

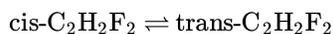
## 13.4: The Law of Chemical Equilibrium

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

Two examples of an [equilibrium constant](#) dealt with [in other sections](#), namely:

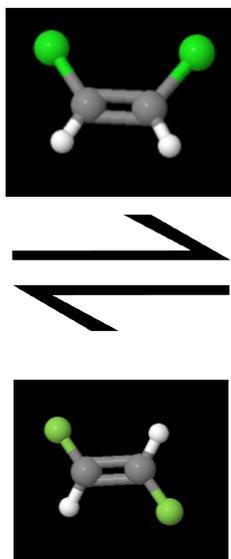
$$K_c = \frac{[trans-C_2H_2F_2]}{[cis-C_2H_2F_2]}$$

for the reaction



In the equation above, notice that both sides have the same molecular formula, yet in the image below, the elements involved are arranged differently. These molecules are called isomers and to learn more about them, check out the following site:

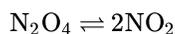
<https://www.thoughtco.com/geometric-isomerism-cis-and-trans-608702>.



and

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

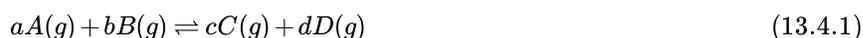
for the reaction



In the equation above, we see the decomposition of  $N_2O_4$  (the clear gas pictured below) into  $NO_2$ , which is the brownish red gas seen below. As you can see in the molecular structure above, this decomposition of  $N_2O_4$  occurs when the middle bond holding  $N_2O_4$  together is broken, leaving two  $NO_2$  molecules. For more information on this specific equilibrium, check out the page on [The Effect of a Change in Temperature](#).



Both the trans-cis transition of  $C_2H_2F_2$  and the decomposition of  $N_2O_4$  are particular examples of a more general law governing chemical equilibrium in gases. If we write an equation for a gaseous equilibrium in general in the form



then the equilibrium constant defined by the equation

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (13.4.2)$$

is found to be a constant quantity depending only on the temperature and the nature of the reaction. This general result is called the **law of chemical equilibrium**, or the **law of mass action**.

#### ✓ Example 13.4.1: Equilibrium Constant

Write expressions for the equilibrium constant for the following reactions:



#### Solution

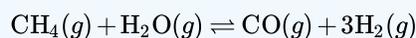
a. 
$$K_c = \frac{[H_2][I_2]}{[HI]^2}$$

b. 
$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

c. 
$$K_c = \frac{[H_2O]^2 [Cl_2]^2}{[O_2] [HCl]^4}$$

#### ✓ Example 13.4.2: Methane and Steam Equilibrium Constant

A mixture containing equal concentrations of methane and steam is passed over a nickel catalyst at 1000 K. The emerging gas has the composition  $[CO] = 0.1027 \text{ mol dm}^{-3}$ ,  $[H_2] = 0.3080 \text{ mol dm}^{-3}$ , and  $[CH_4] = [H_2O] = 0.8973 \text{ mol dm}^{-3}$ . Assuming this mixture is at equilibrium, calculate the equilibrium constant  $K_c$  for the reaction



#### Solution

The equilibrium constant is given by the following equation:

$$K_c = \frac{[CO][H_2]^3}{[CH_4][H_2O]} = \frac{0.1027^{-3} \times (0.3080^{-3})^3}{0.8973^{-3} \times 0.8973^{-3}}$$

$$= 3.727 \times 10^{-3}$$

Note: The yield of  $\text{H}_2$  at this temperature is quite poor. In the commercial production of  $\text{H}_2$  from natural gas, the reaction is run at a somewhat higher temperature where the value  $K_c$  is larger.

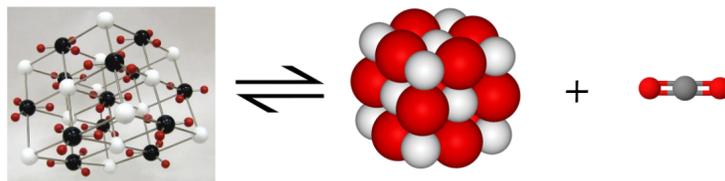
As the above example shows, the equilibrium constant  $K_c$  is a dimensionless quantity. This lack of units is a result of the derivation of  $K_c$  from  $K_{eq}$  which uses the **activities** of the reactants and products in the equilibrium system instead of their concentrations. The activity of a substance is a measure of its effective concentration under specified conditions. While a detailed discussion of this important quantity is beyond the scope of an introductory text, it is necessary to be aware of a few important aspects:

- Activities are dimensionless (**unitless**) quantities and are in essence “adjusted” concentrations.
- For relatively dilute solutions, a substance's activity and its molar concentration are roughly equal. However, to obtain a unitless quantity, each molar concentration is divided by a standard state defined as  $1 \frac{\text{mole}}{\text{dm}^3}$ . By using this standard state, the numerical value of the concentration remains unchanged, but the units cancel out.
- Activities for pure condensed phases (solids and liquids) are equal to 1.
- Activities for solvents in dilute solutions are equal to 1.

Thus, when we apply the equilibrium law to reactions which involve pure **solids** and pure **liquids**, we find in such cases that as long as some solid or liquid is present, the actual amount does not affect the position of equilibrium. Accordingly, only the molar concentrations of gaseous species are explicitly written in the expression for the equilibrium constant. For example, the equilibrium constant for the reaction



Notice below the molecular representation of the above reaction, with the ionic structure of  $\text{CaCO}_3$  'breaking apart' to form the simpler ionic structure  $\text{CaO}$  as well as gaseous  $\text{CO}_2$ .



is given by the expression

$$K_c = [\text{CO}_2] \quad (13.4.4)$$

in which only the concentration of the gas appears explicitly because the two solids each have an activity with a value equal to 1. Equation 13.4.4 suggests that if we heat  $\text{CaCO}_3$  to a high temperature so that some of it decomposes, the concentration of  $\text{CO}_2$  at equilibrium will depend only on the temperature and will not change if the ratio of amount of solid  $\text{CaCO}_3$  to amount of solid  $\text{CaO}$  is altered. Experimentally this is what is observed.

#### ✓ Example 13.4.3 : Equilibrium Constant Expression

Write expressions for the equilibrium constants for the following reactions:



#### Solution

Since only gaseous species need be included, we obtain

a. 
$$K_c = \frac{[\text{CO}][\text{H}_2]}{[\text{H}_2\text{O}]}$$

b.

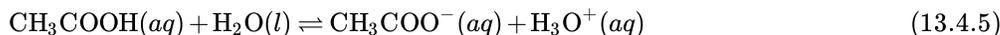
$$K_c = \frac{[\text{CO}]^2}{[\text{CO}_2]}$$

c.

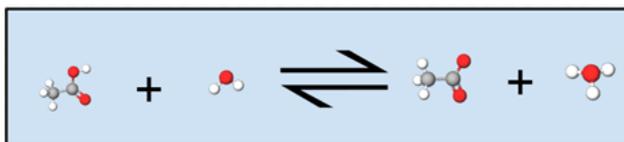
$$K_c = \frac{[\text{H}_2\text{O}]}{[\text{H}_2]}$$

The equilibrium law can be shown experimentally to apply to dilute liquid solutions as well as to mixtures of gases, and the equilibrium-constant expression for a solution reaction can be obtained in the same way as for a gas-phase reaction.

Acetic acid, for example, reacts as follows when it dissolves in water:



Notice in the figure below how the white hydrogen attached to the red oxygen on the acetic acid molecule is transferred to water, forming acetate (acetic acid minus a hydrogen) and a hydronium ion. Symbolically in the equation above, we can see this same transfer, except hydrogen is represented as an H rather than a white ball.



In solution only the concentrations of the solute species are explicitly shown in the equilibrium law. Even though the solvent may be a reactant or product, as long as the solution is dilute, any small amount of water produced or used by the chemical reaction will not change the amount of water to an appreciable extent because it is the solvent. As the solvent, water is assigned an activity equal to 1. Thus the activity of water is conventionally not explicitly written as part of the equilibrium law for a reaction in aqueous solution. Since it applies to a weak acid,  $K_a$  is called an **acid constant**. (The  $a$  stands for acid.) Other equilibrium constants in which the activity of the solvent water has a value of 1 and is thus not explicitly included in the equilibrium law are the **base constant**,  $K_b$ , for ionization of a weak base and the solubility product constant,  $K_{sp}$ , for dissolution of a slightly soluble compound.

#### Definition: Activity of the Solvent

The activity of the solvent in a dilute solution has a defined value of 1. This activity is part of the equilibrium law, but it is conventionally not written in the equilibrium law because its numerical value of 1 does not change the numerical value of the equilibrium constant.

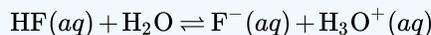
#### Note

It is a common error to claim that the molar concentration of the solvent is in some way involved in the equilibrium law. This error is a result of a misunderstanding of solution thermodynamics. For example, it is often claimed that  $K_c = K_{eq}[\text{H}_2\text{O}]$  for aqueous solutions. This equation is incorrect because it is an erroneous interpretation of the correct equation  $K_c = K_{eq}(a_{\text{H}_2\text{O}})$ . Because  $a_{\text{H}_2\text{O}} = 1$  for a dilute solution,  $K_a = K_{eq}(1)$ , or  $K_a = K_{eq}$ .

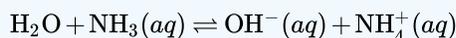
#### Example 13.4.4: Ionic Equilibria

Write out expressions for the equilibrium constants for the following ionic equilibria in dilute aqueous solution:

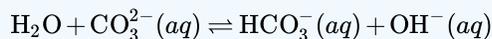
a.



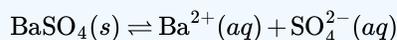
b.



c.



d.



**Solution**

We do not explicitly include the activity of  $\text{H}_2\text{O}$  in the first three examples and the activity of solid  $\text{BaSO}_4$  in the fourth because in all of these cases, the activity of the specific species is equal to 1, and thus would not change the numerical value of the equilibrium constant.

$$\text{a.} \quad K_a = K_c = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]}$$

$$\text{b.} \quad K_b = K_c = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

$$\text{c.} \quad K_b = K_c = \frac{[\text{HCO}_3^-][\text{OH}^-]}{[\text{CO}_3^{2-}]}$$

$$\text{d.} \quad K_{sp} = K_c = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$$

### ✓ Example 13.4.5 : Acetic Acid

Measurements of the conductivities of acetic acid solutions indicate that the fraction of acetic acid molecules converted to acetate and hydronium ions is

- a. 0.0296 at a concentration of  $0.020\ 00\ \text{mol dm}^{-3}$
- b. 0.5385 at a concentration of  $2.801 \times 10^{-5}\ \text{mol dm}^{-3}$

Use these data to calculate the equilibrium constant for Equation (5) at each concentration.

#### Solution

Consider first  $1\ \text{dm}^3$  of solution *a*. This originally contained  $0.02\ \text{mol CH}_3\text{COOH}$  of which the fraction 0.0296 has ionized. Thus  $(1 - 0.0296) \times 0.02\ \text{mol}$  undissociated  $\text{CH}_3\text{COOH}$  is left, while  $0.0296 \times 0.02\ \text{mol H}_3\text{O}^+$  and  $\text{CH}_3\text{COO}^-$  have been produced. In tabular form

Substance	Original Amount	Amount Produced	Equilibrium Amount	Equilibrium Concentration
$\text{CH}_3\text{COOH}$	$0.02\ \text{mol}$	$-0.0296 \times 0.02\ \text{mol}$	$(0.02 - 0.000\ 592)\ \text{mol}$	$0.0194\ \text{mol dm}^{-3}$
$\text{H}_3^+$	$0\ \text{mol}$	$+0.0296 \times 0.02\ \text{mol}$	$0.000\ 592\ \text{mol}$	$5.92 \times 10^{-4}\ \text{mol dm}^{-3}$
$\text{CH}_3\text{COO}^-$	$0\ \text{mol}$	$+0.0296 \times 0.02\ \text{mol}$	$0.000\ 592\ \text{mol}$	$5.92 \times 10^{-4}\ \text{mol dm}^{-3}$

Substituting into the expression for  $K_a$  gives

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = \frac{(5.92 \times 10^{-4})^2}{0.0194} = 1.81 \times 10^{-5}$$

A similar calculation on the second solution yields

$$K_a = \frac{(1.5083 \times 10^{-5})^2}{1.2926 \times 10^{-5}} = 1.760 \times 10^{-5}$$

#### Note

The two values of the equilibrium constant are only in approximate agreement. In more concentrated solutions the agreement is worse. If the concentration is  $1\ \text{mol dm}^{-3}$ , for instance,  $K_a$  has the value  $1.41 \times 10^{-5}$ . This is the reason for our statement that the equilibrium law applies to *dilute* solutions.

### Acknowledgements

molview.org was used to create the molecular representations found on this webpage. Check out the site at the following link: [Molview](https://molview.org).

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