# Equilibrium

**Unit 13A:** Equilibrium Constants and Expressions

### Knowledge/Understanding:

* what equilibrium means
* where the equilibrium constant comes from

### Skills:

* predict which direction equilibrium will shift based on Le Châtelier’s Principle

### Notes:

equilibrium: when the overall concentrations or partial pressures of chemicals in a reaction are not changing; or, in other words, when the rate of the forward reaction equals the rate of the reverse reaction.

A reaction that is at equilibrium is usually written with double “harpoon” arrows, showing that the reaction is proceeding in both directions.

A + B  C + D

Note that in a chemical reaction that has reached equilibrium, both the forward and reverse reactions are happening, often very rapidly. Equilibrium simply means that the rates of these two reactions are the same, which means the overall amounts of A, B, C, and D are not changing.

All chemical reactions proceed to equilibrium. However, it is possible for the equilibrium to lie so far to the right that the amount of reactants left is essentially zero, or so far to the left that the reaction essentially does not occur.

## Arrows Used in Equilibrium Reactions

|  |  |
| --- | --- |
| **Arrow** | **Meaning** |
| A + B  C + D | A + B react to produce C + D Either there is little or no reverse reaction, or no information is given about equilibrium. |
| A + B  C + D | A + B are in equilibrium with C + D No information is given about whether products or reactants are favored. |
| A + B  C + D | A + B are in equilibrium with C + D Products are favored. (*I.e.,* the concentrations of products are higher than the concentrations of reactants.) |
| A + B  C + D | A + B are in equilibrium with C + D Reactants are favored. (*I.e.,* the concentrations of reactants are higher than the concentrations of products.) |
| A  B | A and B are different resonance structures of the same compound. This is different from a chemical reaction that is at equilibrium. |

\*Note that the short arrows to show favoritism are not common. More than likely you’ll be presented a double arrow and will have to discern for yourself whether or not reactants/products are favored.

equilibrium constant: a number that indicates whether a reaction favors the products (Keq > 1) or reactants (Keq < 1).

Recall from Kinetics that the equilibrium constant equals the rate constant for the forward reaction divided by the rate constant for the reverse reaction.

Later, in thermodynamics, we will discuss the relation between energy (ΔG) and the rate constant (Keq). For now, understand that ΔG describes the combination of the enthalpic (ΔH) and entropic (ΔS) energy of a system:

* When ΔG = 0, Keq = 1. This means the free energy change for the reaction is zero, and neither products nor reactants are favored.
* When ΔG = −20 kJ/mol, Keq ≈ 1,000. The free energy change for the reaction is large, and the energy is *released*. This means products are strongly favored, and that the reaction essentially goes to completion.
* When ΔG = +20 kJ/mol, Keq ≈ 0.001. The free energy change for the reaction is large, and the energy is *absorbed.* This means reactants are strongly favored, and that the reaction essentially does not occur.

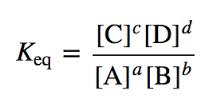
Hopefully this meshes with your understanding of system energy discussed earlier in thermochemistry. Any process that takes a system to a lower energy state (gives off energy, or has a – ΔG) is favorable.

* So, - ΔG and Keq > 1 is favorable as it shows you are releasing energy from the system and the formation of products is favorable.

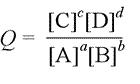
equilibrium expression: an equation that relates the equilibrium constant to the partial pressures (gases) or concentrations (aqueous solutions) of the reactants and products.

As we saw in the kinetics unit when we related the ratio of the forward and reverse rate constants (Keq = k1/k-1), Keq describes the relative amount of products and reactants present in the system at equilibrium.

For reaction:

The equilibrium constant expression would be:

\*The superscripts represent the molar coefficients of the balanced equation.

If the system is not at equilibrium, the ratio of products to reactants no longer represents Keq, but a reaction quotient (Q) value for that moment in time.

## The Equilibrium Expression

For gases, we use partial pressures to measure the amount of reactants and products present. The resulting equilibrium constant is called a pressure-based equilibrium constant, which we denote as *Kp*.

For the reaction:

N2 (g) + 3 H2 (g)  2 NH3 (g)

the equilibrium expression would be:



Where PNH3, for example, is the partial pressure of ammonia.

For aqueous solutions, we use concentration (molarity) to measure the amount of reactants and products present. The resulting equilibrium constant is called a concentration-based equilibrium constant, which we denote as *Kc*.

For the reaction:

I2 (aq) + 2 S2O32− (aq)  2 S4O62− (aq) + 2 I− (aq)

the equilibrium expression would be:

 = [products] / [reactants]

where [S4O62−], for example, is the concentration of S4O62− in .

\*note again that the exponents for the equilibrium expression are the coefficients from the balanced chemical equation.

**Manipulating Equilibrium Expressions**

If you reverse the reaction, the products and reactants switch places. For example, suppose we have:

N2 (g) + 3 H2 (g)  2 NH3 (g) *Kp*= 5.3 × 10−5

This means that for the reaction:

2 NH3 (g)  N2 (g) + 3 H2 (g) 

If you multiply the coefficients by a factor, the new K value is the old K value raised to that power. For example:

NH3 (g)   N2 (g) +  H2 (g) 

Similarly, if you combine two reactions (in Hess’s Law fashion), the overall equilibrium constant is the product of the two equilibrium constants. For example, if we combine:

SO2 (g) + ½ O2 (g)  SO3 (g) *K* = 2.2

NO2 (g)  NO (g) + ½ O2 (g) *K* = 4.0

If we add these two reactions together, we get:

SO2 (g) + NO2 (g)  SO3 (g) + NO (g) *K* = (2.2)(4.0) = 8.8

In summary:

|  |  |
| --- | --- |
| **Action on Equation(s)** | **Effect on *K*** |
| add (Rxn1 + Rxn2) | multiply (*K*1*K*2) |
| subtract (Rxn1 - Rxn2) | divide (*K*1 /*K*2) |
| multiply all coefficients by *x* | raise *K* to the *x* power (*Kx*) |
| divide all coefficients by *x* | *x*th root of *K* |
| reverse reaction | reciprocal |

## Relationship Between *Kp* and *Kc*

It is important to realize that *Kp* and *Kc* measure equilibrium under different conditions, and the equilibria themselves can be quite different. For instance, it is entirely possible for *Kp* to indicate an equilibrium that lies in a particular direction, and for *Kc* for the same system to indicate an equilibrium that lies in the opposite direction. In this instance, both equilibria are correct—they measure different parts of the system, which can be quite different from each other.

In a multi-phase system, the relationship between *Kp* and *Kc* is:



where *R* is the gas constant, *T* is the temperature (Kelvin), and Δ*n* is the change in moles of gas as the reaction proceeds from reactants to products.

Khan Academy Videos to watch:

1. Introduction to kinetics
2. Reactions in equilibrium
3. Keq intuition
4. Heterogeneous equilibrium
5. Le Chatelier’s principle