CHAPTER 6

Chemical Equilibria

It is wrong to think that all chemical reactions proceed to completion and all reactions are irreversible. In fact, there are many chemical reactions that are reversible. For such reversible reactions, not all the reactants are converted into products. We would simply have a mixture of unreacted reactants and products co-existing.

What then can be used to characterise a reversible reaction? How do we know if one system is more reversible than another? What are the factors that affect a reversible reaction? Can we modify a reversible reaction to optimise the formation of the desired products that manufacturers want? These are the questions that we will seek to answer in this chapter.

6.1 Reversible Reactions

What we usually consider as irreversible reactions, i.e., reactions that proceed in one direction (as commonly represented by a single-headed arrow, →) are in actual fact reversible reactions under specific conditions. All chemical reactions are reversible to a certain extent. Products formed in these reactions combine and react to re-form the original reactants. Both forward and backward reactions continue for as long as there are reactants combining to give products.

For example, given the reaction $A + B \rightarrow C + D$ (forward reaction), the products C and D can react to re-form A and B: $C + D \rightarrow A + B$ (backward reaction).

As we can now see, A can be a reactant and also a product. For clarity's sake, the term "reactants" is conventionally used for the species on the left-hand side of the equation and "products" are those species on the right-hand side.

Equations of reversible reactions are represented with a double-headed arrow ($\rightleftharpoons$):

$$A + B \rightleftharpoons C + D.$$

The extent of reversibility depends on the magnitude of the activation energy (E_a) of the backward reaction. For an exothermic reversible reaction, if E_a of the backward reaction is too large, the backward reaction is essentially non-occurring compared to the forward reaction (see Fig. 6.1). Hence, one can assume the forward reaction proceeds almost to completion. In contrast, for an endothermic reversible reaction, higher E_a for the forward reaction makes it less likely for it to proceed as compared to the backward reaction.

The energy profile diagram for a reversible reaction is shown in Fig. 6.2. As can be seen from the diagram, E_a of the backward reaction is comparable to that of the forward reaction. Or in short, ΔH of reaction is about zero!

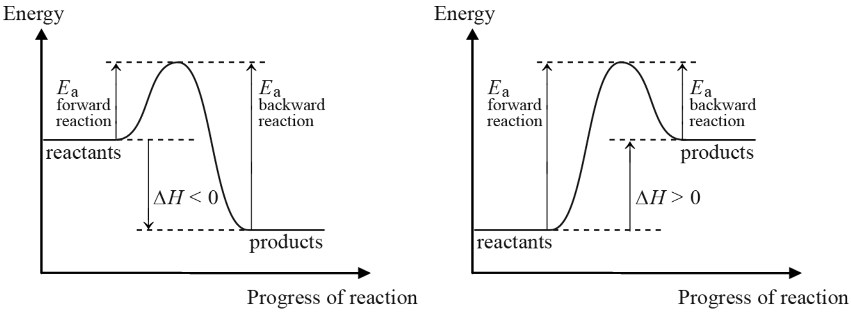


Fig. 6.1. Energy profile diagrams for an exothermic reversible reaction (left) and an endothermic reversible reaction (right).

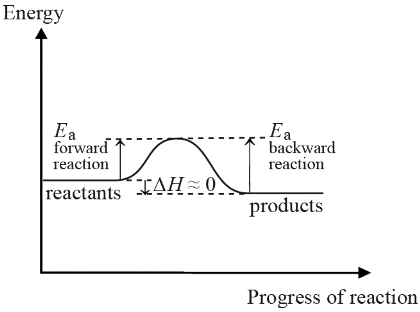
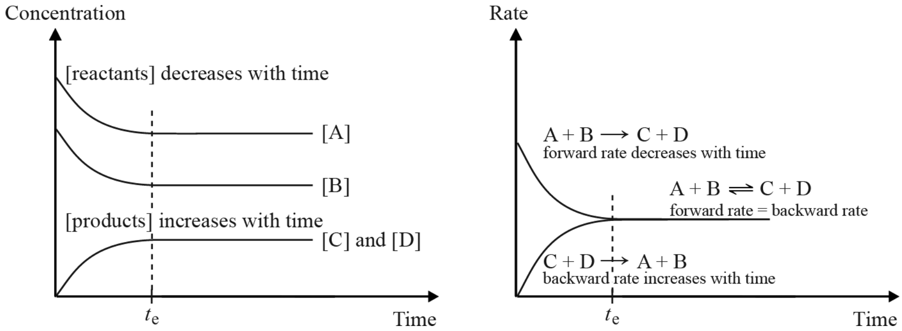


Fig. 6.2. Energy profile diagram for a reversible reaction.

6.2 Equilibrium Systems

Consider the following reaction: $A + B \rightleftharpoons C + D$.



At the start of the reaction, with just A and B present, only the forward reaction will occur. The rate of the forward reaction (determined by the gradient of the tangent drawn to the concentration versus time plot) is at its peak since [reactants] is at its highest while the rate of the backward reaction is zero.

As the reaction progresses, the rate of the forward reaction (R_f) decreases as [A] and [B] decrease, since these are used to form the products C and D.

At the same time, as soon as C and D are formed, the backward reaction proceeds, albeit at a slow rate initially since [products] is low. This helps to regenerate A and B. As [C] and [D] increase over time, the rate of the backward reaction (R_b) also increases.

There will come a point in time (t_e) when both the forward and backward reactions occur at the same rate, i.e., forward rate (R_f) = backward rate (R_b). When this happens, the concentration of every reactant and product remains constant, and the system is in a state of balance, known as equilibrium.

More specifically, the system is said to be in **dynamic equilibrium**. As the rates of these reactions are equal, it may seem that the reactions have completely stopped but this is not true.

Although the concentrations of the substances remain unchanged (as indicated by the term "equilibrium"), there is still activity going on: both forward and backward reactions are continually occurring (as indicated by the term "dynamic") but since they proceed at the same rate, each species is formed as fast as it is consumed, resulting in a constant concentration term.

6.3 Equilibrium Constants K_c and K_p

Every reversible reaction will attain equilibrium at different times; some take minutes while others take weeks. The composition of a system at equilibrium also differs. How can we then determine if equilibrium has been achieved?

Consider the following reaction:

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D}.$$

The mass action expression or reaction quotient Q_c is expressed as the ratio of the concentration of the products to the reactants, each raised to the power corresponding to their stoichiometric coefficient in the balanced chemical equation:

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

Q_c embraces the concentration values of the reactants and products at any point of time. Its value therefore continuously changes with the progress of the reaction until equilibrium is reached.

At equilibrium, Q_c becomes a constant value, which is more appropriately known as the equilibrium constant, K_c:

$$K_c = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b} = \text{constant at a fixed temperature},$$

where [A], [B], [C] and [D] are concentrations of species at equilibrium.

The unit of K_c varies depending on the terms in its expression but since units of concentration are in terms of mol dm^{-3}, the unit of K_c can be computed as "mol$^{(c+d)-(a+b)}$ dm$^{-3[(c+d)-(a+b)]}$".

The equilibrium constant K_c can also be conceptualised from the following mathematical derivation. Consider the **elementary** reaction:

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D}.$$

For the forward reaction: $a\mathrm{A} + b\mathrm{B} \rightarrow c\mathrm{C} + d\mathrm{D}$, $\mathrm{Rate_f} = k_f[\mathrm{A}]^a[\mathrm{B}]^b$.

For the backward reaction: $c\mathrm{C} + d\mathrm{D} \rightarrow a\mathrm{A} + b\mathrm{B}$, $\mathrm{Rate_b} = k_b[\mathrm{C}]^c[\mathrm{D}]^d$.

When equilibrium is achieved, $\mathrm{Rate_f} = \mathrm{Rate_b} \Rightarrow k_f[\mathrm{A}]^a[\mathrm{B}]^b = k_b[\mathrm{C}]^c[\mathrm{D}]^d$.

Rearranging, we get $k_f/k_b = [\mathrm{C}]^c[\mathrm{D}]^d/[\mathrm{A}]^a[\mathrm{B}]^b$ = constant (which is defined as K_c), i.e.,

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

The advantage of this definition is that it allows us to perceive the equilibrium constant K_c as the ratio of the rate constants.

Importantly, the Equilibrium Law expresses K_c as a relationship between the concentrations of products and reactants in a system at equilibrium, and it **provides us with a quantifying means to determine the position of the equilibrium**.

The magnitude of the equilibrium constant informs us of the relative proportion of products to reactants, providing us information on the **extent of reaction** (but not reaction rate).

- When $K_c > 1$, there is a higher proportion of products to reactants. The formation of products is favoured, i.e., the position of equilibrium lies more to the right.
- When $K_c < 1$, there is a high proportion of reactants as not many of these are converted to products, i.e., the position of equilibrium lies towards the left.
- A K_c value close to 1 indicates that the concentrations of both reactants and products are almost the same.

Reaction	**K_c Value**
$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$	$1.8 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$ (at 25°C)
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	$1.7 \times 10^{2}\,\mathrm{mol^{-2}\,dm^{6}}$ (at 227°C)
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	$4.1 \times 10^{8}\,\mathrm{mol^{-2}\,dm^{6}}$ (at 25°C)

At 25°C, the formation of $NH_3(g)$ is spontaneous, whereas the ionisation of ammonia does not occur as readily. If you notice, there is a temperature value tied to the K_c value stipulated. As the rate constants are temperature-dependent [assuming the Arrhenius rate constant, $k = A\exp(-E_a/RT)$], so too is K_c that is derived from them.

Altering temperature actually creates a stress or disturbance in an equilibrium system and thus brings changes to its composition. We will cover this aspect in Section 6.4 on "Le Chatelier's Principle," which helps us to predict the effects of changing conditions on equilibrium systems.

The magnitude of Q_c, relative to that of K_c, indicates where the position of equilibrium lies:

- When $Q_c = K_c$, the system is at equilibrium, i.e., $R_f = R_b$; there is no change in the position of equilibrium.

- If $Q_c < K_c$, then $R_f > R_b$, i.e., the position of equilibrium shifts to the right.
- If $Q_c > K_c$, then $R_f < R_b$, i.e., the position of equilibrium shifts to the left.

Q: Why when $Q_c < K_c$, does the position of equilibrium shift towards the product side?

A: From a kinetics perspective, $Q_c < K_c$ implies that the concentrations of the reactant particles are greater than the product particles as compared to if the system is at equilibrium. Thus, we expect a higher effective collision frequency for the forward reaction than that for the backward reaction. As a result, more products form and the position of equilibrium shifts towards the product side.

Q: But as more products form, wouldn't the rate of the backward reaction increase and deplete the amount of products present, which in turn cause the backward rate to decrease?

A: There is a fallacy here. As more products form, the rate of the backward reaction does increase. But this increase does not deplete the concentration of the products because the rate of the forward reaction is still greater than the rate of the backward reaction at this time (refer to the rate versus time plot in Section 6.2). In fact, the concentration of the products continues to increase and fuel an increase in the rate of the backward reaction. All these changes pertaining to the concentrations and rate will stop once a state of dynamic equilibrium is established.

Example 6.1:

$$\mathrm{CO(g)} + 2\mathrm{H_2(g)} \rightleftharpoons \mathrm{CH_3OH(g)}.$$

At a particular temperature, a system contains 0.5 mol of CO(g), 0.8 mol of H_2(g) and 0.9 mol of CH_3OH(g) in a 5 dm^3 vessel. Is this system at equilibrium? If not, in which direction does the reaction proceed? The given value of K_c is 54 at this particular temperature.

Solution: As the system may not be at equilibrium, we calculate Q_c and compare it against K_c:

$$Q_c = \frac{[\mathrm{CH_3OH}]}{[\mathrm{CO}][\mathrm{H_2}]^2} = \frac{\frac{0.9}{5}}{\frac{0.5}{5} \times \left(\frac{0.8}{5}\right)^2} = 70.3\,\mathrm{mol^{-2}\,dm^6}.$$

Since $Q_c > K_c$, the backward reaction proceeds at a higher rate than the forward reaction. The position of equilibrium shifts to the left.

Back to the reversible reaction: $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$.

Equilibrium of the above system comprising the species A, B, C and D can be attained via either the forward or the backward reaction. If you start off with A and B reacting only, without any C and D present, equilibrium can be achieved. The equilibrium composition can be exactly the same if you start off with only C and D, without any A and B present.

It must be noted that the expression for K_c and thus its value are dependent on the balanced chemical equation written. Whenever K_c is quoted, it must be accompanied by the balanced chemical equation.

Example 6.2: At 500 K, an equilibrium mixture is found to contain $0.053\,\text{mol}\,\text{dm}^{-3}$ of $N_2(g)$, $1.00\,\text{mol}\,\text{dm}^{-3}$ of $H_2(g)$ and $3.00\,\text{mol}\,\text{dm}^{-3}$ of $NH_3(g)$.

Based on the data given, calculate K_c for the following reactions:

(i) $N_2(g) + 3H_2(g) \rightleftharpoons 2\,NH_3(g)$,
(ii) $2N_2(g) + 6H_2(g) \rightleftharpoons 4NH_3(g)$,
(iii) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$.

Solution:

(i) $K_{\text{c},1} = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{3^2}{0.053\times 1} = 1.7 \times 10^2\,\text{mol}^{-2}\,\text{dm}^6$,
(ii) $K_{\text{c},2} = \frac{[NH_3]^4}{[N_2]^2[H_2]^6} = \frac{3^4}{(0.053)^2\times 1} = 2.9 \times 10^4\,\text{mol}^{-4}\,\text{dm}^{12}$,
(iii) $K_{\text{c},3} = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{0.053\times 1}{3^2} = 5.9 \times 10^{-3}\,\text{mol}^2\,\text{dm}^{-6}$.

- When the equation is written in the reverse order, the K_c value is inverted, i.e., $K_{\text{c},3} = \frac{1}{K_{\text{c},1}}$
- When the coefficients in the equation are multiplied by a factor of n, the K_c value is raised to the power of n, i.e., $K_{\text{c},2} = {K_{\text{c},1}}^2$.

For gases, we usually express their concentrations in terms of partial pressures since these are much easier to measure.

The equilibrium constant, expressed in terms of the partial pressures of the substances, is known as K_p (subscript "p" stands for partial pressure). Consider the following equation:

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

Instead of expressing the equilibrium constant as $K_\text{c} = \frac{[NH_3]^2}{[N_2][H_2]^3}$, we can express it as:

$$K_\text{p} = \frac{{p_{NH_3}}^2}{p_{N_2}{p_{H_2}}^3}$$

where p_X is partial pressure of gas X at equilibrium.

The unit of partial pressure can be in terms of either Pa or atm, and thus the unit of K_p varies depending on the terms in its expression. For instance, the unit for $K_p = \frac{p_{NH_3}{}^2}{p_{N_2}p_{H_2}{}^3}$ is Pa^{-2} or atm^{-2}.

6.3.1 *Writing K_c or K_p for heterogeneous equilibria*

An equilibrium system in which all the species are in the same phase is in **homogeneous equilibrium**, e.g., $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$.

Heterogeneous equilibrium refers to an equilibrium system that contains species in different phases.

In writing the K_c or K_p expression for heterogeneous equilibria, the concentrations and partial pressures of pure solids and liquids (but not aqueous solutions) are excluded.

For instance, given the equilibrium $Ti(s) + 2Cl_2(g) \rightleftharpoons TiCl_4(l)$, we have the following expressions:

$$K_c = \frac{1}{[Cl_2(g)]^2} \quad \text{and} \quad K_p = \frac{1}{p_{Cl_2}{}^2}.$$

Q: Why are the terms involving solids and liquids not included in the equilibrium constant expression for heterogeneous equilibrium?

A: For a given temperature, the saturated vapour pressures of solids (and that of liquids) are constant. In addition, even though their actual amounts may change, both solids and liquids have constant concentrations, as explained in the following.

Recall that concentration = amount (in mol)/volume. Since amount (in mol) is calculated as mass/molar mass, concentration = mass/(molar mass × volume) = density/molar mass. For pure solids and liquids, both density and molar mass are constant values.

Q: What is saturated vapour pressure?

A: In a closed vessel containing a liquid or solid, the particles at the surface tend to evaporate and the gas particles formed tend to condense back into the liquid or solid phase. In time, an equilibrium is established between the gas particles and their condensed form. The pressure exerted by the gas particles at this equilibrium is known as the saturated vapour pressure. As saturated vapour pressure is dependent only on temperature, it is a constant at a fixed temperature.

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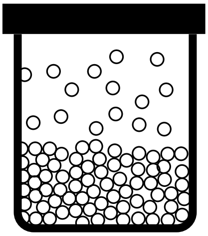

Pure solvent

Exercise 6.1:

(i) Write the K_p expression and state its units for $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(l)$.
(ii) Write the K_c expression and state its units for $Ag^+(aq) + Cl^-(aq) \rightleftharpoons AgCl(s)$.

Solution:

(i) $K_p = \frac{p_{CO}}{p_{CO_2}p_{H_2}}$; unit of K_p is Pa^{-1} or atm^{-1}.
(ii) $K_c = \frac{1}{[Ag^+][Cl^-]}$; units of K_c are $mol^{-2}\,dm^6$.

6.3.2 *Calculations involving K_c*

Calculations that seek to solve for K_c or K_p values require the following information:

- the balanced chemical equation,
- the K_c or K_p expression, and
- equilibrium concentrations of all species.

Example 6.3: Calculating K_c given concentration data

1.5 mol of $CH_3OH(l)$ and 1.5 mol of $CH_3COOH(l)$ are allowed to react in a $0.5\,dm^3$ vessel to form the ester $CH_3COOCH_3(l)$:

$$CH_3OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOCH_3(l) + H_2O(l).$$

The equilibrium mixture is found to contain 0.3 mol of $CH_3COOCH_3(l)$ and 0.3 mol of $H_2O(l)$ at 298 K. Calculate K_c for the reaction.

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Approach:

- Write the K_c expression: $K_c = \frac{[CH_3COOCH_3(l)][H_2O(l)]}{[CH_3OH(l)][CH_3COOH(l)]}$.
- Do we have values for the equilibrium concentrations of species? No, but we can find these using the following steps:

Step 1: Construct an "I.C.E." table that shows the Initial concentration, Change in concentration and Equilibrium concentration of the species concerned.

Step 2: Fill in all the known values into the table.

	$\mathbf{CH_3OH(l)}$ +	$\mathbf{CH_3COOH(l)}$ ⇌	$\mathbf{CH_3COOCH_3(l)}$	+ $\mathbf{H_2O(l)}$
Initial conc. (mol dm^{-3})	$1.5/0.5 = 3.0$	$1.5/0.5 = 3.0$	0	0
Change in conc. (mol dm^{-3})				
Equilibrium conc. (mol dm^{-3})			$0.3/0.5 = 0.6$	$0.3/0.5 = 0.6$

Since equilibrium $[CH_3COOCH_3]$ is $0.6\,\text{mol dm}^{-3}$, the change in $[CH_3COOCH_3]$ is $+0.6\,\text{mol dm}^{-3}$ (the "+" sign indicates a gain).

Based on the stoichiometric ratios in the balanced equation, 0.3 mol of ester is produced from 0.3 mol each of CH_3OH and CH_3COOH.

Thus, the change in concentration of these reactants is $-0.6\,\text{mol dm}^{-3}$ (the "−" sign indicates a loss).

Hence, equilibrium $[CH_3OH]$ and $[CH_3COOH] = 3.0 - 0.6 = 2.4\,\text{mol dm}^{-3}$.

	$\mathbf{CH_3OH(l)}$ +	$\mathbf{CH_3COOH(l)}$ ⇌	$\mathbf{CH_3COOCH_3(l)}$	+ $\mathbf{H_2O(l)}$
Initial conc. (mol dm^{-3})	3.0	3.0	0	0
Change in conc. (mol dm^{-3})	−0.6	−0.6	+0.6	+0.6
Equilibrium conc. (mol dm^{-3})	2.4	2.4	0.6	0.6

Step 3: Calculate K_c and determine its units:

$$K_c = \frac{[CH_3COOCH_3(l)][H_2O(l)]}{[CH_3OH(l)][CH_3COOH(l)]} = \frac{0.6 \times 0.6}{2.4 \times 2.4} = 0.0625.$$

K_c in this instance has no units.

Example 6.4: Calculating concentration data given a K_c value

2 mol of $CH_3OH(l)$ and 2 mol of $CH_3COOH(l)$ are allowed to react to form the ester $CH_3COOCH_3(l)$:

$$CH_3OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOCH_3(l) + H_2O(l).$$

Given that K_c is 0.0625 at 298 K,

(i) determine the equilibrium amount of $CH_3COOCH_3(l)$, and
(ii) hence determine the percentage yield of ester.

Approach:

- Since the value of K_c is given, we start off by writing the K_c expression, i.e., $K_c = \frac{[CH_3COOCH_3(l)][H_2O(l)]}{[CH_3OH(l)][CH_3COOH(l)]} = 0.0625$.
- Although concentration of the species and the volume of the vessel are not stated, we can still construct an I.C.E. table in terms of the amount of species and assign "x mol" as the amount of ester produced at equilibrium.

Solution (i): Let the equilibrium amount of ester be x mol.

	$CH_3OH(l)$	+	$CH_3COOH(l)$	$\rightleftharpoons$	$CH_3COOCH_3(l)$	$+ H_2O(l)$
Initial amount (mol)	2		2		0	0
Change in amount (mol)	$-x$		$-x$		$+x$	$+x$
Equilibrium amount (mol)	$2-x$		$2-x$		x	x

Since volume is not given, assume the volume of mixture to be V dm^3 so that concentration can be expressed in terms of V:

$$K_c = \frac{[CH_3COOCH_3(l)][H_2O(l)]}{[CH_3OH(l)][CH_3COOH(l)]} = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{2-x}{V}\right)\left(\frac{2-x}{V}\right)}$$
$$= 0.0625.$$

For the quadratic equation:

$$ax^2 + bx + c = 0;$$
$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}.$$

Solving the quadratic equation, we get

$$x = 0.4 \text{ or } -0.7.$$

Rejecting the negative value, the equilibrium amount of ester is 0.4 mol.

Solution (ii): The balanced chemical equation gives the theoretical yield, which is, ideally, the maximum amount of product obtainable if the reaction proceeds to completion.

Since the reaction does not go to completion, the actual yield attained is less than the theoretical yield.

Percentage yield is thus the ratio, expressed as a percentage, of the equilibrium amount of product obtained to the theoretical yield.

Percentage yield

$$= \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%.$$

Percentage yield $= \frac{0.4}{2.00} \times 100\% = 20\%$.

6.3.3 *Calculations involving K_p*

As seen in earlier examples involving expressions for K_c, there are cases when the numerical value for concentration is not given up front. However, we can arrive at a value for concentration through manipulation of data (if the amount and volume are known) or express it in terms of an unknown V (when data is given only in terms of moles).

It is the same when we work with questions involving K_p.

To find the partial pressure of gas W, p_w, we can use the following:

- If the number of moles of each of the species and total pressure p_T, of the system are given, we can find the partial pressure of W using:

$$p_w = \chi_w p_T = \frac{n_w}{n_T} \times p_T,$$

  where χ_w is the mole fraction of W.

- If the amount of gas (n_w), temperature (T) and volume (V) of the reaction vessel are all known, we can apply the Ideal Gas equation, assuming that W is an ideal gas:

$$p_w = (n_w RT)/V.$$

Example 6.5:

$$2A(g) + B(g) \rightleftharpoons 2C(g).$$

Calculate K_p for the reaction given that the equilibrium mixture contains 0.2 mol of A(g), 0.5 mol of B(g) and 0.3 mol of C(g) and the pressure of the reaction vessel is 4 atm.

Solution:

$$p_{\mathrm{A}} = \frac{0.2}{0.2+0.5+0.3} \times 4 = 0.8\,\mathrm{atm},$$
$$p_{\mathrm{B}} = \frac{0.5}{0.2+0.5+0.3} \times 4 = 2.0\,\mathrm{atm},$$
$$p_{\mathrm{C}} = \frac{0.3}{0.2+0.5+0.3} \times 4 = 1.2\,\mathrm{atm},$$
$$K_{\mathrm{p}} = \frac{{p_{\mathrm{C}}}^2}{{p_{\mathrm{A}}}^2 p_{\mathrm{B}}} = 1.13\,\mathrm{atm}^{-1}.$$

There are gases that break down to form smaller gaseous components in a process called dissociation. The degree of dissociation tells us the extent of the dissociation. It can be expressed as a percentage or fraction of gas that has dissociated.

Example 6.6: Calculations involving degree of dissociation of a gas

Dinitrogen tetraoxide dissociates into its monomer on heating:

$$\mathrm{N_2O_4(g)} \rightleftharpoons \mathrm{2NO_2(g)}.$$

In a particular reaction, it is found that only 40% of N_2O_4(g) has dissociated and the total pressure of the equilibrium mixture is 2 atm. Calculate the value of K_{p}.

Method 1

Approach: 40% of N_2O_4(g) dissociates into NO_2(g). This means that 60% of the initial amount of N_2O_4(g) remains in its original form, i.e., undissociated. Thus, we need to define the initial amount of N_2O_4(g), which was not given.

Solution: Let w be the initial amount of N_2O_4(g). Since 1 mol of N_2O_4(g) dissociates to give 2 mol of NO_2(g), $0.4w$ mol of N_2O_4(g) dissociates to give $2 \times 0.4w = 0.8\,w$ mol of NO_2(g).

	N_2O_4(g)	**⇌**	**$2NO_2$(g)**
Initial amount (mol)	w		0
Change in amount (mol)	$-0.4w$		$+0.8w$
Equilibrium amount (mol)	$0.6w$		$0.8w$

Total amount of gases n_T at equilibrium $= 0.6w + 0.8w = 1.4w$. Total pressure p_T at equilibrium $= 2$ atm.

$$p_{N_2O_4} = \frac{n_{N_2O_4}}{n_T} \times p_T = \frac{0.6w}{1.4w} \times 2 = 0.857\,\text{atm}$$
$$p_{NO_2} = \frac{n_{NO_2}}{n_T} \times p_T = \frac{0.8w}{1.4w} \times 2 = 1.143\,\text{atm}.$$

Hence,

$$K_p = \frac{{p_{NO_2}}^2}{p_{N_2O_4}} = \frac{(1.143)^2}{0.857} = 1.52\,\text{atm}.$$

Method 2

Approach: Instead of defining the initial amount of $N_2O_4(g)$, we can choose to work with defining the initial pressure of $N_2O_4(g)$.

Solution: Let y be the initial partial pressure of $N_2O_4(g)$. Note that the initial pressure is not 2 atm.

	$\mathbf{N_2O_4(g)}$	$\rightleftharpoons$	$\mathbf{2NO_2(g)}$
Initial partial pressure (atm)	y		0
Change in partial pressure (atm)	$-0.4y$		$+0.8y$
Equilibrium partial pressure (atm)	$0.6y$		$0.8y$

Total pressure, p_T at equilibrium $= 2$ atm.

$$\begin{aligned} p_T = p_{N_2O_4} + p_{NO_2} &= 2, \\ 0.6y + 0.8y &= 2, \\ y &= 1.429\,\text{atm}. \end{aligned}$$

Hence,

$$K_p = \frac{{p_{NO_2}}^2}{p_{N_2O_4}} = \frac{(0.8y)^2}{0.6y} = \frac{0.64 \times 1.429}{0.6} = 1.52\,\text{atm}.$$

Exercise:

(i) At a particular temperature, 2.5 mol of $CO(g)$ and 2.5 mol of $H_2(g)$ are allowed to react in a 2 dm^3 vessel:

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g).$$

The equilibrium mixture was found to contain 0.4 mol of $CH_4(g)$. Calculate K_c for the reaction.

(ii) 4.0 mol of NOCl(g) is allowed to decompose. It is found that only 28% of NOCl(g) has dissociated and the total pressure of the equilibrium mixture is 2 atm. Calculate the value of K_p.

$$2\mathrm{NOCl(g)} \rightleftharpoons 2\mathrm{NO(g)} + \mathrm{Cl_2(g)}.$$

[**Answer:** (i) $0.139\,\mathrm{mol^{-2}\,dm^6}$, and (ii) 3.71×10^{-2} atm.]

6.4 Le Chatelier's Principle

Le Chatelier's Principle is a helpful rule for predicting the effects of changes applied to a system that is already at equilibrium.

It states that, "When a system in equilibrium is subjected to a change, the system responds in such a way as to counteract the imposed change and reestablish the equilibrium state."

The change can be brought about by changes in *concentration, pressure, volume, presence of catalyst, or temperature.*

The principle helps us to predict in which direction the equilibrium position will shift (favouring either the forward or backward reaction) in response to the change.

When a change in conditions is introduced to an equilibrium system, the system will no longer be in equilibrium since the change will affect the rates of both forward and backward reactions to different extents. The system will then readjust itself to attain a new equilibrium where the concentrations of reactants and products become constant again. These concentration values will, however, be **different from the previous equilibrium state**.

However, the values of K_c and K_p remain unchanged as these are only affected by changes in temperature.

Q: Why are the equilibrium constants only affected by a temperature change?

A: Remember that K_c can be perceived as the ratio of rate constants? Now, rate constant can be perceived as $k = A\exp(-E_\mathrm{a}/RT)$. So do you see now that temperature affects the rate constant and thus the equilibrium constant?

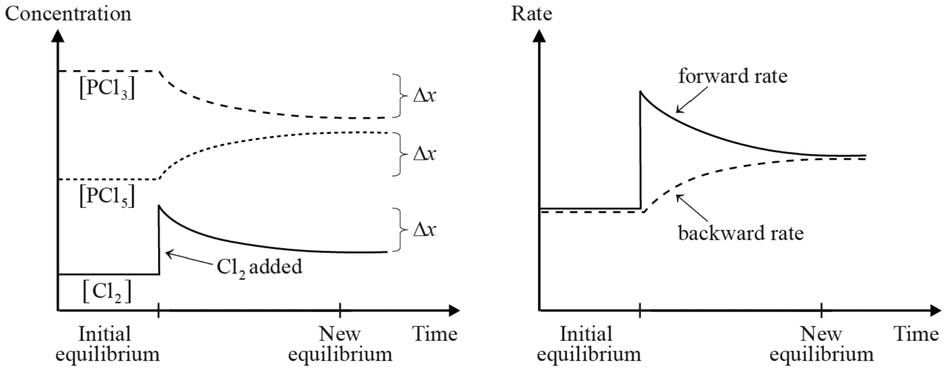
6.4.1 *Effect of concentration changes*

Let us consider the reaction $\mathrm{PCl_3(g)} + \mathrm{Cl_2(g)} \rightleftharpoons \mathrm{PCl_5(g)}$.

6.4.1.1 *Effect of adding a reactant (at constant volume)*

When extra $Cl_2(g)$ is added at constant volume to the equilibrium mixture, its concentration increases.

According to Le Chatelier's Principle, the system will attempt to remove some of the extra $Cl_2(g)$ by favouring the forward reaction. The equilibrium position will shift to the right. More $PCl_3(g)$ and $Cl_2(g)$ will react to form $PCl_5(g)$ until a new equilibrium is established.



Note: Δx = change in [substance]

This new equilibrium mixture has a different composition compared to the initial equilibrium mixture before the change is introduced, but K_c remains unchanged. At the new position of equilibrium, $[Cl_2]$ increases (as not all the $Cl_2(g)$ added has been completely removed) while $[PCl_3]$ decreases (as it was consumed in order to remove the additional Cl_2 that has been added) and $[PCl_5]$ increases.

Q: How do we use kinetics to explain the way the system responds to the change?

A: When extra $Cl_2(g)$ is added while keeping the volume constant, the forward rate rapidly increases because the effective collisional frequency increases as there are now more Cl_2 molecules in the system. The increased amount of PCl_5 formed soon results in an increase in the backward rate. As time passes, the forward rate and backward rate become equal again, but at a higher value than the previous equilibrium state.

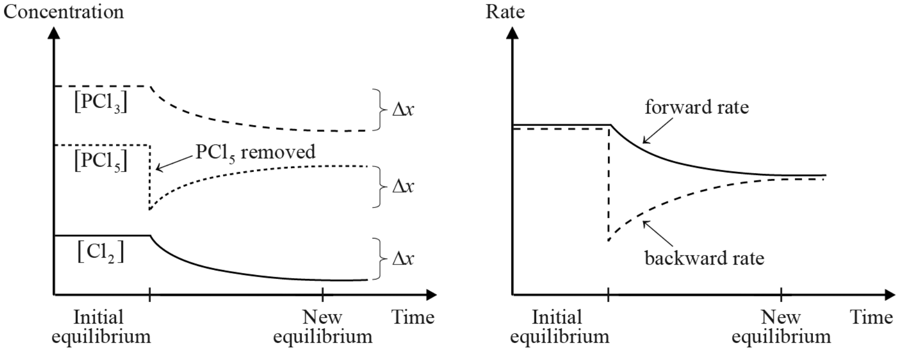
Q: But shouldn't the new forward rate be lower than the old forward rate since $[PCl_3]$ has decreased because it was being consumed to remove the Cl_2?

A: Based on the decrease in $[PCl_3]$, the forward rate should be lower. But do not forget that at the new equilibrium position, $[Cl_2]$ is higher than at the old equilibrium position. So the higher $[Cl_2]$ and lower $[PCl_3]$ together ensures a new higher forward rate. Now, if you are still not convinced, the $[PCl_5]$ at the new equilibrium position is higher than at the old equilibrium position. This leads to a new higher backward rate. Since both the forward rate and backward rate at the new equilibrium position are the same, then a new higher backward rate also means a new higher forward rate!

6.4.1.2 *Effect of removing a reactant (at constant volume)*

With reference to the same reaction, $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$, when $PCl_5(g)$ is removed at constant volume from the equilibrium mixture, its concentration decreases.

According to Le Chatelier's Principle, the system will attempt to replace the removed $PCl_5(g)$ by favouring the forward reaction. The equilibrium position will shift to the right. More $PCl_3(g)$ and $Cl_2(g)$ will react to form $PCl_5(g)$ until a new equilibrium is established.



Note: Δx = change in [substance]

Not all the $PCl_5(g)$ removed has been completely replenished. In all, $[PCl_5]$ changes by the same extent as both $[PCl_3]$ and $[Cl_2]$, but K_c remains unchanged.

Q: How do we use kinetics to explain the way the system responds to the change?

A: When some $PCl_5(g)$ is removed, the backward rate decreases rapidly because the effective collisional frequency decreases as there are now fewer PCl_5 molecules in the system. The forward rate also decreases as there are smaller amounts of PCl_3 and Cl_2 formed. The backward rate slowly picks up as more PCl_5 forms. As time passes, the forward rate and backward rate become equal again, but at a lower value than the previous eqiuilibrium state.

Removal of a species can also be achieved by introducing a new substance that will react with it (see Example 6.7 below).

Example 6.7: What will be observed when $OH^-(aq)$ is added to the following system at equilibrium?

$$\underset{\text{yellow}}{2CrO_4^{2-}(aq)} + 2H^+(aq) \rightleftharpoons \underset{\text{orange}}{Cr_2O_7{}^{2-}(aq)} + H_2O(l).$$

Solution: The added $OH^-(aq)$ will react with $H^+(aq)$ and cause $[H^+]$ to decrease. According to Le Chatelier's Principle, the system will attempt to increase $[H^+]$ by favouring the backward reaction. The equilibrium position will shift to the left. The solution will thus change colour from orange to yellow.

6.4.2 *Effect of pressure changes*

Changes in pressure only affect reactions that involve gases. A pressure change can be introduced through the following ways:

(a) addition/removal of a gaseous component of the equilibrium mixture under conditions of constant volume,
(b) expansion or compression of the reaction vessel,
(c) addition of an inert gas at constant volume, and
(d) addition of an inert gas at constant pressure.

6.4.2.1 *Addition/removal of a gaseous component of the equilibrium mixture*

Addition or removal of a gaseous component in the equilibrium mixture affects the partial pressure of that particular component. The effect of partial pressure changes is similar to that of concentration changes since $p \propto n/V$ (assuming ideal behaviour).

Let us consider the same reaction: $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$.

When extra $Cl_2(g)$ is **added** at constant volume to the equilibrium mixture, its partial pressure increases since n increases.

According to Le Chatelier's Principle, the system will attempt to **remove some of the extra** $Cl_2(g)$ by favouring the forward reaction. The equilibrium position will shift to the right. More $PCl_3(g)$ and $Cl_2(g)$ will react to form $PCl_5(g)$ until a new equilibrium is established.

Does this sound familiar? Refer to Sec. 6.4.1 for more details.

6.4.2.2 *Expansion or compression of reaction vessel*

Expansion or compression of the reaction vessel affects the total pressure (p_T) of the system:

Recall: Boyle's Law

$$V \propto \frac{1}{p}.$$

- Expansion (an increase in volume) causes p_T of system to decrease, which means that the partial pressure of each of the component gases also decreases.
- Compression (a decrease in volume) causes p_T of system to increase, which means that the partial pressure of each of the component gases also increases.

The effect of changes in p_T of a gaseous system depends on the relative number of gaseous molecules on the right and left sides of the balanced chemical equation. There are two different scenarios as shown in the examples below:

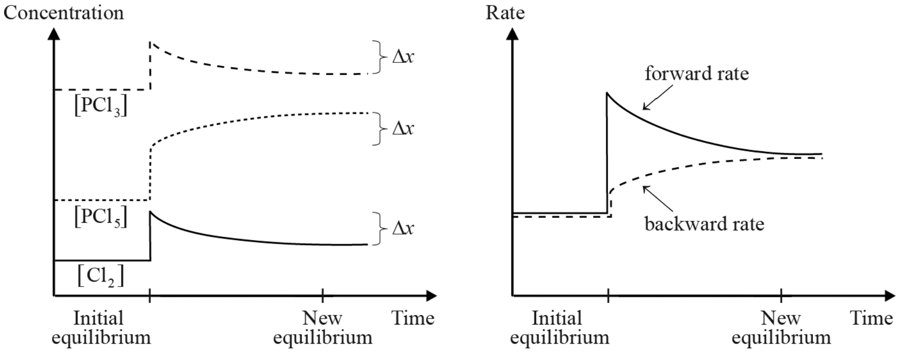
- **Changing the total pressure of a system in which the number of gas molecules on each side of the chemical equation is different:**

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

According to Le Chatelier's Principle, when the **total pressure** of the system is **increased**, concentrations of all species (both reactants and products) also increase. The system will attempt to **decrease the overall pressure**, **by favouring the reaction that decreases the overall number of gaseous molecules**, i.e., the forward reaction is favoured.

Recall:
$pV = nRT$, $p \propto n$.

The equilibrium position will shift to the right. More $PCl_3(g)$ and $Cl_2(g)$ will react to form $PCl_5(g)$ until a new equilibrium is established.



Note: Δx = change in [substance]

Since $p \propto n/V$ (assuming ideal behaviour), when p_T of the system is increased, concentrations of all species (both reactants and products) also increase. In terms of the number of moles, the new equilibrium mixture has a higher percentage of $PCl_5(g)$ but lower percentages of $PCl_3(g)$ and $Cl_2(g)$, as compared to the old equilibrium position, but the equilibrium constant remains unchanged.

The reverse can be said when total pressure is decreased.

Q: How do we use kinetics to explain the way the system responds to the change?

A: When the total pressure increases due to a decrease in the volume of the container, the volume of the system shrinks. The gaseous particles now occupy a smaller volume. As a result, the effective collisional frequencies of both the forward and backward reactions increase. These lead to increases in the rates of both the forward and backward reactions. BUT the rate of the reaction that involves a greater number of particles colliding is increased by a greater extent. So, in this case, since the forward reaction involves the collision of two particles whereas the backward reaction only one, the percentage increase of the forward rate is higher than the backward rate. As time passes, the forward rate and backward rate become equal again, but at a higher value than the previous equilibrium state.

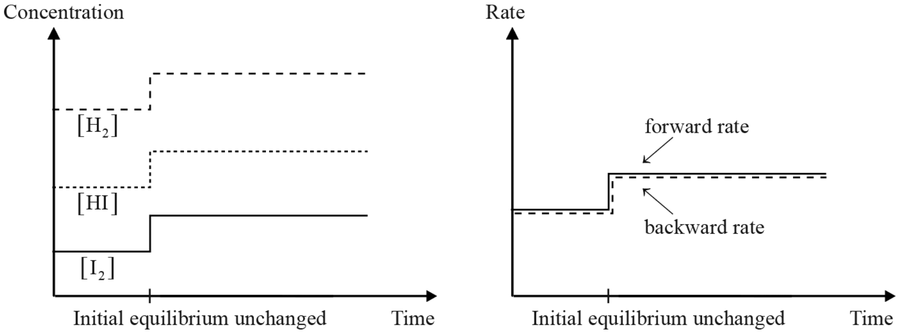
- **Changing the total pressure of a system in which the number of gas molecules on each side of the chemical equation is the same:**

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g).$$

According to Le Chatelier's Principle, when the total pressure of the system is increased, concentrations of all species (both reactants and products) also increase. The system will attempt to decrease the overall pressure by favouring the reaction that decreases the overall number of gaseous molecules.

However, since both forward and backward reactions produce the same number of gaseous molecules, none of these reactions is favoured over the other.

The equilibrium position will not shift as the system remains at equilibrium. In terms of the number of moles, the equilibrium composition is unchanged and so is the equilibrium constant, BUT both the forward and backward rates do increase!



Q: How do we use kinetics to explain the way the system responds to the change?

A: When the total pressure increases, the volume of the system shrinks. The gaseous particles now occupy a smaller volume. As a result, the effective collisional frequencies of both the forward and backward reactions increase. These lead to increases in the rates of both the forward and backward reactions. Since both reactions involve the collision of the same number of particles, both rates increase by the same extent. As time passes, the forward rate and backward rate remain equal, but at a higher value than the previous equilibrium state.

6.4.2.3 *Addition of an inert gas at constant volume*

Consider the reaction: $A(g) + B(g) \rightleftharpoons C(g)$.

When an inert gas is added at constant volume to the equilibrium mixture, the total pressure of the system increases:

$$p_T = p_A + p_B + p_C + p_{\text{inert gas}}.$$

The increase in p_T is due to an increase in n_T since $n_T = n_A + n_B + n_C + n_{\text{inert gas}}$.

However, there are no changes in the partial pressures of the reacting gases since for each gas, concentration is unchanged (i.e., both n and V are constant).

Thus, the equilibrium position will not shift as the system remains at equilibrium. The equilibrium composition is unchanged and so is the equilibrium constant.

Recall:

$$p_A = \frac{n_A}{n_T} \times p_T,$$

where n_A is the amount of A(g) and n_T is the total amount of gas molecules.

Q: When inert gas particles are added into the system, wouldn't the inert gas particles take up the space in between the reactant particles and inhibit them from reacting?

A: Take note that in the gaseous state, the separation between two gas particles is huge. Moreover, all the gas particles are constantly in rapid motion. Thus, **introducing inert gas particles at constant volume does not affect the position of equilibrium no matter what the chemical equation for the reaction is**!

6.4.2.4 *Addition of an inert gas at constant pressure*

When an inert gas is added at constant pressure to the equilibrium mixture, the volume of the vessel increases (i.e., expansion takes place) to keep total pressure constant.

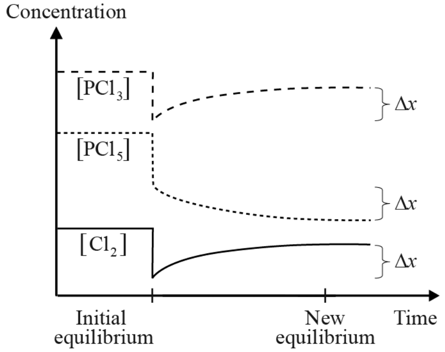
The expansion leads to a decrease in the concentrations of all gases and also their partial pressures (since the same number of molecules now occupy a bigger volume). Whether there is a change in the position of equilibrium depends on the following:

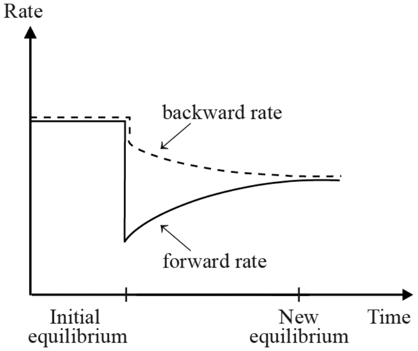
- **If the numbers of gas molecules are not the same for both sides of the equation:**

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

According to Le Chatelier's Principle, the system will attempt to counteract the change by favouring the reaction that increases the overall number of gaseous molecules, i.e., the backward reaction is favoured.

The equilibrium position will shift to the left. More PCl_5(g) will dissociate to form PCl_3(g) and Cl_2(g) until a new equilibrium is established.





Note: Δx = change in [substance]

The concentrations of all species (both reactants and products) decrease. In terms of the number of moles, the new equilibrium mixture has a higher percentage of $PCl_3(g)$ and $Cl_2(g)$ but a lower percentage of $PCl_5(g)$ as compared to the old equilibrium position. The equilibrium constant remains unchanged.

Q: How do we use kinetics to explain the way the system responds to the change?

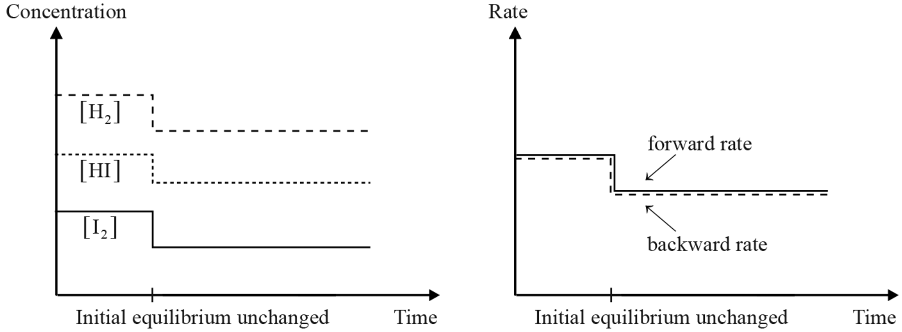
A: When the volume increases due to the addition of an inert gas at constant pressure, the concentration of each reacting gas decreases. As a result, the effective collisional frequencies of both the forward and backward reactions decrease. These lead to decreases in the rates of both the forward and backward reactions. BUT the rate of the reaction that involves a greater number of particles colliding is decreased by a greater extent. So, in this case, since the forward reaction involves the collision of two particles whereas the backward reaction only one, the percentage decrease of the forward rate is higher than the backward rate. As time passes, the forward rate and backward rate become equal again, but at a lower value than the previous equilibrium state.

- **If the numbers of gas molecules are the same for both sides of the equation:**

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g).$$

The addition of inert gas at constant pressure results in an increase in the volume of the system. The concentrations of the reacting gases decrease. According to Le Chatelier's Principle, the system will attempt to counteract the change by favouring the reaction that increases the overall number of gaseous molecules.

However, since both forward and backward reactions produce the same number of gaseous molecules, none of these reactions is favoured over the other. Thus, the equilibrium position will not shift as the system remains at equilibrium. In terms of the number of moles, the equilibrium composition is unchanged and so is the equilibrium constant.



Q: How do we use kinetics to explain the way the system responds to the change?

A: When inert gas is added at constant pressure, the volume of the system expands. The gaseous particles now occupy a bigger volume. As a result, the effective collisional frequencies of both the forward and backward reactions decrease. These lead to decreases in the rates of both the forward and backward reactions. Since both reactions involve the collision of the same number of particles, both rates decrease by the same extent. As time passes, the forward rate and backward rate remain equal, but at a lower value than the previous equilibrium state.

6.4.3 *Effect of temperature changes*

Increasing the temperature of an equilibrium system will result in the following:

- a change in the equilibrium position, and
- **a change in the value of the equilibrium constant**.

Consider the hypothetical reaction below whereby the forward reaction is exothermic:

$$a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}, \quad \Delta H < 0.$$

- **Effect of an increase in temperature**
  According to Le Chatelier's Principle, when there is an **increase in temperature**, the system will attempt to **decrease** the **overall temperature**

by **favouring** the **reaction** that **absorbs heat**, i.e., the **endothermic** reaction.

Since the backward reaction is endothermic, the equilibrium position will shift to the left. Greater amounts of C and D will react to form A and B until a new equilibrium is established.

This new equilibrium mixture will contain more of the reactants A and B, and less of the products C and D.

As a result, the value of the equilibrium constant becomes smaller (recall: $K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$).

Q: How do we use kinetics to explain the way the system responds to the change?

A: When the temperature of the system is increased, the rates of both the forward and backward reactions increase as the rate constant is temperature dependent ($k = A\exp(-E_a/RT)$). **The percentage increase in rate is greater for the reaction with the greater activation energy** (refer to Chap. 5 on Reaction Kinetics), i.e., the backward reaction for the reaction here. So as time passes, the position of equilibrium shifts to the left. This explains how the system "gets rid" of the added heat.

Q: I am still not convinced! Can you please prove it to me?

A: Look at the following calculations which assume the value of A to be one:

E_a (kJ mol^{-1})	$k = A\exp(-E_a/RT)$ at T = 300 K	$k = A\exp(-E_a/RT)$ at T = 400 K	Percentage Change in Rate Constant
500 (backward)	0.818	0.860	5.13
200 (forward)	0.923	0.942	2.06

As can be seen from the above, an increase in temperature leads to an increase in the rate constant for both the forward and backward reactions. BUT there is a greater percentage increase for the reaction that has a higher activation energy (E_a).

- **Effect of a decrease in temperature**
  According to Le Chatelier's Principle, when there is a **decrease in temperature**, the system will attempt to **increase** the **overall temperature** by **favouring** the **reaction** that **releases heat**, i.e., the **exothermic** reaction.

Since the forward reaction is exothermic, the equilibrium position will shift to the right. Greater amounts of A and B will react to form C and D until a new equilibrium is established.

This new equilibrium mixture will contain less of the reactants A and B, and more of the products C and D.

As a result, the value of the equilibrium constant becomes larger.

Similar arguments can be applied to the case where the forward reaction is endothermic:

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D}, \quad \Delta H > 0.$$

Just remember that,

- an increase in temperature favours the endothermic reaction, and
- a decrease in temperature favours the exothermic reaction.

6.4.4 *Effect of temperature changes on the value of the equilibrium constant*

K_c can be expressed as a ratio of the rate constants of a reversible reaction as follows:

$$K_\mathrm{c} = k_\mathrm{f}/k_\mathrm{b}.$$

Since the rate constant is dependent on temperature, $k = A\exp(-E_\mathrm{a}/RT)$, so too is the equilibrium constant. How is it actually affected? We know that reaction rate increases when temperature increases. This means that equilibrium can be attained at a faster rate if temperature is raised.

We also know that when temperature is raised, the endothermic reaction is favoured, i.e., there is a greater proportional increase for its rate constant as compared to the exothermic reverse reaction.

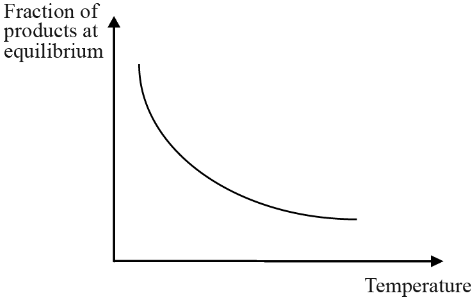
The reverse is true when temperatures are lowered. Both the reaction rates decrease and equilibrium is attained at a slower rate. The exothermic reaction is favoured, i.e., there is a smaller proportional decrease for its rate constant as compared to the endothermic forward reaction.

All in all, given that $K_\mathrm{c} = k_\mathrm{f}/k_\mathrm{b}$, and that a larger rate constant k indicates a faster rate:

- For an exothermic forward reaction $a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D}$, $\Delta H < 0$,
  - an increase in temperature will result in K_c becoming smaller since the rate of the backward reaction has increased by a greater proportion than the rate of the forward reaction, i.e., $\Delta k_\mathrm{f} < \Delta k_\mathrm{b}$;

  - a decrease in temperature will result in K_c becoming larger since the rate of the backward reaction has decreased by a greater proportion than the rate of the forward reaction, i.e., $|\Delta k_f| < |\Delta k_b|$.
- For an endothermic forward reaction $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$, $\Delta H > 0$,
  - an increase in temperature will result in K_c becoming larger since the rate of the forward reaction has increased by a greater proportion than the rate of the backward reaction, i.e., $\Delta k_f > \Delta k_b$;
  - a decrease in temperature will result in K_c becoming smaller since the rate of the forward reaction has decreased by a greater proportion than the rate of the backward reaction, i.e., $|\Delta k_f| > |\Delta k_b|$.

Example 6.8:



For which system is the profile of the graph correct?

(a) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$, $\Delta H = -910\,\text{kJ mol}^{-1}$.
(b) $2NOBr(g) \rightleftharpoons 2NO(g) + Br_2(g)$, $\Delta H = +30\,\text{kJ mol}^{-1}$.

Solution: The profile of the graph fits system (a). Based on the graph, the proportion of products at equilibrium decreases as temperature increases. This implies that the backward reaction is favoured at higher temperatures.

According to Le Chatelier's Principle, when there is an increase in temperature, the system will attempt to decrease the overall temperature by favouring the endothermic reaction.

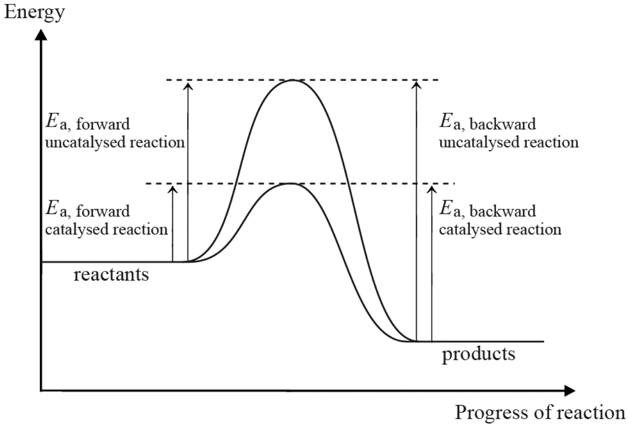
Therefore, the backward reaction is endothermic and thus the forward reaction is exothermic as shown here:

$$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g), \quad \Delta H = -910\,\text{kJ mol}^{-1}.$$

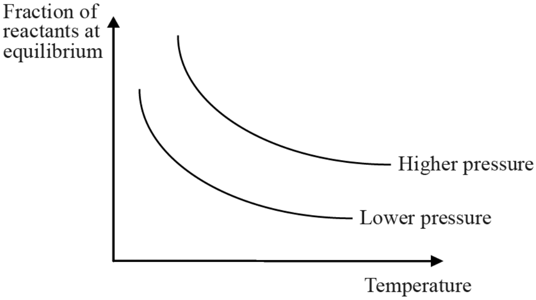
6.4.5 *Effect of catalyst*

A catalyst only aids a reaction in attaining equilibrium in a shorter time. It does not cause any changes to the position of the equilibrium and hence the value of the equilibrium constant.

This is because a catalyst lowers the activation energies of both the forward and backward reactions to the same extent. This, in turn, leads to the rates of both the forward and backward reactions being increased to the same extent.



Example 6.9:



Which of the following system(s) will give the graphs shown?

(a) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$, $\Delta H = -910\,\text{kJ mol}^{-1}$.
(b) $2NOBr(g) \rightleftharpoons 2NO(g) + Br_2(g)$, $\Delta H = +30\,\text{kJ mol}^{-1}$.
(c) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $\Delta H = -92\,\text{kJ mol}^{-1}$.
(d) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, $\Delta H = +53\,\text{kJ mol}^{-1}$.
(e) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, $\Delta H = +57\,\text{kJ mol}^{-1}$.

Solution: According to Le Chatelier's Principle, when there is an increase in temperature, the system will attempt to decrease the overall temperature by favouring the endothermic reaction.

Based on the graph, the proportion of reactants at equilibrium decreases as temperature increases. This implies that the **forward reaction is endothermic**.

According to Le Chatelier's Principle, when there is an increase in pressure, the system will attempt to decrease the overall pressure by favouring the reaction that decreases the overall number of gaseous molecules.

Since the graph indicates that at a given temperature, the proportion of reactants at equilibrium increases when pressure is increased, the backward reaction must be favoured at higher pressures. This implies that the **number of molecules on the left-hand side of the equation is lower than that on the right-hand side.**

Based on the two features discussed, the systems to which the graphs correspond to are:

(b) $2NOBr(g) \rightleftharpoons 2NO(g) + Br_2(g), \quad \Delta H = +30\,kJ\,mol^{-1}$, and
(e) $N_2O_4(g) \rightleftharpoons 2NO_2(g), \quad \Delta H = +57\,kJ\,mol^{-1}$.

Exercise: Predict how the position of equilibrium will be affected when the following changes are made to the equilibrium system:

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g), \quad \Delta H = -206\,kJ\,mol^{-1}.$$

(i) Temperature is increased.
(ii) Total pressure is increased.
(iii) Some CO is removed.
(iv) A catalyst is added.
(v) An inert gas is added at constant volume.

Solution:

(i) It shifts to the left.
(ii) It shifts to the right.
(iii) It shifts to the left.
(iv) It does not shift.
(v) It does not shift.

Exercise: For which of these systems is the formation of products favoured when

(i) temperature is decreased;
(ii) pressure is decreased;
(iii) both temperature and pressure are increased?

(a) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g), \quad \Delta H = -198\,kJ\,mol^{-1}$.
(b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g), \quad \Delta H = +181\,kJ\,mol^{-1}$.
(c) $2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g), \quad \Delta H = +566\,kJ\,mol^{-1}$.
(d) $N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g), \quad \Delta H = +66\,kJ\,mol^{-1}$.
(e) $2O_3(g) \rightleftharpoons 3O_2(g), \quad \Delta H = -427\,kJ\,mol^{-1}$.

Solution:

(i) (a) and (e).
(ii) (c) and (e).
(iii) d only.

The discussion on Le Chatelier's Principle and the changes that affect an equilibrium system help us to understand why certain conditions are employed in trying to achieve production yield, which is especially important in the manufacturing industry amidst other considerations such as cost, time and environmental concerns.

One classic textbook example is the manufacturing conditions for the production of $NH_3(g)$, which will be discussed in the following section.

6.5 The Haber Process

The aim of the manufacturing industry is to produce the maximum yield of products in the shortest, most efficient time possible and at minimum cost.

$NH_3(g)$ is an important industrial product which has various uses such as in the manufacturing of fertilizers, household cleaners and in producing nitrogen-containing derivatives like nitric acid, which are useful for bomb making.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g), \quad \Delta H^{\ominus}{}_{(298\,\mathrm{K})} = -92.4\,\mathrm{kJ\,mol^{-1}}.$$

To maximise the yield of $NH_3(g)$ and minimise production cost, the following conditions are applied to the production process:

- *Temperature*: *450°C*
  Reason for choice: Lowering the temperature of the reaction vessel will favour the forward reaction since it is exothermic, and hence a higher yield of $NH_3(g)$ can be obtained.

  On the other hand, the rate of production can be too slow at low temperatures. Therefore, it has been found that at 450°C, a substantial yield and production rate can be achieved. Higher temperatures than this will result in lower yield and high operating costs. The latter comes from the investment in expensive reactors that can withstand the high temperature and the continuous requirement for large amounts of energy needed to maintain the high temperature.

- *Pressure*: *about 200 atm*
  Reason for choice: Increasing the pressure of the reaction vessel will favour the forward reaction since it will decrease the overall number of gaseous molecules and hence the pressure. This will increase the yield of $NH_3(g)$. However, operating at very high pressures will increase production cost, so a moderate pressure of 200 atm is used.
- *The use of catalyst*: *finely divided iron catalyst with aluminium oxide as promoter*
  Reason for use: Although the use of catalyst does not affect the yield of $NH_3(g)$, it will enable production to be faster.

My Tutorial (Chapter 6)

1. Ethanol, which is an important motor fuel nowadays, can be manufactured by direct catalytic hydration of ethene with steam, using a phosphoric acid catalyst. Assume that the reaction of ethene (C_2H_4) with steam to give ethanol (C_2H_5OH, which is gaseous at the temperature of the reaction), is at equilibrium.
   (a) Write the equation for the reaction (with state symbols).
   (b) Write the expression for the *equilibrium constant* K_c for the reaction in terms of the concentrations of reactants and products.
   (c) Use the information below to calculate the equilibrium concentration of ethanol vapour under these conditions:

$$\begin{aligned}\text{Temperature} &= 570\,\text{K},\\ \text{Pressure} &= 60 \times 10^5\,\text{Pa},\\ K_c &= 24\,\text{dm}^3\,\text{mol}^{-1} \text{ at } 570\,\text{K},\\ \text{equilibrium } [\text{H}_2\text{O(g)}] &= 0.050\,\text{mol}\,\text{dm}^{-3},\\ \text{equilibrium } [\text{C}_2\text{H}_4\text{(g)}] &= 0.45\,\text{mol}\,\text{dm}^{-3}.\end{aligned}$$

   (d) The enthalpy change for the forward reaction is $\Delta H = -46\,\text{kJ}\,\text{mol}^{-1}$. Why is a temperature of 570 K used for the reaction, rather than
      (i) a higher temperature?
      (ii) a lower temperature?
   (e) Why is a pressure of 60×10^5 Pa used for the reaction, rather than
      (i) a higher pressure?
      (ii) a lower pressure?
2. The Haber process is an important industrial process for the synthesis of ammonia, an important precursor for making industrial fertilizers.

Iron is a common catalyst used in this process. The process does not go to completion on its own and would reach the following dynamic equilibrium state:

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

(a) Define the terms *partial pressure* of a gas in a mixture of gases and *dynamic equilibrium.*

(b) In an equilibrium mixture consisting of nitrogen, hydrogen and ammonia at 800 K, the partial pressures of the three gases are 20.4, 57.2 and 11.7 atm, respectively.

   (i) Calculate the total pressure in the system.
   (ii) What is the mass of ammonia present under these conditions in a vessel of volume 200 m^3? (Take $R = 8.20 \times 10^{-5}\,\mathrm{m^3\,atm\,mol^{-1}\,K^{-1}}$.)
   (iii) Write an expression for K_p for the formation of ammonia.
   (iv) Calculate the value of K_p under these conditions.
   (v) What would the effect on the equilibrium yield of ammonia be under the conditions in part (b)(ii) if a better catalyst were used?
   (vi) Predict and explain the effect of an increase in temperature on the value of K_p.
   (vii) Predict and explain the effect of an increase in temperature on the rate of the forward reaction.
   (viii) Give two reasons why a new catalyst might be preferred to the existing one even though it costs more.

(c) The gases are passed through a conversion chamber containing granulated iron as a catalyst. Describe and explain the effect of the iron on:

   (i) the rate of the production of ammonia, and
   (ii) the amount of ammonia in the equilibrium mixture.

(d) The equilibrium mixture formed is then passed into a refrigeration plant. Explain why this is done and what happens after this stage?

3. At high temperatures, phosphorus pentachloride is a gas that dissociates as follows:

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

(a) Write an expression for the equilibrium constant K_p for this equilibrium.

(b) At a given temperature, the degree of dissociation of an original sample of $PCl_5(g)$ is 0.52 and the system reaches equilibrium. If the total equilibrium pressure is 2 atm, calculate the values of the equilibrium partial pressures of PCl_5 and PCl_3.

(c) Hence calculate the value of K_p and give its units.

4. This question concerns the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g),$$

which is slow even at high temperature.

(a) (i) Using your Data Booklet, calculate ΔH for the reaction between hydrogen and iodine.

(ii) Sketch an energy profile diagram for this reaction.

(b) Indicate on your sketch in (a)(ii):

(i) ΔH for the reaction,

(ii) the activation energy for the forward reaction ($E_{a(f)}$), and

(iii) the activation energy for the reverse reaction ($E_{a(b)}$).

(c) For an analogous reaction involving the formation of hydrogen chloride

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g),$$

explain how you would expect the activation energy of the forward reaction to be compared with that shown for the formation of HI.

(d) The reaction for the formation of hydrogen iodide does not go to completion but reaches an equilibrium state.

(i) Write an expression for the equilibrium constant K_c for this reaction.

(ii) A mixture of 2.9 mol of H_2 and 2.9 mol of I_2 is prepared and allowed to reach equilibrium in a closed vessel of 250 cm^3 capacity at 700°C. The resulting equilibrium mixture is found to contain 4.5 mol of HI. Calculate the value of K_c at this temperature.

(iii) Explain why the formation of hydrogen chloride goes to completion in contrast to the formation of hydrogen iodide.

(e) In an experiment to establish the equilibrium concentration in (d)(ii), the reaction is allowed to reach equilibrium at 723 K and then quenched by addition of a large known volume of water. The concentration of iodine in this solution is then determined by titration with standard sodium thiosulfate solution.

(i) Explain the purpose of quenching.

(ii) Write an equation for the reaction between sodium thiosulfate and iodine.
(iii) What indicator would you use? Give the colour change when the end point is reached.
(iv) In this titration and in titrations involving potassium manganate(VII), a colour change occurs during the reaction. Why is an indicator usually added in iodine/thiosulfate titrations but not in titrations that involve potassium manganate(VII)?

(f) The rate expression for the forward reaction between hydrogen and iodine is

$$\text{Rate} = k[\text{H}_2][\text{I}_2].$$

(i) What is the order of the reaction with respect to iodine?
(ii) When 0.20 mol each of H_2 and I_2 are mixed at 600°C in a vessel of $500\,\text{cm}^3$ capacity, the initial rate of formation of HI is found to be $2.3 \times 10^{-5}\,\text{mol}\,\text{dm}^{-3}\,\text{s}^{-1}$. Calculate a value for k at 600°C, stating the units.