Biophysical chemistry

Part A
Chapter: 2
Chemical Equilibrium
Lecture - 1

Fahmida Akter Lia
Department of Biochemistry
National Institute of Science and Technology(NIST)

Chemical Equilibrium

NATURE OF CHEMICAL EQUILIBRIUM :

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

When a chemical reaction has reached the equilibrium state, the concentrations of reactants and products remain constant over time, and there are no visible changes in the system.
However, there is much activity at the molecular level because reactant molecules continue to form product molecules while product molecules react to yield reactant molecules

Let us consider the reaction

$$A + B \leftrightarrow C + D$$

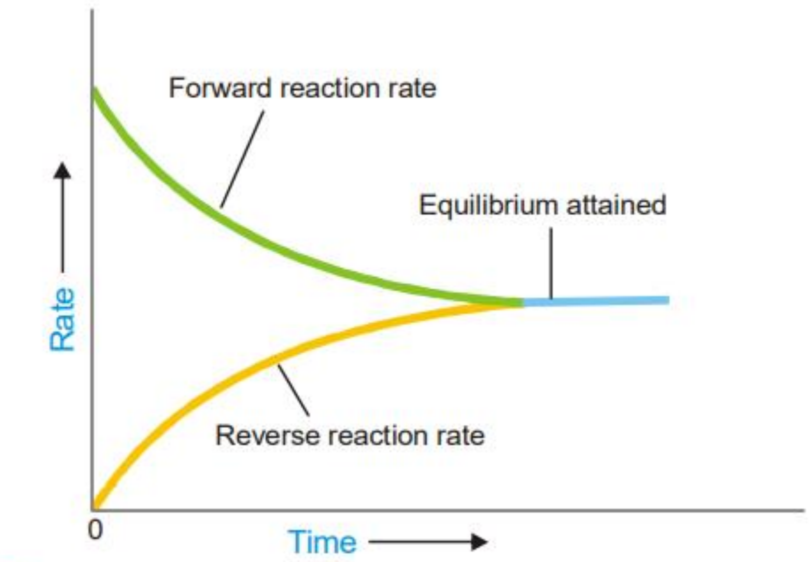
If we start with A and B in a closed vessel, the forward reaction proceeds to form C and D. The concentrations of A and B decrease and those of C and D increase continuously. As a result the rate of forward reaction also decreases and the rate of the reverse reaction increases. Eventually, the rate of the two opposing reactions equals and the system attains a state of equilibrium

Chemical Equilibrium

Chemical equilibrium may be defined as:

the state of a reversible reaction when the two opposing reactions occur at the same rate and the concentrations of reactants and products do not change with time.

Furthermore, the true equilibrium of a reaction can be attained from both sides. Thus the equilibrium concentrations of the reactants and products are the same whether we start with A and B, or C and D



■ **Figure 17.1**
At equilibrium the forward reaction rate equals the reverse reaction rate.

Chemical Equilibrium

Chemical Equilibrium is Dynamic Equilibrium

The dynamic nature of chemical equilibrium can be easily understood on the basis of the kinetic molecular model. The molecules of A and B in the equilibrium mixture collide with each other to form C and D. Likewise C and D collide to give back A and B. The collisions of molecules in a closed system is a ceaseless phenomenon. Therefore collisions of A and B giving C and D (Forward reaction) and collisions of C and D giving back A and B (reverse reaction) continue to occur even at equilibrium, while concentrations remain unchanged.

LAW OF MASS ACTION

Two Norwegian chemists, Guldberg and Waage, studied experimentally a large number of equilibrium reactions. In 1864, they postulated a generalization called the Law of Mass action. It states that :

the rate of a chemical reaction is proportional to the active masses of the reactants.

By the term 'active mass' is meant the molar concentration i.e., number of moles per litre. It is expressed by enclosing the formula of the substance in square brackets.

$$\text{Rate of reaction} \propto [A]\,[B]$$
$$= k\,[A]\,[B]$$

EQUILIBRIUM CONSTANT : EQUILIBRIUM LAW

Let us consider a general reaction

$$A + B \leftrightarrow C + D$$

and let [A], [B], [C] and [D] represent the molar concentrations of A, B, C and D at the equilibrium point. According to the Law of Mass action.

Rate of forward reaction ∝ [A] [B] = k1 [A] [B]

Rate of reverse reaction ∝ [C][D] = k2 [C][D]

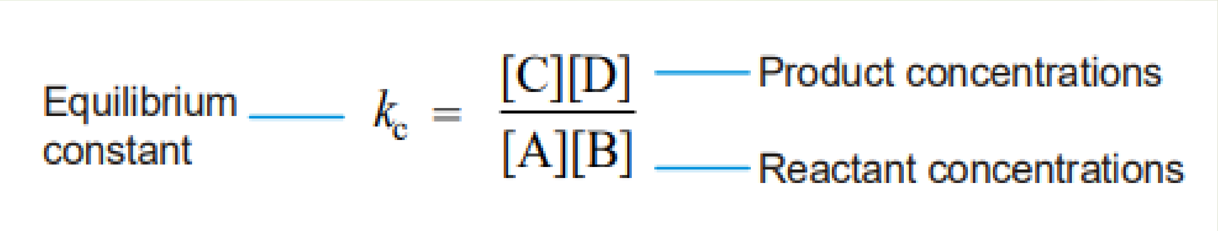
where k1 and k2 are rate constants for the forward and reverse reactions. At equilibrium,

rate of forward reaction = rate of reverse reaction. Therefore,

k1[A] [B] = k2 [C] [D] or

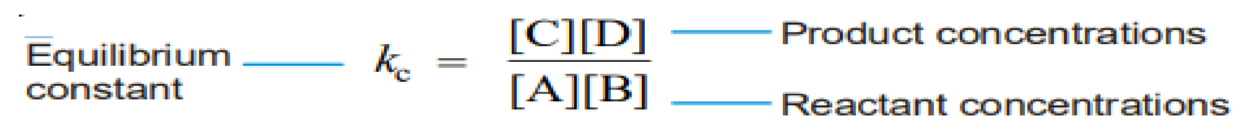
$$= \frac{K_1}{K_2} = \frac{[C]\ [D]}{[A]\ [B]}$$

At any specific temperature k1/k2 is constant since both k1 and k2 are constants. The ratio k1/k2 is called Equilibrium constant and is represented by the symbol Kc , or simply k.



$$k_c = \frac{[C][D]}{[A][B]}$$

EQUILIBRIUM CONSTANT : EQUILIBRIUM LAW



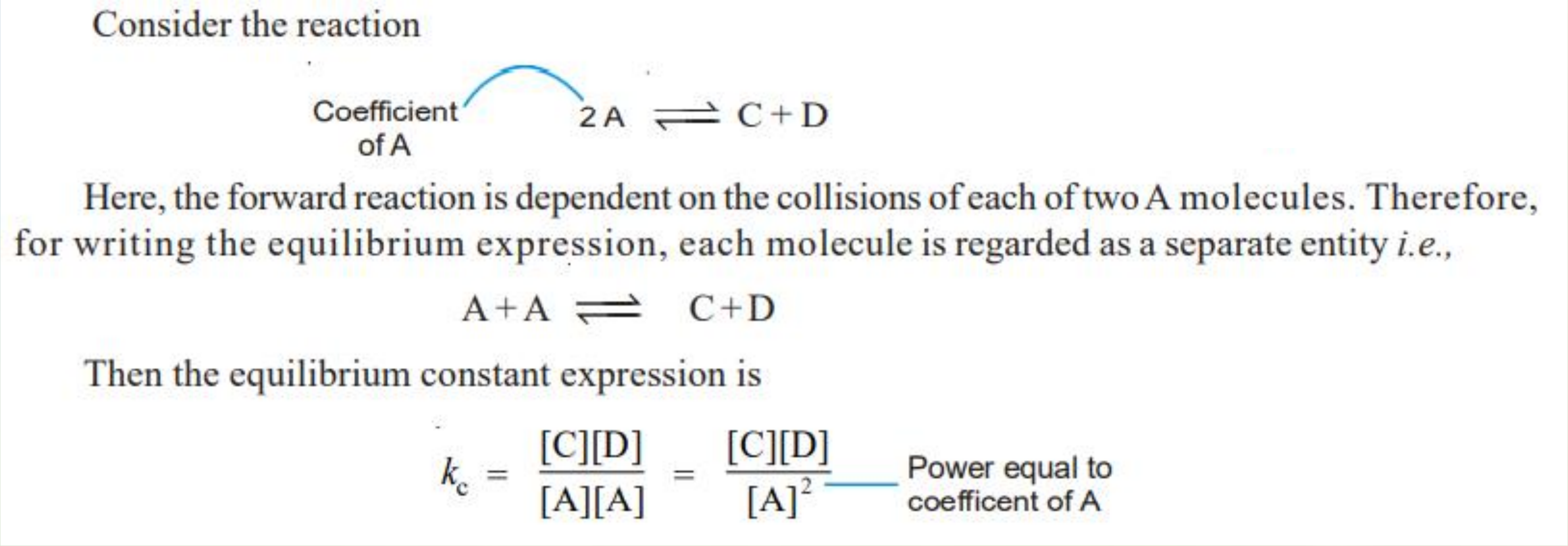
Equilibrium constant

$$k_c = \frac{[C][D]}{[A][B]}$$

Product concentrations

Reactant concentrations

This equation is known as the Equilibrium constant expression or Equilibrium law



Consider the reaction

Coefficient of A

$$2\,A \rightleftharpoons C + D$$

Here, the forward reaction is dependent on the collisions of each of two A molecules. Therefore, for writing the equilibrium expression, each molecule is regarded as a separate entity *i.e.,*

$$A + A \rightleftharpoons C + D$$

Then the equilibrium constant expression is

$$k_c = \frac{[C][D]}{[A][A]} = \frac{[C][D]}{[A]^2}$$

Power equal to coefficent of A

As a general rule, if there are two or more molecules of the same substance in the chemical equation, its concentration is raised to the power equal to the numerical coefficient of the substance in the equation

EQUILIBRIUM CONSTANT : EQUILIBRIUM LAW

Equilibrium Constant Expression for a Reaction in General Terms The general reaction may be written as

$$aA + bB \leftrightarrow cC + dD$$

where a, b, c and d are numerical quotients of the substance, A, B, C and D respectively.

The equilibrium constant expression is

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

It is the mathematical expression of their law of mass action, which holds that for a reversible reaction at equilibrium and a constant temperature, a certain ratio of reactant and product concentrations has a constant value, K (the equilibrium constant).

EQUILIBRIUM CONSTANT EXPRESSION IN TERMS OF PARTIAL PRESSURES

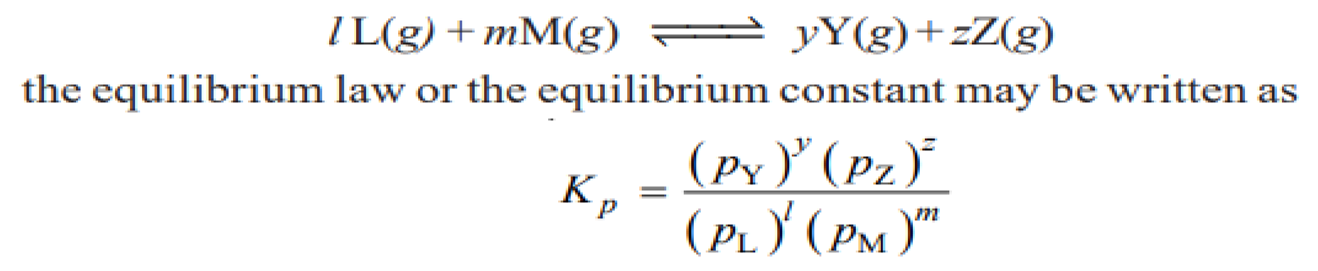
The relationship between the partial pressure (p) of any one gas in the equilibrium mixture and the molar concentration follows from the general ideal gas equation

$$pV = nRT \quad \text{or} \quad p = \left(\frac{n}{V}\right) RT$$

The quantity n/V is the number of moles of the gas per unit volume and is simply the molar concentration. Thus,

p = (Molar concentration) × RT

i.e.,the partial pressure of a gas in the equilibrium mixture is directly proportional to its molar concentration at a given temperature. Therefore, we can write the equilibrium constant expression in terms of partial pressure instead of molar concentrations. For a general reaction

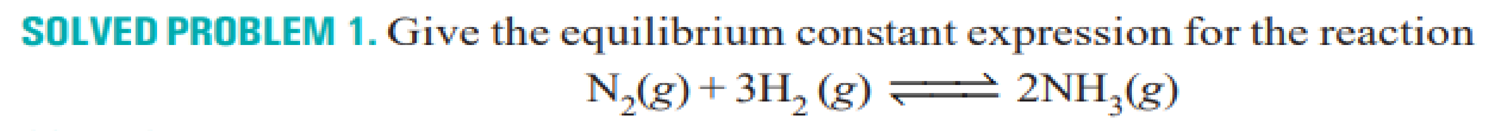


$$l\,\mathrm{L}(g) + m\mathrm{M}(g) \rightleftharpoons y\mathrm{Y}(g) + z\mathrm{Z}(g)$$

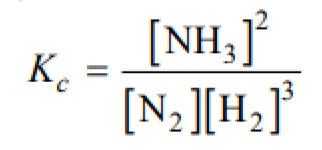
the equilibrium law or the equilibrium constant may be written as

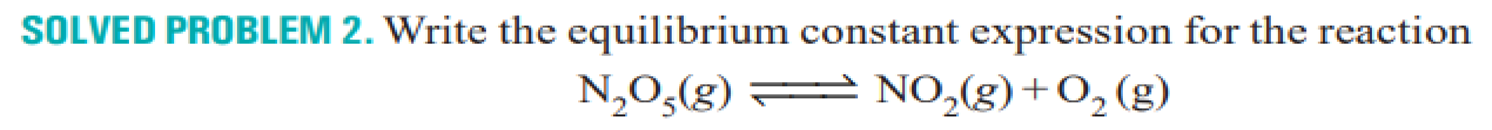
$$K_p = \frac{(p_\mathrm{Y})^y\,(p_\mathrm{Z})^z}{(p_\mathrm{L})^l\,(p_\mathrm{M})^m}$$

EQUILIBRIUM CONSTANT : EQUILIBRIUM LAW


SOLVED PROBLEM 1. Give the equilibrium constant expression for the reaction

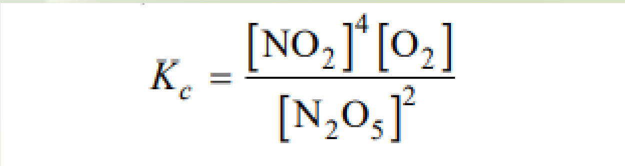
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

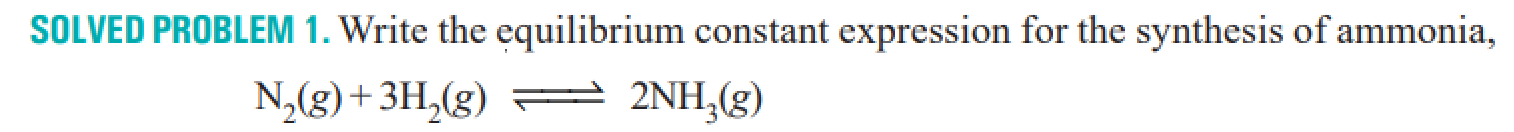

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$


SOLVED PROBLEM 2. Write the equilibrium constant expression for the reaction

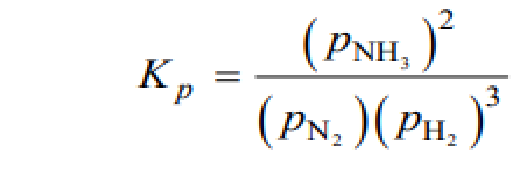
$$N_2O_5(g) \rightleftharpoons NO_2(g) + O_2(g)$$


$$2N_2O_5 \rightleftharpoons 4NO_2(g) + O_2$$


$$K_c = \frac{[NO_2]^4[O_2]}{[N_2O_5]^2}$$


SOLVED PROBLEM 1. Write the equilibrium constant expression for the synthesis of ammonia,

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


$$K_p = \frac{(p_{NH_3})^2}{(p_{N_2})(p_{H_2})^3}$$

HOW Kc AND Kp ARE RELATED?

Let us consider a general reaction

$$jA + kB \leftrightarrow lC + mD$$

where all reactants and products are gases. We can write the equilibrium constant expression in terms of partial pressures as

$$K_p = \frac{(p_C)^l (p_D)^m}{(p_A)^j (p_B)^k} \qquad ...(1)$$

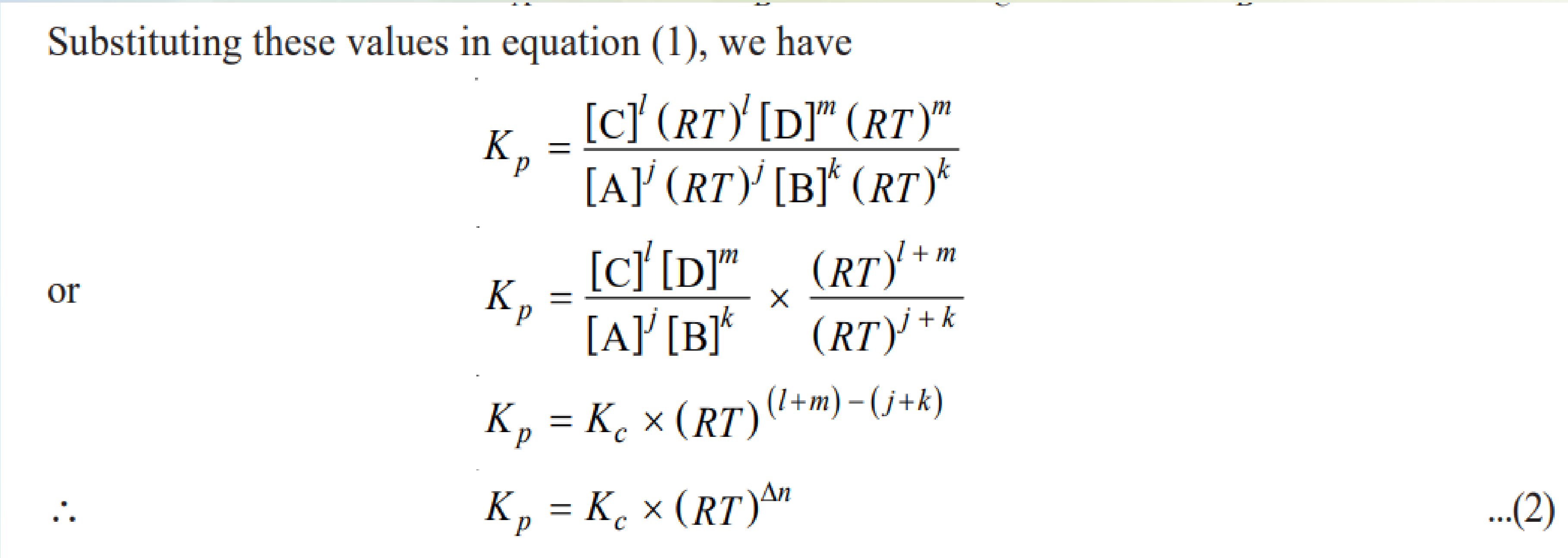
Assuming that all these gases constituting the equilibrium mixture obey the ideal gas equation, the partial pressure (p) of a gas is

$$p = (n/V)RT$$

Where n/V is the molar concentration. Thus the partial pressures of individual gases, A, B, C and D are:

$$P_A = [A]RT;\ p_B = [B]RT;\ p_C = [C]RT;\ p_D = [D]RT$$

HOW Kc AND Kp ARE RELATED?



Substituting these values in equation (1), we have

$$K_p = \frac{[C]^l (RT)^l [D]^m (RT)^m}{[A]^j (RT)^j [B]^k (RT)^k}$$

or

$$K_p = \frac{[C]^l [D]^m}{[A]^j [B]^k} \times \frac{(RT)^{l+m}}{(RT)^{j+k}}$$

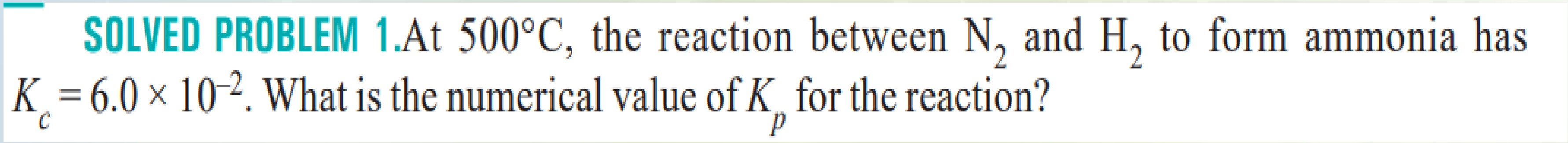
$$K_p = K_c \times (RT)^{(l+m)-(j+k)}$$

∴

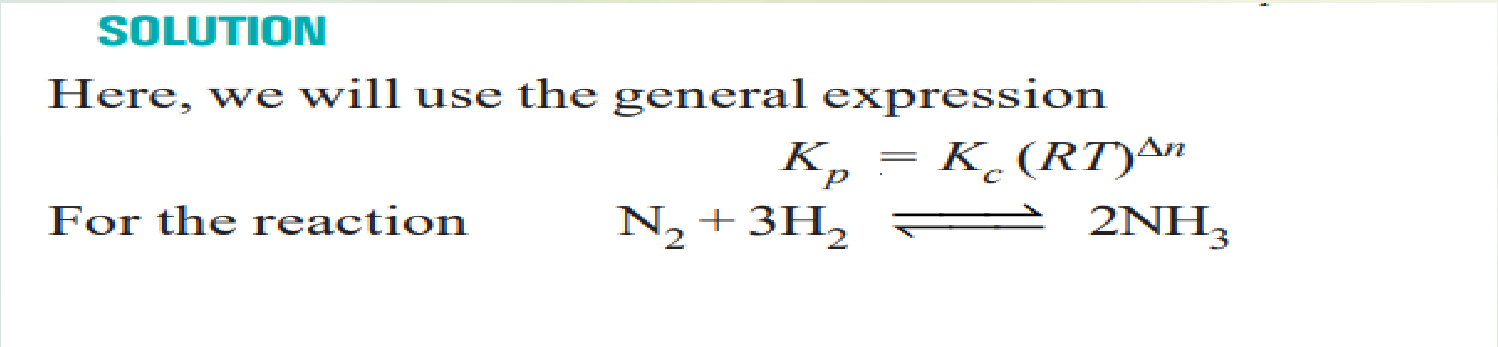
$$K_p = K_c \times (RT)^{\Delta n} \qquad ...(2)$$

From the expression (2) it is clear that when $\Delta n = 0$, $Kp = Kc$.

HOW Kc AND Kp ARE RELATED?



SOLVED PROBLEM 1. At 500°C, the reaction between N_2 and H_2 to form ammonia has $K_c = 6.0 \times 10^{-2}$. What is the numerical value of K_p for the reaction?

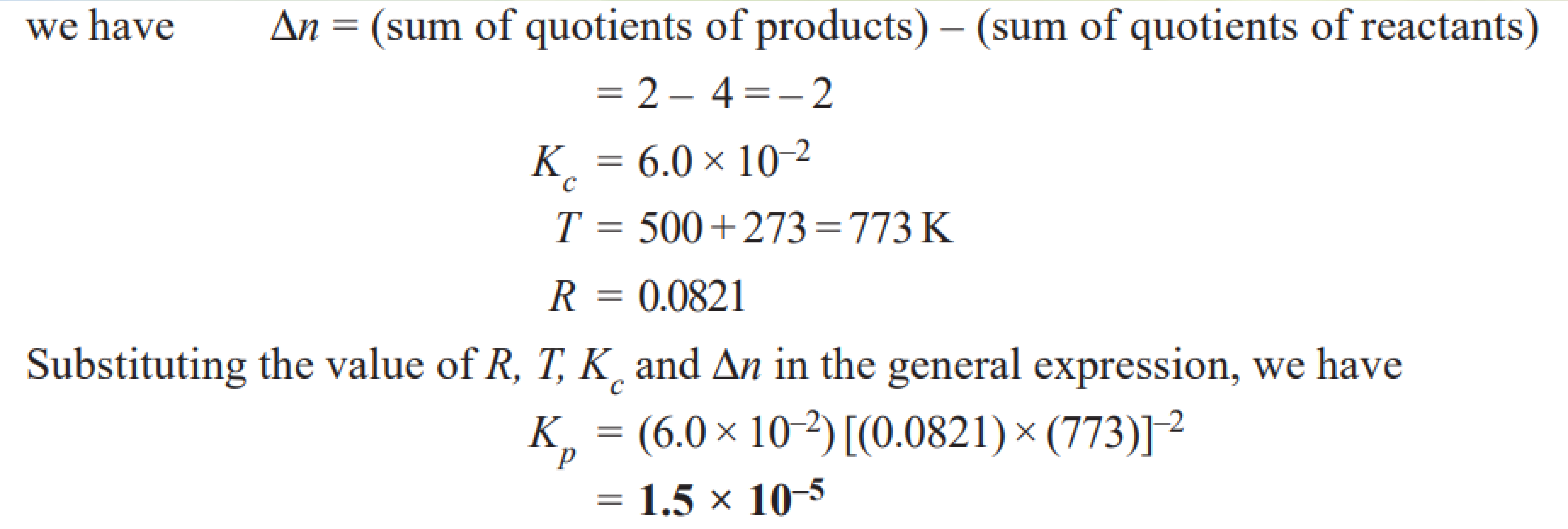


SOLUTION

Here, we will use the general expression

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

For the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$



we have Δn = (sum of quotients of products) – (sum of quotients of reactants)

$$= 2 - 4 = -2$$

$$K_c = 6.0 \times 10^{-2}$$

$$T = 500 + 273 = 773\text{ K}$$

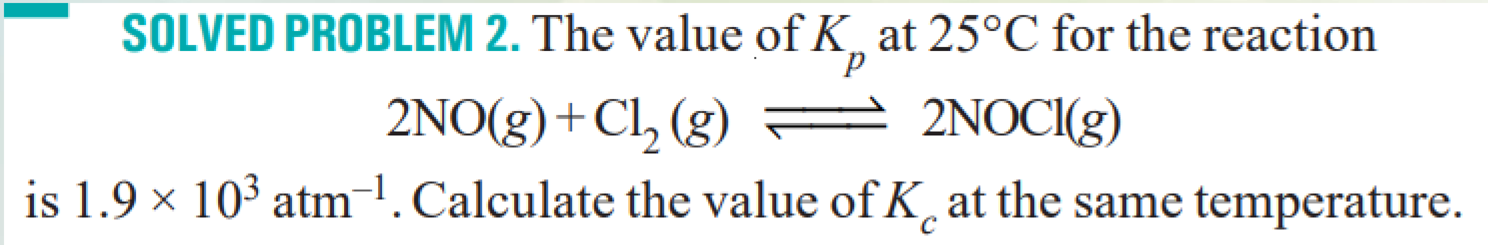
$$R = 0.0821$$

Substituting the value of R, T, K_c and Δn in the general expression, we have

$$K_p = (6.0 \times 10^{-2})\,[(0.0821) \times (773)]^{-2}$$

$$= \mathbf{1.5 \times 10^{-5}}$$

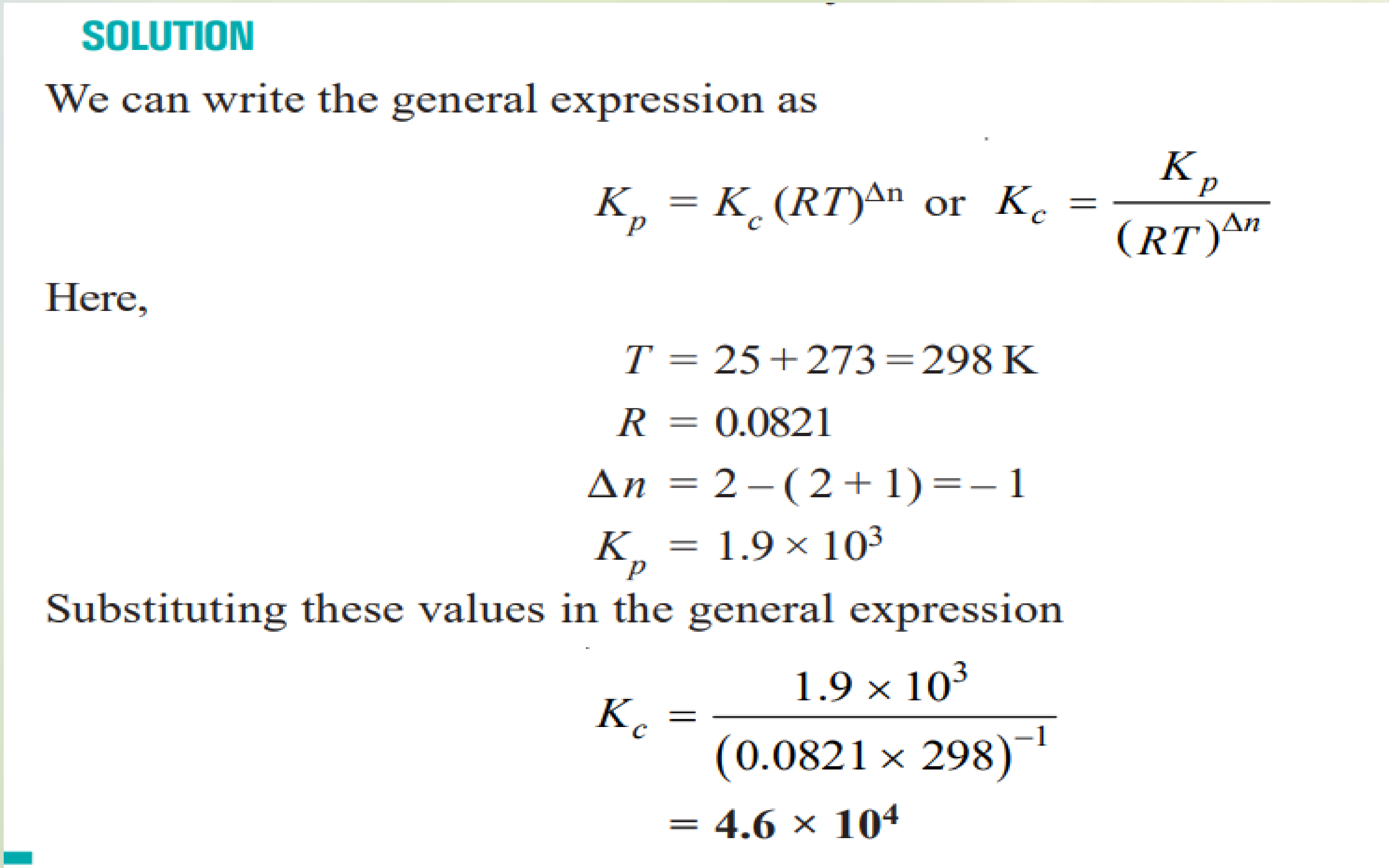
HOW Kc AND Kp ARE RELATED?



SOLVED PROBLEM 2. The value of K_p at 25°C for the reaction

$$2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$$

is 1.9×10^3 atm^{-1}. Calculate the value of K_c at the same temperature.



SOLUTION

We can write the general expression as

$$K_p = K_c(RT)^{\Delta n} \quad \text{or} \quad K_c = \frac{K_p}{(RT)^{\Delta n}}$$

Here,

$$T = 25 + 273 = 298\ \text{K}$$

$$R = 0.0821$$

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

$$K_p = 1.9 \times 10^3$$

Substituting these values in the general expression

$$K_c = \frac{1.9 \times 10^3}{(0.0821 \times 298)^{-1}}$$

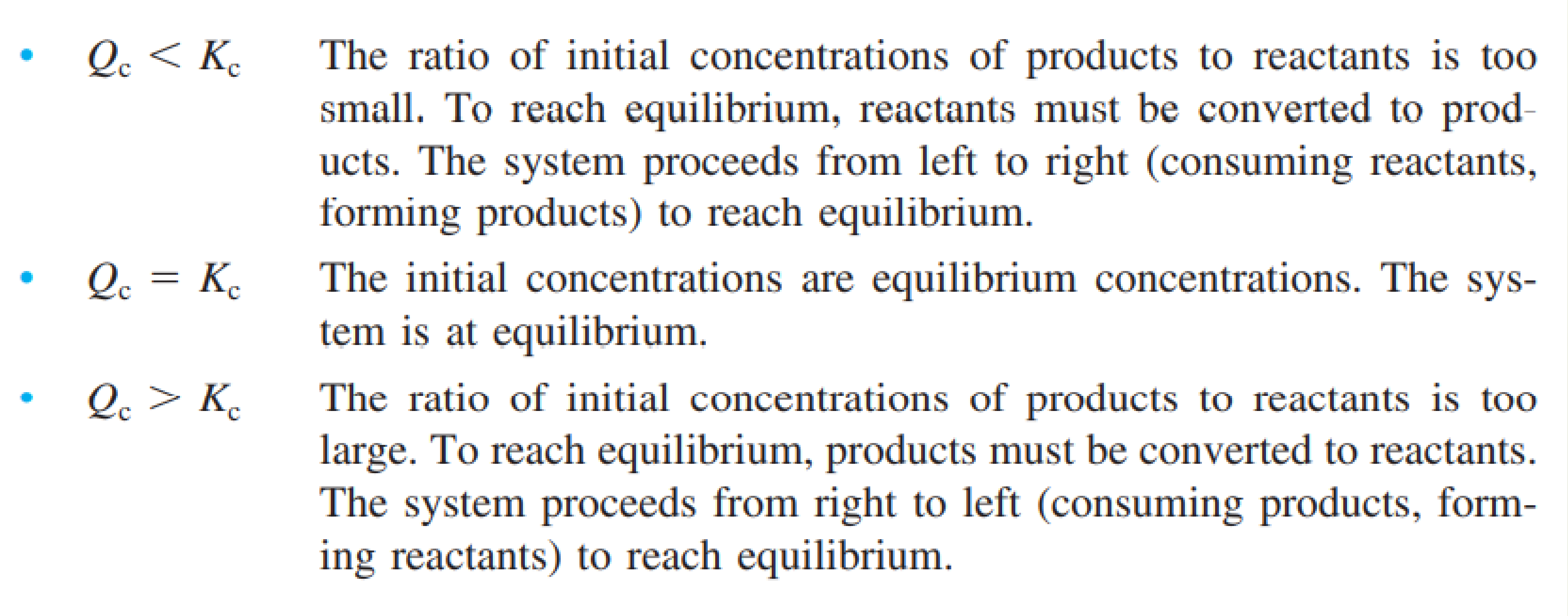
$$= \mathbf{4.6 \times 10^4}$$

What Does the Equilibrium Constant Tell Us?

Predicting the Direction of a Reaction

For reactions that have not reached equilibrium, we obtain the reaction quotient (Qc), The reaction quotient (Qc) measures the relative amounts of products and reactants present during a reaction at a particular point in time.

To determine the direction in which the net reaction will proceed to achieve equilibrium, we compare the values of Qc and Kc. The three possible cases are as follows



- $Q_c < K_c$ The ratio of initial concentrations of products to reactants is too small. To reach equilibrium, reactants must be converted to products. The system proceeds from left to right (consuming reactants, forming products) to reach equilibrium.
- $Q_c = K_c$ The initial concentrations are equilibrium concentrations. The system is at equilibrium.
- $Q_c > K_c$ The ratio of initial concentrations of products to reactants is too large. To reach equilibrium, products must be converted to reactants. The system proceeds from right to left (consuming products, forming reactants) to reach equilibrium.