}(aq)$ .

Step 2: Write given information: Solid                      2s                      s (let s = solubility).

Steps 3 and 4: Use expression written in part (a) and substitute and solve:

$$2.6 \times 10^{-12} = (2s)^2(s) = 4s^3,$$

$$s = 8.7 \times 10^{-5}.$$

This equals [CrO<sub>4</sub><sup>2-</sup>] as defined in step 2.

Looking at the equation, [Ag<sup>+</sup>] = 2s = 1.7 × 10<sup>-4</sup> M. (Note the tricky assumption, for beginners, that the unitless K value provides results in molar units!)

(c) Calculate the maximum mass, in grams, of Ag<sub>2</sub>CrO<sub>4</sub> that can dissolve in 100 mL of water at 25°C.

**Solution**

Steps 1–4 lead the student to realize that the solubility of silver chromate is 8.7 × 10<sup>-5</sup> M.

If the student realizes that the solubility is the maximum amount that can be dissolved in a particular volume of solution, the solubility may be used to determine the required mass as follows: 100 mL × 8.7 × 10<sup>-5</sup> mol/1000 mL × 331.7 g/mol = 0.0029 g.

In a saturated solution of Ag<sub>3</sub>PO<sub>4</sub> at 25°C, the concentration of Ag<sup>+</sup>(aq) is 5.3 × 10<sup>-5</sup> M. The equilibrium-constant expression for the dissolving of Ag<sub>3</sub>PO<sub>4</sub>(s) in water is shown below.

$$K_{sp} = [\text{Ag}^+]^3[\text{PO}_4^{3-}]$$

## Special Focus: Chemical Equilibrium

(e) Write the balanced equation for the dissolving of  $\text{Ag}_3\text{PO}_4$  in water.

(f) Calculate the value of  $K_{sp}$  for  $\text{Ag}_3\text{PO}_4$  at  $25^\circ\text{C}$ .

### Solution

Step 1:  $\text{Ag}_3\text{PO}_4(s) \rightleftharpoons 3\text{Ag}^+(aq) + \text{PO}_4^{3-}(aq)$ , then applying the ratio of 3:1 gives

Step 2: solid  $5.3 \times 10^{-5}$   $1.8 \times 10^{-5}$ .

Step 3: The equilibrium expression is given above.

Step 4: Substitute  $K_{sp} = (5.3 \times 10^{-5})^3(1.8 \times 10^{-5}) = 2.6 \times 10^{-18}$ .

Note that all digits should be carried through the entire calculation, and rounding should only be done to the correct number of significant figures at the end. Note also that no units are given for  $K_{sp}$ .



### Useful Analogies for Chemical Processes

**The Cereal Bowl Analogy for Solubility:** Most students will smile and recognize the situation when so much sugar has been added to a bowl of cereal that some solid sugar can be seen sitting in their milk at the bottom of the bowl. Explain that the milk is now saturated with sugar. The crystals of sugar are dissolving at the same rate as the sugar is recrystallizing. This is a good example of a saturated solution. However, be clear that sugar is not a sparingly soluble salt, and so the  $K_{sp}$  treatment is not used for sugar.

**The Bicycle Analogy for Mole Ratios:** Many students have difficulty understanding that 1 mole of  $\text{AB}(s)$  will dissociate into 1 mole of  $\text{A}^+(aq)$  and 1 mole of  $\text{B}^-(aq)$ . Some are not comfortable with the idea that 1 gives  $1 + 1$ . They think that 1 should give  $0.5 + 0.5$ . Sketch a bicycle. Ask the question, if I have one bicycle, how many front wheels do I have? How many rear wheels? You may wish to use different colors for the wheels and place the bicycle under an equation, using corresponding colors for the cation and anion. For  $\text{AB}_2$  salts, use a tricycle analogy, asking for the number of front and rear wheels. Continue the ratio analogy with two or three cycles. (This analogy is useful for lower-level chemistry concepts such as moles of atoms in a compound like  $\text{CaCO}_3$ . For example, let the Ca represent the handlebar, the C represent the seat, and the O represent the wheels in a tricycle.)



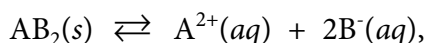
### **Predicting Whether a Precipitate Will Form When Two Solutions Combine**

As with all types of equilibrium, it is possible to substitute concentrations from nonequilibrium systems into an equilibrium constant expression to calculate a reaction quotient, or “Q” value. This might be called a “Trial  $K$ .” This is especially useful in the case of  $K_{sp}$  to answer questions about whether or not a precipitate will form.

The major difference between this type of calculation and the solubility calculations discussed previously is that precipitation generally involves ions from two different sources. It is crucial that students understand that **the concentration of each ion in any solution is directly related to the salt that is the source of that ion**. As two solutions of soluble salts that might form a precipitate are poured together, the student must calculate the initial concentration of each ion in the final solution. This may require either dilution calculations or determining the moles of each ion and dividing by the final solution volume. Once the concentration of each ion is known, they are substituted into the equilibrium expression, **assuming no reaction or precipitation occurs**, and a value for  $Q$  is determined. The  $Q$  value is then compared to the actual  $K_{sp}$  value for the “insoluble” salt that may form at a particular temperature (generally 25°C).

Consider the combination, in water, of soluble salts  $\text{NaB}$  and  $\text{A}(\text{NO}_3)_2$  that can form a precipitate,  $\text{AB}_2$ .

The solubility equilibrium equation is



and the equilibrium expression is

$$K_{sp} = [\text{A}^{2+}][\text{B}^{-}]^2.$$

The concentration of  $\text{A}^{2+}$  is equal to the concentration of  $\text{A}(\text{NO}_3)_2$ , and the concentration of  $\text{B}^{-}$  is equal to the concentration of  $\text{NaB}$ , both in the final solution (recall the crucial point above—students frequently attempt to double the concentration of  $\text{NaB}$ ).

Since  $Q = [\text{A}^{2+}][\text{B}^{-}]^2$ , it follows that  $Q$  equals  $K_{sp}$  when the solution is at equilibrium or exactly saturated with both solid present in the system and ions in the solution.



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If  $Q$  is calculated to be *larger* than  $K_{sp}$ , the reaction must shift left, lowering the concentrations of ions by forming precipitate until  $Q$  becomes equal to  $K_{sp}$ .

If, however, the calculated  $Q$  is found to be *smaller* than the  $K_{sp}$ , there are not enough ions present to produce a precipitate. All the ions will remain in solution, and equilibrium will not be reached with a solid salt.

To summarize:

If  $Q = K_{sp}$ , the solution is saturated.

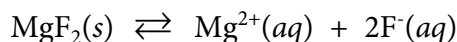
If  $Q > K_{sp}$ , a precipitate will form.

If  $Q < K_{sp}$ , all ions remain in solution; no precipitate forms.

$Q$  may also be used to determine the concentration of cation required to precipitate a known concentration of anion (or vice versa). For this type of calculation, it is crucial for students to understand that **when  $Q$  is equal to  $K_{sp}$ , the solution has just become saturated.**



### Sample AP Question: 1994 1(a) and (c)



In a saturated solution of  $\text{MgF}_2$  at  $18^\circ\text{C}$ , the concentration of  $\text{Mg}^{2+}$  is  $1.21 \times 10^{-3}$  molar. The equilibrium is represented by the equation above.

- (a) Write the expression for the solubility-product constant,  $K_{sp}$ , and calculate its value at  $18^\circ\text{C}$ .

#### Solution

Step 1:  $\text{MgF}_2(s) \rightleftharpoons \text{Mg}^{2+}(aq) + 2\text{F}^{-}(aq)$ ; applying the 2:1 ratio gives

Step 2: Solid                       $1.21 \times 10^{-3}$        $2.42 \times 10^{-3}$

Steps 3 and 4: Writing the equilibrium-constant expression and substituting:

$$K_{sp} = [\text{Mg}^{2+}][\text{F}^{-}]^2 = (1.21 \times 10^{-3})(2.42 \times 10^{-3})^2 = 7.09 \times 10^{-9}.$$

- (b) Predict whether a precipitate of  $\text{MgF}_2$  will form when 100.0 milliliters of a  $3.00 \times 10^{-3}$  molar  $\text{Mg}(\text{NO}_3)_2$  solution is mixed with 200.0 milliliters of a  $2.00 \times 10^{-3}$  molar NaF solution at  $18^\circ\text{C}$ . Calculations to support your prediction must be shown.

**Solution**

From the given equation,  $Q = [\text{Mg}^{2+}][\text{F}^-]^2$ , and noting the source of ions from the fully soluble salts and the final total volume to be  $200 \text{ mL} + 100 \text{ mL} = 300 \text{ mL}$ , then

$$\begin{aligned} [\text{Mg}^{2+}] &= [\text{Mg}(\text{NO}_3)_2] = 0.00300 \text{ M} \times 100.0 \text{ mL}/300.0 \text{ mL} = 0.00100 \text{ M}, \\ [\text{F}^-] &= [\text{NaF}] = 0.00200 \text{ M} \times 200.0 \text{ mL}/300.0 \text{ mL} = 0.00133 \text{ M}, \\ Q &= (0.00100)(0.00133)^2 = 1.78 \times 10^{-9}. \end{aligned}$$

Since  $Q < K_{sp}$ , there is no precipitate.



**Predicting the Effect of Addition of a Common Ion to a Solution**

The common ion effect deals with the addition of ions that are already part of an existing equilibrium. The effect of adding such ions can be examined qualitatively or quantitatively. The qualitative effect is most easily predicted using Le Chatelier's principle (see chapter 2).

In an aqueous equilibrium such as  $\text{AB}_2(\text{s}) \rightleftharpoons \text{A}^{2+}(\text{aq}) + 2\text{B}^-(\text{aq})$ , the addition of a soluble salt, NaB, by adding a solution or a solid will result in an increased concentration of  $\text{B}^-$  ions. As a result, the equilibrium will shift to the left, increasing the amount of solid  $\text{AB}_2$ . Although  $K_{sp}$  remains constant for the salt  $\text{AB}_2$ , it can be said that  $\text{AB}_2$  is less soluble in a solution of NaB than it is in water. A similar effect could be achieved by adding a source of  $\text{A}^{2+}$  ions.

It should be noted that the common ion effect is sometimes discussed in terms of the removal of ions from an equilibrium system. In this case, there really is no "common ion" but the introduction of a "new" reaction, which has its own equilibrium constant at work. Ions are most frequently removed by one of three means:

1. Neutralization: The hydroxide ion is neutralized by the addition of a strong acid. For example, nitric acid is added to a saturated aqueous solution of lead (II) hydroxide. The hydrogen ion from the acid will react with the hydroxide ion, reducing  $[\text{OH}^-]$

## Special Focus: Chemical Equilibrium

and causing a right shift in the equilibrium,  $\text{Pb(OH)}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2\text{OH}^-(aq)$ . More lead hydroxide will dissolve so that the  $K_{sp}$  value is held constant. Lead hydroxide is more soluble in nitric acid than in pure water.

2. Precipitation: Anions or cations are removed *from solution* by precipitation with a cation or anion with which they form an “insoluble” salt. For example, silver nitrate is added to a saturated solution of lead(II) chloride. The silver ion from the silver nitrate will precipitate the chloride ion, causing a right shift in the equilibrium,  $\text{PbCl}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2\text{Cl}^-(aq)$ . More lead chloride will dissolve to keep  $K_{sp}$  constant. Lead chloride is more soluble in a solution of silver nitrate than it is in pure water.
3. Complex ion formation: Anions or cations are removed through the formation of a complex ion with some added species. For example, ammonia is added to a saturated solution of silver chloride. The ammonia will make a complex with the silver ion, forming silver diammine,  $\text{Ag(NH}_3)_2^+$ , causing a right shift in the equilibrium,  $\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)$ . More silver chloride will dissolve; silver chloride is more soluble in a solution of ammonia than it is in pure water. Strictly speaking, this is not an application of a solubility equilibrium but of a complex ion formation equilibrium, since the species stays in solution.

Regardless of the method used, removal of a product ion will always cause a shift of equilibrium, effectively increasing the solubility of the salt. The only instance where this is tricky is when there is no reservoir of additional solid to dissolve, and a nonequilibrium system results.

To summarize, students should recognize that **the addition of a common ion will reduce solubility, while the removal of an ion by an alternative reaction will increase solubility.**

The attack plan for a quantitative problem involving the common ion effect is very similar to that for a standard solubility calculation, except that additional salts are involved. Once again, a series of four steps are followed:

1. Write the equations for each substance side by side. Note that the low solubility substance's equation is written first, and it is written as an equilibrium. The freely soluble substance equation(s) follows and is written with a single arrow.

2. Write given information, such as the concentrations, below each species. (Be sure to express concentrations in moles per liter. Pay attention to the stoichiometry [mole ratios]. If a concentration is unknown, represent it with a variable.)
3. Write the expression for the equilibrium constant for the low solubility substance. Students frequently have difficulty discerning which expression to write. It is crucial to point out that we are interested in the **expression for the low solubility substance. It is the one whose  $K_{sp}$  value is given or implied. Students may be expected to know solubility rules (which salts are soluble and which are not).**
4. Substitute and solve the problem.

Note that one of the ions will be present in both equations. This is the common ion. The substitution of two concentrations, one represented by a variable, may result in a quadratic equation. It is often possible to eliminate the need for solving a quadratic equation by making a simplifying assumption. The assumption is that one of the common ion concentrations is negligible compared with the other. It is crucial to clarify that the negligible concentration will be the one whose source is the low solubility substance. By assuming this concentration is negligible, students can eliminate the need for a quadratic equation, and the problem becomes easier to solve.



Always emphasize the need for students to **remember the chemistry. Don't just rely on the mathematics. Does the final answer make sense?** If a common ion was added, was the solubility reduced compared to that in water? If an ion was removed, was the solubility increased?



### AP Sample Question: 2004 1(d)—Qualitative

A 0.100 mol sample of solid  $\text{AgNO}_3$  is added to a 1.00 L saturated solution of  $\text{Ag}_2\text{CrO}_4$ . Assuming no volume change, does  $[\text{CrO}_4^{2-}]$  increase, decrease, or remain the same? Justify your answer.

#### Solution

Steps are not strictly used in this qualitative question.

The low solubility substance is the  $\text{Ag}_2\text{CrO}_4$ .

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$\text{Ag}_2\text{CrO}_4(s) \rightleftharpoons 2\text{Ag}^+(aq) + \text{CrO}_4^{2-}(aq)$  is given in the stem of the question.

Students should recognize that nitrates are freely soluble. (No solubility table is provided with the exam.) The common ion,  $\text{Ag}^+$ , is being added. Nitrate is merely a spectator ion. As a result of adding a product, the equilibrium shifts left. A consequence of this shift is a decrease in  $[\text{CrO}_4^{2-}]$ .

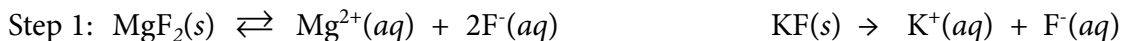
Should the student prefer, a mathematical explanation could be employed. In this case, the student would indicate that  $[\text{Ag}^+]^2[\text{CrO}_4^{2-}]$  must =  $2.6 \times 10^{-12}$  (the  $K_{sp}$  value is given in the question). When  $[\text{Ag}^+]$  is increased by adding silver nitrate, substituting in the expression for  $Q$  will give a value greater than  $K_{sp}$ .  $[\text{CrO}_4^{2-}]$  must decrease in order for  $Q$  to become equal to  $K_{sp}$ .



### Sample AP Question: 1994 1(b)—Quantitative

Calculate the equilibrium concentration of  $\text{Mg}^{2+}$  in 1.000 liter of saturated  $\text{MgF}_2$  solution at  $18^\circ\text{C}$  to which 0.100 mole of solid  $\text{KF}$  has been added. The  $\text{KF}$  dissolves completely. Assume the volume change is negligible.

#### Solution



Step 2: Solid                       $x$                        $2x$                       Solid                      0.100                      0.100  
(Notice the variable  $x$  is used instead of  $s$ , as  $x$  is *not* the solubility in pure water, and the  $\text{KF}$  is assumed to be completely dissociated into ions.)

Step 3:  $K_{sp} = [\text{Mg}^{2+}][\text{F}^-]^2$  (the equilibrium expression for the low solubility salt).

Step 4: Substitute and solve:

$$7.09 \times 10^{-9} = (x)(2x + 0.100)^2.$$

( $K_{sp}$  was calculated in part (a) of the problem; see above, “Sample AP Problem: 1994 1(a) and (c).”)

Simplify by assuming the  $[\text{F}^-]$  contributed from  $\text{MgF}_2$  is negligible, then

$$7.09 \times 10^{-9} = (x)(0.100)^2 = (x)(0.0100).$$
$$\text{Hence } x = [\text{Mg}^{2+}] = 7.09 \times 10^{-7} \text{ M}.$$



### Useful Demonstrations

Be sure to follow good safety and disposal practices.

1. Make a precipitate of  $\text{Al}(\text{OH})_3$  by adding 15 mL of 0.1 M aluminum nitrate to 15 mL of 0.1 M sodium hydroxide. Filter and divide the saturated solution into two portions of approximately 10 mL in separate test tubes. Add two drops of 0.1 M aluminum nitrate to one of the tubes. Have students predict the result before the addition. Repeat with two drops of 0.1 M sodium hydroxide in the second tube. Should the quantity of precipitate produced be the same? Calculations may be performed to verify that the hydroxide reduces the solubility more than the aluminum ion. (For simplicity, assume the volume of two drops is 0.10 mL.)
2. The remaining solid aluminum hydroxide and its saturated supernatant solution may be placed into a third test tube. Add 3 M nitric acid to this tube several drops at a time until the solid dissolves. Students need to explain that the hydrogen ion from the strong acid is neutralizing the hydroxide, resulting in a right shift that dissolves the precipitate.
3. A more interesting visual is the dissolution of  $\text{Cu}(\text{OH})_2$  by the addition of 6 M ammonia. In this case, the copper(II) ion is removed due to the formation of the complex ion copper(II) tetrammine,  $\text{Cu}(\text{NH}_3)_4^{2+}$ . Copper(II) hydroxide may be made by combining copper(II) nitrate with sodium hydroxide (0.1 M is a suitable concentration). The precipitate is a light blue, jellylike substance. The complex formation will result in a deep blue solution.



### Useful Labs

Note that safety regulations may inhibit performing some of these laboratory exercises in some schools.

1. Varying concentrations of lead(II) ion (from lead(II) nitrate) and chloride ion (from sodium chloride) are combined to determine the combination where the TIP (trial ion product) or Q value just equals the  $K_{sp}$ .

**Reference:** Experiment 12C from *Essential Experiments for Chemistry* by Morrison and Scodellaro (2005). For more information on this manual, along with a correlation guide for all recommended AP Chemistry labs, see [www.smgllabbooks.com](http://www.smgllabbooks.com).

## Special Focus: Chemical Equilibrium

2. A saturated solution of calcium hydroxide (lime water) is titrated with standardized hydrochloric acid using methyl red as an indicator. The  $K_{sp}$  of calcium hydroxide is calculated from the data. The titration is repeated using calcium hydroxide with calcium chloride added to it. The solubilities of the calcium hydroxide in water and in calcium chloride are compared. Differences are compared and explained.

## Equilibria with $K_a$ , $K_b$ , and $K_w$

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$K_a$ ,  $K_b$ , and  $K_w$  are specialized representations of equilibrium constants operating in an aqueous solution.  $K_a$  refers to the expression for the reaction of a weak acid,  $K_b$  refers to a weak base, and  $K_w$  refers to the ionization of water itself. Related problems are solved in the same way as for other equilibrium problems, but additional terminology is in common usage as weak acid-base reactions are important in chemistry, biochemistry, and medicinal chemistry. In fact, the simple treatments at this level are only accurate in very dilute solutions, and most problems assume ideal dilute solution behavior.

Rather than attempting to be a complete account of acid-base theory and practice, this chapter concentrates on those types of problems typically used in AP Examinations that deal with equilibrium aspects of weak acid-base reactions.

It is important for students to understand and become familiar with the terminology as well as how to solve typical equilibrium problems in this realm. The interesting, and difficult, aspect for many students is that this is their first encounter with systems where two or more simultaneous equilibria are operating. Students find it difficult to imagine that one solution system must obey at least two sets of equations at the same time.



### Types of Acids and Bases

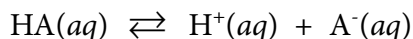
Weak acids and bases are those substances that do not ionize completely in water but give rise to changes in concentrations of  $H^+$  and  $OH^-$  ions when added to pure water. In contrast, strong acids and bases are almost completely ionized in dilute aqueous solutions. Usually, no equilibrium constant values are listed for most strong acids or bases, though they can be determined by highly specialized experiments. Weak acids and bases have equilibrium constant values for their reaction with water of less than 1. The  $K_a$  or  $K_b$  values are greater than 1 for strong acids and bases.

Many substances are amphiprotic—meaning that in the right conditions, they can act as an acid or a base. Water itself is such a substance, reacting as an acid with stronger bases than itself and as a base with stronger acids.

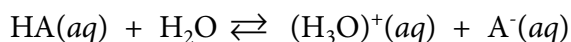


## Special Focus: Chemical Equilibrium

A typical acid has a formula that can be written HA, and its reaction equation is conventionally written:



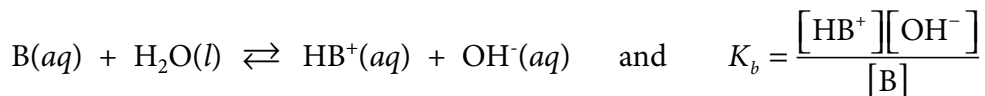
While the reaction is actually between the acid and water, the water is usually omitted to simplify thinking. A more complete reaction might be written:



For either reaction, the appropriate equilibrium expression is written:

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

For a weak base, the corresponding (simplified) equations are:



$K_w$  deals with the autoionization of water:  $\text{H}_2\text{O}(l) \rightleftharpoons \text{H}^+(aq) + \text{OH}^-(aq)$ . Students need to understand that every solution contains both the hydrogen ion  $[\text{H}^+]$  and hydroxide ion  $[\text{OH}^-]$ . The equilibrium constant expression for water is written:

$$K_w = [\text{H}^+][\text{OH}^-]$$

No denominator is used because water is a pure liquid. The numerical value of  $K_w$  is  $1.0 \times 10^{-14}$  for any aqueous solution at 298 K (25°C). A solution with more  $\text{H}^+$  than  $\text{OH}^-$  is termed acidic, and basic solutions have more  $\text{OH}^-$  than  $\text{H}^+$ .  $K_w$  is sometimes known as the “ion product constant” for water.

To conveniently express and track ion concentrations in aqueous solutions at very low concentrations, the pX system was devised.

The negative of the logarithm (to base 10) of the concentration ( $-\log [X]$ ) is termed pX.

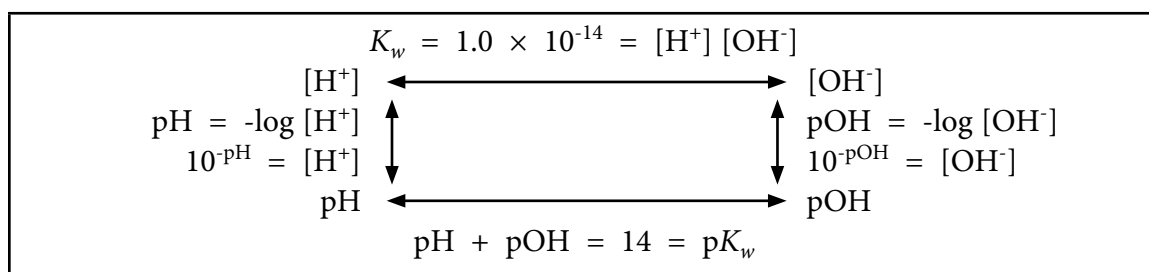
This system is also frequently applied to the values for equilibrium constants  $K_x$ , such that  $\text{p}K_x = (-\log K_x)$ . Students are often asked to make conversions between the two systems.

## Special Focus: Chemical Equilibrium

The equilibrium for water autoionization connects pH and pOH.

Since  $K_w = [\text{H}^+][\text{OH}^-]$ , then  $\text{p}K_w = \text{pH} + \text{pOH} = 14$  (at 298 K)

The following chart can help students with the steps of converting values of  $[\text{H}^+]$  and  $[\text{OH}^-]$  to pH and/or pOH values. This helps them remember they can't go directly from an  $\text{OH}^-$  concentration to pH. On the AP Examination, the pathway the student uses does not matter as long as work is shown.



There is a further interesting relationship among weak acids and bases.

In the reaction  $\text{HA}(aq) \rightleftharpoons \text{H}^+(aq) + \text{A}^-(aq)$ , HA is an acid.

However, the ion  $\text{A}^-$  can itself react with water in a “reverse” way, as shown by  $\text{A}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HA}(aq) + \text{OH}^-(aq)$  to form HA and  $\text{OH}^-$ . Thus  $\text{A}^-$  is a weak base. Because it forms from the acid, it is termed the conjugate base of HA. In a similar manner, HA can be thought of as the conjugate acid of the weak base  $\text{A}^-$ .

The equilibrium constants of a conjugate pair are closely related:

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

it is readily seen that  $K_a \times K_b = [\text{H}^+][\text{OH}^-] = K_w$  and so  $\text{p}K_a + \text{p}K_b = \text{p}K_w = 14$ .

This makes it easy to calculate a conjugate equilibrium constant if the value for the other member of the pair is known.

## Special Focus: Chemical Equilibrium



### Weak Acid Calculations

For the general weak acid represented by HA,  $\text{HA}(aq) \rightleftharpoons \text{H}^+(aq) + \text{A}^-(aq)$ , the equilibrium expression would be:

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

An example of a typical  $K_a$  problem would be as follows:

Given a 0.50 M solution of HA, calculate the pH of the solution at 25°C.  
Assume  $K_a = 2.6 \times 10^{-5}$ .

It is imperative students understand that when an HA breaks apart, there is one ion of  $\text{H}^+$  and one ion of  $\text{A}^-$ . **This concept—from one species, you get two species—is difficult for students.** Using models and pictures can help them understand this concept. Students must understand this to do any of the different types of equilibrium problems. It may be useful to have students draw simple pictures with every problem. However, it is also important to have them look at realistic pictures in texts or computer simulations that show the ions properly surrounded by oriented water molecules.



### Solution

It is convenient to use an ICE table (as shown below), where I is initial concentration, C is change in concentration, and E is concentration at equilibrium. We can determine the values of  $[\text{H}^+]$  and then the pH using the formula  $\text{pH} = -\log [\text{H}^+]$ .

Students should begin with an equation:  $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$ , then write the equilibrium expression and fill out an ICE chart below the equation:

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

	$[\text{HA}] \rightleftharpoons$	$[\text{H}^+]$	$+ [\text{A}^-]$
<b>Initial M</b>	0.50 M	0	0
<b>Change</b>	- x	+ x	+ x
<b>Equilibrium</b>	0.50 M - x	x	x

The  $-x$  value represents the amount of acid (in concentration units) breaking into ions.

Substituting, we get  $2.6 \times 10^{-5} = [x][x] / [0.50 M - x]$ .

- Many students will understand that the  $-x$  value is so small that when subtracted from the  $0.50 M$ , the overall value using correct significant figures will still be  $0.50 M$ . The students will want to drop the  $-x$  from the expression. This is okay as long as they show the  $-x$  and then put a line through it indicating that a simplifying assumption has been made.
- Always have students calculate the percent ionization to prove the assumption may be made. Percent ionization should be less than 5 percent for the  $-x$  value to be dropped. Otherwise, the student must be able to solve the quadratic equation. To get the percent ionization, the value of  $x$  is placed over the initial concentration of the acid, then multiplied by 100. In this case, since  $x = 3.6 \times 10^{-3} M$ ,  $(0.0036 M / 0.50 M) \times 100 = 0.72$  percent, it was okay to drop the  $-x$  value.
- Once the  $[H^+]$  is determined, taking the  $-\log$  of the value will give the pH. In this example, the  $[H^+]$  concentration ( $x$ ) of  $3.6 \times 10^{-3} M$  results in a pH of 2.44. The number of significant figures in the concentration is two, resulting in two places past the decimal in the pH value.



**Sample AP Weak Acid Question with a Starting Concentration:  
1996 1(a)**



Hypochlorous acid, HOCl, is a weak acid commonly used as a bleaching agent. The acid-dissociation constant,  $K_a$ , for the reaction represented above is  $3.2 \times 10^{-8}$ .

(a) Calculate the  $[H^+]$  of a  $0.14 M$  solution of HOCl.

**Solution**

$$K_a = \frac{[\text{OCl}^-][\text{H}^+]}{[\text{HOCl}]} = 3.2 \times 10^{-8}$$

- If  $x$  is the amount of the acid changing into ions, then  $x = [\text{OCl}^-] = [\text{H}^+]$ .
- The amount of  $[\text{HOCl}]$  remaining would be  $(0.14 - x)$ .

## Special Focus: Chemical Equilibrium

- Substituting into the equilibrium expression  $3.2 \times 10^{-8} = x^2 / (0.14 - x)$ ;
- $x = 6.7 \times 10^{-5} M = [H^+]$  assuming  $x$  is small compared to 0.14.

The same process in reverse can be used if given the pH and asked to determine the  $K_a$  value. Students often make a mistake doing this calculation with the use of significant figures and doing the proper math. If  $pH = -\log [H^+]$ , then  $10^{-pH} = [H^+]$ . The number of significant figures in the  $[H^+]$  from a pH is the number of places past the decimal. A pH of 7.97 leads to a concentration with two significant figures or  $1.1 \times 10^{-8} M$ . On the AP Examination, the number of significant figures calculated from a pH or expressed in a pH is often given incorrectly, as many textbooks discuss this only in the appendix, if at all.

For example, if a 0.50 M solution of an unknown monoprotic acid has a pH of 5.32, the  $K_a$  of the unknown acid can be calculated. To solve, the student has to recognize that the pH indirectly gives the  $[H^+]$  and the  $[A^-]$ . It gives the  $[A^-]$  because it is monoprotic; hence when the acid ionizes, one  $H^+$  is generated for one  $A^-$ .  $10^{-pH}$  is  $10^{-5.32} = 4.8 \times 10^{-6} M$ .

Substituting into the ICE chart gives the values shown below.

	[HA] $\rightleftharpoons$	[H <sup>+</sup> ]	+ [A <sup>-</sup> ]
<b>I</b>	0.50 M	0	0
<b>C</b>	$-4.8 \times 10^{-6} M$	$4.8 \times 10^{-6} M$	$4.8 \times 10^{-6} M$
<b>E</b>	0.4999952 M	$4.8 \times 10^{-6} M$	$4.8 \times 10^{-6} M$

Substituting into the equilibrium expression,

$$K_a = \frac{[4.8 \times 10^{-6} M][4.8 \times 10^{-6} M]}{[0.50 M]},$$

and the  $K_a$  value is  $4.6 \times 10^{-11}$ .

In this case, even though  $[H^+]$  is negligible with respect to the initial  $[HA]$ , the subtraction step is still shown. This is a good habit to develop as the percent ionization may sometimes exceed 5 percent in this type of problem.



**Sample AP Weak Acid Question with a pH: 2002 1(a)**



Hypobromous acid, HOBr, is a weak acid that dissociates in water, as represented by the equation above.

(a) Calculate the value of  $[\text{H}^+]$  in an HOBr solution that has a pH of 4.95.

**Solution**

$$10^{-4.95} = [\text{H}^+] = 1.1 \times 10^{-5} M$$

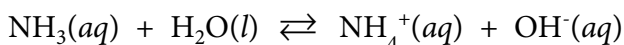


**Weak Base Calculations**

Weak base calculations involve the same types of computations, except bases generate an increased  $[\text{OH}^-]$ . This can be changed to either pOH using  $\text{pOH} = -\log$  of  $[\text{OH}^-]$  and then to pH using  $\text{pH} + \text{pOH} = 14$  or using the steps  $[\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$  ( $K_w$ ) and then  $\text{pH} = -\log [\text{H}^+]$ . (See the pH “box” on page 49.)

A common weak base, ammonia ( $\text{NH}_3$ ), is used in the following example. Here water is shown as a reactant; otherwise the source of  $\text{OH}^-$  ions is not obvious. However, note that it is incorrect to put water in the equilibrium constant expression.

Calculate the pH of an 0.50 M solution of ammonia if  $K_b = 1.8 \times 10^{-5}$ .



The  $K_b$  expression is written  $K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$ .

To solve, use the ICE format to get the values at equilibrium

	$\text{NH}_3 \rightleftharpoons$	$\text{NH}_4^+$	+ $\text{OH}^-$
<b>I</b>	0.50 M	0	0
<b>C</b>	- x	+ x	+ x
<b>E</b>	0.50 M - x	x	x

## Special Focus: Chemical Equilibrium

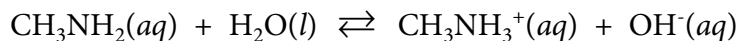
Using the  $K_b$  value for  $\text{NH}_3$ , and substituting, we get  $1.8 \times 10^{-5} = \frac{[x][x]}{[0.50 - x]}$ .

Solving for  $x$  gives  $x = 0.0030 \text{ M}$ , but  $x = [\text{OH}^-]$ , which can be converted to a pOH of 2.52 and then to a pH of  $(14 - 2.52) = 11.48$ .

Problems that need a  $K_b$  value may require the student to also calculate the  $K_b$  value from the relationship,  $K_a \times K_b = K_w$ , for a conjugate pair or vice versa.



### Sample AP Question: 1993 1(a)



Methylamine,  $\text{CH}_3\text{NH}_2$ , is a weak base that reacts according to the equation above. The value of the ionization constant,  $K_b$ , is  $5.25 \times 10^{-4}$ . Methylamine forms salts such as methylammonium nitrate,  $(\text{CH}_3\text{NH}_3^+)(\text{NO}_3^-)$ .

(a) Calculate the hydroxide ion concentration,  $[\text{OH}^-]$ , of a 0.225-molar aqueous solution of methylamine.

### Solution

$$K_b = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]}$$

	$\text{CH}_3\text{NH}_2$	+ $\text{H}_2\text{O}$	$\rightleftharpoons$ $\text{CH}_3\text{NH}_3^+$	+ $\text{OH}^-$
<b>I</b>	0.225 M		0	0
<b>C</b>	- $x$		+ $x$	+ $x$
<b>E</b>	0.225 M - $x$		$x$	$x$

$$K_b = 5.25 \times 10^{-4} = \frac{[x][x]}{[0.225 \text{ M} - x]} \cong \frac{[x^2]}{[0.225 \text{ M}]}$$

$$x = [\text{OH}^-] = 1.09 \times 10^{-2} \text{ M}$$

Solving using the quadratic instead of approximating:  $x = 1.06 \times 10^{-2} \text{ M}$ .



### Weak Conjugate Pair (Buffer) Calculations

In some problems, students will be required to determine the pH of a solution containing a weak acid *and* the salt of its conjugate base, or a weak base *and* the salt of its conjugate acid. Such solutions are termed “buffer solutions” owing to their ability to absorb reasonable quantities of acids and bases with only modest changes in pH. Problems such as these may be solved in a manner that is very similar to those previously discussed, with a slight modification. The initial concentration of the conjugate will not be zero. The initial concentration of both components of the pair may need to be calculated by dilution or through a typical molarity calculation.



### Sample AP Question: 1993 1(b)

Recall the given information from the previous page:

- (b) Calculate the pH of a solution made by adding 0.0100 mole of solid methylammonium nitrate to 120.0 milliliters of a 0.225-molar solution of methylamine. Assume no volume change occurs.

#### Solution

$$[\text{CH}_3\text{NH}_3^+] = 0.0100 \text{ mol} / 0.1200 \text{ L} = 0.0833 \text{ M}$$

$$K_b = 5.25 \times 10^{-4} = \frac{[0.0833\text{M} + x][x]}{[0.225\text{M} - x]} \cong \frac{[0.0833\text{M}][x]}{[0.225\text{M}]}$$

$$x = [\text{OH}^-] = 1.42 \times 10^{-3} \text{ M}, \text{pOH} = 2.848, \text{pH} = 11.152$$



### Other Acid-Base Concepts to Consider

Students will need to recognize that buffer solutions may be made directly by mixing, or they may be formed by neutralizing strong bases with an excess of weak acid or by neutralizing strong acids with an excess of weak base. In addition, neutralizations such as these which involve equimolar quantities of acid and base will result in salts that undergo hydrolysis.

The formation of buffers by neutralization and the behavior of ions as weak acids or bases are topics that are often important for the correct completion of an AP Examination equilibrium problem. These topics will be dealt with in detail in a forthcoming segment on acid/base chemistry.



## Special Focus: Chemical Equilibrium

### Suggested Laboratory Activities

A wide variety of acid-base labs should be performed. One suggestion is to have students determine the molarity of household vinegar (acetic acid). Students only need the  $K_a$  value and the pH, read from a pH meter. Consider using open-ended labs where the students have to write an experiment to determine the answer. This way, they have to think about what they need. Of course, the teacher should approve the steps students have suggested before they may start their experiment. A set of steps might include the following:

1. Look up the  $K_a$  value of acetic acid in a text or a handbook.
2. Research the safety considerations for acetic acid.
3. Following safe procedures, including wearing goggles, obtain a 50.0 mL sample of household vinegar, noting the brand used.
4. Using a pH meter, determine the pH of the sample.
5. Do the following calculations:  $10^{-\text{pH}} = [\text{H}^+] = [\text{CH}_3\text{COO}^-]$
6. Then substitute into an ICE diagram and determine molarity from:

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

If you give different students different brands, they can compare the molarities.

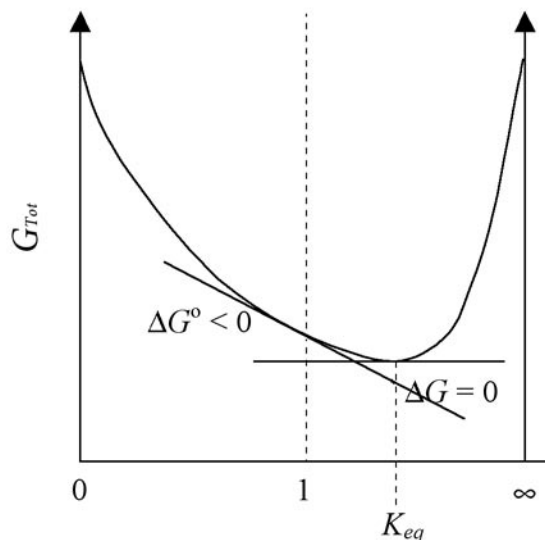
In a similar way, students could determine the molarity of household ammonia.

## Thermodynamic Relationships of Equilibrium Constants

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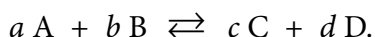


When a chemical system reaches a state of dynamic equilibrium, two conditions are satisfied. In terms of reaction kinetics, the rate of the forward reaction must be equal to the rate of the reverse reaction. Systems that can attain a state of equilibrium are represented with a double-headed arrow ( $\rightleftharpoons$ ) reflecting this observation. Thermodynamically, a chemical system is in a state of equilibrium when the free energy,  $G_{Rxn}$ , has attained a minimum value. In this case, a shift in either direction would result in an increase in the free energy of the system. Since the equilibrium state represents a minimum point on the Free Energy vs. Reaction Quotient graph, the condition that must be met at equilibrium is  $\Delta G = 0$ .



An equilibrium constant,  $K$ , is an expression of the concentrations (or partial pressures if dealing with gases) of reactants and products at equilibrium. Free-energy change,  $\Delta G$ , is an expression that indicates whether a reaction will have a higher forward or reverse reaction rate and thereby “move” in the forward or reverse direction in order to achieve equilibrium. As you might imagine, a relationship exists between these two expressions since one defines equilibrium and the other indicates the change necessary for it to be achieved.

As noted previously, the equilibrium constant expression and its value for a specific chemical reaction are derived from the law of mass action. Thus, for the reaction:



The expression for the equilibrium constant is  $K_{eq} = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}$ .

## Special Focus: Chemical Equilibrium

The value of the equilibrium constant is related to the value of  $\Delta G^\circ$ , the change in free energy, when all substances (reactants and products) are present in their standard states (1 molar concentrations for solutions, or 1 atmosphere pressure for gases), by the relations:

$$\Delta G^\circ = -R \cdot T \cdot \ln K_{eq}, \text{ or equivalently } K_{eq} = e^{-\Delta G^\circ / R \cdot T},$$

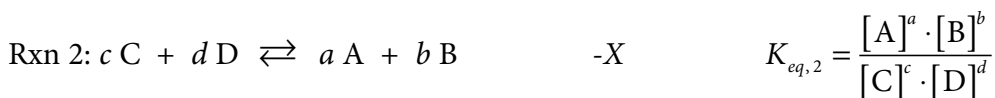
where  $R$  represents the ideal gas constant expressed, conventionally, in  $\text{kJ}/\text{mol}\cdot\text{K}$ , and  $T$  represents the Kelvin temperature. Note that “standard state” does *not* mean at standard temperature, for temperature is included in the relation and thus is a variable. This is a common source of confusion for students. Even the “ $^\circ$ ” on the  $\Delta G^\circ$  does not imply “at standard temperature,” though tables usually list values at a *stated* temperature of 298 K.

It is important to note the qualitative relationship between the standard free-energy change of a reaction,  $\Delta G^\circ$ , and the magnitude of the equilibrium constant. For a typical exothermic reaction (ignoring entropy effects, which are very small),  $\Delta G^\circ < 0$ , implying that the products are lower in free energy than the reactants, and  $K_{eq} > 1$ , indicating that the concentration of products (the numerator of the equilibrium expression) is greater than the concentration of the reactants. Conversely, an endothermic reaction would typically have a value of  $\Delta G^\circ > 0$  and consequently  $K_{eq} < 1$ , with reactants favored over products. Only for the very unlikely reaction where reactants and products are in equilibrium at their standard states is  $\Delta G^\circ = 0$  and  $K_{eq} = 1$ . Note carefully that this statement is *not* in conflict with the general statement above that  $\Delta G = 0$  at equilibrium. There *is* an important conceptual difference between  $\Delta G^\circ$  and  $\Delta G$ .

The values of  $\Delta G^\circ$  and  $K_{eq}$  depend on the form of the balanced chemical equation. We can see why and how by investigating manipulations of the above example:



Since the reaction is reversible, the equation can be reversed, writing the original products as reactants and the original reactants as products. Note that this will change the sign of the  $\Delta G^\circ$  value for the reaction.



A moment's inspection will show that the expression for the equilibrium constant for Rxn 2 is simply the reciprocal of the expression for Rxn 1, that is:

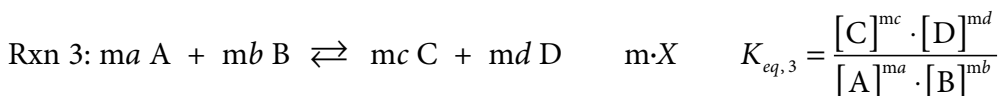
$$K_{eq,2} = \frac{[A]^a \cdot [B]^b}{[C]^c \cdot [D]^d} = \frac{1}{\left(\frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}\right)} = \frac{1}{K_{eq,1}}$$

This is also consistent with the change in sign of  $\Delta G^\circ$ , since:

$$K_{eq,2} = e^{-\Delta G^\circ_{Rxn2}/R \cdot T} = e^{-(-X)/R \cdot T} = \frac{1}{e^{-X/R \cdot T}} = \frac{1}{e^{-\Delta G^\circ_{Rxn1}/R \cdot T}} = \frac{1}{K_{eq,1}}$$

Thus, reversing the chemical equation will change the sign of the value of  $\Delta G^\circ$  and cause it to take the reciprocal of the value of the equilibrium constant.

Consider now the effect of multiplying the chemical equation by a constant, m:



It can be shown that the expression for the equilibrium constant for Rxn 3 is the expression for Rxn 1 raised to the m<sup>th</sup> power:

$$K_{eq,3} = \frac{[C]^{mc} \cdot [D]^{md}}{[A]^{ma} \cdot [B]^{mb}} = \left(\frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b}\right)^m = (K_{eq,1})^m$$

Again, this is consistent with the multiplication of the value of  $\Delta G^\circ$ :

$$K_{eq,3} = e^{-\Delta G^\circ_{Rxn3}/R \cdot T} = e^{-(mX)/R \cdot T} = \left(e^{-X/R \cdot T}\right)^m = \left(e^{-\Delta G^\circ_{Rxn1}/R \cdot T}\right)^m = (K_{eq,1})^m$$



### Reaction Systems Not at Equilibrium

For a system that has not reached equilibrium, the equations can be rewritten as follows:

$$\Delta G = \Delta G^\circ + R \cdot T \cdot \ln Q, \text{ or equivalently, } Q = e^{\frac{\Delta G - \Delta G^\circ}{RT}}$$

Obviously, at equilibrium, when  $\Delta G = 0$ , these equations become identical to those given above.

## Special Focus: Chemical Equilibrium

These are less useful since the values of  $\Delta G$  are not normally known, but they can be derived from these equations.

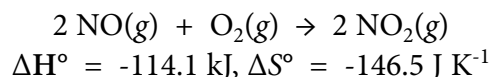
It is important for students not to confuse consideration of “spontaneity” with “equilibrium.” A reaction system at equilibrium cannot proceed in either direction unless a stress is applied.

However, a reaction equation can still be described as “spontaneous” if  $\Delta G^\circ$  is negative, since  $\Delta G^\circ$  does not relate to the equilibrium concentrations of reactants and products but to the tendency of the reaction to proceed if *reactants and products* are all at *standard* concentrations (1 molar) or standard partial pressures (1 atmosphere). From such conditions, a reaction will proceed in the forward direction toward equilibrium from the standard concentration or pressure values if  $\Delta G^\circ$  is negative, or in the reverse direction toward equilibrium from the standard concentrations or pressures if  $\Delta G^\circ$  is positive.

Not surprisingly, students become easily confused on this issue, and discussion of spontaneity should be avoided in answering AP questions unless specifically asked for.



### Sample AP Question: 2001 2(b) (i)



The reaction above is one that contributes significantly to the formation of photochemical smog.

(b) For the reaction at 25°C, the value of the standard free-energy change,  $\Delta G^\circ$ , is -70.4 kJ.

(i) Calculate the value of the equilibrium constant,  $K_{eq}$ , for the reaction at 25°C.

### Solution

$$K_{eq} = e^{-\Delta G^\circ/RT} = e^{-(-70400)/(8.31)(298)}$$
$$= 2.22 \times 10^{12}$$



**Sample AP Question: 1989 2(a)**

At 25°C, the equilibrium constant,  $K_p$ , for the reaction,  $\text{Br}_2(l) \rightleftharpoons \text{Br}_2(g)$ , is 0.281 atmosphere.

(a) What is the  $\Delta G^\circ_{298}$  for this reaction?

**Solution**

$$\begin{aligned}\Delta G^\circ &= -RT \ln K \\ &= -(8.314 \text{ J mol}^{-1} \text{ K}^{-1}) (298 \text{ K}) (\ln 0.281) \\ &= 3.14 \times 10^3 \text{ J mol}^{-1}\end{aligned}$$

## Special Focus: Chemical Equilibrium

### Combining Equilibrium Constants

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St. Francis High School  
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Though there are multiple possible forms for the chemical equation and equilibrium constant, the value of any physically observable quantity, such as concentration or pressure, *must* be *independent* of the form of the equation used. What changes is the  $K_{eq}$  value.

For example, at 1100 K, for the gas phase reaction of sulfur dioxide and oxygen to form sulfur trioxide, the value of the equilibrium constant,  $K_p$ , is 0.25.

What will be the equilibrium pressures of each gas if the initial pressures are

$$P_{SO_2} = P_{O_2} = 0.500 \text{ atm and } P_{SO_3} = 0.000 \text{ atm?}$$

One possible setup of the problem uses the following balanced equation and the ICE method:

		$2SO_2(g)$	$+ O_2(g)$	$\rightleftharpoons 2SO_3(g)$	$K_p = 0.25$
<b>Initial</b>	$P_o(atm)$	0.500	0.500	0.000	
<b>Change</b>		$- 2x$	$- x$	$+ 2x$	
<b>Equilibrium</b>	$P_{eq}$	$0.500 - 2x$	$0.500 - x$	$2x$	

Solving for  $x$ :

$$K_p = \frac{(P_{SO_3})^2}{(P_{SO_2})^2 \cdot (P_{O_2})} = 0.25$$
$$\frac{(2x)^2}{(0.500 - 2x)^2 \cdot (0.500 - x)} = 0.25$$

Solve for  $x$ :  $x = 0.062$

## Special Focus: Chemical Equilibrium

Substituting into the equilibrium expression:

$$P_{\text{SO}_2} = 0.376 \text{ atm} \quad P_{\text{O}_2} = 0.438 \text{ atm} \quad P_{\text{SO}_3} = 0.124 \text{ atm}$$

If, instead, the problem is set up with the chemical equation “reversed,” we have:

		2SO <sub>3</sub> (g)	⇌ 2SO <sub>2</sub> (g)	+ O <sub>2</sub> (g)
<b>I</b>	$P_o(\text{atm})$	0.000	0.500	0.500
<b>C</b>		+ 2x	- 2x	- x
<b>E</b>	$P_{eq}$	2x	0.500 - 2x	0.500 - x

$$K_p = \frac{1}{0.250} = 4.00$$

Solving for x:

$$K_p = \frac{(P_{\text{SO}_2})^2 \cdot (P_{\text{O}_2})}{(P_{\text{SO}_3})^2} = 4.00$$

$$\frac{(0.500 - 2x)^2 \cdot (0.500 - x)}{(2x)^2} = 4.00$$

Solve for x:  $x = 0.062$

$$\text{Substituting: } P_{\text{SO}_3} = 0.124 \text{ atm} \quad P_{\text{SO}_2} = 0.376 \text{ atm} \quad P_{\text{O}_2} = 0.438 \text{ atm}$$

The alternative setup of the problem leads to the *same values* of the partial pressures of each gas.

Examine one more setup of the same problem, in which the balanced equation is written to form one mole of sulfur trioxide:

		SO <sub>2</sub> (g)	+ 1/2 O <sub>2</sub> (g)	⇌ SO <sub>3</sub> (g)
<b>I</b>	$P_o(\text{atm})$	0.500	0.500	0.000
<b>C</b>		- x	-x/2	+ x
<b>E</b>	$P_{eq}$	0.500 - x	0.500 - x/2	x

$$K_p = \sqrt{0.25} = 0.50$$



## Special Focus: Chemical Equilibrium

Solving for  $x$ :

$$K_p = \frac{(P_{\text{SO}_3})}{(P_{\text{SO}_2}) \cdot (P_{\text{O}_2})^{1/2}} = 0.50$$

$$\frac{(x)}{(0.500 - x) \cdot (0.500 - x/2)^{1/2}} = 0.50$$

Solve for  $x$ :  $x = 0.124$

Substituting, we get:

$$P_{\text{SO}_2} = 0.376 \text{ atm} \quad P_{\text{O}_2} = 0.438 \text{ atm} \quad P_{\text{SO}_3} = 0.124 \text{ atm}$$

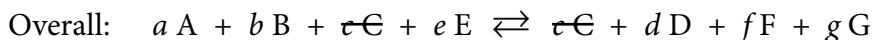
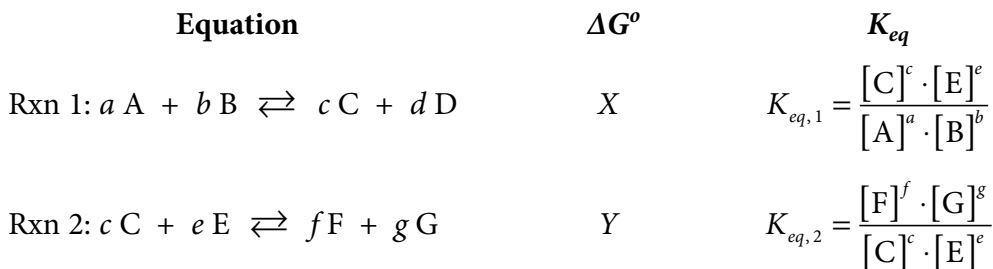
And again, the physically observable partial pressures are independent of the form of the balanced equation and  $K_p$  used.



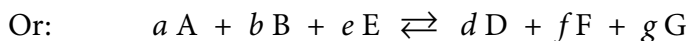
### Combining Equations and Equilibrium Constants

As described in chapter 1, when two chemical equations share a common species—typically a product of one reaction becomes a reactant in a subsequent reaction—the equations can be combined to give one “overall” equation. In this case, the equilibrium constants of each reaction can be combined to give an equilibrium constant for the overall equation. Further examples are given here.

In general, consider the following reactions and their equilibrium constants:



## Special Focus: Chemical Equilibrium



$$\Delta G^\circ = X + Y$$

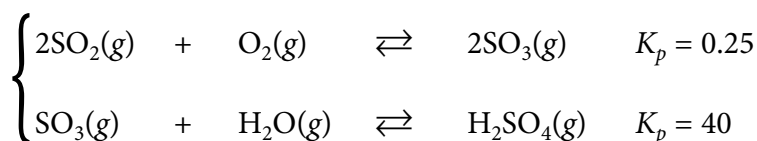
$$K_{eq, overall} = \frac{[D]^d \cdot [F]^f \cdot [G]^g}{[A]^a \cdot [B]^b \cdot [E]^e}$$

Note that the  $K_{eq}$  of the overall reaction can be obtained by multiplying the  $K_{eq}$  constants of the individual reactions:

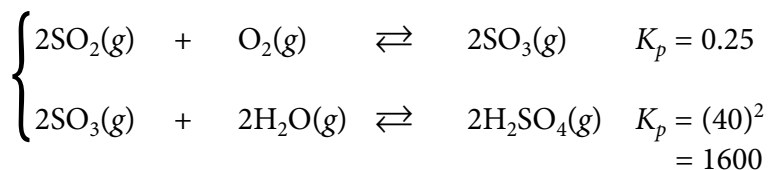
$$K_{eq,1} \times K_{eq,2} = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b} \times \frac{[F]^f \cdot [G]^g}{[C]^c \cdot [E]^e} = \frac{[D]^d \cdot [F]^f \cdot [G]^g}{[A]^a \cdot [B]^b \cdot [E]^e} = K_{eq, overall}$$

Thus, when two chemical equations are added, the equilibrium constants are *multiplied*.

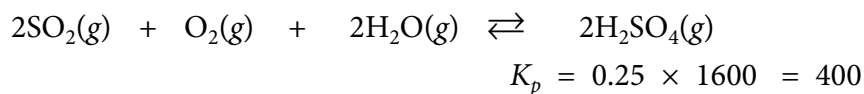
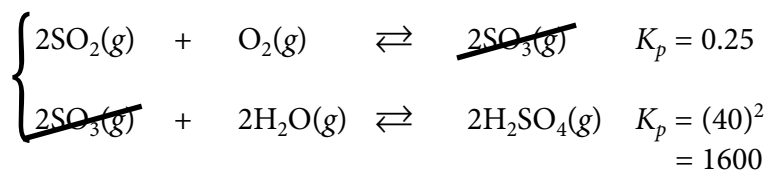
As an example, consider the sulfur dioxide/oxygen/sulfur trioxide system at 1100 K, but assume that sulfur trioxide produced also exists in equilibrium with water vapor to form sulfuric acid, according to the equations:



These equations can be combined by first multiplying through the second equation by 2:



And then adding these equations:



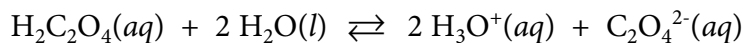
## Special Focus: Chemical Equilibrium

In summary, it should be stressed that the equilibrium constant expression  $K_{eq}$ , as well as its numerical value, depends on the form of the chemical equation that describes the equilibrium system. The equations and the equilibrium constants can be manipulated and are “coupled,” but the physically observable concentrations are independent of the form of the chemical equation.



### Examples from AP<sup>®</sup> Chemistry Released Examinations

#### Sample AP Question: 1994 Multiple-Choice Question 31

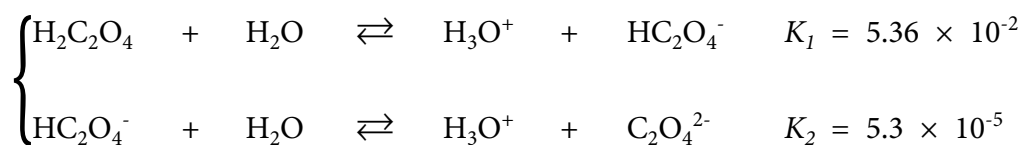


Oxalic acid,  $\text{H}_2\text{C}_2\text{O}_4$ , is a diprotic acid with  $K_1 = 5.36 \times 10^{-2}$  and  $K_2 = 5.3 \times 10^{-5}$ . For the reaction above, what is the equilibrium constant?

- (a)  $5.36 \times 10^{-2}$
- (b)  $5.3 \times 10^{-5}$
- (c)  $2.8 \times 10^{-6}$
- (d)  $1.9 \times 10^{-10}$
- (e)  $1.9 \times 10^{-13}$

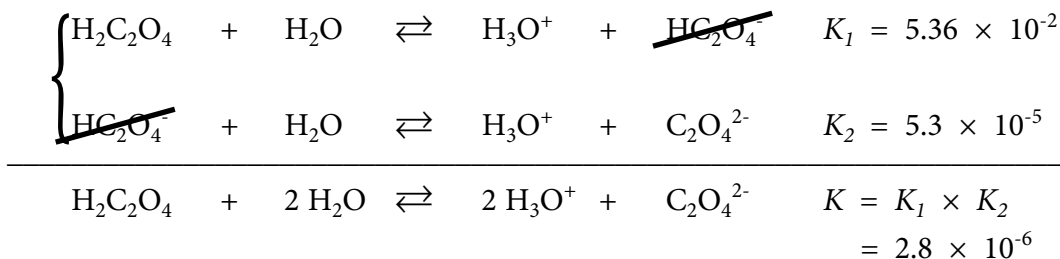
#### Solution

$K_1$  and  $K_2$  represent the first and second ionizations of the diprotic oxalic acid, as represented by the following equations:



## Special Focus: Chemical Equilibrium

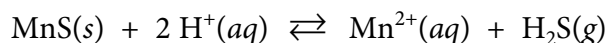
The overall equation can be expressed as the sum of these two dissociation equations, so the overall equilibrium constant is equal to the product of  $K_1$  and  $K_2$ :



The correct answer is therefore (b).



### Sample AP Question: 1989 Multiple-Choice Question 66



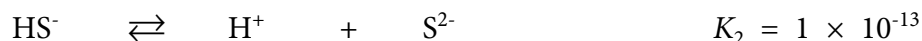
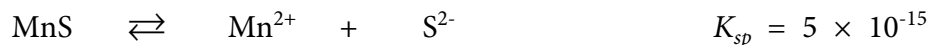
At 25°C the solubility product constant,  $K_{sp}$ , for MnS is  $5 \times 10^{-15}$  and the acid dissociation constants  $K_1$  and  $K_2$  for  $\text{H}_2\text{S}$  are  $1 \times 10^{-7}$  and  $1 \times 10^{-13}$ , respectively. What is the equilibrium constant for the reaction represented by the equation above at 25°C?

- (a)  $\frac{1 \times 10^{-13}}{5 \times 10^{-15}}$
- (b)  $\frac{5 \times 10^{-15}}{1 \times 10^{-7}}$
- (c)  $\frac{1 \times 10^{-7}}{5 \times 10^{-15}}$
- (d)  $\frac{5 \times 10^{-15}}{1 \times 10^{-20}}$
- (e)  $\frac{1 \times 10^{-20}}{5 \times 10^{-15}}$

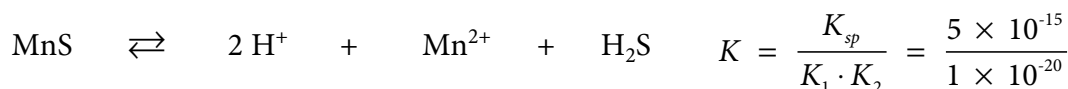
## Special Focus: Chemical Equilibrium

### Solution

The equilibrium constants given above refer to the following processes:



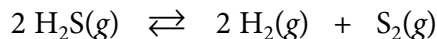
These equations can be rearranged and combined to give the overall equation above:



The correct answer is therefore (d).



### Sample AP Question: 2000 Free-Response Question 1(e)



When heated, hydrogen sulfide gas decomposes according to the equation above. A 3.40 g sample of  $\text{H}_2\text{S}(g)$  is introduced into an evacuated rigid 1.25 L container. The sealed container is heated to 483 K, and  $3.72 \times 10^{-2}$  mol of  $\text{S}_2(g)$  is present at equilibrium.

(a)–(d) These parts of the question establish the form and value of the equilibrium constant.  $K_c$  for this reaction at 483 K is determined to have the value 0.25.

(e) For the reaction  $\text{H}_2(g) + \frac{1}{2} \text{S}_2(g) \rightleftharpoons \text{H}_2\text{S}(g)$  at 483 K, calculate the value of the equilibrium constant,  $K_c$ .

**Solution**

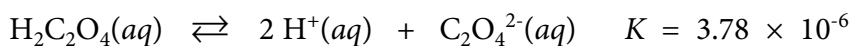
Because this equation has been reversed and divided through by 2, the value of the equilibrium constant is the square root of the reciprocal of the  $K_c$  of the original equation:

$$K_c = \frac{1}{\sqrt{0.25}} = 2.0$$



**Sample AP Question: 1997 Free-Response Question 1(b) and (d)**

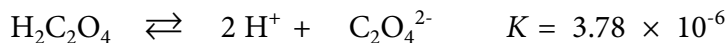
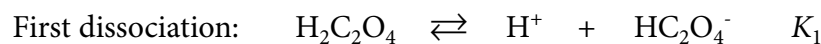
The overall dissociation of oxalic acid,  $\text{H}_2\text{C}_2\text{O}_4$ , is represented below. The overall dissociation constant is also indicated.



- (b) Give the equations representing the first and second dissociations of oxalic acid. Calculate the value of the first dissociation constant,  $K_1$ , for oxalic acid if the value of the second dissociation constant,  $K_2$ , is  $6.40 \times 10^{-5}$ .
- (d) Calculate the value of the equilibrium constant,  $K_b$ , for the reaction that occurs when solid  $\text{Na}_2\text{C}_2\text{O}_4$  is dissolved in water.

**Solution**

- (b) The first and second dissociations refer to the loss of the first and second protons; this is shown below. They combine to give the overall equation given above, so  $K_1 \times K_2 = K$ .

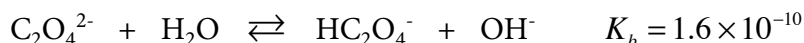


$$K_1 \times K_2 = K$$

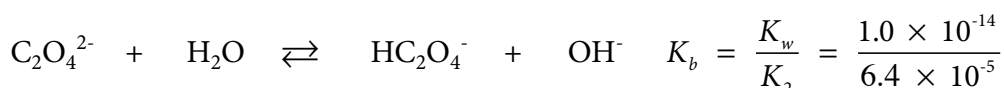
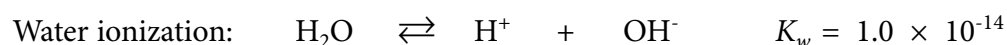
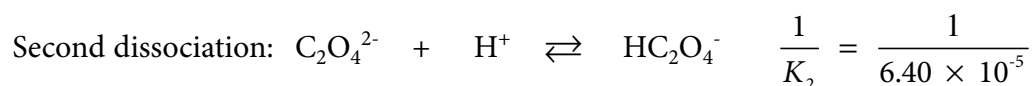
$$K_1 = \frac{K}{K_2} = \frac{3.78 \times 10^{-6}}{6.40 \times 10^{-5}} = 0.0591$$

## Special Focus: Chemical Equilibrium

- (d) Sodium oxalate dissolves into water to give the weak base, the oxalate ion,  $\text{C}_2\text{O}_4^{2-}$ . This ion will hydrolyze (react with water) in water according to the equation:



This equation can be derived as the combination of the reverse of the second dissociation of oxalic acid and the autoionization of water:



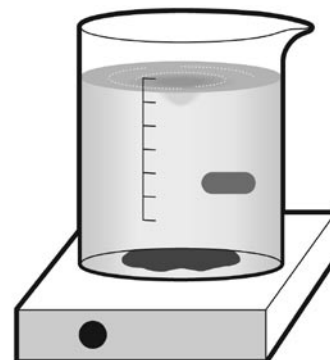
### Suggested Demonstration The Silver “One-Pot” Reactions

When two equilibrium reactions share a common species, the equilibria may be in competition for that common species. In such a case, the reactions are “coupled,” and the overall reaction is a combination of both equilibrium reactions. The  $K_{eq}$  for the overall reaction is the product or quotient of the equilibrium constants for the individual reactions.

In this demonstration, several clear, colorless solutions are added in sequence to a stirred solution of  $\text{Ag}^+(aq)$  ion. Each addition changes the appearance of the contents of the beaker. A precipitate either forms or dissolves, or the mixture changes color. The precipitates are, in turn,  $\text{Ag}_2\text{CO}_3$ ,  $\text{AgOH}$  (actually  $\text{Ag}_2\text{O}$ ),  $\text{AgCl}$ ,  $\text{AgBr}$ ,  $\text{AgI}$ , and  $\text{Ag}_2\text{S}$ ; the soluble complexes are  $\text{Ag}(\text{NH}_3)_2^+$ ,  $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ , and  $\text{Ag}(\text{CN})_2^-$ .

#### Procedure

1. Fill a clean 600 mL beaker with 200 mL of distilled water and place it on the magnetic stirrer at a moderate rate of stirring. Add 10 mL of 0.1 M  $\text{AgNO}_3$  solution and allow time for complete mixing.
2. Add 2 mL of 0.1 M  $\text{NaHCO}_3$ . A white-yellow precipitate of  $\text{Ag}_2\text{CO}_3$  will form.



3. Add 10 mL of 0.10 M NaOH solution. The light-colored silver carbonate precipitate darkens to brown due to the formation of AgOH (Ag<sub>2</sub>O).
4. Add the following in sequence. Note the changes in the appearance of the mixture upon each addition.
  1. 30 mL of 0.1 M NaCl solution (a source of Cl<sup>-</sup> ion)
  2. 30 mL of 6.0 M ammonia (a source of NH<sub>3</sub>)
  3. 10 mL of 0.1 M NaBr (a source of Br<sup>-</sup> ion)
  4. 50 mL of 0.10 M sodium thiosulfate (a source of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> ion)
  5. 10 mL of 0.1 M KI (a source of I<sup>-</sup> ion)
  6. 20 mL of 0.1 M KCN (a source of cyanide ion, CN<sup>-</sup>)
  7. 10 mL of 1.0 M Na<sub>2</sub>S (a source of S<sup>2-</sup> ion)

### Discussion

This demonstration is particularly attractive due to the number of steps required before reaching a material that is so insoluble as to defy easy solution. It illustrates simple solubility and the competitive equilibrium between two insoluble substances and between insoluble substances and soluble complexes. Most of these substances have a 1:1 stoichiometry, though some do have a 2:1 stoichiometry that must be accounted for.

Note that the cyanide ligand is extremely toxic and must be handled judiciously. This step can be omitted, and the yellow silver(I) iodide can be converted directly to the black silver(I) sulfide by adding Na<sub>2</sub>S(aq), omitting the formation of the Ag(CN)<sub>2</sub><sup>-</sup> complex.

If viewing conditions are good, the amounts can be reduced and hence waste disposal and chemical use minimized.

The  $K_{sp}$  and  $K_{eq}$  of the relevant Ag<sup>+</sup> species are given below:

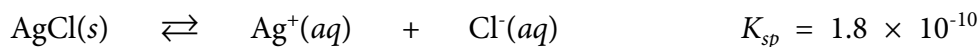
Species	Equation	$K_{eq}$
Ag <sub>2</sub> CO <sub>3</sub> (s)	Ag <sub>2</sub> CO <sub>3</sub> (s) ⇌ 2 Ag <sup>+</sup> (aq) + CO <sub>3</sub> <sup>2-</sup> (aq)	$K_{sp} = 8.1 \times 10^{-12}$
AgOH(s)	AgOH(s) ⇌ Ag <sup>+</sup> (aq) + OH <sup>-</sup> (aq)	$K_{sp} = 4.3 \times 10^{-8}$
AgCl(s)	AgCl(s) ⇌ Ag <sup>+</sup> (aq) + Cl <sup>-</sup> (aq)	$K_{sp} = 1.8 \times 10^{-10}$
AgBr(s)	AgBr(s) ⇌ Ag <sup>+</sup> (aq) + Br <sup>-</sup> (aq)	$K_{sp} = 8.0 \times 10^{-13}$
AgI(s)	AgI(s) ⇌ Ag <sup>+</sup> (aq) + I <sup>-</sup> (aq)	$K_{sp} = 4.5 \times 10^{-17}$
Ag <sub>2</sub> S(s)	Ag <sub>2</sub> S(s) ⇌ 2 Ag <sup>+</sup> (aq) + S <sup>2-</sup> (aq)	$K_{sp} = 2.0 \times 10^{-50}$
Ag(NH <sub>3</sub> ) <sub>2</sub> <sup>+</sup>	Ag <sup>+</sup> (aq) + 2 NH <sub>3</sub> (aq) ⇌ Ag(NH <sub>3</sub> ) <sub>2</sub> <sup>+</sup> (aq)	$K_{eq} = 1.6 \times 10^7$
Ag(S <sub>2</sub> O <sub>3</sub> ) <sub>2</sub> <sup>3-</sup> (aq)	Ag <sup>+</sup> (aq) + 2 S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> (aq) ⇌ Ag(S <sub>2</sub> O <sub>3</sub> ) <sub>2</sub> <sup>3-</sup> (aq)	$K_{eq} = 4.3 \times 10^{12}$
Ag(CN) <sub>2</sub> <sup>-</sup> (aq)	Ag <sup>+</sup> (aq) + 2 CN <sup>-</sup> (aq) ⇌ Ag(CN) <sub>2</sub> <sup>-</sup> (aq)	$K_{eq} = 1.0 \times 10^{20}$



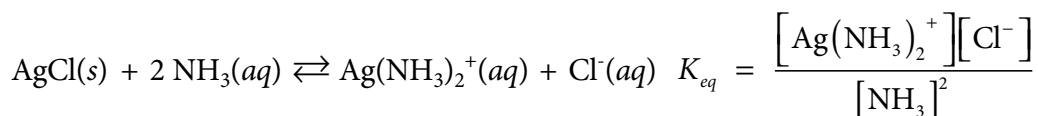
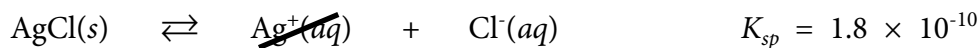
## Special Focus: Chemical Equilibrium

From the values given in the above table, the equilibrium constants for the reactions in this demonstration can be calculated. The combination of equilibrium constants is accomplished by treating the reaction as a competition between two ligands for the same metal ion, which must have only one concentration in the solution. This single concentration must satisfy both equilibrium constants.

Consider, for example, the conversion of AgCl to  $\text{Ag}(\text{NH}_3)_2^+$ . The relevant chemical equations from the above list are:



These equations can be combined directly to give:



Note that though the value of  $K_{eq}$  for the overall reaction is less than 1, the large excess of  $\text{NH}_3$  drives the reaction toward the product side, and the AgCl is seen to dissolve.

$$\begin{aligned} K_{eq} &= K_{sp}[\text{AgCl}] \times K_{eq}[\text{Ag}(\text{NH}_3)_2^+] \\ &= (1.8 \times 10^{-10}) \times (1.6 \times 10^7) \\ &= 0.0029 \end{aligned}$$

### Discussion Questions

Using the values in the table given, calculate the  $K_{eq}$  constants for the other reactions in this demonstration. Calculate the  $\Delta G^\circ_{298 \text{ K}}$  for each step (see chapter 6). Be careful to account for the different stoichiometries in some of the steps.

## Difficulties Students Experience with Equilibrium Problems and Ways Teachers Can Help Them

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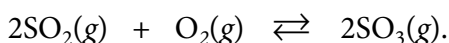
There are several reasons that students find chemical equilibrium challenging:

1. Equilibrium reactions, by their very nature, do not go to completion.
2. In acid-base equilibria, students often confuse the strength of acids and/or bases with their concentrations. In addition, the simultaneous water equilibrium tends to lead students to assume there are two separate, distinguishable values for  $[H^+]$  (or  $[OH^-]$ ) in solution—one from the water and one from the acid.
3. Different designations are assigned to different equilibrium situations.
4. Equilibrium expressions are written differently (and equilibrium constants have different values) depending on the way the chemical equation is written or the terms in which  $K$  is expressed.
5. Equilibrium constants are quoted without units, but students have been taught to rigorously include units in computations (factor-label method); this is highly confusing.
6. Equilibrium is often taught (and learned) as a pattern of calculations rather than for the understanding. Students have much difficulty when following rote procedures in making time-saving and valid approximations.
7. Students fail to develop a sense of reasonable answers when doing calculations.

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### 1. Equilibrium reactions do not go to completion.

For example, consider the familiar equilibrium system:



The chemical equation tells a beginning student that 1.0 mol of  $\text{SO}_2(g)$  should react with 0.50 mol of  $\text{O}_2(g)$  to form 1.0 mol of  $\text{SO}_3(g)$ . Indeed, this would occur if the reaction went to completion. However, because the equilibrium constant for this reaction is typically less than 1.0, the actual amount of  $\text{SO}_3(g)$  produced is substantially lower than expected. The amount of  $\text{SO}_3(g)$  formed cannot be determined from the coefficients in the equation alone but must be calculated by using a new abstract relationship—one that is obtained by raising the concentrations (or pressures) of the reactants and products to the powers of the coefficients in the balanced equation. There is little in a student's previous chemistry experience to support the idea of the law of mass action. Indeed, it is the direct opposite of the rules for chemical kinetics, where reaction orders must be determined experimentally rather than by examining the balanced equation. (The typical course sequence in which kinetics precedes equilibrium emphasizes this contrast.)

Further, even though the quantity of  $\text{SO}_3(g)$  present in the equilibrium mixture for other ratios of  $\text{SO}_2(g)$  and  $\text{O}_2(g)$  is determined by the value of  $K$ , stoichiometric ratios still need to be invoked. Thus to calculate the equilibrium amounts of each component in an equilibrium mixture, the ratios of  $\text{SO}_2(g)$ ,  $\text{O}_2(g)$ , and  $\text{SO}_3(g)$  must be taken into account when defining the amounts of reactants that disappear (and products that appear). That is, for a situation where equilibrium shifts to the right, the equilibrium amount of  $\text{SO}_2(g) = (\text{initial} - 2x)$  while the equilibrium amount of  $\text{O}_2(g) = (\text{initial} - x)$  and that of  $\text{SO}_3(g) = (\text{initial} + 2x)$ . These values must then be substituted into the equilibrium expression in the appropriate spots. Students often ignore either the stoichiometric ratios or their powers in the equilibrium expression, or both. It must be very confusing, indeed, to a student who has just developed some measure of comfort with stoichiometry calculations to have to consider these additional features.

### 2. The strength and concentration of weak acids and bases are not synonymous.

Students often fail to distinguish between the strength and concentration of electrolytes such as acids and bases. This point is closely related to the first one because the ionization process goes to completion for strong acids and bases but not for weak ones. Students

who fail to make the distinction between strength and concentration may not realize which aspects of acid or base behavior require the use of an equilibrium expression and which do not. Obviously those characteristics that depend on the total number of moles of  $H^+$ , such as the volume of acid needed to neutralize a base or the volume of gas produced in a reaction, depend on the concentration of an acid rather than on its strength and, consequently, do not require the use of an equilibrium expression. On the other hand, those properties of a solution that change with the  $[H^+]$ , such as the pH or the rate of a reaction, depend on the strength (as well as the concentration) of an acid.

On the other hand, students doing titration problems, such as titrating a weak acid with a solution of a strong base, are often fooled by the notion that a weak acid can only contribute its equilibrium  $H^+$  concentration to an added strong base, so a large amount of unreacted acid remains acid. Thus they employ equilibrium ideas when complete reaction does occur. The time to apply equilibrium is usually only at the equivalence point, where anion hydrolysis can be considered as shifting the true equivalence point pH to something other than 7.

Beginning students often fail to appreciate that any substance (ionic or otherwise) can have but one concentration in a given solution, no matter how many individual contributions from the added solution or solid, or the solvent (usually water), there may be. Suggesting that there are not red  $H^+$  from an acid and blue  $H^+$  from the water in the solution, but that  $H^+$  ions have neither memory nor identification tags of where they came from, sometimes helps students through this thinking.

### **3. Different symbols for equilibrium constants create confusion.**

In earlier chapters we listed many different  $K$  values with different subscripts to be applied in different situations. Although each refers to a special situation that teachers and other practitioners understand, such a range of choices may be more intimidating than interesting to the inexperienced.

Students often believe that different rules apply when equilibria are designated by different symbols, but the different designations for  $K$  create a complexity that doesn't really exist. Regardless of the type of equilibrium under consideration, the rules for writing equilibrium expressions are always the same. These are:

- a. The products are always in the numerator.
- b. The reactants are always in the denominator.

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- c. Only substances whose concentrations (or pressures) can change are included, i.e., solids and pure liquids are not included.
- d. The concentration (or pressure) of each substance is raised to the power of its coefficient in the balanced equation.

The confusion in the minds of some students about these different types of equilibrium is illustrated by describing a question and responses from the 2004 AP Chemistry Examination. This question asked students to write the equilibrium constant expression

for the dissolving of solid  $\text{Ag}_2\text{CrO}_4$ . Some students wrote  $K = \frac{[\text{Ag}^+][\text{CrO}_4^{2-}]}{[\text{Ag}_2\text{CrO}_4]}$ , followed

by  $K_{sp} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}]$ , as if the rules for including solids changed depending on the type of equilibrium specified.

Another example of the confusion created by the conventions surrounding equilibrium involves using  $K_b$  for the ionization of a weak base and also for the hydrolysis of the conjugate base of a weak acid (its anion). In addition, the value of  $K_b$  for the conjugate acid of a weak acid is obtained by dividing  $K_w$  by  $K_a$ . Some students must wonder why the value of  $K_b$  isn't  $1/K_a$  (rather than  $K_w/K_a$ ), since the hydrolysis process seems to be the reverse of the ionization. (The correct relationship is derived in chapter 5.) While this works well in teaching situations, students may not recall this derivation when they need it for their calculations, even though the equation is provided in the test booklet.

### 4. Equilibrium expressions and constants change with the chemical equation.

The inversion of an equilibrium expression that accompanies the reversal of a chemical equation certainly makes sense to an experienced chemist but may not be apparent to a student encountering it for the first time. Nor will the relation between  $K_c$  and  $K_p$  be obvious without considerable practice and thought. Several examples of typical situations are described in earlier chapters.

In general, a student who understands what the ratio leading to the  $K_{eq}$  expression is, and how it relates to the stoichiometric equation, will easily be able to decide which is the appropriate formulation for the system.

All the relationships described in this section represent confusing complications for beginning students who are used to thinking in a linear “plug and chug” fashion. They may be troubled further if their qualitative and quantitative math skills (see number 7 below) are not as strong as they should be.

**5. Equilibrium constants are unitless.**

This is a vexing issue for many, since in all other areas of beginning chemistry a heavy emphasis is given to tracking units because it works as a problem-solving device.  $K$  is unitless (for rationale see the appendix), not just when moles of reactants equals moles of products. So the concentrations resulting from algebraic manipulation of equilibrium expressions have “assumed” units—a very difficult idea for beginners (and even advanced students). For example, in the case of the sulfur trioxide equilibrium described in number 1 above, one might assume that from the correctly written expression for  $K$  its units should be  $(\text{moles/liter})^{-1}$ , and a value provided with these units would be a helpful designation that the correct expression had been written. No such assistance is available, however, which removes a “crutch” for many students that is provided in formulations used, for example, in chemical kinetics or in gas law calculations.

**6. Equilibrium is often treated in a mechanical fashion.**

Some teachers present equilibrium calculations in a rote manner, but even teachers who do not follow this practice may have students who decide that success can be achieved by memorizing a set pattern of operations. While it is true that various types of equilibrium calculations (gaseous, acid-base, solubility product) have specific features that distinguish them from other types, there are more similarities than differences. Thus, equilibrium expressions are the same regardless of the type of equilibrium (see number 3 above, and earlier chapters). For example, solids are not included in equilibrium expressions, regardless of whether the equilibrium under consideration involves a gas phase reaction that happens to include a solid or the dissolution of a slightly soluble salt.

Students can improve their success on equilibrium problems when they can be convinced to think about the chemistry involved in a problem rather than to begin calculating immediately. For example, taking the time to define variables in a convenient way may make solving a problem much easier in the long run. For the reaction system in number 1 above,  $2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g)$ , the arithmetic is easier if the change in the concentration or pressure of  $\text{O}_2(g)$  is defined as  $x$  rather than as  $x/2$ . Further, the calculation will make more sense if a decision is made about the direction that the reaction proceeds to reach equilibrium so that the  $x$  value defined and calculated is positive rather than negative. In cases where the  $K$  value is very large or very small (compared to 1.0), it makes considerable sense to start with either “no reaction” if  $K$  is small or “complete reaction” if  $K$  is large, to set up new starting conditions (as in the ICE protocol) and proceed to the equilibrium conditions from that point.

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A common question about an acid-base reaction is to find the pH at the equivalence point of a titration or to select an appropriate indicator. In order to answer such a question, a student must take into account the hydrolysis of the salt formed (see number 3 above and chapter 5), but many students assume that all salts are neutral and neglect further reaction of the ions formed with water. Alternatively, some students may treat all salts as only partly dissociated in solution and fail to calculate correct resulting ion concentrations in common ion effect problems.

However, nothing in this section should be taken to indicate that certain rote practices should be abandoned. For instance, always writing and balancing the equation for a reaction system (even if not directly asked for) is essential. Writing out all the equilibrium expressions operating in the system (e.g., water dissociation *and* the weak acid equilibrium in a solution of a weak acid), even if not specifically requested, makes good sense. Carefully and neatly laying out the assumed starting conditions, the appropriate changes, and the equilibrium or ending conditions can save confusion.

### **7. Students often don't bother checking their answers.**

It is important at the end of a complicated, multistep calculation (like many equilibrium problems) to ask oneself if the answer obtained makes sense. Regrettably, due to the increased reliance on sophisticated calculators by students and a decreased emphasis on mental arithmetic, many students lack the skills to carry out such a task. An even better strategy is to check one's calculations by substituting the answer into the  $K$  expression to see if the original  $K$  value is regenerated. Too many students do not bother to carry this out, preferring to rely on the answer in their calculator, even if it is nonsensical (such as calculating a pH above 7 for an acid solution or deciding more of a substance reacts than was initially present). Time spent on this aspect in an examination is well spent since it may recover several lost points, even if another portion of a different question cannot be completed owing to time constraints.

Students who write numbers so they are barely legible need to be warned that this is a common way to lose points on a question. Such students frequently misread their own numbers, carrying the incorrect values into the remainder of the problem, with disastrous results, even though the method may have been correct.

## Appendix: Chemical Equilibrium—Beyond AP

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### Introduction

There are several topics in chemical equilibrium for which the level of discussion is mostly beyond our expectations of AP Chemistry students. Usually such areas are discussed in analytical chemistry and/or physical chemistry courses in college. However, the ramifications of these can extend into the beginning levels of understanding equilibrium phenomena and so are briefly discussed here. Teachers and students wishing to learn more may explore the topic in analytical chemistry or physical chemistry texts, including those suggested below. Some of these concepts may be introduced in more advanced versions of introductory chemistry texts.

### Solution Concentrations and Activities

Strictly speaking, “analytical” molar concentrations are not a true measure of the *effective* concentration of a chemical species, as local effects can change the availability of a species for reaction. Chemists use the term *activity* for the “effective concentration.” Activity is defined as equal to the conventional molar concentration multiplied by an *activity coefficient*. The size of the latter is determined by the circumstances. Chemical equilibrium expressions and the values of equilibrium constants are correctly expressed as ratios of activities rather than concentrations.

For the usual solution concentrations encountered, activity coefficients vary between 0.5 and 1.0. As solutions become more dilute, the activity coefficients do approach unity, and molar concentrations become more accurate representations of activities. Ironically, for many substances, the coefficients also approach unity at some concentration close to 1 molar. In more concentrated solutions, activity coefficients become greater than 1.0.

Activity effects are due to ion clustering and interactions with water molecules as a result of the charge and polarities of the substances, not allowed for in a simple model of isolated free ions. This causes activity coefficients to change with solution ionic composition (ionic strength) even when the ions present are not part of the chemical reaction under consideration but rather are “spectator ions” in the normal definition. In college, this concept is usually taught thoroughly in most quantitative analysis



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courses, with some attention given in physical chemistry, when chemical potential and/or Debye-Hückel theory and alternative models may be discussed.

These considerations are one of the reasons why  $K_{eq}$  values for a specific reaction sometimes will differ from one reference source to another—the conditions of solution ionic strength from spectator ions in the measurement may not be identical, and as a result, activities may differ.

### Unitless Equilibrium Constants

An important consequence of the use of activities is that, by convention, chemists express activities for use in equilibrium expressions as the ratio of the actual activity to that of the same substance in its standard state at the temperature of interest. Standard states for substances in solution are defined as having an activity of 1 (equivalent to a 1-molar solution only if the activity coefficient is unity); pure solids and liquids, also by definition, have an activity equal to unity (1) in their standard state at the temperature of the system. Gases are defined relative to 1 atmosphere partial pressure.

Since these activity *ratios* are unitless quantities, when they are entered into an equilibrium expression, the quotient or constant derived is also unitless. This explains the difficult idea that students have to accept—that we seemed to have casually dropped units on equilibrium constants and equilibrium quotient expressions, while retaining them meticulously in rate expressions and for rate constants!

### Temperature Effects on Equilibrium Constants

This has been discussed in a qualitative way in the main chapters. In most college texts, the quantitative relationship that permits calculating the  $K_{eq}$  at a new temperature if the  $K_{eq}$  is provided at a given temperature is derived and used. On past AP Examinations, this issue was addressed in questions.

The relation derives from the following overall relationships:

$$-RT \ln K_{eq} = \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ.$$

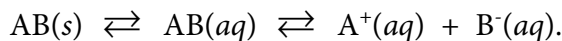
If we write the equations at two different temperatures,  $T_1$  and  $T_2$ , and subtract and do a little algebra, we obtain:

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

The assumption (which is not totally valid) is that  $\Delta H^\circ$  and  $\Delta S^\circ$  do not vary with temperature. This is valid if  $T$  is not changed dramatically.

### Incomplete Solution and Presence of Undissociated Salts

The simple approach that assumes complete dissociation of all “ionic” substances on entering aqueous solution is sometimes far from accurate. Solubility equilibria might more realistically be represented as

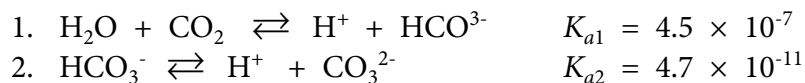


In which case, neither  $[A^+]$  nor  $[B^-]$  properly represents the true solubility,  $s$ , of the solid substance AB in solution. This is especially true for salts that are far from completely ionic in character, such as silver halides.

### Polyprotic Acids and Bases

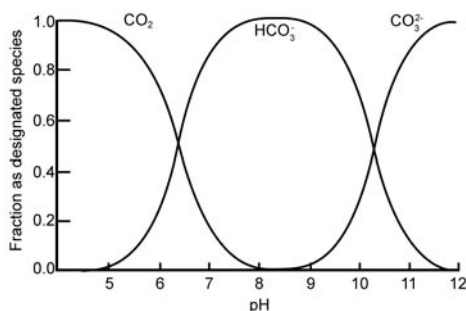
Many substances encountered in biochemical systems have multiple sites for acid and base reaction (acceptance or donation of a proton). Such substances include amino acids and proteins. Multiple equilibria result, and computation of simple results (such as how the pH of 0.05 M leucine varies as a strong base is added) becomes tedious unless handled by “dominant species” approximations. Consideration of the two (or more)  $K_a$  values leads to the understanding that providing they differ by  $10^3$  or more, the conditions of the solution will predetermine that one of the two equilibria (only) will be operative and that one of the species (e.g.,  $H_2L^+$ , HL, or  $L^-$ ) will be in excess of the other two.

For the simple and familiar case of carbon dioxide in water, we find, for example:



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From this information, a fractional composition diagram as a function of solution pH can be constructed, as shown below. This demonstrates that in the pH range from 1 to 9, the first equilibrium is operative; in the pH range from 9 to 14, the second is operative.



Furthermore, below pH = 6, the CO<sub>2</sub> species is dominant; between pH = 8 and pH = 9, the HCO<sub>3</sub><sup>-</sup> species dominates; and above pH = 11, the CO<sub>3</sub><sup>2-</sup> species dominates.

### The Ultimate Solution

Students (and their teachers) may sometimes ask, isn't there a master equation that doesn't make approximations? The answer is yes, and more advanced quantitative analysis texts derive the equation (for example, see Harris) and show how a spreadsheet can be used to solve it. For a weak acid equilibrium, the iterative equation is

$$[\text{H}^+] = \frac{-K_a + \sqrt{K_a^2 + 4(K_w + K_a F + K_a K_w / [\text{H}^+])}}{2},$$

where  $F$  is the "formal" concentration of the acid (the amount put in).

### How Are Unusual $K_{eq}$ Values Determined?

In a textbook, you may find that the  $K_{sp}$  value for mercury (II) sulfide, HgS, is quoted as equal to  $4 \times 10^{-53}$ .

In a saturated solution,  $[\text{Hg}^{2+}] = [\text{S}^{2-}] = \sqrt{4 \times 10^{-53}} = 6 \times 10^{-27} \text{ M}$ .

Avogadro's number is  $6 \times 10^{23}$ , so you would need 280 liters to be sure of having 1 ion of mercury and 1 of sulfide! How can this be?

While it is an interesting philosophical question for one of those after-exam parties, the answer is in the thermodynamic connection. Even though this seems impossible, the electrochemical potential of a cell involving HgS and its saturated solution can be measured, and thus the  $K_{sp}$  value may be determined using the equations connecting standard cell potentials to equilibrium constants. Electrochemical measurements are powerful tools in exploring both thermodynamic (free energy values) and equilibrium phenomena. No direct measure of such solution concentrations is possible. Many other  $K$  values have been determined in this way.

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### **Representative Texts**

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Petrucci, Ralph H., and William S. Harwood. *General Chemistry*. 6th ed. McMillan, 1993. (Introduces activities,  $K_{eq}$  variation with temperature, and polyprotic acid equilibrium calculations.)

Rammette, Richard W. *Chemical Equilibrium and Analysis*. Addison Wesley, 1981.

### **Web Site**

One sample of many, this site has a PowerPoint presentation based on the Harris 6th edition text: <http://employees.oneonta.edu/schaumjc/chem361/chem361.html>.

## Special Focus: Chemical Equilibrium

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*Information current as of original publish date of September 2005.*

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