13.6: Calculating the Extent of a Reaction

Once we know the equilibrium constant for a reaction, we can calculate what will happen when any arbitrary mixture of reactants and products is allowed to come to equilibrium. To take a simple case: What would happen if we mixed 1 mol cis isomer with 1 mol trans isomer of difluoroethene in a 10-dm³ flask at 623 K? From what we know of this reaction, it is easy to guess that some of the trans isomer will be converted to cis isomer, since an equilibrium mixture of the isomers always contains more of the cis than of the trans form. If we want to know the exact amount of trans isomer converted in this way, we can use the equilibrium constant to calculate it.

In all calculations of this sort we need to concentrate on the *increase in the amount of one of the products or the reactants.* Since this quantity is unknown, we label it algebraically, calling it x mol, where x indicates a pure number.[1] In the case under consideration, we would label the amount of cis isomer produced as the system moves to equilibrium as x mol. Once this step has been taken, the amount of each of the other products and reactants transformed by the reaction can be deduced from the equation and the appropriate stoichiometric factors. In our current case the equation is

$$cis - \mathrm{C_2H_2F_2} \rightleftharpoons trans - \mathrm{C_2H_2F_2}$$

and it is obvious that if x mol cis isomer have been produced, x mol trans isomer have been *consumed.*

[1]If x is used to indicate a quantity rather than a number, the units become much more difficult to handle in the algebra which follows.

We can now construct a table showing the initial amounts, the amounts transformed by reaction, the amounts present at equilibrium, and finally the equilibrium concentrations of each product and reagent:

Substance	Initial Amount	Amount Produced	Equilibrium Amount	Equilibrium Concentration
cis-C₂H₂F₂	1 mol	x mol	$(1 + x)$ mol	$((1 + x)/10)$ mol/L
trans-C₂H₂F₂	1 mol	-x mol	$(1 - x)$ mol	$((1 - x)/10)$ mol/L

Once the final concentration of each species has been obtained in this way, an algebraic equation can be set up linking the equilibrium concentrations to the value of the equilibrium constant:

$$K_c = 0.500 = \frac{[\textit{trans}\text{-}\mathrm{C_2H_2F_2}]}{[\textit{cis}\text{-}\mathrm{C_2H_2F_2}]} = \frac{((1-x)/10)\ \mathrm{mol/L}}{((1+x)/10)\ \mathrm{mol/L}} \tag{13.6.1}$$

$$0.500 = \frac{1-x}{1+x} \tag{13.6.2}$$

At this stage we are left with an algebraic equation to solve for x. Inevitably this equation involves *only numbers*. If any units remain, a mistake must have been made. From

by cross-multiplying, we have

$1 - \mathrm{x} = 0.500 + 0.500\mathrm{x}$

which rearranges to

$0.500 = 1.500\mathrm{x}$

so that $x = \dfrac{0.500}{1.500x} = 0.333$

We thus conclude that 0.333 mol trans isomer is converted to the cis form when the original mixture is allowed to equilibrate. The final equilibrium concentrations are as follows:

$$[cis\text{-}C_2H_2F_2] = \frac{1+x}{10} \text{ mol/L} = \frac{1.333}{10} \text{ mol/L}$$

$$[cis\text{-}C_2H_2F_2] = 0.1333 \text{ mol/L}$$

While

$$[trans\text{-}C_2H_2F_2] = \frac{1-x}{10} \text{ mol/L} = 0.0667 \text{ mol/L}$$

We can easily cross check that the ratio of these two concentrations is actually equal to the equilibrium constant, that is, to 0.5.

In calculating the extent of a chemical reaction from an equilibrium constant, it is often useful to realize that if the equilibrium constant is very small, the reaction proceeds to only a limited extent, while if it is very large, the reaction goes almost to completion. This point is easiest to see in the case of an equilibrium between two isomers of the type

$$A \rightleftharpoons B$$

If K_c for this reaction is very small, say 10^{-6}, then the ratio [B]/[A] = 10^{-6}. There will thus be a million times more molecules of the A isomer than of the B isomer in the equilibrium mixture. For most purposes we can regard the equilibrium mixture as being pure A. Conversely if K_c has a very large value like 10^6, the very opposite is true. In an equilibrium mixture governed by this second constant, there would be a million times more B isomer than A isomer, and for most purposes the equilibrium mixture could be regarded as pure B.

The realization that an equilibrium mixture can contain only small concentrations of some of the reactants or products is often very useful in solving equilibrium problems, as the 3rd example below demonstrates.

> ### ✔ Example 13.6.1: Concentration
>
> When colorless hydrogen iodide gas is heated, a beautiful purple color appears, indicating that some iodine gas has been produced and that the compound has decomposed partially into its elements according to the equation
>
> $$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$
>
> At 745 K (471.8°C), K_c for this reaction has the value 0.0200. Calculate the concentration of I_2 produced when 1.00 mol HI is heated to this temperature in a flask of volume 10.0 dm^3. Also calculate the fraction of the HI which has dissociated.
>
> **Solution**
>
> Let us denote the amount of I_2 produced by the reaction as x mol. The equation then tells us that the amount of H_2 produced will also be x mol, while the amount of HI consumed by the decomposition will be $2x$ mol. The initial amount of HI, 1 mol, will thus be reduced to $(1 - 2x)$ mol at equilibrium. Dividing the above amounts by the volume 10 dm^3, we easily obtain the equilibrium concentrations
>
> | Substance | Initial Amount | Amount Produced | Equilibrium Amount | Equilibrium Concentration |
> |---|---|---|---|---|
> | I_2 | 0.00 mol | x mol | x mol | (x/10) mol dm^{-3} |
> | H_2 | 0.00 mol | x mol | x mol | (x/10) mol dm^{-3} |
> | HI | 1.00 mol | (-2)x mol | (1 - 2x) mol | ((1 - 2x)/10) mol dm^{-3} |
>
> We can now write an expression for the equilibrium constant
>
> $$K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{(x/10) \text{ mol dm}^{-3} \times (x/10) \text{ mol dm}^{-3}}{((1-2x)/10) \text{ mol dm}^{-3} \times ((1-2x)/10) \text{ mol dm}^{-3}}$$
>
> or
>
> $$0.0200 = \frac{x^2}{(1-2x)^2}$$
>
> which is the required algebraic expression, free of units. This equation is easily solved by taking the square root of both sides.

$$\sqrt{2 \times 10^{-2}} = \sqrt{2} \times 10^{-1} = 0.1414 = \frac{x^2}{1-2x}$$

Thus $0.1414 - 0.2828x = x$

or $1.2828x = 0.1414$

so that $x = \frac{0.1414}{1.2828} = 0.110$

Thus $[I_2] = \frac{x}{10} \text{mol dm}^{-3} = 1.10 \times 10^{-2} \text{ mol dm}^{-3}$

Since $2x$ mol HI dissociated and 1 mol HI was originally present, we concluded that the fraction of HI which dissociated is

$$\frac{2x \text{ mol}}{1 \text{ mol}} = 0.220$$

It is wise at this point to check the answer. We found $x = 0.110$. If this is the correct value, we should also find that

$$\frac{x^2}{(1-2x)^2} = 0.0200$$

The value obtained using a calculator is 0.019 888 2 (which rounds to 0.0199 to three significant figures). The difference is due to errors introduced by rounding off during the calculation.

✔ **Example 13.6.2 : Equilibrium Mixture**

A mixture of 1.00 mol HI pas and 1.00 mol H_2 gas is heated in a 10.0-dm³ flask to 745 K. Calculate the concentration of I_2 produced in the equilibrium mixture and also the fraction of HI which dissociates.

Solution:

Again we let x mol represent the amount of I_2 produced. Our table then becomes

Substance	Initial Amount	Amount Produced	Equilibrium Amount	Equilibrium Concentration
I_2	0.00 mol	x mol	x mol	(x/10) mol dm⁻³
H_2	1.00 mol	x mol	(1 + x) mol	((1 + x)/10) mol dm⁻³
HI	1.00 mol	(-2x) mol	(1 - 2x) mol	((1 - 2x)/10) mol dm⁻³

Substituting the final concentrations in an expression for the equilibrium constant, we then have

$$K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{(1 + x/10) \text{ mol dm}^{-3} \times (x/10) \text{ mol dm}^{-3}}{((1-2x)/10) \text{ mol dm}^{-3} \times ((1-2x)/10) \text{ mol dm}^{-3}}$$

or

$$0.0200 = \frac{(1+x)x}{(1-2x)^2}$$

Because of the added H_2, it is no longer possible to take a square root as in the previous example. Instead we need to multiply out and rearrange in order to obtain a quadratic equation of the form $ax^2 + bx + c = 0$. Accordingly we have

$0.0200(1 - 2x)^2 = (1 + x)x$

or $0.0200(1 - 4x + 4x^2) = x + x^2$

multiplying both sides by 50, we obtain

$1 - 4x + 4x^2 = 50x + 50x^2$

which on rearrangement has the required form

$$46x^2 + 54x - 1 = 0$$

where

- $a = 46$
- $b = 54$
- $c = -1$

We can now use the conventional quadratic formula

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-54 \pm \sqrt{54^2 + 4 \times 46 \times 1}}{2 \times 46}$$

$$= \frac{-54 \pm 55.678}{92} = 0.0182 \text{ or } -1.192$$

The negative root, $x = -1.192$, implies that 1.192 mol I_2 was consumed. Since no I_2 was present to begin with, this is impossible. We conclude that the positive root, namely $x = 0.0182$, is the correct one. Thus

$$[I_2] = \frac{x}{10} \text{mol dm}^{-3} = 1.82 \times 10^{-3} \text{ mol dm}^{-3}$$

Again the fraction dissociated is given by $2x$ mol/1 mol and is thus equal to 0.0364. To check this solution, we can substitute x = 0.0182 in the expression

$$\frac{(1+x)x}{(1-2x)^2}$$

We then obtain the value 0.019 96, which rounds to the correct value of 0.0200.

> **Note:**
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> The inclusion of one of the products (H_2 gas) in the mixture reduces the extent to which the hydrogen iodide dissociates quite appreciably. We will explore this phenomenon more extensively in the next section.

✔ Example 13.6.3 : Fraction of Dissociation

The equilibrium constant K_c for the dissociation of dinitrogen tetroxide according to the equation

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

changes from a very small to a very large value as the temperature is increased, as shown in the table. Calculate the fraction of N_2O_4 dissociated at

Temperature/K	K_c/mol×dm^{-3}
200	1.09×10^{-7}
400	1.505
600	1.675×10^3

each temperature if 1.00 mol N_2O_4 is sealed in a container of volume 4.00 dm^3.

Solution

Let the amount of N_2O_4 dissociated at the temperature under consideration be x mol. From the equation, $2x$ mol NO_2 will be produced. In tabular form we then have

Substance	Initial Amount	Amount Produced	Equilibrium Amount	Equilibrium Concentratioin
N_2O_4	1.00 mol	-x mol	(1-x) mol	((1-x)/4) mol×dm^{-3}
NO_2	0.00 mol	+2x mol	2x mol	(2x/4) mol×dm^{-3}

We thus have

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(2x/4)\text{ mol dm}^{-3} \times (2x/4)\text{ mol dm}^{-3}}{((1-x)/4)\text{ mol dm}^{-3}}$$

$$= \frac{4x^2}{16} \times \frac{4}{1-x}\text{ mol dm}^{-3} = \frac{x^2}{1-x}\text{ mol dm}^{-3}$$

a) At 200 K, $K_c = 1.09 \times 10^{-7}$ mol dm^{-3}, so that

$\frac{x^2}{1-x}$ mol dm$^{-3} = 1.09 \times 10^{-7}$ mol dm^{-3}

or $\frac{x^2}{1-x} = 1.09 \times 10^{-7}$

Since K_c is so small, we guess that very little N$_2$O$_4$ is dissociated at this temperature. This means that x is very small, and it is probably valid to make the approximation

$$1 - x \approx 1$$

(The symbol $\approx$ means approximately equal.) With this approximation our equation becomes:

$x^2 = 1.09 \times 10^{-7} mol$

or

$$x = \sqrt{1.09 \times 10^{-8}}\text{ mol} = \sqrt{1.09} \times 10^{-4} = 3.30 \times 10^{-4}$$

Our guess about x was thus correct. It is a small number, especially in comparison with 1. The approximation $1 - x \approx 1$ is valid to three decimal-place accuracy since $1 - x = 0.9997$.

Since x mol has dissociated, the fraction of N$_2$O$_4$ dissociated is given by x mol/1 mol = x. The fraction dissociated is thus 3.30 × 10^{-4}.

b) At 400 K, $K_c = 1.505$ mol dm^{-3}, so that:

$\frac{x^2}{1-x}$ mol dm$^{-3} = 1.505$ mol dm^{-3}

or $\frac{x^2}{1-x} = 1.505$

Since K_c is not small, we can no longer use the approximation:

$$1 - x \approx 1$$

Indeed, such an assumption leads to a ridiculous conclusion, since if $1 - x \approx 1$, then $x^2 = 1.505$, or $x = 1.227$. This result is impossible since it tells us that more N$_2$O$_4$ has dissociated (1.227 mol) than was originally present (1 mol).

Accordingly we return to the orthodox method for solving quadratic equations. Multiplying out our equation, we obtain:

$x^2 = 1.505 - 1.505x$

or $x^2 + 1.505x - 1.505 = 0$

so that

$$x = \frac{-1.505 \pm \sqrt{(1.505)^2 + 4(1.505)}}{2} = \frac{-1.505 \pm 2.878}{2}$$

$= -2.19$ or 0.6865

Since a negative result has no physical meaning, we conclude that 0.6865 is the correct answer. (As a cross check we can feed this result back into our original equation.) The fraction of N$_2$O$_4$ dissociated at this temperature is accordingly 0.6865.

c) At 600 K, $K_c = 1.675 \times 10^3$ mol dm^{-3}, so that:

$\frac{x^2}{1-x} = 1.675 \times 10^3$

Since K_c is fairly large, we guess that almost all the N$_2$O$_4$ has dissociated at this temperature and that x is accordingly close to 1. A valid approximation for these circumstances is then $x \approx 1$. With this approximation our equation becomes:

$\frac{1}{1-x} = 1.675 \times 10^3$

or 1-x $= \frac{1}{1.675 \times 10^3} = 5.97 \times 10^{-4}$

Thus

$$x = 1 - 5.97 \times 10^{-4} = 0.999\ 40$$

and our approximation is a good one. Since the fraction dissociated is *x*, we conclude that 0.9994 of the original N_2O_4 has dissociated.

> 📌 **Note:**
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> We did not use the approximation $x \approx 1$ to say that $1 - x \approx 0$. This is not a productive way to solve the problem because we would end up dividing by zero. Common sense tells us that it will not work. Similarly, in part a of this example we used the fact that *x* was very small to say that $1 - x \approx 1$. Saying that $x^2 \approx 0$ would not make sense because it would lead to the algebraic equation
>
> $\frac{0}{1-x} = 1.09 \times 10^{-7}$
>
> that is, that $0 = 1.09 \times 10^{-7} - (1.09 \times 10^{-7})x$. This would lead to the solution $x = 1$ which is rather far from the original assumption.