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

$$\text{A}\ (g) \rightleftharpoons \text{B}\ (g) \tag{13.3.1}$$

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

$$K_c = \frac{[\text{B}]}{[\text{A}]} \tag{13.3.2}$$

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,

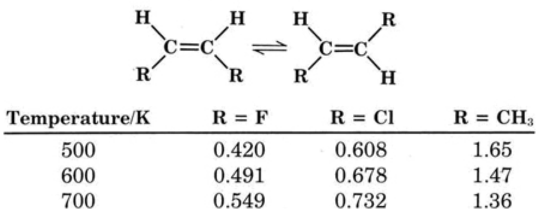
$$\text{B}\ (g) \rightleftharpoons \text{A}\ (g)$$

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

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

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.

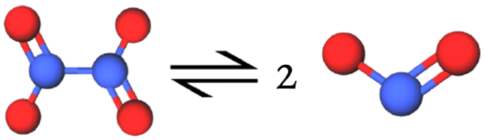
TABLE 13.3.1 *The Equilibrium Constant* K_c *for some Cis-Trans Interconversions.*



Temperature/K	R = F	R = Cl	R = CH_3
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_2O_4. This compound is a colorless gas, but even at room temperature it dissociates partly into a vivid red-brown gas, NO_2, according to the equation

$$\text{N}_2\text{O}_4\ (g) \rightleftharpoons 2\text{NO}_2\ (g) \tag{13.3.3}$$



If 1 mol N_2O_4 contained in a flask of volume 1 L is heated to 407.2 K, exactly one-half of it dissociates into NO_2. If the volume is now increased, the ratio of $[NO_2]$ to $[N_2O_4]$ 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_2O_4 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

$$\frac{[\mathrm{NO_2}]^2}{[\mathrm{N_2O_4}]}$$

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

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

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 N_2O_4 is placed in a 10 L flask at 407 K, 0.854 mol dissociate.

TABLE 13.3.2 The Dissociation of 1 mol N_2O_4 into NO2 at 407.2 K (134°C) and Various Volumes.

	Amount of N_2O_4 Added mol	**Volume of Flask L**	**Fraction N_2O_4 Dissociated**	**Amount N_2O_4 at Equilibrium mol**	**Amount NO_2 at Equilibrium mol**	**Concentration N_2O_4 at Equilibrium mol/L**	**Concentration NO_2 at Equilibrium mol/L**	**Equilibrium Constant K_c 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 NO_2, there will be

$$0.854\ \mathrm{mol\ N_2O_4} \times \frac{2\ \mathrm{mol\ NO_2}}{1\ \mathrm{mol\ N_2O_4}} = 1.708\ \mathrm{mol\ NO_2}$$

present in the reaction vessel. There will also be (1 – 0.854) mol = 0.146 mol N_2O_4 left undissociated in the flask. Since the total volume is 10 L, the equilibrium concentrations are

$$[\mathrm{NO_2}] = \frac{1.708\ \mathrm{mol}}{10\ \mathrm{L}} = 0.1708\ \mathrm{mol/L}$$

and

$$[\mathrm{N_2O_4}] = \frac{0.146\ \mathrm{mol}}{10\ \mathrm{L}} = 0.0146\ \mathrm{mol/L}$$

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 forK_c.

✓ Example 13.3.1 : Equilibrium Constant

When 2 mol N_2O_4 gas is heated to 407 K in a vessel of volume 5 dm^3, it is found that 0.656 of the molecules dissociate into NO_2. Show that these data are in agreement with the value for K_c of 2.00 mol dm^{-3} 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 N_2O_4 dissociates. Since 2 mol was used, a total of 0.656 × 2 = 1.312 mol N_2O_4 is *consumed*. The amount of 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 N_2O_4 dissociated out of an original 2 mol, we have (2 – 1.312) mol = 0.688 mol N_2O_4 left. The equilibrium concentration of N_2O_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 NO_2 was originally present, the amount of NO_2 present at equilibrium is the amount produced by the dissociation, namely, 2.624 mol 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 N_2O_4 in this example) has been *consumed*. There is less of that substance when equilibrium is reached than was present initially.

Substance	Initial Amount mol	Amount Produced mol	Equilibrium Amount mol	Equilibrium Concentration mol dm^{-3}
N_2O_4	2.00	-1.312	0.688	0.688/5
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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