

## 13.3: The Equilibrium Constant

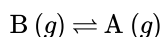
The constancy of the ratio of [the equilibrium concentration](#) of one isomer to the [concentration](#) of the other at a given temperature is characteristic of all gaseous equilibria between isomers, i.e., of all reactions of the general type



The constant ratio of concentrations is called the **equilibrium constant** and is given the symbol  $K_c$ . For reactions of the type given by Equation 13.3.1 the equilibrium constant is thus described by the equation

$$K_c = \frac{[B]}{[A]} \quad (13.3.2)$$

where, by convention, the concentration of the product B appears in the numerator of the ratio. If, for some reason, we wish to look at this reaction in reverse,



then the equilibrium constant is denoted as the reciprocal of the constant given in Equation 13.3.2

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

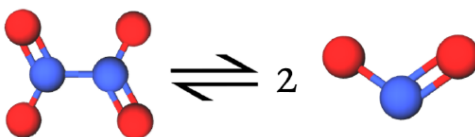
In general the equilibrium constant  $K_c$  [varies with temperature](#) and also differs based on the substances involved. Examples illustrating this behavior are given in Table 13.3.1 where the experimentally determined equilibrium constants for various cis-trans isomerization equilibria are recorded at various temperatures. Note that the equilibrium changes as the temperature and the composition of the molecule changes.

**TABLE 13.3.1** *The Equilibrium Constant  $K_c$  for some Cis-Trans Interconversions.*

$$\begin{array}{ccc}
 \text{H} & & \text{H} \\
 & \backslash & / \\
 & \text{C} = \text{C} \\
 & / & \backslash \\
 \text{R} & & \text{R}
 \end{array}
 \rightleftharpoons
 \begin{array}{ccc}
 \text{H} & & \text{R} \\
 & \backslash & / \\
 & \text{C} = \text{C} \\
 & / & \backslash \\
 \text{R} & & \text{H}
 \end{array}$$

| Temperature/K | R = F | R = Cl | R = CH <sub>3</sub> |
|---------------|-------|--------|---------------------|
| 500           | 0.420 | 0.608  | 1.65                |
| 600           | 0.491 | 0.678  | 1.47                |
| 700           | 0.549 | 0.732  | 1.36                |

When we turn our attention to more complex equilibrium reactions, we find that the relationship between the concentrations of the various species is no longer a simple ratio. A good demonstration of this fact is provided by the dissociation of dinitrogen tetroxide, N<sub>2</sub>O<sub>4</sub>. This compound is a colorless gas, but even at room temperature it dissociates partly into a vivid red-brown gas, NO<sub>2</sub>, according to the equation



If 1 mol N<sub>2</sub>O<sub>4</sub> contained in a flask of volume 1 L is heated to 407.2 K, exactly one-half of it dissociates into NO<sub>2</sub>. If the volume is now increased, the ratio of [NO<sub>2</sub>] to [N<sub>2</sub>O<sub>4</sub>] does not remain constant but increases as more dissociates. As shown in Table 13.3.2, if we increase the volume still further, even more dissociation occurs. By the time we have increased the volume to 10 L, the fraction of N<sub>2</sub>O<sub>4</sub> molecules dissociated has increased to 0.854 (i.e., to 85.4 percent).



Obviously the situation is now not quite so straightforward as in the previous example. Nevertheless there is a simple relationship between the equilibrium concentrations of the reactant and product in this case too. We find that it is the quantity

$$\frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

rather than the simple ratio of concentrations, which is now constant. Accordingly we also call this quantity an equilibrium constant and give it the symbol  $K_c$ . Thus  $K_c$  for Equation 13.3.3 is given by the relationship

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

where again by convention the product appears in the numerator. It is easy to check that  $K_c$  actually is a constant quantity with the value 2.00 mol/L from the data given in Table 13.3.2. Thus if we take the result from line **d**, we find that when 1 mol  $\text{N}_2\text{O}_4$  is placed in a 10 L flask at 407 K, 0.854 mol dissociate.

TABLE 13.3.2 The Dissociation of 1 mol  $\text{N}_2\text{O}_4$  into  $\text{NO}_2$  at 407.2 K (134°C) and Various Volumes.

|   | Amount of<br>$\text{N}_2\text{O}_4$<br>Added<br>mol | Volume of<br>Flask<br>L | Fraction<br>$\text{N}_2\text{O}_4$<br>Dissociated | Amount<br>$\text{N}_2\text{O}_4$ at<br>Equilibrium<br>mol | Amount<br>$\text{NO}_2$ at<br>Equilibrium<br>mol | Concentrati<br>on $\text{N}_2\text{O}_4$ at<br>Equilibrium<br>mol/L | Concentrati<br>on $\text{NO}_2$ at<br>Equilibrium<br>mol/L | Equilibrium<br>Constant $K_c$<br>mol/L |
|---|---|-------------------------|---|---|--|---|--|--|
| a | 1   | 1                       | 0.500   | 0.500   | 1.000  | 0.500   | 1.000  | 2.000                                  |
| b | 1   | 2                       | 0.618   | 0.382   | 1.236  | 0.191   | 0.618  | 2.000                                  |
| c | 1   | 5                       | 0.766   | 0.234   | 1.532  | 0.0468  | 0.3064   | 2.006                                  |
| d | 1   | 10                      | 0.854   | 0.146   | 1.708  | 0.0146  | 0.1708   | 1.998                                  |

Since from Equation 13.3.3 each mole which dissociates yields 2 mol  $\text{NO}_2$ , there will be

$$0.854 \text{ mol } \text{N}_2\text{O}_4 \times \frac{2 \text{ mol } \text{NO}_2}{1 \text{ mol } \text{N}_2\text{O}_4} = 1.708 \text{ mol } \text{NO}_2$$

present in the reaction vessel. There will also be  $(1 - 0.854) \text{ mol} = 0.146 \text{ mol } \text{N}_2\text{O}_4$  left undissociated in the flask. Since the total volume is 10 L, the equilibrium concentrations are

$$[\text{NO}_2] = \frac{1.708 \text{ mol}}{10 \text{ L}} = 0.1708 \text{ mol/L}$$

and

$$[\text{N}_2\text{O}_4] = \frac{0.146 \text{ mol}}{10 \text{ L}} = 0.0146 \text{ mol/L}$$

Accordingly

$$K_c = \frac{1.708 \text{ mol/L} \times 0.1708 \text{ mol/L}}{0.0146 \text{ mol/L}} = 2.00 \text{ mol/L}$$

In exactly the same way, if we use the data from line a in Table 13.3.2, we find

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{(1.00 \text{ mol/L})^2}{0.5 \text{ mol/L}} = 2.00 \text{ mol/L}$$

You can check for yourself that lines **b** and **c** also yield the same value for  $K_c$ .

### ✓ Example 13.3.1 : Equilibrium Constant

When 2 mol  $\text{N}_2\text{O}_4$  gas is heated to 407 K in a vessel of volume 5 dm<sup>3</sup>, it is found that 0.656 of the molecules dissociate into  $\text{NO}_2$ . Show that these data are in agreement with the value for  $K_c$  of 2.00 mol dm<sup>-3</sup> given in the text.

#### Solution

Many equilibrium problems can be solved in a fairly standardized fashion in three stages.

**a)** Calculate the amount of each substance transformed by the reaction as it comes to equilibrium, i.e., the amount of each reactant *consumed* by the reaction and the amount of each product *produced* by the reaction. Stoichiometric ratios derived from the equation must always be used in these calculations.

In this particular example we note that 0.656 of the original  $\text{N}_2\text{O}_4$  dissociates. Since 2 mol was used, a total of  $0.656 \times 2 = 1.312$  mol  $\text{N}_2\text{O}_4$  is *consumed*. The amount of  $\text{NO}_2$  *produced* is accordingly

$$n_{\text{NO}_2} = 1.312 \text{ mol N}_2\text{O}_4 \times \frac{2 \text{ mol NO}_2}{1 \text{ mol N}_2\text{O}_4} = 2.624 \text{ mol NO}_2$$

**b)** Use the amounts calculated in the first stage to calculate the amount of each substance present at equilibrium. Dividing by the volume, we can obtain the equilibrium concentrations.

Since 1.312 mol  $\text{N}_2\text{O}_4$  dissociated out of an original 2 mol, we have  $(2 - 1.312)$  mol = 0.688 mol  $\text{N}_2\text{O}_4$  left. The equilibrium concentration of  $\text{N}_2\text{O}_4$  is thus

$$[\text{N}_2\text{O}_4] = \frac{0.688 \text{ mol N}_2\text{O}_4}{5.00 \text{ dm}^3} = 0.1376 \text{ mol dm}^{-3}$$

Since no  $\text{NO}_2$  was originally present, the amount of  $\text{NO}_2$  present at equilibrium is the amount produced by the dissociation, namely, 2.624 mol  $\text{NO}_2$ . Thus

$$[\text{NO}_2] = \frac{2.624 \text{ mol NO}_2}{5.00 \text{ dm}^3} = 0.525 \text{ mol dm}^{-3}$$

It is usually worthwhile tabulating these calculations, particularly in more complex examples.

Note that a *negative* quantity in the column headed Amount Produced indicates that a given substance (such as  $\text{N}_2\text{O}_4$  in this example) has been *consumed*. There is less of that substance when equilibrium is reached than was present initially.

| Substance              | Initial Amount<br>mol | Amount Produced<br>mol | Equilibrium Amount<br>mol | Equilibrium<br>Concentration<br>mol dm <sup>-3</sup> |
|------------------------|-----------------------|------------------------|---------------------------|--|
| $\text{N}_2\text{O}_4$ | 2.00                  | -1.312                 | 0.688                     | 0.688/5  |
| $\text{NO}_2$          | 0.00                  | 2.624                  | 2.624                     | 2.624/5  |

**c)** In the third stage we insert the equilibrium concentrations in an expression for the equilibrium constant:

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{0.525 \text{ mol dm}^{-3} \times 0.525 \text{ mol dm}^{-3}}{0.1376 \text{ mol dm}^{-3}} = 2.00 \text{ mol dm}^{-3}$$

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