Chemical Equilibrium

Chapter 14

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Chapter Outline

14.1 The Concept of Equilibrium and the Equilibrium Constant

14.2 Writing Equilibrium Constant Expressions

14.3 The Relationship Between Chemical Kinetics and Chemical Equilibrium

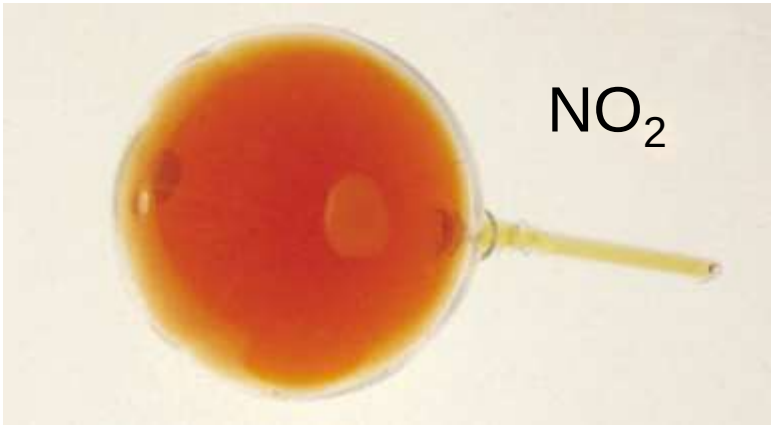
14.4 What Does the Equilibrium Constant Tell Us?

14.5 Factors that Affect Chemical Equilibrium

Equilibrium is a state in which there are no observable changes as time goes by.

Chemical equilibrium is achieved when:

- the rates of the forward and reverse reactions are equal and
- the concentrations of the reactants and products remain constant



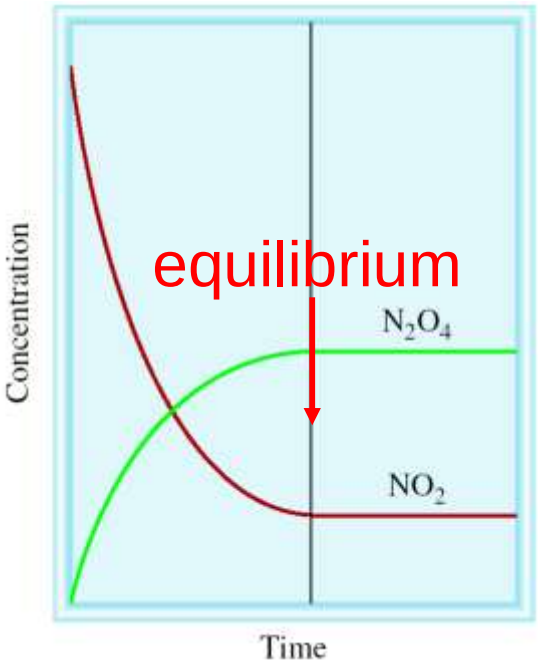
Physical equilibrium

$$H_2O\ (l) \rightleftharpoons H_2O\ (g)$$

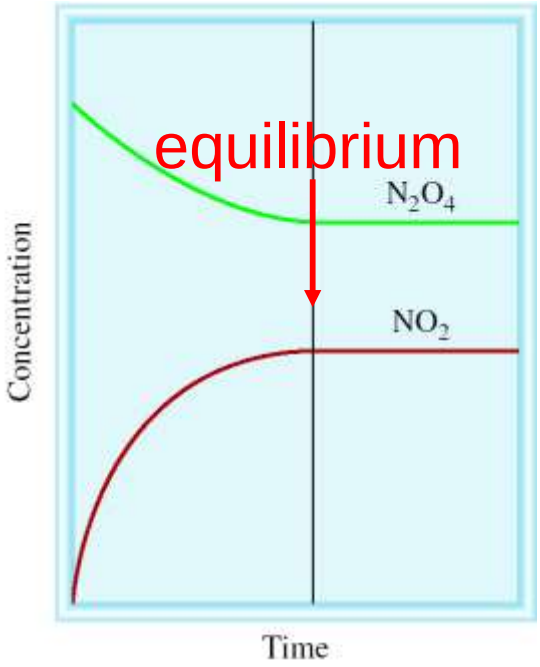
Chemical equilibrium

$$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$$

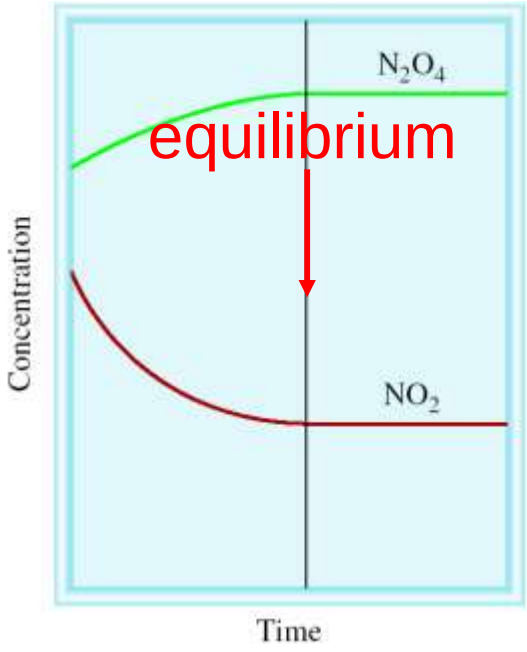
$$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$$



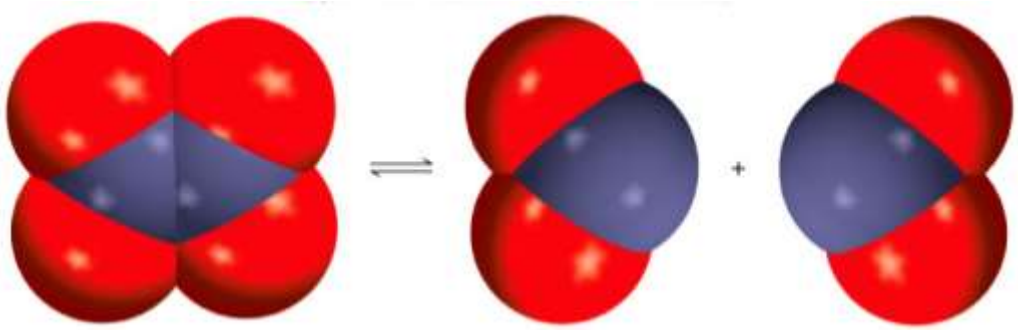
Start with NO_2

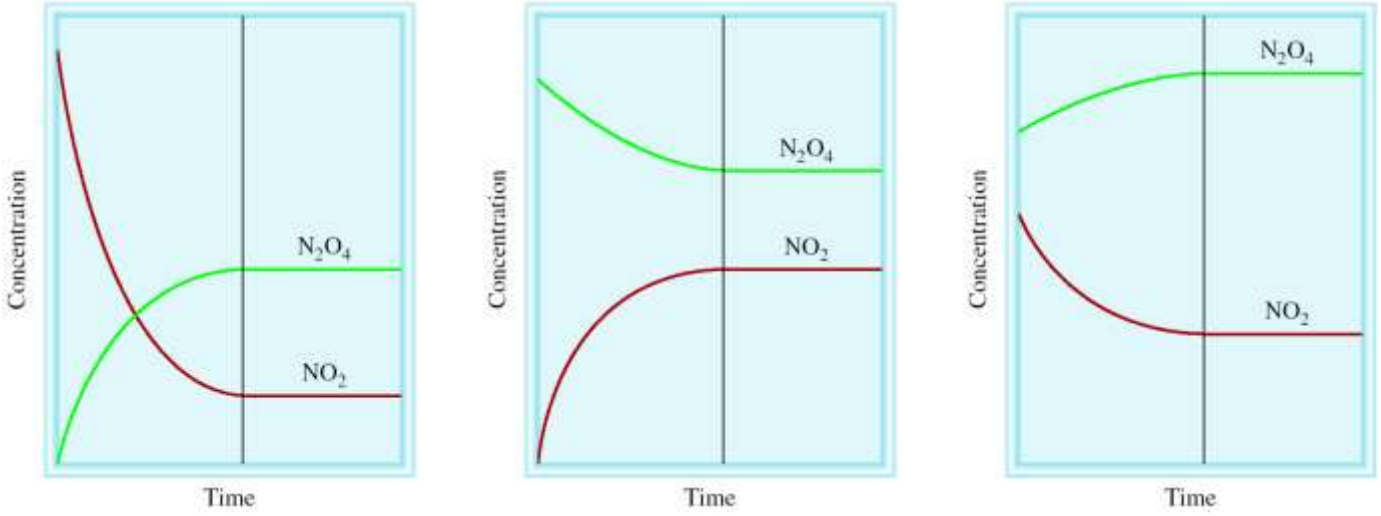


Start with N_2O_4



Start with NO_2 & N_2O_4





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constant

Table 15.1 The NO_2–N_2O_4 System at 25°C

Initial Concentrations (M)		Equilibrium Concentrations (M)		Ratio of Concentrations at Equilibrium	
$[NO_2]$	$[N_2O_4]$	$[NO_2]$	$[N_2O_4]$	$\frac{[NO_2]}{[N_2O_4]}$	$\frac{[NO_2]^2}{[N_2O_4]}$
0.000	0.670	0.0547	0.643	0.0851	4.65×10^{-3}
0.0500	0.446	0.0457	0.448	0.102	4.66×10^{-3}
0.0300	0.500	0.0475	0.491	0.0967	4.60×10^{-3}
0.0400	0.600	0.0523	0.594	0.0880	4.60×10^{-3}
0.200	0.000	0.0204	0.0898	0.227	4.63×10^{-3}

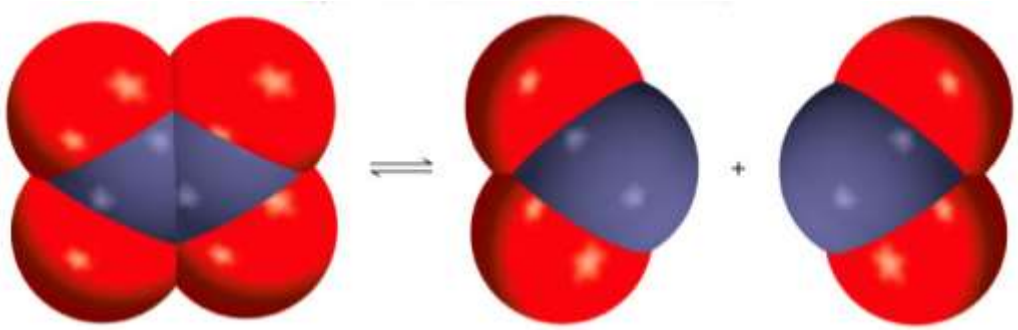
$$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$$

$$K = \frac{[NO_2]^2}{[N_2O_4]} = 4.63 \times 10^{-3}$$

$$aA + bB \rightleftharpoons cC + dD$$

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

Law of Mass Action

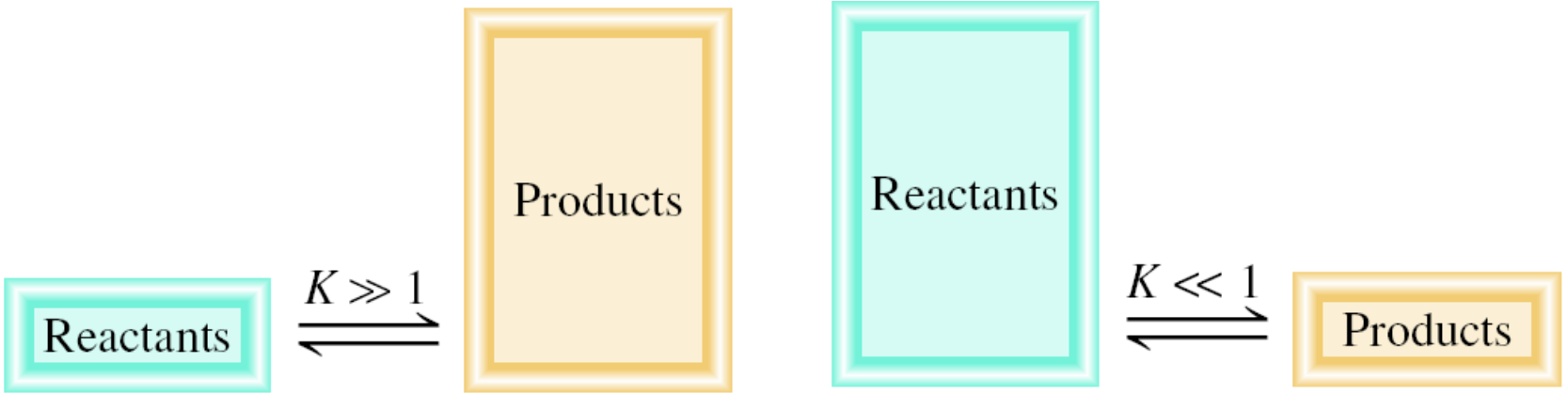


$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$$aA + bB \rightleftharpoons cC + dD$$

Equilibrium Will

$K >> 1$	Lie to the right	Favor products
$K << 1$	Lie to the left	Favor reactants



Homogenous equilibrium applies to reactions in which all reacting species **are in the same phase.**

$$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} \qquad K_p = \frac{P_{NO_2}^{\,2}}{P_{N_2O_4}}$$

In most cases

$$K_c \neq K_p$$

$$a\mathrm{A}\,(g) + b\mathrm{B}\,(g) \rightleftharpoons c\mathrm{C}\,(g) + d\mathrm{D}\,(g)$$

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

Δn = moles of gaseous products – moles of gaseous reactants

= $(c + d) - (a + b)$

Homogeneous Equilibrium

$$CH_3COOH\,(aq) + H_2O\,(l) \rightleftharpoons CH_3COO^-\,(aq) + H_3O^+\,(aq)$$

$$K_c' = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH][H_2O]} \qquad [H_2O] = \text{constant}$$

$$K_c = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = K_c'\,[H_2O]$$

General practice **not** to include units for the equilibrium constant.

Example 15.1

Write expressions for K_c, and K_P if applicable, for the following reversible reactions at equilibrium:

(a) $HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$

(b) $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

(c) $CH_3COOH(aq) + C_2H_5OH(aq) \rightleftharpoons CH_3COOC_2H_5(aq) + H_2O(l)$

Example 15.1

Strategy

Keep in mind the following facts: (1) the K_P expression applies only to gaseous reactions and (2) the concentration of solvent (usually water) does not appear in the equilibrium constant expression.

Example 15.1

Solution

(a) Because there are no gases present, K_P does not apply and we have only K_c.

$$K_c' = \frac{[H_3O^+][F^-]}{[HF][H_2O]}$$

HF is a weak acid, so that the amount of water consumed in acid ionizations is negligible compared with the total amount of water present as solvent. Thus, we can rewrite the equilibrium constant as

$$\boldsymbol{K_c = \frac{[H_3O^+][F^-]}{[HF]}}$$

Example 15.1

(b)

$$K_c = \frac{[NO_2]^2}{[NO]^2[O_2]} \qquad K_p = \frac{P_{NO_2}^2}{P_{NO}^2 P_{O_2}}$$

(c) The equilibrium constant K_c' is given by

$$K_c' = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

Because the water produced in the reaction is negligible compared with the water solvent, the concentration of water does not change. Thus, we can write the new equilibrium constant as

$$K_c = \frac{[CH_3COOC_2H_5]}{[CH_3COOH][C_2H_5OH]}$$

Example 15.2

The equilibrium constant K_P for the decomposition of phosphorus pentachloride to phosphorus trichloride and molecular chlorine

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

is found to be 1.05 at 250°C. If the equilibrium partial pressures of PCl_5 and PCl_3 are 0.875 atm and 0.463 atm, respectively, what is the equilibrium partial pressure of Cl_2 at 250°C?

Example 15.2

Strategy

The concentrations of the reacting gases are given in atm, so we can express the equilibrium constant in K_P. From the known K_P value and the equilibrium pressures of PCl_3 and PCl_5, we can solve for P_{Cl_2}.

Example 15.2

Solution

First, we write K_P in terms of the partial pressures of the reacting species

$$K_p = \frac{P_{PCl_3} P_{Cl_2}}{P_{PCl_5}}$$

Knowing the partial pressures, we write

$$1.05 = \frac{(0.463)(P_{Cl_2})}{(0.875)}$$

or

$$P_{Cl_2} = \frac{(1.05)(0.875)}{(0.463)} = \mathbf{1.98\ atm}$$

Example 15.2

Check

Note that we have added atm as the unit for P_{Cl_2}.

Example 15.3

Methanol (CH_3OH) is manufactured industrially by the reaction

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

The equilibrium constant (K_c) for the reaction is 10.5 at 220°C. What is the value of K_P at this temperature?

Example 15.3

Strategy

The relationship between K_c and K_P is given by Equation (15.5). What is the change in the number of moles of gases from reactants to product? Recall that

Δn = moles of gaseous products - moles of gaseous reactants

What unit of temperature should we use?

Example 15.3

Solution

The relationship between K_c and K_P is

$$K_P = K_c(0.0821T)^{\Delta n}$$

Because $T = 273 + 220 = 493$ K and $\Delta n = 1 - 3 = -2$, we have

$$K_P = (10.5)\ (0.0821 \times 493)^{-2}$$
$$= \mathbf{6.41 \times 10^{-3}}$$

Example 15.3

Check

Note that K_P, like K_c, is a dimensionless quantity. This example shows that we can get a quite different value for the equilibrium constant for the same reaction, depending on whether we express the concentrations in moles per liter or in atmospheres.

Heterogenous equilibrium applies to reactions in which reactants and products **are in different phases.**

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

$$K_c' = \frac{[CaO][CO_2]}{[CaCO_3]}$$

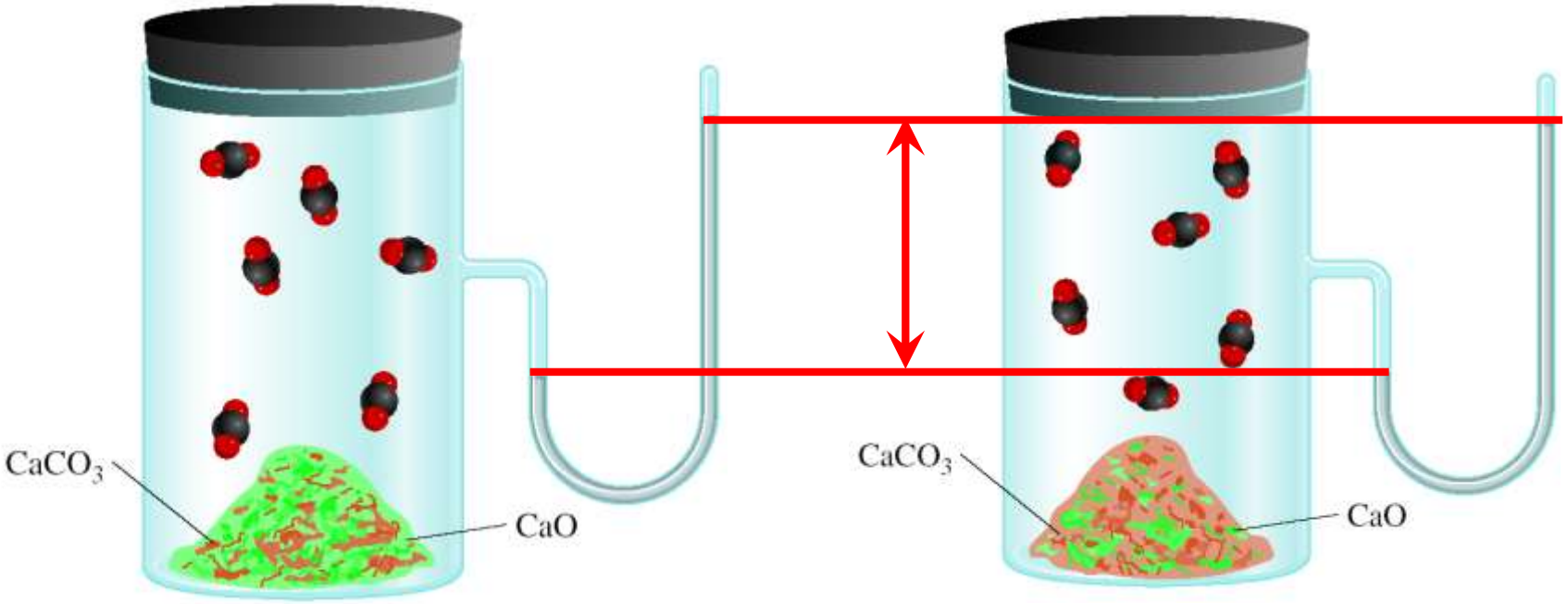
$[CaCO_3]$ = constant
$[CaO]$ = constant

$$K_c = [CO_2] = K_c' \times \frac{[CaCO_3]}{[CaO]}$$

$$K_p = P_{CO_2}$$

The concentration of **solids** and **pure liquids** are not included in the expression for the equilibrium constant.

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$$



$$P_{CO_2} = K_p$$

P_{CO_2} does not depend on the amount of $CaCO_3$ or CaO

Example 15.4

Consider the following heterogeneous equilibrium:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

At 800°C, the pressure of CO_2 is 0.236 atm. Calculate (a) K_P and (b) K_c for the reaction at this temperature.

Example 15.4

Strategy

Remember that pure solids do not appear in the equilibrium constant expression. The relationship between K_P and K_c is given by Equation (15.5).

Solution

(a) Using Equation (15.8) we write

$$K_P = P_{CO_2}$$
$$= \mathbf{0.236}$$

Example 15.4

(b) From Equation (15.5), we know

$$K_P = K_c(0.0821T)^{\Delta n}$$

In this case, $T = 800 + 273 = 1073$ K and $\Delta n = 1$, so we substitute these values in the equation and obtain

$$0.236 = K_c(0.0821 \times 1073)$$
$$K_c = \mathbf{2.68 \times 10^{-3}}$$

$$A + B \rightleftharpoons \cancel{C} + \cancel{D} \qquad K_c'$$

$$\cancel{C} + \cancel{D} \rightleftharpoons E + F \qquad K_c''$$

$$A + B \rightleftharpoons E + F \qquad K_c$$

$$K_c' = \frac{[C][D]}{[A][B]} \qquad K_c'' = \frac{[E][F]}{[C][D]}$$

$$K_c = \frac{[E][F]}{[A][B]}$$

$$K_c = K_c' \times K_c''$$

If a reaction can be expressed as the sum of two or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.

$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$

$$K = \frac{[NO_2]^2}{[N_2O_4]} = 4.63 \times 10^{-3}$$

$2NO_2\ (g) \rightleftharpoons N_2O_4\ (g)$

$$K' = \frac{[N_2O_4]}{[NO_2]^2} = \frac{1}{K} = 216$$

When the equation for a reversible reaction is written in the opposite direction, the equilibrium constant becomes the reciprocal of the original equilibrium constant.

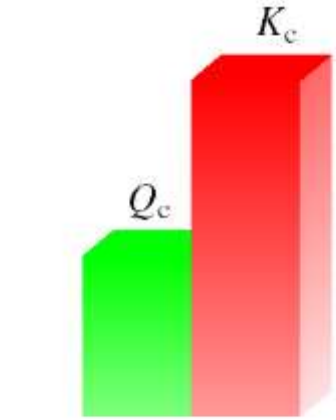
Writing Equilibrium Constant Expressions

1. The concentrations of the reacting species in the condensed phase are expressed in *M*. In the gaseous phase, the concentrations can be expressed in *M* or in atm.
2. The concentrations of pure solids, pure liquids and solvents do not appear in the equilibrium constant expressions.
3. The equilibrium constant is a dimensionless quantity.
4. In quoting a value for the equilibrium constant, you must specify the balanced equation and the temperature.
5. If a reaction can be expressed as a sum of two or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.

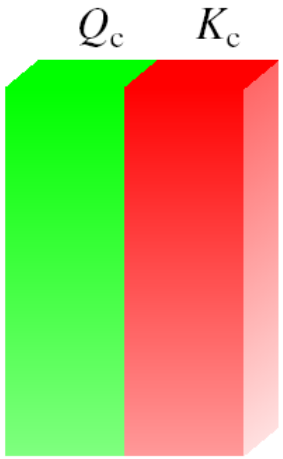
The ***reaction quotient (Q_c)*** is calculated by substituting the initial concentrations of the reactants and products into the equilibrium constant (K_c) expression.

IF

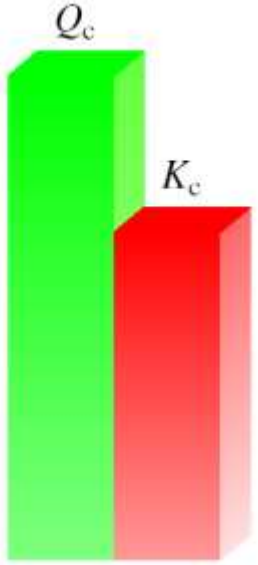
- $Q_c < K_c$ system proceeds from left to right to reach equilibrium
- $Q_c = K_c$ the system is at equilibrium
- $Q_c > K_c$ system proceeds from right to left to reach equilibrium



Reactants → Products



Equilibrium : no net change



Reactants ← Products

Example 15.5

At the start of a reaction, there are 0.249 mol N_2, 3.21 x 10^{-2} mol H_2, and 6.42 x 10^{-4} mol NH_3 in a 3.50-L reaction vessel at 375°C. If the equilibrium constant (K_c) for the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

is 1.2 at this temperature, decide whether the system is at equilibrium. If it is not, predict which way the net reaction will proceed.

Example 15.5

Strategy

We are given the initial amounts of the gases (in moles) in a vessel of known volume (in liters), so we can calculate their molar concentrations and hence the reaction quotient (Q_c). How does a comparison of Q_c with K_c enable us to determine if the system is at equilibrium or, if not, in which direction will the net reaction proceed to reach equilibrium?

Example 15.5

Solution

The initial concentrations of the reacting species are

$$[N_2]_o = \frac{0.249 \text{ mol}}{3.50 \text{ L}} = 0.0711\ M$$

$$[H_2]_o = \frac{3.21 \times 10^{-2} \text{ mol}}{3.50 \text{ L}} = 9.17 \times 10^{-3}\ M$$

$$[NH_3]_o = \frac{6.42 \times 10^{-4} \text{ mol}}{3.50 \text{ L}} = 1.83 \times 10^{-4}\ M$$

Example 15.5

Next we write

$$Q_c = \frac{[NH_3]_o^2}{[N_2]_o[H_2]_o^3} = \frac{(1.83 \times 10^{-4})^2}{(0.0711)(9.17 \times 10^{-3})^3} = 0.611$$

Because Q_c is smaller than K_c (1.2), the system is not at equilibrium. The net result will be an increase in the concentration of NH_3 and a decrease in the concentrations of N_2 and H_2. That is, the net reaction will proceed from left to right until equilibrium is reached.

Calculating Equilibrium Concentrations

1. Express the equilibrium concentrations of all species in terms of the initial concentrations and a single unknown *x*, which represents the change in concentration.
2. Write the equilibrium constant expression in terms of the equilibrium concentrations. Knowing the value of the equilibrium constant, solve for *x*.
3. Having solved for *x*, calculate the equilibrium concentrations of all species.

Example 15.6

A mixture of 0.500 mol H_2 and 0.500 mol I_2 was placed in a 1.00-L stainless-steel flask at 430°C. The equilibrium constant K_c for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is 54.3 at this temperature. Calculate the concentrations of H_2, I_2, and HI at equilibrium.

Example 15.6

Strategy

We are given the initial amounts of the gases (in moles) in a vessel of known volume (in liters), so we can calculate their molar concentrations. Because initially no HI was present, the system could not be at equilibrium. Therefore, some H_2 would react with the same amount of I_2 (why?) to form HI until equilibrium was established.

Example 15.6

Solution We follow the preceding procedure to calculate the equilibrium concentrations.

Step 1: The stoichiometry of the reaction is 1 mol H_2 reacting with 1 mol I_2 to yield 2 mol HI. Let *x* be the depletion in concentration (mol/L) of H_2 and I_2 at equilibrium. It follows that the equilibrium concentration of HI must be 2*x*. We summarize the changes in concentrations as follows:

	H_2 +	I_2	$\rightleftharpoons$	2HI
Initial (*M*):	0.500	0.500		0.000
Change (*M*):	- *x*	- *x*		+ 2*x*
Equilibrium (*M*):	(0.500 - *x*)	(0.500 - *x*)		2*x*

Example 15.6

Step 2: The equilibrium constant is given by

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

Substituting, we get

$$54.3 = \frac{(2x)^2}{(0.500 - x)(0.500 - x)}$$

Taking the square root of both sides, we get

$$7.37 = \frac{2x}{0.500 - x}$$

$$x = 0.393\ M$$

Example 15.6

Step 3: At equilibrium, the concentrations are

$$[H_2] = (0.500 - 0.393)\ M = \mathbf{0.107\ M}$$
$$[I_2] = (0.500 - 0.393)\ M = \mathbf{0.107\ M}$$
$$[HI] = 2 \times 0.393\ M = \mathbf{0.786\ M}$$

Check You can check your answers by calculating K_c using the equilibrium concentrations. Remember that K_c is a constant for a particular reaction at a given temperature.

Example 15.7

For the same reaction and temperature as in Example 15.6, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, suppose that the initial concentrations of H_2, I_2, and HI are 0.00623 *M*, 0.00414 *M*, and 0.0224 *M*, respectively. Calculate the concentrations of these species at equilibrium.

Example 15.7

Strategy

From the initial concentrations we can calculate the reaction quotient (Q_c) to see if the system is at equilibrium or, if not, in which direction the net reaction will proceed to reach equilibrium. A comparison of Q_c with K_c also enables us to determine if there will be a depletion in H_2 and I_2 or HI as equilibrium is established.

Example 15.7

Solution

First we calculate Q_c as follows:

$$Q_c = \frac{[HI]_0^2}{[H_2]_0[I_2]_0} = \frac{(0.0224)^2}{(0.00623)(0.00414)} = 19.5$$

Because Q_c (19.5) is smaller than K_c (54.3), we conclude that the net reaction will proceed from left to right until equilibrium is reached (see Figure 15.4); that is, there will be a depletion of H_2 and I_2 and a gain in HI.

Example 15.7

Step 1: Let *x* be the depletion in concentration (mol/L) of H_2 and I_2 at equilibrium. From the stoichiometry of the reaction it follows that the increase in concentration for HI must be 2*x*. Next we write

	H_2 +	I_2	$\rightleftharpoons$	2HI
Initial (*M*):	0.00623	0.00414		0.0224
Change (*M*):	- *x*	- *x*		+ 2*x*
Equilibrium (*M*):	(0.00623 - *x*)	(0.00414 - *x*)		(0.0224 + 2*x*)

Example 15.7

Step 2: The equilibrium constant is

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

Substituting, we get

$$54.3 = \frac{(0.0224 + 2x)^2}{(0.00623 - x)(0.00414 - x)}$$

It is not possible to solve this equation by the square root shortcut, as the starting concentrations $[H_2]$ and $[I_2]$ are unequal. Instead, we must first carry out the multiplications

$$54.3(2.58 \times 10^{-5} - 0.0104x + x^2) = 5.02 \times 10^{-4} + 0.0896x + 4x^2$$

Example 15.7

Collecting terms, we get

$$50.3x^2 - 0.654x + 8.98 \times 10^{-4} = 0$$

This is a quadratic equation of the form $ax^2 + bx + c = 0$. The solution for a quadratic equation (see Appendix 4) is

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Here we have $a = 50.3$, $b = -0.654$, and $c = 8.98 \times 10^{-4}$, so that

$$x = \frac{0.654 \pm \sqrt{(-0.654)^2 - 4(50.3)(8.98 \times 10^{-4})}}{2 \times 50.3}$$

$$x = 0.0114\ M \qquad \text{or} \qquad x = 0.00156\ M$$

Example 15.7

The first solution is physically impossible because the amounts of H_2 and I_2 reacted would be more than those originally present. The second solution gives the correct answer. Note that in solving quadratic equations of this type, one answer is always physically impossible, so choosing a value for *x* is easy.

Step 3: At equilibrium, the concentrations are

$$[H_2] = (0.00623 - 0.00156)\ M = \mathbf{0.00467\ M}$$

$$[I_2] = (0.00414 - 0.00156)\ M - \mathbf{0.00258\ M}$$

$$[HI] = (0.0224 + 2 \times 0.00156)\ M = \mathbf{0.0255\ M}$$

Example 15.7

Check

You can check the answers by calculating K_c using the equilibrium concentrations. Remember that K_c is a constant for a particular reaction at a given temperature.