

Chapter 15

Chemical Equilibrium

* Note: On the AP exam, the required question has always been on equilibrium. All possible types of equilibrium will be discussed in chapters 15,16,17. Throughout these chapters, I will be giving you past AP equilibrium questions.

Chemical equilibrium: The condition in a reaction when the concentrations of reactants and products cease to change. At this point opposing reactions are occurring at equal rates.

Previous examples of equilibrium:

- vapor pressure above a liquid is in equilibrium with the liquid. The rate at which molecules of the gas phase strike the surface and become part of the liquid is equal to the rate in which molecules of liquid phase evaporate
- A saturated solution of ferrous alum: The rate at which the ions come out of solution as a solid equal the rate at which the ions dissolve (dissociate)

I. The Concept of Equilibrium

At equilibrium, the rate of the forward reaction is equal to the rate of the reverse.

Forward reaction: $A \rightarrow B$ rate = $k_f [A]$

Reverse reaction: $B \rightarrow A$ rate = $k_r [B]$

where k_f and k_r are the rate constants for the forward and reverse reactions.

Figure 15.3

Suppose we start with pure compound A in a closed container. As A reacts to form compound B, the concentration of A decreases while the concentration of B increases. As A decreases, the rate of the forward reaction decreases. Likewise, as B increases, the rate of the reverse reaction increases. Eventually, the reaction reaches a point where the forward and reverse reactions are the same. At equilibrium:

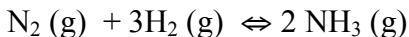
$$k_f [A] = k_r [B]$$

Rearranging

$$[B]/[A] = k_f / k_r = \text{a constant}$$

This **does not** mean A and B stop reacting. On the contrary, the equilibrium is *dynamic*. (compound $A \rightarrow B$ and $B \rightarrow A$, signified by $A \rightleftharpoons B$)

A famous equilibrium reaction is the **Haber process** for synthesizing ammonia.



The Haber process consists of putting together N_2 and H_2 in a high pressure tank in the presence of a catalyst and a temperature of several hundred degrees Celsius. Eventually, an equilibrium will be reached where there is a mixture of N_2 , H_2 , and NH_3 . If only ammonia is placed in the tank, again, a mixture of the three will occur. therefore, equilibrium can be reached from either direction.

II. The Equilibrium Constant

A relationship between the concentrations of reactants and products at equilibrium can be determined. This is referred to as the Law of mass action.



where A,B,P,Q are the chemicals involved and a,b,p,q are the coefficients in the balanced equation.

According to this law, the equilibrium condition is expressed by the equation:

$$K_c = \frac{[\text{P}]^p [\text{Q}]^q}{[\text{A}]^a [\text{B}]^b}$$

the square brackets signify molar concentrations. The constant K_c is called the equilibrium constant. The c indicates that concentrations expressed in molarity are used.

The value of the equilibrium constant will vary with temperature.

Equilibrium constants can also be expressed in terms of pressure.

When the reactants and products in a chemical equation are gases, we can formulate the equilibrium expression in terms of partial pressures (usually in atms) instead of molar concentrations

When using partial pressures, the equilibrium constant is K_p

$$K_p = \frac{(P_P)^p (P_Q)^q}{(P_A)^a (P_B)^b}$$

where P_A is the partial pressure of a and so forth. The numerical values for K_c and K_p will obviously be different so be careful.

For gases, we can use the ideal gas law to convert between K_s and K_p .

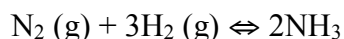
$PV = nRT$ rearranging $P = (n/V)RT$ and since n/V is expressed as moles per liter, this is molarity.

$$P = MRT$$

For substance A, $P_A = [A](RT)$; for substance B, $P_B = [B](RT)$ and so on.

Substitute each equation into the K_p equation, you will end up with

$K_p = K_c (RT)^{\Delta n}$ where Δn is the change in number of moles going from reactants to products. It is equal to the number of moles of gaseous products minus number of moles of gaseous reactants. For example



$$\Delta n = 2 - (3+1) = -2$$

Example: A mixture of nitrogen and hydrogen in a reaction vessel is allowed to attain equilibrium at 472°C. the equilibrium mixture of gases was analyzed and found to contain 0.127 M H_2 , 0.0402 M N_2 , and 0.00272 M NH_3 . From this data calculate K_c . Then, using the value for K_c calculate K_p .

(answers: $K_c = 0.105$; $K_p = 2.81 \times 10^{-5}$)

III. Magnitude and direction of the Chemical Equation and K.

If the equilibrium constant is very large, the products are favored and it is said equilibrium lies to the right.

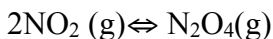
If the equilibrium constant is much less than one, we say the reactants are favored and the equilibrium lies to the left.

Because an equilibrium can be approached from either direction, the direction in which we write the equilibrium is arbitrary.



$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.212 \text{ (at } 100^\circ\text{C)}$$

OR



$$K_c = [N_2O_4] \quad 1$$

$$\frac{\text{-----}}{[\text{NO}_2]^2} = \frac{\text{-----}}{0.212} = 4.72 \text{ (at } 100^\circ\text{C)}$$

Notice: The equilibrium constant for the reaction written in one direction is the reciprocal of the reaction written in the reverse direction.

It is very important then to specify not only temperature, but how the equilibrium expression is written.

IV. Heterogeneous Equilibria

Equilibria in which all reactants and products are of the same phase are called Homogeneous equilibria. If different phases are involved, it is referred to as heterogeneous equilibria.



$$K_c = \frac{[\text{CaO}][\text{CO}_2]}{[\text{CaCO}_3]}$$

When we are looking at concentrations of liquids and solids, we are really looking at density divided by molar mass.

$$\frac{\text{Density/MM} = \text{g/cm}^3}{\text{g/mol}} = \frac{\text{mol}}{\text{cm}^3}$$

since the density of any given liquid or solid is constant and changes very little with temperature, we can effectively say it is a constant.

$$K_c = \frac{(\text{constant 1}) [\text{CO}_2]}{(\text{constant 2})}$$

$$K_c' = K_c \text{ constant 2/constant 1} = [\text{CO}_2]$$

We can therefore exclude liquids and solids from the expression. However, even though they do not appear in the expression, they must be present for an equilibrium to be established.

V. Applications of equilibrium constants

A. To determine Concentrations of other species in a chemical reaction if one species is known.

use the following procedure:

1. Tabulate the known initial and equilibrium concentrations of all species involved.
2. For those species for which both the initial equilibrium concentrations are known, calculate the change in concentration that occurs as the system reaches equilibrium.
3. Use the stoichiometry of the reaction to calculate the changes in concentration for all other species in the equilibrium.
4. From the initial concentrations and changes in concentration, calculate the equilibrium concentrations. these are used to evaluate the equilibrium constant.

Example 2:

A mixture of 5.000×10^{-3} mol of H_2 and 1.000×10^{-2} mol of I_2 is placed in a 5.000 L container at $448^\circ C$ and allowed to come to equilibrium. Analysis of the equilibrium mixture shows that the concentration of HI is 1.87×10^{-3} M. Calculate K_c at $448^\circ C$ for the reaction: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$.

First, tabulate the initial and equilibrium concentrations of all species as well as the change in concentrations. It is convenient to use the equation as a heading for the table.

In this example, the initial concentrations of H_2 and I_2 must be calculated.

$$[H_2]_{initial} = (5.000 \times 10^{-3} \text{ mol}) / (5.000 \text{ L}) = 1.000 \times 10^{-3} \text{ M}$$
$$[I_2]_{initial} = (1.000 \times 10^{-2} \text{ mol}) / (5.000 \text{ L}) = 2.000 \times 10^{-3} \text{ M}$$

	$H_2(g)$	+ $I_2(g)$	\rightleftharpoons	$2HI(g)$
Initial	$1.000 \times 10^{-3} \text{ M}$	$2.000 \times 10^{-3} \text{ M}$		0 M
Change				
Equilibrium				$1.87 \times 10^{-3} \text{ M}$

Second, calculate the change in concentration of HI using initial and equilibrium values. The change is $1.87 \times 10^{-3} \text{ M}$.

third, use the stoichiometry of the reaction to calculate the other species. The balanced chemical equation shows for 2 mol of HI formed, 1 mol of H_2 must be consumed. Thus the amount of H_2 consumed is:

$$(1.87 \times 10^{-3} \text{ mol HI/liter}) (1 \text{ mol } H_2 / 2 \text{ mol HI}) = 9.35 \times 10^{-4} \text{ mol } H_2/\text{liter}$$

The same line of reasoning gives the same value for I_2

Fourth, calculate the equilibrium concentrations using initial and change values. the equilibrium concentration is the initial minus that consumed. The table now looks like:

	$H_2(g)$	+ $I_2(g)$	\rightleftharpoons	$2HI(g)$
Initial	$1.000 \times 10^{-3} \text{ M}$	$2.000 \times 10^{-3} \text{ M}$		0 M
Change	$-0.935 \times 10^{-3} \text{ M}$	$-0.935 \times 10^{-3} \text{ M}$		$+1.87 \times 10^{-3} \text{ M}$
Equilibrium	$0.065 \times 10^{-3} \text{ M}$	$1.065 \times 10^{-3} \text{ M}$		$1.87 \times 10^{-3} \text{ M}$

Finally, calculate the equilibrium constant.

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.87 \times 10^{-3})^2}{(0.065 \times 10^{-3})(1.065 \times 10^{-3})} = 51$$

B. Predicting the direction of a reaction

When we substitute reactant and product information into the equilibrium expression, the result is known as the **reaction quotient** and is represented by the letter Q. The reaction quotient will equal the equilibrium constant K only if the concentrations are such that the system is at equilibrium. When $Q > K$ substances on the right side of the equation will react to form those on the left. If $Q < K$, the reaction will achieve equilibrium by forming more products.

Example 3:

At 448 °C the K_c for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is 51. Predict how the reaction will proceed to reach equilibrium if we start with $1.0 \times 10^{-2} M HI$, $5.0 \times 10^{-3} M H_2$, and $1.5 \times 10^{-2} M I_2$.

Solution: the reaction quotient is

$$Q = \frac{[HI]^2}{[H_2][I_2]} = \frac{(1.0 \times 10^{-2})^2}{(5.0 \times 10^{-3})(1.5 \times 10^{-2})} = 1.3$$

$Q < K$ therefore, $[HI]$ will need to increase and $[H_2]$ and $[I_2]$ decrease to reach equilibrium. the reaction will proceed to the left.

C. Calculation of Equilibrium Concentrations

Example 4:

For the Haber process, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3$, $K_p = 1.45 \times 10^{-5}$ at 500 °C. In an equilibrium mixture of the three gases, the partial pressure of H_2 is 0.928 atm and that of N_2 is 0.432 atm. What is the partial pressure of NH_3 ?



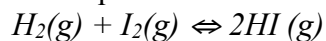
Equilibrium pressure (atm): 0.432 0.928 x

At equilibrium, the pressures must satisfy the equilibrium expression:

$$K_p = \frac{P_{NH_3}^2}{P_{N_2}P_{H_2}^3} = \frac{x^2}{(0.432)(0.928)^3} = 1.45 \times 10^{-5}$$

Solving for x gives 2.24×10^{-3} atm

Example 4: A 1.000 l flask is filled with 1.000 mol H₂ and 2.000 mol I₂ at 448°C. The value of the equilibrium constant, K_c, for the reaction



at 448°C is 50.5. What are the concentrations of H₂, I₂ and HI at equilibrium?

Solution: In this case we are not given any of the equilibrium concentrations. We proceed by first constructing a table with initial concentrations as follows.

	$H_2(g)$	+ $I_2(g)$	\rightleftharpoons	$2HI(g)$
Initial	1.000 M	2.000 M		0 M
Change				
Equilibrium				

At equilibrium, the concentration of HI must be greater than 0 and the concentrations of H₂ and I₂ must decrease. Let's represent the change in concentration of H₂ by the variable x . Since the moles of I₂ are in a 1:1 ratio with H₂ the change in concentration of I₂ can also be x . However, 2 moles of HI are formed so its concentration change is $2x$.

	$H_2(g)$	+ $I_2(g)$	\rightleftharpoons	$2HI(g)$
Initial	1.000 M	2.000 M		0 M
Change	- x M	- x M		+ $2x$ M
Equilibrium	(1.000- x)M	(2.000- x)M		$2x$ M

Substitute the equilibrium concentrations into the equilibrium expression.

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(2x)^2}{(1.000-x)(2.000-x)} = 50.5$$

Through the use of the quadratic equation, $x = 2.323$ or 0.935 .

Using the first value, we will end up with negative concentrations. Since a negative concentration is not meaningful, we reject that value and use 0.935 .

The equilibrium concentrations are then found to be

$$[\text{H}_2] = (1.000 - 0.935) = 0.065\text{M}$$

$$[\text{I}_2] = 1.065\text{M}$$

$$[\text{HI}] = 1.870\text{M}$$

You can double check for correctness by plugging these values into the equilibrium expression and see if you end up with a K_c around 50.5 .

VI. Le Châtelier's Principle

If a system at equilibrium is disturbed by a change in temperature, pressure, or concentration of one of the components, the system will shift its equilibrium position so as to contract the disturbance.

A. Change in reactant or product concentrations.

If a chemical substance is at equilibrium and we add more of a reactant or product, the reaction will shift to consume whatever is added. Conversely, removal of some of the reactants or products will result in the reaction moving in the direction that forms more of what was removed.

B. Effect of volume and pressure changes.

Reducing the volume (hence increasing pressure), causes the reaction to shift to the direction that produces less moles.

Note: keep in mind this shifts of volume, pressure and concentrations do not change the value of K_c only the concentrations of reactants and products.

C. The effect of temperature changes

Changes in temperature will change the value of the equilibrium constant.

To notice the shifts in equilibrium, we need to be aware whether the reaction is endothermic or exothermic and place heat either as a reactant or product:

Endothermic: Reactants + *heat* \rightleftharpoons products

Exothermic: Reactants \rightleftharpoons products + *heat*.

When the temperature is increased, the equilibrium shifts to the direction to use up the heat. For example, in an endothermic reaction, this would mean a shift to the right in the direction of the products. What would this do the value of K?

Endothermic: Increasing T results in _____ of K

Exothermic: Increasing T results in _____ of K