

# 12

## BIG IDEA 6: EQUILIBRIUM

### Big Idea 6

Any bond or intermolecular attraction that can be formed can be broken. These two processes are in a dynamic competition, sensitive to initial conditions and external perturbations.

In this chapter, you will review the characteristics of equilibrium and calculations involving the concentrations of reactants and products for a given system at equilibrium. Your knowledge of the basic equilibrium problems in this chapter will enable you to qualitatively and quantitatively explain pH of acids, bases, salts, and buffers as well as the solubility of ionic compounds.

### AP Tip

Equilibrium is one of the big ideas in AP Chemistry that underpins much of what you study. Make sure you are comfortable with particle and graphical representations as well as with the calculations.

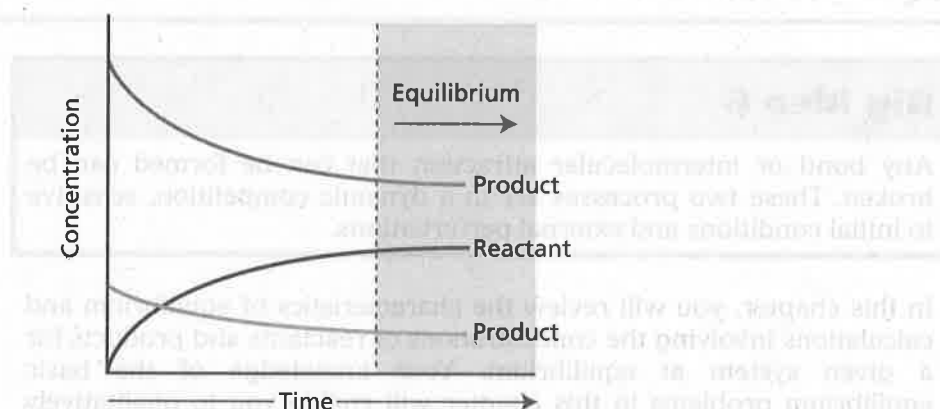
You should be able to

- Write equilibrium expressions for a given reaction.
- Calculate  $Q$  and compare it to  $K$  to determine if a reaction is at equilibrium.
- Manipulate  $K$  if a reaction is reversed or multiplied by a coefficient.
- Calculate  $K$  from given equilibrium concentrations, or if given  $K$  and all except one equilibrium concentration, solve for the missing value.

- Calculate equilibrium concentrations (or one of the missing variables) if given any two of the following values:  $K$ , the initial concentrations, one equilibrium concentration.
- Do calculations involving gaseous equilibria, partial pressures, and  $K_p$ .
- Use Le Châtelier's principle to determine in what direction the position of equilibrium will shift when a change is imposed.
- Calculate the value of  $K$  from thermodynamic values such as  $\Delta G^\circ$ .

## EQUILIBRIUM CONDITION

Many chemical and physical changes are reversible. When equilibrium is reached, the rate of the forward reaction equals the rate of the reverse reaction. The ratio of the product concentrations to the reactant concentrations is constant at equilibrium. At a given set of conditions, macroscopic variables such as concentrations, partial pressures, and temperature do not change over time.



Some examples of reversible processes include biological processes such as oxygen binding to hemoglobin in red blood cells and the sense of smell due to molecules binding to receptor sites in the nose. Environmental examples include nitrogen and carbon biogeochemical cycles. Chemistry examples include dissolution of solids as well as proton transfer in acid–base reactions and electron transfer in redox reactions.

## THE EQUILIBRIUM EXPRESSION

(Chemistry 8th ed. pages 597–598/9th ed. pages 610–611)

The equilibrium constant,  $K$ , measures the ratio of product concentrations to reactant concentrations.

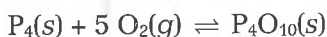
For a hypothetical reaction  $aA + bB \rightleftharpoons cC + dD$

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

$K$  is the equilibrium constant, usually given without units. Brackets, [ ], represent the concentration of the reactants and products at equilibrium in moles/liter. The concentrations of products and reactants are raised to the powers of their respective coefficients in the balanced chemical equation. Note that this is different from kinetics where the orders of each reactant must be determined by empirical evidence.

You will be expected to write the equilibrium expression for a given reaction. Remember, the concentrations of solids and liquids are not included because the concentration (amount per volume) is constant. Individual particles in a pure substance have fixed volume. Since the concentration is expressed in mol L<sup>-1</sup>, changing the number of particles (mol) of a pure substance must also change the volume (L) of the pure substance.

**EXAMPLE:** Write the equilibrium expression for the reaction



**SOLUTION:** The equilibrium expression for the reaction is

$$K = \frac{1}{[\text{O}_2]^5}$$

The concentrations of the solids are not included in the expression because the concentration of a solid or liquid is a constant, so it is included in the value of  $K$ .

The value of the equilibrium constant measures the extent to which a reaction occurs.

$K \gg 1$ : The concentrations of the products are much greater than the concentrations of the reactants so the reaction is product-favored.

$K \ll 1$ : The concentrations of the reactants are much greater than the concentrations of the products. In this case, the reaction does not proceed in the direction written to any great extent and is called a reactant-favored reaction.

$K \approx 1$ : Reactants and products are present in significant concentrations at equilibrium.

## REACTION QUOTIENT

(Chemistry 8th ed. pages 608–609/9th ed. pages 620–621)

When reactants and products are mixed together, they may not be at equilibrium. The reaction quotient,  $Q$ , compared to the equilibrium constant,  $K$ , will determine which way a system will shift to reach equilibrium. If a system is not at equilibrium, it will move in a direction to reach equilibrium.

If a reactant or product in a reaction is not present and is at zero concentration, the reaction will move in the direction that produces the missing component.

If all reactants and products are present and have an initial concentration, you must determine the value of  $Q$ , the reaction quotient.

To determine if the reaction is at equilibrium or the direction it will shift to attain equilibrium, plug all of the initial concentrations into the reaction quotient, which is the same as the equilibrium expression (also called the law of mass action), and compare the value of  $Q$  to  $K$ .

### Comparison of $Q$ to $K$

If  $Q = K$ , the reaction is at equilibrium and the rate of the forward and reverse reactions are the same.

If  $Q > K$ , the reaction will shift to the left. A shift toward the reactants will consume products because the rate of the reverse reaction is greater than the rate of the forward reaction until equilibrium is established.

If  $Q < K$ , the reaction will shift to the right. A shift to produce more products will consume reactants because the rate of the forward reaction is greater than the rate of the reverse reaction until equilibrium is established.

**EXAMPLE:** For the reaction  $2 \text{NO}(g) \rightleftharpoons \text{N}_2(g) + \text{O}_2(g)$ ,  $K = 2.4 \times 10^3$  at a particular temperature.

- If the initial concentrations are  $0.024 \text{ M NO}$ ,  $2.0 \text{ M N}_2$ , and  $2.6 \text{ mol O}_2$ , is the system at equilibrium?
- If it is not at equilibrium, in which direction will the reaction shift?

**SOLUTION:** The reaction is not at equilibrium,  $Q > K$ , so it will shift to the left.

$$Q = \frac{[\text{N}_2][\text{O}_2]}{[\text{NO}]^2} = \frac{(2.0)(2.6)}{(0.024)^2} = 9.0 \times 10^3$$

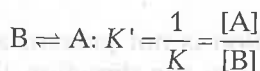
## TYPES OF EQUILIBRIUM PROBLEMS

(Chemistry 8th ed. pages 598, 612–620/9th ed. pages 611, 625–633)

The types of equilibrium problems you can expect to solve on the AP Chemistry exam include:

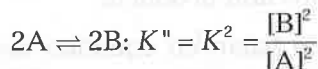
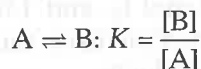
- Manipulation of the equilibrium constant,  $K$ .
  - If the reaction is reversed, the equilibrium expression is the reciprocal of the expression for the forward reaction.

**EXAMPLE:**



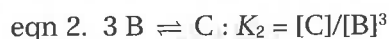
- b. If the coefficients in a balanced equation are multiplied by a number,  $n$ , the equilibrium constant is raised to the power  $n$ .

EXAMPLE:



- c. If two reactions are added together through the presence of a common intermediate, the equilibrium constant of the resulting reaction is a product of the values of  $K$  for the original reactions.

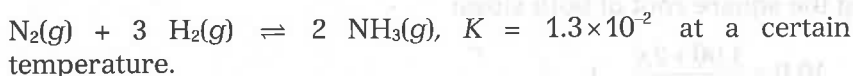
EXAMPLE:



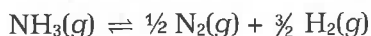
- Given all equilibrium concentrations, calculate the value of the constant,  $K$ .
- Given the value of the equilibrium constant,  $K$ , and all but one of the equilibrium concentrations, solve for the missing concentration.
- Given the value of the initial concentrations of the reactants and one of the equilibrium concentrations of either the reactants or products, solve for all equilibrium concentrations and the value of  $K$ .
- Given the initial concentrations and the value of  $K$ , solve by approximation for the equilibrium concentrations.

The first four types of problems listed above can be solved using basic algebra. An example of a Type 1 problem follows.

EXAMPLE: (Type 1) For the reaction



Calculate the value of  $K$ , called  $K'$ , for the reaction

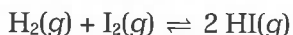


SOLUTION: The reaction is the reverse and one-half of the one which is given.

$$K' = [N_2]^{1/2}[H_2]^{3/2} / [NH_3] = (1/K)^{1/2}; \left( \frac{1}{1.3 \times 10^{-2}} \right)^{1/2} = 8.8$$

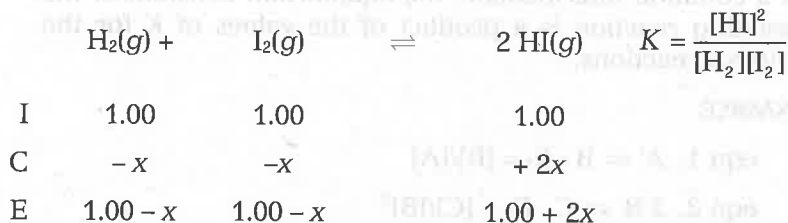
The fifth type of problem can be solved by approximation, using an ICE chart. ICE is an acronym for Initial, Change, Equilibrium and is a convenient method for organizing your work. The use of an ICE chart is illustrated below.

**EXAMPLE:** (Type 5) At a particular temperature,  $K = 1.00 \times 10^2$  for the reaction



In an experiment, 1.00 mol  $\text{H}_2$ , 1.00 mol  $\text{I}_2$ , and 1.00 mol  $\text{HI}$  are introduced into a 1.00-L container. Calculate the equilibrium concentrations of all reactions and products.

**SOLUTION:** To begin, write the balanced equation for the reaction and the equilibrium expression, omitting pure solids and liquids.



Make an ICE chart under the balanced chemical equation.

**I = initial concentration** in mol/L (note units are omitted from chart)

**C = the change to reach equilibrium** represented by + or - x. A minus sign indicates a decrease in concentration; a plus sign indicates an increase. The coefficient in front of the reactant in the balanced equation is placed in front of the x in the change line.

**E = Equilibrium concentrations** which are obtained by adding the I and C lines together.

Plug the equilibrium values into the expression and solve for x:

$$K = 100. = \frac{(1.00 + 2x)^2}{(1.00 - x)^2}$$

Taking the square root of both sides:

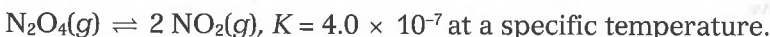
$$\begin{aligned} 10.0 &= \frac{1.00 + 2x}{1.00 - x} \\ 10.0 - 10.0x &= 1.00 + 2x \\ 12x &= 9.0 \\ x &= 0.75 \text{ M} \end{aligned}$$

Use this value of x to solve for the equilibrium concentrations of all reactants and products.

$$[\text{H}_2] = [\text{I}_2] = 1.00 - 0.75 = 0.25 \text{ M}; [\text{HI}] = 1.00 + 2(0.75) = 2.50 \text{ M}$$

Last, check your equilibrium concentrations by making sure that they equal the correct value of K.

**EXAMPLE:** (Type 4) For the reaction



In an experiment, 1.0 mol of  $\text{N}_2\text{O}_4$  is placed in a 10.0-L vessel.

Calculate the equilibrium concentrations of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$ .

**SOLUTION:** At equilibrium,  $[\text{N}_2\text{O}_4] = 0.10 \text{ M}$  and

$[\text{NO}_2] = 2.0 \times 10^{-4} \text{ M}$ . To solve this problem, proceed as in the previous example.

	$\text{N}_2\text{O}_4(\text{g})$	$\rightleftharpoons$	$2 \text{NO}_2(\text{g})$
I	0.10		0
C	$-x$		$+2x$
E	$0.10 - x$		$2x$

$$K = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{(2x)^2}{(0.10 - x)} = 4.0 \times 10^{-7}$$

Since the value of  $K$  is much smaller than 1, you can assume that the change from the initial concentration,  $x$  in  $0.10 - x$ , is so small that it is negligible, that is,  $0.10 - x$  is about equal to 0.10.

This greatly simplifies the math to

$$K = \frac{(2x)^2}{(0.10)} = 4.0 \times 10^{-7}$$

$$4x^2 = 4.0 \times 10^{-8}, x = 1.0 \times 10^{-4} \text{ M}$$

It is okay to make this assumption if the change from the initial concentration, in this case,  $x$  is less than 5% of the initial concentration.

$$\frac{x}{0.10} \times 100 = \frac{1.0 \times 10^{-4}}{0.10} \times 100\% = 0.10\%$$

This is less than 5%, so, it is okay to make the assumption.

The equilibrium concentrations are as follows:

$$[\text{N}_2\text{O}_4] = 0.10 - x = 0.10 - 1.0 \times 10^{-4} = 0.10 \text{ M}$$

$$[\text{NO}_2] = 2x = 2(1.0 \times 10^{-4}) = 2.0 \times 10^{-4} \text{ M}$$

## GASEOUS EQUILIBRIUM

(Chemistry 8th ed. pages 601–604, 610–612/9th ed. pages 614–616, 622–624)

For equilibrium in the gas phase, the equilibrium expression can be written in terms of the partial pressures of the gases.

For the reaction  $\text{AsH}_3(\text{g}) \rightleftharpoons 2 \text{As}(\text{s}) + 3 \text{H}_2(\text{g})$

$$K_p = \frac{(P_{\text{H}_2})^3}{P_{\text{AsH}_3}}$$

$K_p$  is the equilibrium constant in terms of the partial pressures of the gases.

$P$  represents the partial pressure of the gases raised to their coefficients in the balanced chemical equation. Notice that parentheses, ( ), are used for the partial pressure. The use of brackets, [ ], in this instance would result in deduction of points on the exam since brackets represent concentration in mol/L.

**EXAMPLE:** Given the following reaction:



The equilibrium partial pressure of  $\text{Br}_2 = 0.0159 \text{ atm}$  and  $\text{NOBr} = 0.0768 \text{ atm}$ . Calculate the equilibrium partial pressure of  $\text{NO}$ .

**SOLUTION:**

$$K_p = \frac{(P_{\text{NOBr}})^2}{(P_{\text{NO}})^2 (P_{\text{Br}_2})}$$

$$109 \text{ atm}^{-1} = \frac{(.0768 \text{ atm})^2}{(P_{\text{NO}})^2 (0.0159 \text{ atm})}$$

$$P_{\text{NO}} = 0.0583 \text{ atm}$$

The relationship between  $K_p$  and  $K$  is given by  $K_p = K(RT)^{\Delta n}$ .

$K_p$  is the equilibrium constant in terms of partial pressures.

$K$  is the equilibrium constant in terms of concentration.

$R$  is the ideal gas constant ( $0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1}$ ).

$T$  is the absolute (Kelvin) temperature.

$\Delta n$  is the sum of the coefficients of the gaseous products minus the sum of the coefficients of the gaseous reactants.

**EXAMPLE:**  $2 \text{NO}(g) + \text{Cl}_2(g) \rightleftharpoons 2 \text{NOCl}(g)$   $K_p = 1.9 \times 10^3$  at  $25^\circ\text{C}$ . Calculate the value for  $K_c$  at  $25^\circ\text{C}$ .

$$\Delta n = 2 - (2 + 1) = -1$$

$$K_p = K(RT)^{-1} = K/RT$$

$$K = K_p RT = (1.9 \times 10^3)(0.08206)(298) = 4.6 \times 10^4$$

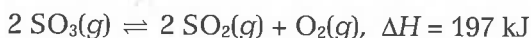
## LE CHÂTELIER'S PRINCIPLE

(Chemistry 8th ed. pages 620–625/9th ed. pages 633–639)

The value of  $K$  is a constant at a particular temperature. The only factor that changes the value of  $K$  is temperature. Pressure, a catalyst, and changes in concentration will not affect the value of  $K$ .

Le Châtelier's principle states that if a change is imposed in a system at equilibrium, the position of the equilibrium will shift in a direction that will counteract the change.

**EXAMPLE 1:** Consider the following changes on the system below at equilibrium.





(a) Addition of  $O_2$ 

**SOLUTION:** The equilibrium will shift to the left to form more reactants. The addition of oxygen increases the rate of the reverse reaction so more reactants will form, until the rate of the forward reaction again equals the rate of the reverse reaction. On the particulate level, more  $O_2$  is available to collide with the  $SO_2$  so more reactant will be made. Another way to explain the shift is that with the added  $O_2$ ,  $Q$  is now greater than  $K$ . The reverse reaction is favored so the product concentrations decrease and reactant concentrations increase until  $Q = K$  again.

(b) Removal of  $SO_2$ 

**SOLUTION:** Removal of an equilibrium component such as  $SO_2$  at constant pressure and temperature will cause the equilibrium to shift toward the removed component to increase its concentration. The reaction in this example will shift to products. When  $SO_2$  is removed,  $Q$  is less than  $K$ . The forward reaction is favored until enough product has been made for  $Q = K$ .

## (c) Increase in temperature

**SOLUTION:** The direction of the shift can be predicted in the same way as the addition or removal of a reactant or product.

The decomposition of  $SO_3$  is endothermic. Treating heat as a reactant, an increase in temperature will cause the reaction to shift right, producing more products, increasing the value of  $K$ . More  $SO_3$  molecules will have sufficient energy to break the bonds and make products. A decrease in temperature will cause a shift to the left, increasing the reactant concentrations, and lowering the value of  $K$ .

## (d) An increase in pressure

**SOLUTION:** If the pressure is increased in an equilibrium system, the reaction will shift toward the side with fewer moles of gas. Decreasing the volume has the same effect because the only way the pressure can be increased without changing the temperature or number of moles is to decrease the volume. In this example, the reaction will shift to the left, toward  $SO_3$ , when the pressure is increased or the volume is decreased. If the moles of gas are the same on both sides of the reaction, no shift will occur.

## (e) Addition of a solid or inert gas, such as Ne

**SOLUTION:** If a solid or an inert gas (with no change in volume) is added to the reaction, there will be no shift in equilibrium. Neither the solid nor the inert gas is part of the equilibrium expression. The concentrations of all the components of the equilibrium expression remain unchanged.

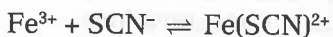
## (f) An inert gas, such as Ne, is added at constant pressure.

**SOLUTION:** There will be a shift in the equilibrium to the side of the equation with more moles of gas. To add Ne at constant pressure, the volume of the container must increase so the concentrations or partial pressures of all gases have decreased.

If the moles of gas are greater in the reactants, then  $Q < K$ , so equilibrium can be reestablished only by increasing the products.

**EXAMPLE 2:** Dilution of a reaction system with a solvent may have an effect on the equilibrium concentrations. Consider how the following will affect equilibrium.

Water is added to a dilute  $\text{Fe}(\text{SCN})^{2+}$  solution.

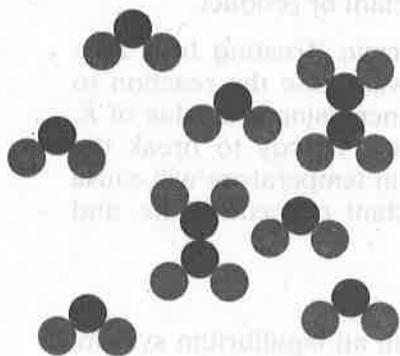


**SOLUTION:** This is the opposite of the acetic acid example. When water is added to this equilibrium, the reaction will shift to the reactants because the more dilute the solution, the fewer chances the individual ions have of colliding to make the complex ion.

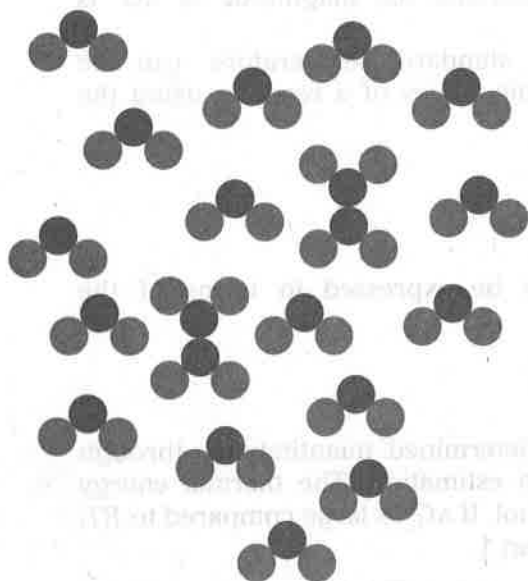
**EXAMPLE 3:** Create a particulate model to illustrate the system described below.

6 molecules of  $\text{NO}_2$  and 2 molecules of  $\text{N}_2\text{O}_4$  are at equilibrium. 10 molecules of  $\text{NO}_2$  are added and equilibrium is reestablished. Temperature and pressure remain constant.

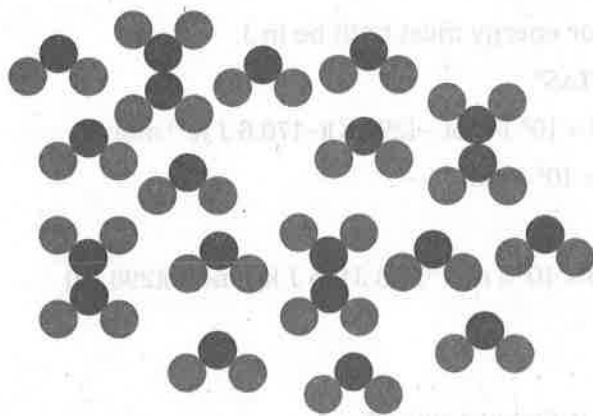
**SOLUTION:**



<p>Initial Equilibrium          6 <math>\text{NO}_2</math> molecules          2 <math>\text{N}_2\text{O}_4</math> molecules          3 : 1 ratio</p>
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Disturb Equilibrium  
add 10  $\text{NO}_2$  molecules



Restore Equilibrium  
12  $\text{NO}_2$  molecules  
4  $\text{N}_2\text{O}_4$  molecules  
3 : 1 ratio

## RELATIONSHIP OF $K$ TO FREE ENERGY, $\Delta G^\circ$

(Chemistry 8th ed. pages 798–802/9th ed. pages 813–817)

The magnitude of the equilibrium constant,  $K$ , is directly related to the change in Gibbs free energy associated with the reaction,  $\Delta G^\circ$ . The species that have lower free energy will have larger relative concentrations at equilibrium. When both reactants and products have

significant concentrations at equilibrium, the magnitude of  $\Delta G^\circ$  is similar to the thermal energy ( $RT$ ).

The equilibrium constant at standard temperature can be determined from the thermodynamic values of a reaction using the equation:

$$\Delta G^\circ = -RT \ln K$$

$$R = 8.314 \text{ J/(K}\cdot\text{mol)}$$

Alternatively, the equation can be expressed in terms of the equilibrium constant:

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

The equilibrium constant can be determined quantitatively through calculation or qualitatively through estimation. The thermal energy ( $RT$ ) at room temperature is 2.4 kJ/mol. If  $\Delta G^\circ$  is large compared to  $RT$ , then  $K$  will be significantly larger than 1.

**EXAMPLE:** Calculate the value of  $K$  at 25.0°C for the reaction  $2 \text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$

The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  are  $-58.03 \text{ kJ/mol}$  and  $-176.6 \text{ J/K}\cdot\text{mol}$ , respectively.

**SOLUTION:**

Notice that the units for energy must both be in J.

$$\begin{aligned} \text{At } 25^\circ\text{C}, \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -58.03 \times 10^3 \text{ J/mol} - (298 \text{ K})(-176.6 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= -5.40 \times 10^3 \text{ J mol}^{-1} \end{aligned}$$

$$\Delta G^\circ = -RT \ln K$$

$$\begin{aligned} \ln K &= -\Delta G^\circ/RT = (-5.40 \times 10^3 \text{ J mol}^{-1})/[(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})] \\ &= 2.18 \end{aligned}$$

$$K = 8.846$$

This reaction is product-favored since  $K > 1$ .

### Comparison of $\Delta G^\circ$ to $K$

If  $\Delta G^\circ < 0$ , then  $K > 1$  and the reaction is product-favored.

If  $\Delta G^\circ > 0$ , then  $K < 1$  and the reaction is reactant-favored.

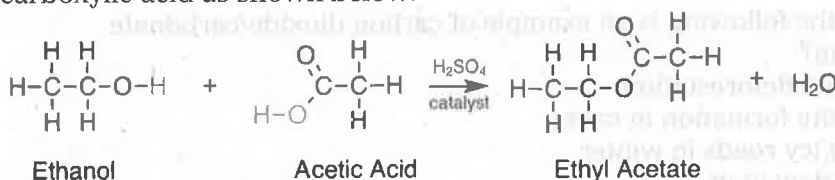
Exergonic reactions ( $\Delta G^\circ < 0$ ) and endergonic reactions ( $\Delta G^\circ > 0$ ) are important in many biological applications where the magnitude of the equilibrium constant is important.

**MULTIPLE-CHOICE QUESTIONS**

No calculators are to be used in this section.

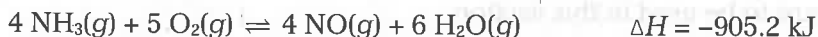
- In the reaction  $3W + X \rightleftharpoons 2Y + Z$ , all substances are gases. The reaction is initiated by adding an equal number of moles of W and of X. When equilibrium is reached,
  - $[Y] = [Z]$
  - $[X] = [Y]$
  - $[W] = [X]$
  - $[X] > [W]$

- An esterification reaction occurs when an alcohol reacts with a carboxylic acid as shown below.



- The equilibrium constant is approximately 5 at room temperature, but the rate of reaction without a catalyst is very slow. How do the rates of the forward and reverse reactions compare at equilibrium?
- The forward rate is 5 times faster than the reverse rate.
  - The reverse rate is the same as the forward rate.
  - The reverse rate is 5 times faster than the forward rate.
  - The rate can only be determined experimentally.
- The reaction  $3\text{H}_2(g) + \text{N}_2(g) \rightleftharpoons 2\text{NH}_3(g)$  has an enthalpy of change of  $-92 \text{ kJ}$ . Increasing the temperature of this equilibrium system causes
    - an increase in  $[\text{NH}_3]$
    - an increase in  $[\text{N}_2]$
    - a decrease in  $[\text{H}_2]$
    - an increase in  $K$
  - Consider  $\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{NO}(g)$ . The reaction was initiated by adding 15.0 moles of NO to a 1.0-L flask. At equilibrium, 3.0 moles of oxygen are present in the 1.0-L flask. The value of  $K$  must be
    - 0.33
    - 3.0
    - 5.0
    - 9.0
  - At a certain temperature, the synthesis of ammonia gas from nitrogen and hydrogen gases, shown as  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ , has a value for  $K$  of  $3.0 \times 10^{-2}$ . If  $[\text{H}_2] = [\text{N}_2] = 0.10 \text{ M}$  and  $[\text{NH}_3] = 0.20 \text{ M}$ ,
    - the reaction would shift toward the ammonia
    - the reaction would shift toward the  $\text{N}_2$  and the  $\text{H}_2$
    - the system is at equilibrium, therefore no shifting will occur
    - the reaction will shift toward a new equilibrium position, but the direction cannot be determined from these data

6. One way to produce nitric acid is through the Ostwald process. In the first reaction ammonia is oxidized to nitrogen monoxide.



Which of the following would shift equilibrium to products?

- (A) Raise the temperature of the reaction and remove nitrogen monoxide as it is made.  
 (B) Lower the temperature of the reaction and remove nitrogen monoxide as it is made.  
 (C) Raise the temperature of the reaction to keep water in its gaseous form.  
 (D) Lower the temperature of the reaction to condense ammonia into a liquid.
7. Which of the following is an example of carbon dioxide/carbonate equilibrium?
- (A) acid rain deforestation  
 (B) stalagmite formation in caves  
 (C) salting icy roads in winter  
 (D) ozone depletion
8. Which of the following systems at equilibrium are not affected by a change in pressure caused by changing the volume at constant temperature?
- (A)  $\text{H}_2(g) + \text{Cl}_2(g) \rightleftharpoons 2 \text{HCl}(g)$   
 (B)  $\text{H}_2(g) + \text{I}_2(s) \rightleftharpoons 2 \text{HI}(g)$   
 (C)  $\text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g)$   
 (D)  $2 \text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3 \text{H}_2(g)$
9. The equilibrium  $\text{P}_4(g) + 6 \text{Cl}_2(g) \rightleftharpoons 4 \text{PCl}_3(l)$  is established at  $-10^\circ\text{C}$ . The equilibrium constant expression is

(A)  $K = \frac{[\text{PCl}_3]}{[\text{P}_4][\text{Cl}_2]}$

(B)  $K = \frac{[\text{PCl}_3]^4}{[\text{P}_4][\text{Cl}_2]^6}$

(C)  $K = \frac{[\text{P}_4][\text{Cl}_2]^6}{[\text{PCl}_3]^4}$

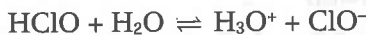
(D)  $K = \frac{1}{[\text{P}_4][\text{Cl}_2]^6}$

10. Ammonium hydrogen sulfide will decompose into ammonia gas and hydrogen sulfide gas when heated. Consider the equilibrium system

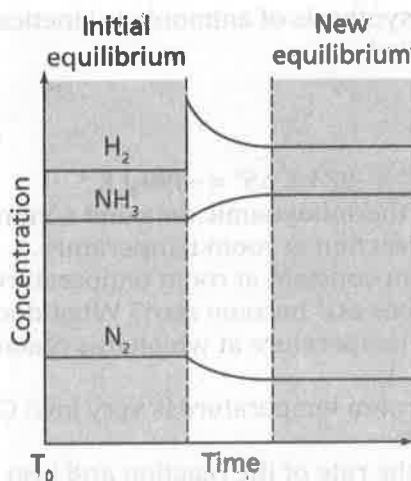


which is developed from 1.000 mole of  $\text{NH}_4\text{HS}$  in a 100-L cylinder. At equilibrium the total pressure is found to be 0.400 atm.  $K_p$  will be equal to

- (A)  $2.00 \times 10^{-1}$   
 (B)  $1.00 \times 10^{-2}$   
 (C)  $4.00 \times 10^{-2}$   
 (D) 4.00
11. The equilibrium constant for the ionization of hypochlorous acid is  $3.0 \times 10^{-8}$ . If a 1.0 M solution is at pH 2, what is the equilibrium condition of the system?



- (A) The system is at equilibrium.  
 (B) The system will shift to the right to make products.  
 (C) The system will shift to the left to make reactants.  
 (D) The equilibrium cannot be determined without more information.
12. According to the graph below, what chemical was added to the equilibrium mixture and how did the system respond?

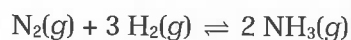


- (A) Hydrogen was added and the concentration of nitrogen decreased.  
 (B) Ammonia was added and the concentration of ammonia increased.  
 (C) Hydrogen was added and the concentration of ammonia decreased.  
 (D) Ammonia was added and the concentration of hydrogen increased.

13. For which of the following values of  $K$  will the equilibrium mixture consist almost entirely of reactants:
- 0.030
  - 1.00
  - $1 \times 10^{10}$
  - 30
14.  $K = 0.25$  for  $2 \text{NOBr}(g) \rightleftharpoons 2 \text{NO}(g) + \text{Br}_2(g)$ . At the same  $T$  and  $P$ , what is the  $K$  for  $\text{NO} + \frac{1}{2} \text{Br}_2 \rightleftharpoons \text{NOBr}$ ?
- 2.0
  - 4.0
  - 0.50
  - 0.63
15. Ammonia and oxygen react to establish the following equilibrium:
- $$4 \text{NH}_3(g) + 3 \text{O}_2(g) \rightleftharpoons 2 \text{N}_2(g) + 6 \text{H}_2\text{O}(g)$$
- If a 1-L flask is filled with 4.0 mol of oxygen and 3.0 mol of ammonia and the system is allowed to come to equilibrium, the flask is found to contain 1.0 mol of nitrogen. How much oxygen is present at equilibrium?
- 0.50 mol
  - 1.0 mol
  - 1.5 mol
  - 2.5 mol

### FREE-RESPONSE QUESTIONS

1. The Haber process for the synthesis of ammonia is kinetically and thermodynamically controlled.



for the reaction above:  $\Delta H^\circ = -92 \text{ kJ}$ ,  $\Delta S^\circ = -199 \text{ J} \cdot \text{K}^{-1}$

- Calculate  $\Delta G^\circ$  from the thermodynamic data and comment on the spontaneity of the reaction at room temperature.
  - Calculate the equilibrium constant at room temperature.
  - At what temperature does  $\Delta G^\circ$  become zero? What does this mean in regards to the temperature at which this reaction can be carried out at?
  - The rate of reaction at room temperature is very low. Give an explanation for this fact.
  - Propose a way to shift the rate of the reaction and also shift equilibrium towards products.
2. Refer to the system  $\text{PCl}_3(g) + \text{Cl}_2(g) \rightleftharpoons \text{PCl}_5(g)$ . To an empty 15.0-L cylinder, 0.500 mol of gaseous  $\text{PCl}_5$  are added and allowed to reach equilibrium. The concentration of  $\text{PCl}_3$  is found to be 0.0220 M. Assume a temperature of 375 K.
- How many mol of  $\text{PCl}_5$  remain at equilibrium?
  - Write the equilibrium constant expression for the above reaction.
  - Determine the value of  $K$ .



- (d) Determine the value of  $K_p$  for this same system at the same temperature.
- (e) How would the value of  $K_p$  be effected by increasing the temperature of the system at equilibrium for this exothermic reaction?

## Answers

### MULTIPLE-CHOICE QUESTIONS

- D** Since every time a mole of X reacts, 3 moles of W must react, so the amount of W remaining must be less than the amount of X remaining (recall that you started with an equal number of moles of W and of X) (*Chemistry* 8th ed. pages 594–597/9th ed. pages 607–610). LO 6.6
- B** Equilibrium is established when the forward rate is equal to the reverse rate (*Chemistry* 8th ed. pages 594–597/9th ed. pages 607–610). LO 6.3
- B** Increasing the temperature causes the equilibrium to shift to the left. For an exothermic reaction, increasing the temperature increases the rate of both the forward and reverse reactions, but proportionally makes a greater increase in the reverse reaction since it has the higher activation energy, favoring the formation of more hydrogen gas and more nitrogen gas, and lowering the concentration of the ammonia. This forms more gaseous particles; therefore, the pressure increases at constant volume (*Chemistry* 8th ed. pages 624–626/9th ed. pages 637–639). LO 6.8

- D** If 3.0 moles of oxygen are formed, 6.0 moles of NO must have reacted, leaving 9.0 moles of NO at equilibrium ( $15.0 - 6.0 = 9.0$  mol/L for [NO]). Each time 3.0 moles of oxygen form, the same number of moles of nitrogen are produced. Since the reaction (take care here) is written showing NO as a product, the equilibrium

constant expression is 
$$K = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = \frac{(9.0)^2}{(3.0)(3.0)} = \frac{81}{9.0} = 9.0$$

(*Chemistry* 8th ed. pages 612–617/9th ed. pages 624–630). LO 6.5

- B**

$$Q = \frac{[\text{NH}_3]^2}{[\text{H}_2]^3 [\text{N}_2]} = \frac{(0.20)^2}{(0.10)^3 (0.10)} = 400$$

Since  $Q$  is greater than  $K$ , the reaction will shift toward  $\text{N}_2$  and  $\text{H}_2$

(*Chemistry* 8th ed. pages 608–610/9th ed. pages 620–622). LO 6.10

- B** The reaction is exothermic so lowering the temperature and removing the nitrogen monoxide will both shift the reaction to

products according to Le Châtelier's principle (*Chemistry* 8th ed. pages 620–626/9th ed. pages 633–639). LO 6.9

7. **B** Chemistry concepts should not be learned in a vacuum. You need to be able to connect chemistry concepts with other science concepts. Cave formations occur when carbon dioxide in the air forms carbonic acid. The very weak acid reacts with calcium carbonate in limestone forming calcium bicarbonate. This compound is also in equilibrium with carbon dioxide, water, and calcium carbonate.



(*Chemistry* 8th ed. pages 620–622, 624–626/9th ed. pages 633–635, 637–639). LO 6.1

8. **A** Because you are seeking an equilibrium system which has not changed with a change in pressure due to a volume change, look for a system with an equal number of moles of both gaseous reactants and products (*Chemistry* 8th ed. pages 621–624/9th ed. pages 634–637). LO 6.8

9. **D** The equilibrium constant is a ratio of the concentration of products divided by the concentration of reactants, each taken to a power represented by their coefficients. Pure liquids and solids are not shown in the equilibrium constant expression (*Chemistry* 8th ed. pages 597–599, 603–606/9th ed. pages 610–612, 615–618). LO 6.2

10. **C** The two gases are formed in equal molar amounts (1:1); therefore half of the pressure is due to each gas  $\left(\frac{0.400 \text{ atm}}{2} = 0.200 \text{ atm}\right)$ .  $K_p = (P_{\text{NH}_3}) (P_{\text{H}_2\text{S}}) = (0.200) \times (0.200) = 0.0400 = 4.00 \times 10^{-2}$  (*Chemistry* 8th ed. pages 602–606/9th ed. pages 615–618). LO 6.6

11. **C** Hypochlorous acid is a weak acid, but the pH can be used to calculate  $[\text{H}_3\text{O}^+]$  and by stoichiometry,  $[\text{ClO}^-]$ .

$$\text{At pH } 2, [\text{H}_3\text{O}^+] = 0.01 \text{ M} = [\text{ClO}^-]$$

$$Q = [\text{H}_3\text{O}^+]_0 [\text{ClO}^-]_0 / [\text{HClO}]_0$$

$$Q = (0.01)(0.01/1) = 1 \times 10^{-4}$$

Recall that  $K = 3.0 \times 10^{-8}$  so  $Q > K$ . Equilibrium with shift to reactants (*Chemistry* 8th ed. pages 608–611/9th ed. pages 620–623). LO 6.4

12. **A** The graph shows a spike where  $\text{H}_2$  was added. This extra  $\text{H}_2$  reacted with some  $\text{N}_2$  and decreased  $[\text{N}_2]$  in the system (*Chemistry* 8th ed. pages 620–622/9th ed. pages 633–635). LO 6.10

13. **C** A small value for  $K$  indicates that in the ratio of products to reactants, there are considerably more reactants than products, resulting in a very small number significantly less than one (*Chemistry* 8th ed. page 608/9th ed. page 620). LO 6.7

14. **A** First, recognize that the reaction requested is the reverse of the one for which the  $K$  is given. The value of  $K$  for the reversed equilibrium reaction is the reciprocal of  $K$  or  $1/K$ , which is  $1/0.25 = 4$ . The new reaction as written is then multiplied by a factor of  $\frac{1}{2}$ , therefore the equilibrium expression for the new reaction is the original  $K$  raised to the  $\frac{1}{2}$  power or in this case, the square root of 4, which is 2.0 (*Chemistry* 8th ed. pages 598–600/9th ed. pages 611–613). LO 6.2
15. **D** Solve the problem using an ICE table. A useful technique is to underline the information given to you in the problem (3.0 mole  $\text{NH}_3$  and 4.0 mole  $\text{O}_2$  as well as 1.0 mole  $\text{N}_2$  at equilibrium).

	$4 \text{ NH}_3(g) +$	$3 \text{ O}_2(g) \rightleftharpoons$	$2 \text{ N}_2(g) +$	$6 \text{ H}_2\text{O}(g)$
initial	<u>3.0</u>	<u>4.0</u>	0	0
change	$-4x = -2.0$	$-3x = -1.5$	$+2x = 1.0$	$+6x = 3.0$
equilibrium	1.0	2.5	<u>1.0</u>	3.0

Since the coefficient for  $\text{N}_2$  is 2, the concentration must increase by  $2x$ . The reactant concentrations decrease by their coefficients times  $x$  and the water concentration increases by its concentration times  $x$  (see chart). Since  $2x = 1$ ,  $x = 0.5$ . Plug that value into the other “change” boxes to calculate the values of all of the species at equilibrium (*Chemistry* 8th ed. pages 606–615/9th ed. pages 618–628). LO 6.6

### FREE-RESPONSE QUESTIONS

1. (a)  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$\Delta G^\circ = -92 \text{ kJ} - (298 \text{ K})(0.199 \text{ kJ/K})$$

$$\Delta G^\circ = -33 \text{ kJ}; \text{ spontaneous at room temperature}$$

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

$$K = e^{-33000\text{J}/(8.314\text{J/K mol})(298\text{K})}$$

$$K = 5.4 \times 10^5$$

LO 6.25

(c)  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$0 \text{ kJ mol}^{-1} = 92 \text{ kJ mol}^{-1} - T(0.199 \text{ kJ K}^{-1}\text{mol}^{-1})$$

$T = 462 \text{ K}$ ; at temperatures higher than 462 K, the reaction becomes nonspontaneous.

- (d) The rate of reaction is probably very low due to a high  $E_a$  that must be overcome. The very stable triple bond of nitrogen requires a lot of energy to break; that is the activation energy for the reaction.

- (e) To maximize the yield of this reaction, raise the temperature up to around 426 K to maximize the thermodynamics. Increase the pressure to force the reaction to products to relieve the stress on the system. Find a suitable catalyst to lower the activation energy by taking a different path from reactants to products (*Chemistry* 8th ed. pages 565–570, 790–794, 798–802/9th ed. pages 577–583, 805–810, 813–817). LO 6.3, LO 6.9
2. (a)  $0.0220 \text{ mol/L PCl}_3 \times 15.0 \text{ L} = 0.330 \text{ mole PCl}_3 = 0.330 \text{ mole PCl}_5$  that reacted.
- $0.500 - 0.330 = 0.170 \text{ mole PCl}_5$  remains.
- (b) 
$$K_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]}$$
- (c) 
$$\frac{\left(\frac{0.170}{15.0 \text{ L}}\right)}{(0.0220)(0.0220)} = 23.4$$
- (d)  $K_p = K_c (RT)^{\Delta n}$
- In this case,  $1 + 1 \text{ mol of gas} \rightarrow 1 \text{ mol of gas}$ , so  $\Delta n = -1 \text{ mol}$
- $K_p = 23.4 (0.08206 \times 375)^{-1} = 0.760$
- (e) Raising the temperature of an exothermic reaction opposes the forward reaction. Further, from  $K_p = K_c(RT)^{\Delta n}$ , if  $T$  increases, the value of  $K_p$  decreases (*Chemistry* 8th ed. pages 602–603, 609–612/9th ed. pages 615–616, 621–625). LO 6.8