Chemical equilibrium

$$CaCO_3(s) + 2HCl \rightarrow CaCl_2 + H_2O(l) + CO_2(g)$$

This reaction is an example of one that proceeds to completion if the correct proportions of reactants are present. The reactants are totally consumed.

Not all reactions proceed to completion. In many reactions, the final reaction mixture consists of both products and reactants.

Dissolution of iodine in water

$$I_2(s) \rightarrow I_2(aq)$$

$$I_2(aq) \rightarrow I_2(s)$$

As iodine dissolves in water, the solution becomes more yellow-orange. The colour deepens over time until a point is reached when there is no further change.

This example shows us that chemical reactions are reversible.

$$I_2(s) \rightleftarrows I_2(aq)$$

Conditions for chemical equilibrium

The previous example showed that chemical equilibria are dynamic and not static. All systems in chemical equilibria exhibit the following characteristics.

- The system is closed.
- The observable or measurable properties of the system are constant. These properties are often called *macroscopic* properties and they include colour, electrical conductivity, concentration and gas pressure.
- The concentrations of reactants and products are constant once equilibrium is achieved.
- The rate of the forward reaction equals the rate of the reverse reaction. Thus the system is dynamic.

- *define Le Chatelier’s principle*

Le Chatelier's principle

'If a system is at equilibrium and a change is made that disturbs the equilibrium, then the system responds in such a way as to counteract the change and eventually a new equilibrium is established.'

- *identify factors which can affect the equilibrium in a reversible reaction*

The factors that may cause a disturbance to a chemical system in equilibrium are:

- temperature
- concentration (or gas partial pressure)
- total gas pressure (in gaseous equilibria).

It should be noted at this point that catalysts do not alter the position of a system already in equilibrium. Also, if a system is not at equilibrium then catalysts reduce the time to reach equilibrium; however, the final equilibrium position is the same whether the catalyst is present or not.

Temperature

Reactions can be classified as endothermic or exothermic on the basis of whether heat is absorbed or released in the forward reaction. Using Le Chatelier's principle, the following predictions can be made.

- For endothermic equilibria, an increase in temperature causes the equilibrium to shift to favour the products.
- For exothermic equilibria, an increase in temperature causes the equilibrium to shift to favour the reactants.

Example:

The reaction of colourless lead (II) ions and colourless chloride ions to form a white precipitate of lead (II) chloride is an exothermic equilibrium.

$$Pb^{2+} + 2Cl^- \rightleftharpoons PbCl_2(s)$$

Experiment:

The effect of temperature on this equilibrium can be demonstrated by adding drops of lead (II) nitrate solution to a sodium chloride solution in a beaker until a faint white suspension of lead (II) chloride appears.

Mix thoroughly.

Divide this mixture into two test tubes.

Place one tube in iced water or leave it at room temperature, and place the other in a beaker of hot water.

Allow the systems to adjust to the temperature change.

Observations:

More precipitate is present in the tube at the lower temperature.

In the hot water, the precipitate should reduce in amount, or even dissolve completely.

The precipitation of lead (II) chloride decreases with increasing temperature. This demonstrates a shift in an exothermic equilibrium.

Explanation:

Heat is a product of the forward reaction. *(Exothermic)*

- If the *tube is cooled, heat is removed*.
- This disturbs the equilibrium and so a change occurs to oppose the disturbance.
- The equilibrium *moves to the right to make more heat*; consequently, more white precipitate forms.

- If the *tube is heated*, the system responds to *remove some of the added heat* by shifting the equilibrium *to the left*.
- Thus, more precipitate dissolves in the heated tube.

Concentration

Increasing or decreasing the concentration of reactants or products can shift the position of a chemical equilibrium. Using Le Chatelier's principle, the following predictions can be made.

- Increasing the concentration of reactants or decreasing the concentration of products shifts the equilibrium to favour the products.
- Decreasing the concentration of reactants or increasing the concentration of products shifts the equilibrium to favour the reactants.

Example:

An equilibrium mixture consisting of colourless NO, colourless O_2 and brown NO_2 is held at a constant temperature. The mixture is pale brown due to NO_2.

$$2NO(g) + O_2(g) \rightleftarrows \underset{\text{brown}}{2NO_2(g)}$$

Gas partial pressure

- Increasing the partial pressure of a reactant gas shifts the equilibrium to favour the products.
- Increasing the partial pressure of a product gas shifts the equilibrium to favour the reactants.

$$2NO(g) + O_2(g) \rightleftarrows \underset{\text{brown}}{2NO_2(g)}$$

Experiment: A gas syringe was used to inject oxygen gas into the equilibrium mixture. The mixture turns from light brown to darker brown.
Explanation: The increase in the oxygen partial pressure has disturbed the equilibrium; to counteract the change, the equilibrium has shifted to the right to reduce the amount of O_2 in the mixture. Thus the depth of brown colour has increased.

Experiment:

A sample of NO_2 is introduced into a gas syringe held at constant temperature.

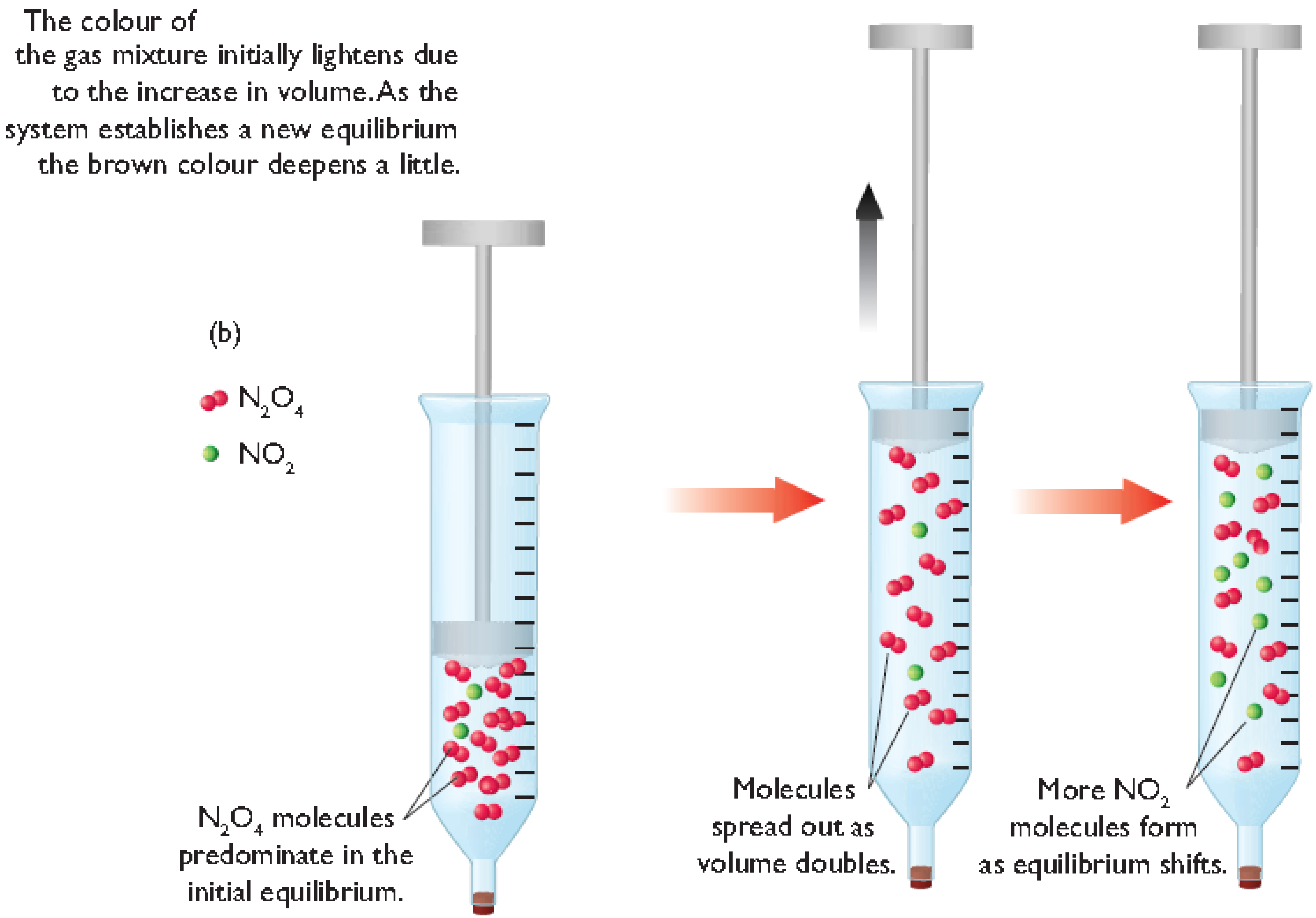
The gas eventually comes to equilibrium with its dimer, N_2O_4.

The plunger is then pulled out to double the volume. This is equivalent to halving the gas pressure.

Observations:

The brown colour of the gas mixture initially lightens as the volume suddenly rises.

The pale brown mixture then slowly darkens in colour.



Explanation:

The *initial lightening* of the brown colour is due to the *doubling in volume* and the *spreading out* of the gaseous *particles*.

This change has *disturbed the equilibrium* and halved the partial pressures of each gas in the reaction vessel.

The system responds by *shifting to the left* to counteract the change.

This shift to the left *increases the number of particles* in the syringe and as these particles are brown, the *brown colouration intensifies*.

- *describe the solubility of carbon dioxide in water under various conditions as an equilibrium process, and explain the process in terms of Le Chatelier's principle*

Carbon dioxide equilibrium in aqueous systems

Carbon dioxide is an acidic oxide. It dissolves in water to produce a solution of carbonic acid (H_2CO_3). Carbonic acid is in equilibrium with hydrogen ions and hydrogen carbonate ions as shown in the following equations.

$$CO_2(g) \rightleftharpoons CO_2(aq) \quad (1)$$

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \quad (2)$$

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \quad (3)$$

This dissolution reaction is exothermic.

Changing the pH

Experiment: Drops of lemon juice are injected into the soda water.
Observation: The soda water degasses.
Explanation: The addition of the lemon juice increased the hydrogen ion concentration of the soda water. This caused the carbonic acid equilibrium to shift to the left to use up some of the added acid.

$$H_2CO_3(aq) \rightleftarrows H^+(aq) + HCO_3^-(aq)$$

The increase in carbonic acid levels causes the following two equilibria to reverse and produce more gaseous carbon dioxide.

$$CO_2(aq) + H_2O(l) \rightleftarrows H_2CO_3(aq)$$

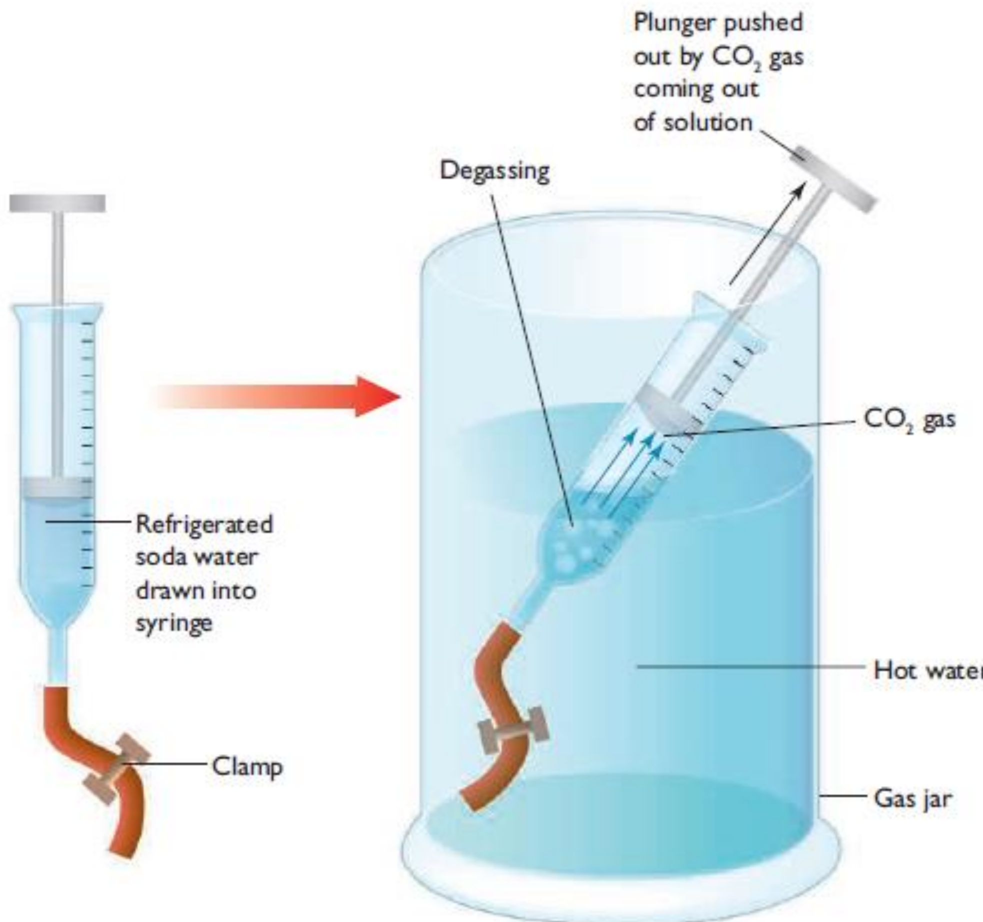
$$CO_2(g) \rightleftarrows CO_2(aq)$$

Changing the temperature (at constant pressure)

Experiment: Warm a sample of soda water (in a gas syringe).
Observation: The soda water degasses.
Explanation: The dissolution of carbon dioxide in water is exothermic. Heat is therefore a product of the reaction.

$$CO_2(g) \rightleftarrows CO_2(aq)$$

If heat is added, the equilibria shift to the left to counteract the change. This causes the soda water to de-gas.



Soda water degasses as it is heated, as the dissolution equilibrium is exothermic.

Question 25 (4 marks)

An indicator is placed in water. The resulting solution contains the green ion, *Ind*$^-$, and the red molecule, *HInd*. 4

Explain why this solution can be used as an indicator. In your response, include a suitable chemical equation that uses *Ind*$^-$ and *HInd*.

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Question 25

Criteria	Marks
• Clearly articulates that indicators work through equilibrium processes, linking cause and effect through Le Chatelier's principle • Includes a chemical equation, correctly using the symbols given	4
• Some links made between the action of indicators and equilibrium reactions, with reference to the symbols given OR • Correct equations and use of symbols for an acid and base showing the action of the indicator without reference to equilibrium	3
• Describes the action of indicators without the use of a chemical equation or reference to equilibrium	2
• States one relevant concept	1

Sample answer:

An indicator needs to change colour in different pH conditions. The solution would have the equilibrium:

$$\underset{\text{red}}{HInd(aq)} + H_2O(l) \rightleftharpoons \underset{\text{green}}{Ind^-(aq)} + H_3O^+(aq)$$

When a base is present, the concentration of H_3O^+ will be reduced. Le Chatelier's principle predicts the equilibrium will shift to the right, increasing the ionisation of the indicator. This shift causes the green colour to dominate.

Alternatively, when an acid is present the increased concentration of H_3O^+ will shift equilibrium left and the red colour will dominate.

Answers could include:

Separate equations to illustrate the response to an acid and a base.

- *calculate volumes of gases given masses of some substances in reactions, and calculate masses of substances given gaseous volumes, in reactions involving gases at 0ºC and 100k Pa or 25ºC and 100 kPa*

Mass–volume calculations involving gases

Avogadro's Law

Equal volumes of gases at the same temperature and pressure contain equal numbers of molecules.

This can be rearranged into:

Equal numbers of molecules of different gases occupy the same volume (at the same temperature and pressure).

Since a mole is a fixed number of molecules (6.02×10^{23}), a mole of any gas has the same volume as a mole of any other gas (at the same temperature and pressure). This volume is called the **molar volume** of a gas—the volume of one mole.

Because the volume of a gas changes quite significantly as its temperature and the pressure acting upon it change, we must always state the temperature and pressure when we give the volume of a gas. The two temperatures commonly used for the molar volume of a gas are 0°C and 25°C.

The molar volume (V_M) of any gas has the following values at the stated temperatures and pressures:

- At 0°C and 100 kPa: $V_M = 22.71$ L/mol
- At 25°C and 100 kPa: $V_M = 24.79$ L/mol

The relationship between the number of moles (n) of a gas and its volume (V) is:

$$n = V/V_M$$

This equation can be used to solve problems involving the quantities of gases involved in chemical changes.

SAMPLE PROBLEM

Figure 7.21 shows two 1-litre vessels (A and B) at the same temperature and pressure. Vessel A contains oxygen (O_2) gas, and vessel B contains an unknown gas (X_2). The mass of gas in vessel A is 9.600 g, and the mass of gas in vessel B is 11.400 g. Identify the gaseous element present in vessel B.

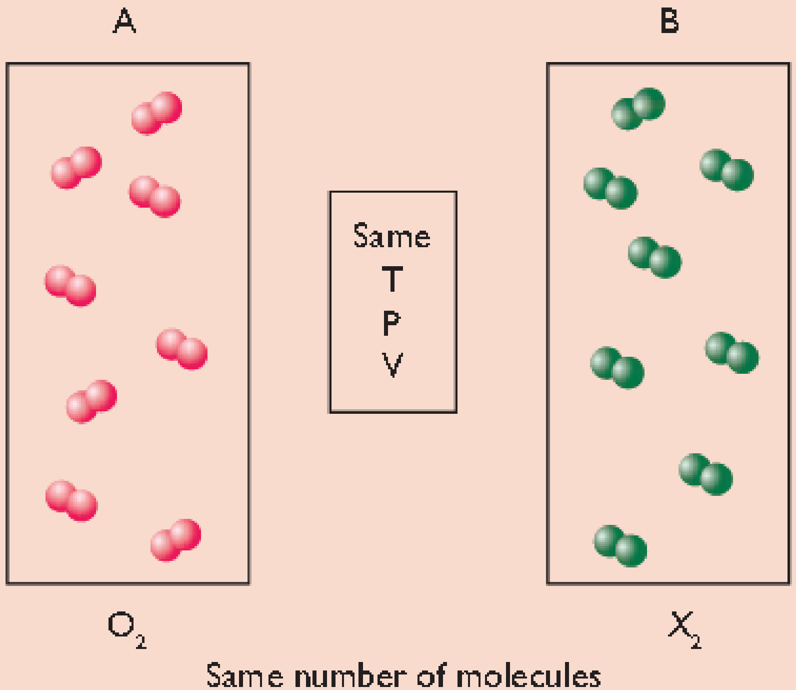

Figure 7.21 Each vessel contains the same number of molecules

According to Avogadro's Law, the same volume of gas (at the same temperature and pressure) contains the same number of molecules.

Thus, 9.600 g of oxygen contains as many molecules as 11.400 g of X_2.

Molecular weight of $O_2 = 32.00$

Let the atomic weight of $X = x$.

Molecular weight of $X_2 = 2x$

The ratio of the molecular weights will be equal to the mass ratio of each gas.

Thus,

$$9.600 : 11.400 = 32.00 : 2x$$

Solve for x.

$$x = 19.0$$

The gaseous element that has an atomic weight of 19.0 is fluorine. The gas in vessel **B** is therefore fluorine (F_2).

SAMPLE PROBLEM

A 0.60 g ribbon of magnesium is dissolved completely in sulfuric acid. Calculate the volume of dry hydrogen produced at 100 kPa and 25°C.

Step 1. Calculate the number of moles of magnesium that have reacted.

$$n(\mathrm{Mg}) = \mathrm{m/M} = 0.60/\ 24.31 = 0.02468\ \mathrm{mol}$$

Step 2. Write a balanced equation for the reaction.

$$\mathrm{Mg(s)} + \mathrm{H_2SO_4} \rightarrow \mathrm{MgSO_4} + \mathrm{H_2(g)}$$

Step 3. Determine the number of moles of hydrogen formed.

The balanced equation shows that 1 mole of magnesium produces 1 mole of hydrogen.

$$\text{Thus: } n(\mathrm{H_2}) = n(\mathrm{Mg}) = 0.02468\ \mathrm{mol}$$

Step 4: Calculate the volume of hydrogen.

$$\begin{aligned} V(\mathrm{H_2}) &= n(\mathrm{H_2}) \times V_{\mathrm{M}} \\ &= (0.02468)(24.79) \\ &= 0.612\ \mathrm{L} \end{aligned}$$

SAMPLE PROBLEM

Sulfur dioxide gas and water vapour form when hydrogen sulfide gas is oxidised by oxygen.

(a) Write a balanced equation for this reaction.

(b) Calculate the mass of sulfur dioxide formed when 100 mL of hydrogen sulfide (at 0°C and 100 kPa) is reacted with excess oxygen.

(a) $2H_2S(g) + 3O_2(g) \rightarrow 2H_2O(g) + 2SO_2(g)$

(b) Step 1. Calculate the number of moles of hydrogen sulfide.

Convert the volume of the gas to litres (0.100 L)

$n(H_2S) = V/V_M = 0.100/22.71 = 4.403 \times 10^{-3}$ mol

Step 2. Use the balanced equation to determine the number of moles of sulfur dioxide formed.

Two moles of hydrogen sulfide form two moles of sulfur dioxide (1 : 1 mole ratio).

$$n(SO_2) = n(H_2S)$$
$$= 4.403 \times 10^{-3} \text{ mol}$$

Step 3. Calculate the mass, m, of sulfur dioxide

$$M(SO_2) = 64.07 \text{ g/mol}$$
$$m = nM$$
$$m(SO_2) = nM(SO_2)$$
$$= (4.403 \times 10^{-3})(64.7)$$
$$= 0.282 \text{ g}$$