

# General Equilibrium

## Chemical Equilibrium

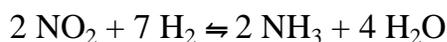
Most chemical reactions that are encountered are *reversible*. In other words, they go fairly easily in either the forward or reverse directions. The thing to remember about reactions that have come to equilibrium is that they have not stopped. The equilibrium is a *dynamic equilibrium*. The reaction is still proceeding as it was previously. However, the reverse reaction is occurring at the same rate as the forward reaction. This means that the concentration of the reactants and products remaining the same after equilibrium has been reached. A particular reactant at any given time may convert to a product and vice versa.

What happens to cause a reaction to come to equilibrium?

Initially the reactant concentrations are large. Because of this, the rate of the forward reaction starts out rather high. As the reaction proceeds the reactant concentrations decrease causing the forward rate to decrease. At the same time, the reverse rate starts out at zero, because the concentration of the products is zero. As the products are created the reverse reaction increases. Eventually a point is reached where the reactants are produced by the reverse reaction just as quickly as they are consumed by the forward reaction. This is the state of chemical equilibrium.

We need to remember that the reaction mixture at equilibrium is dictated by both the forward and reverse rates AND the stoichiometry of the reaction.

The following reaction is allowed to come to equilibrium:



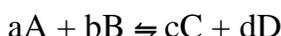
If the reaction starts with 26.56 mol of Hydrogen gas and 8.95 mol of Nitrogen Dioxide in a 15 L container and there are 2.26 mol of Ammonia at equilibrium, what is the composition of the equilibrium mixture?

	[NO]	[H <sub>2</sub> ]	[NH <sub>3</sub> ]	[H <sub>2</sub> O]
Initial conc.	0.597	1.77	0.000	0.000
Change	-0.0755*2	-0.0755*7	+0.0755*2	+0.0755*4
Final conc.	0.597-0.151	1.77-0.5285	0.000+0.151	0.000+0.302
Final	0.446	1.24	0.151	0.302

In this example, the concentration of each compound changes by an amount that is a stoichiometric multiple of some given amount (0.0755 M). The changes are given as positive or negative depending on whether that substance is being produced or consumed. The final concentrations are dependent on the initial concentrations. If we start with different amounts of each we will finish with different amounts.

### ***Equilibrium Constants***

At a given temperature we can define a constant that indicates where along the reaction path the equilibrium lies. This constant is called the equilibrium constant,  $K_c$ . If we consider a general equilibrium reaction:



the equilibrium constant and expression is defined as

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

where the subscript “c” in  $K_c$  denotes that this is derived from concentrations. This constant is the same for a given reaction at a given temperature regardless of the equilibrium concentrations. The expression for the equilibrium constant is derived from the stoichiometric coefficients in the chemical reaction, unlike the exponents in the rate law.

Looking at the above reaction (NO and H<sub>2</sub>) what is the equilibrium expression?

$$K_c = \frac{[NH_3]^2 [H_2O]^4}{[NO]^2 [H_2O]^7}$$

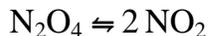
Given that this is the equilibrium expression what is the equilibrium constant?

$$K_c = \frac{[NH_3]^2 [H_2O]^4}{[NO]^2 [H_2O]^7} = \frac{[0.151]^2 [0.302]^4}{[0.466]^2 [1.24]^7} = 1.94 \times 10^{-4}$$

Often the equilibrium constants are given without units. The reason for this lies in thermodynamics where these constants are defined in terms of the *activities* of the species present. The activity is the concentration of the species divided by 1 M. The result is unit-less so the equilibrium constants are unit-less.

## Kinetic argument for equilibrium constants

Look at the decomposition of  $N_2O_4$ . It proceeds according to the following reaction:



This reaction is at equilibrium when the forward and reverse rates are the same. It also proceeds as if the chemical equation is the only step in the mechanism, an elementary step. In that case, the forward rate is given by:

$$\text{rate} = k_1 [N_2O_4],$$

and the reverse rate is given by:

$$\text{rate} = k_{-1}[NO_2]^2,$$

and these rates are equal leading to the expression:

$$k_1 [N_2O_4] = k_{-1}[NO_2]^2.$$

This can be rearranged to give:

$$\frac{k_1}{k_{-1}} = \frac{[NO_2]^2}{[N_2O_4]}$$
$$K_c = \frac{k_1}{k_{-1}}$$
$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

which is just our equilibrium expression. If the reaction occurs by a multi-step mechanism, the equilibrium expression is a combination of ratios of rate constants from each step in the mechanism.

$K_p$

The equilibrium constants can be defined in terms of partial pressures when working with gases. Let's look at the relationship between  $K_c$  and  $K_p$ . We can find the relationship by looking at the relationship between concentration and pressure via the Ideal Gas Law.

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

$$[C] = \frac{n_c}{V_c} = \frac{P_c}{RT}$$

$$K_c = \frac{\left(\frac{P_c}{RT}\right)^c \left(\frac{P_d}{RT}\right)^d}{\left(\frac{P_a}{RT}\right)^a \left(\frac{P_b}{RT}\right)^b} = (RT)^{-(c+d-(a+b))} \left(\frac{P_c^c P_d^d}{P_a^a P_b^b}\right) = K_p (RT)^{-\Delta n}$$

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

Where  $\Delta n$  is the number of moles of *gaseous* products minus the number of moles of *gaseous* reactants.  $RT$  is a constant at a given temperature.  $R$  must be in units of L-atm/mol-K because we are, in effect changing between molarity (mol/L) to atmospheres (atm).

What is the  $K_p$  for the reaction between NO and  $H_2$ ?

$$\begin{aligned} K_p &= K_c (RT)^{\Delta n} = (2.12 \times 10^{-4}) ((0.08206 \text{ L-atm/mol-K}) (298 \text{ K}))^{(6-9)} \\ &= 1.45 \times 10^{-8} \end{aligned}$$

### ***Equilibrium Constants for the sum of reactions***

If we add two more reactions together, the equilibrium constants are multiplied together. If we reverse a reaction the equilibrium constant gets inverted. Dividing a reaction by a constant, we take the corresponding root of the equilibrium constant. Multiplying a reaction by a constant means we raise the equilibrium constant to that power.

### ***Heterogeneous Equilibria***

This is equilibrium in which the species in the reaction are in different phases. When we write the equilibrium expression for this equilibrium we omit the concentrations of pure solids and liquids. The reason for this is that the concentrations of these phases are constant. As a result, the concentrations of these phases are absorbed into the equilibrium constant.

If the solvent takes place in the reaction its concentration is also effectively constant so it is also absorbed into the equilibrium constant. The concentration of the solvent is also not represented in the equilibrium expression.

## *Using the Equilibrium Constant*

We can use the equilibrium constant in one of three ways:

1. Qualitative interpretation of the constant. By looking at the constant we can tell how far toward completion the reaction goes.
2. Predicting the direction of a reaction. Given a mixture of products and reactants, what direction will the reaction go?
3. Finding equilibrium concentrations. Given an initial mixture of products and reactants, what will be the equilibrium concentrations?

### *Qualitative interpretation*

Look at the magnitude of the equilibrium constant. If the constant is much greater than 1, the reaction lies toward the products. If it is much less than 1, the reaction lies toward the reactants. If the equilibrium constant is about 1, the reaction mixture is about equal in products and reactants.

### *Predicting the direction of a reaction*

To predict the direction of a reaction we must first examine a quantity that is called the **reaction quotient**. The reaction quotient is mathematically identical to the Equilibrium expression that gives rise to K. However, the concentrations that are used in quotient are not equilibrium concentrations.

$$K = \frac{[\text{products}]_e^x}{[\text{reactants}]_e^y}$$
$$Q = \frac{[\text{products}]^x}{[\text{reactants}]^y}$$

The subscript e indicates an equilibrium value. We can predict the direction of a reaction by comparing Q and K

$K < Q$	reaction shifts to the left
$K > Q$	reaction shifts to the right
$K = Q$	already at equilibrium so there is no change

### *Finding equilibrium concentrations of reactants*

We can use the equilibrium constant and expression to calculate what the equilibrium concentrations (or partial pressures) will be. Sometimes the resulting

mathematical equation is too complicated to solve directly so we must resort to approximation methods.

Example:

For the reaction:



the equilibrium constant ( $K_c$ ) is  $1.4 \times 10^2$ . If 2.00 mol of Dinitrogen Monoxide and 2.00 mol of Oxygen are placed into a 1.00 L container what will the equilibrium concentrations of everything be?

	$2 \text{N}_2\text{O} (g) + 3 \text{O}_2 (g) \rightleftharpoons 4 \text{NO}_2 (g)$		
init	2.00 M	2.00 M	0.00M
$\Delta$	-2x	-3x	+4x
final	2.00-2x	2.00-3x	4x

The equilibrium expression is:

$$K_c = 1.4 \times 10^2 = \frac{(4x)^4}{(2-2x)^2(2-3x)^3}$$

This is a 5<sup>th</sup> order equation that can be solved using an approximation method. (It can be solved exactly using a computer.) To solve this we need to realize that the largest x can be is 2/3. If it were more than this the denominator would be negative which it can't be. We can guess a value for x and solve for Q. We then adjust the value for x until we get Q to be close to the value for K. Because K is fairly large, we can guess that the x will be fairly close to 2/3. We choose 0.500 initially, which gives:

Initial guess:	0.500	Q = 128
	0.510	Q = 174
	0.505	Q = 149
	0.504	Q = 144
	0.502	Q = 136
	0.503	Q = 140.19 (very close)

The value for x is then 0.503, which means that the equilibrium concentration of  $\text{N}_2\text{O}$  is 0.994 M,  $\text{O}_2$  is 0.491 M, and  $\text{NO}_2$  is 2.01 M.

Using the quadratic equation or taking a root can solve most problems of this sort. Other problems may require other approximation methods. We'll examine the other approximation methods as we come to them.

### *Le Châtelier's Principle*

**Le Châtelier's principle** states that when a system at equilibrium is stressed or strained, the equilibrium will shift so as to relieve the stress or strain.

If we add more reactants to a system at equilibrium, the system will respond by producing more products, thus relieving the stress. If we take reactants away, the system will consume products to make more reactants. When we add anything to either side of the reaction the equilibrium will shift to the opposite side. If we take anything away, the equilibrium will shift to the side that loses molecules.

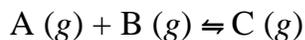
### **Effects of pressure changes**

If we change the pressure by adding an inert gas, such as Argon, the equilibrium will **not** shift because we are not changing the partial pressures of the components of the reaction. We can shift the equilibrium by changing the pressure by other means though. If we reduce the size of the container the partial pressures of everything will increase. The equilibrium will shift to the side of the reaction with fewer moles of gas to relieve the increase in total pressure. Conversely, if we increase the size of the container, which decreases all of the partial pressures, the equilibrium will shift to the side of the reaction with more moles of gas to bring the pressure back up.

The same argument above can be made for aqueous solutions. If we dilute a solution, the equilibrium will shift to the side of the reaction with more moles of solute to increase the overall concentration of the solution.

### **Quantitative changes of Q**

For the following reaction



If we decrease the size of the container by a factor of 2 the partial pressures of everything will double. This will cause Q to become

$$Q = \frac{[C]}{[A][B]} = \frac{2}{2 \times 2} = \frac{1}{2}$$

So  $Q$  will become  $\frac{1}{2}$  of  $K$ . Because  $K$  is bigger than  $Q$  the reaction will shift to the right. This is same conclusion we came to above. The reaction shifts to the side with fewer moles of gas.

### **Effects of temperature changes**

The effect on equilibria due to temperature changes depends on if the reaction is exothermic or endothermic. On a qualitative level we can think of heat as a product (exothermic reaction) or as a reactant (endothermic reaction). Now Le Châtelier's principle is applied. If the reaction is exothermic and we add heat, we drive the reaction to the reactant side. If we remove heat the reaction is driven to the product side.

We must keep in mind; however, that what is changing when we change the temperature is **not  $Q$  but  $K$** . If the reaction is exothermic and we add heat,  $K$  increases which is what actually causes the shift in equilibrium.

### **Effects of a catalyst on equilibrium**

Adding a catalyst to a system already at equilibrium does not change the equilibrium. The catalyst will increase the forward and reverse rates **by the same amount**. If the system is not yet at equilibrium, the catalyst causes the equilibrium to be reached faster than it would have been without the catalyst.