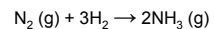


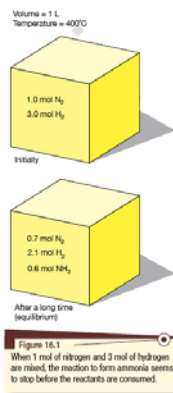
## Week 8 Controlling the Yield of Reactions

Take the industrially important reaction:



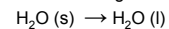
The amount of ammonia obtained upon mixing the reactants is less than stoichiometrically predicted. The reaction seems to be "stuck" when less than 2 mols of ammonia have been formed.

The stage when quantities of reactants and products remain unchanged is called **chemical equilibrium**.

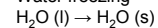


## Reversible reactions

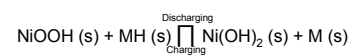
Water melting



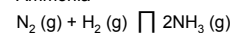
Water freezing



Nickel-metal hydride (NiMH) batteries



Ammonia



## Equilibrium explained

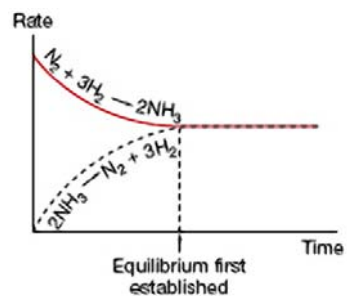


Figure 16.3  
The variation of the rates of the forward and back reactions with time when nitrogen and hydrogen are mixed.

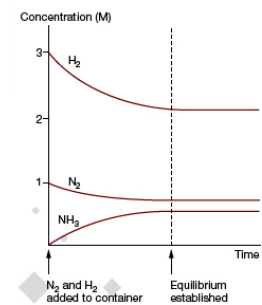


Figure 16.4  
Changes in the concentrations of  $\text{N}_2$ ,  $\text{H}_2$  and  $\text{NH}_3$  as a mixture of nitrogen and hydrogen gas reacts. As indicated by the coefficients of the equation for the reaction, for every amount of  $\text{N}_2$  that reacts, three times as much  $\text{H}_2$  reacts and twice as much  $\text{NH}_3$  is produced.

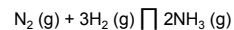
Equilibrium is a **dynamic state** since forward and back reactions occur simultaneously.

During dynamic equilibrium:

- The amounts and concentrations of chemical substances remain constant
- The total gas pressure is constant (if gases are involved)
- The temperature is constant
- The reaction is 'incomplete' (all of the substances are present in the equilibrium mixture)

## The Equilibrium Law

Consider the reaction



An unlimited number of different equilibrium mixtures of  $\text{N}_2$ ,  $\text{H}_2$  and  $\text{NH}_3$  can be prepared:

TABLE 16.1 Concentrations of different equilibrium mixtures for  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$  at  $400^\circ\text{C}$

| Equilibrium mixture | $[\text{N}_2]$ (M) | $[\text{H}_2]$ (M) | $[\text{NH}_3]$ (M)  | $\frac{[\text{NH}_3]}{[\text{N}_2][\text{H}_2]}$ | $\frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$ |
|---------------------|--------------------|--------------------|----------------------|--|--|
| A                   | 0.25               | 0.75               | 0.074                | 0.39   | 0.052  |
| B                   | 0.55               | 0.65               | 0.089                | 0.25   | 0.052  |
| C                   | 0.0025             | 0.0055             | $4.6 \times 10^{-6}$ | 0.33   | 0.051  |
| D                   | 0.0011             | 0.0011             | $2.7 \times 10^{-7}$ | 0.23   | 0.051  |

There is no obvious relationship between  $\text{N}_2$ ,  $\text{H}_2$  or  $\text{NH}_3$ .

No relationship can be seen for the values of  $\frac{[\text{NH}_3]}{[\text{N}_2][\text{H}_2]}$  or many other similar fractions

However, the fraction  $\frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$  gives an almost constant value of each mixture.

This **concentration fraction** is known as the **reaction quotient** for the reaction.

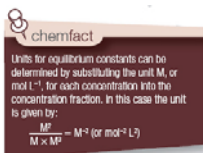
It is only at equilibrium that the reaction quotient has a constant value:

$$K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

Where  $K$  is known as the **equilibrium constant**.

From studies of equilibria, it is found that:

- Different chemical reactions have different values of  $K$ .
- For a particular reaction,  $K$  is constant for all equilibrium mixtures at a fixed temperature.



For the equation

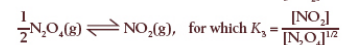
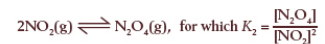
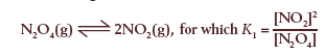
$a\text{W} + b\text{X} \rightleftharpoons c\text{Y} + d\text{Z}$  at a particular temperature then:

$$K = \frac{[\text{Y}]^c [\text{Z}]^d}{[\text{W}]^a [\text{X}]^b}$$

where  $K$  is a constant.

This is known as the **equilibrium law**.

Note that the Equilibrium Law depends on the equation used for the reaction e.g.



Therefore, it is important that the equation be specified when an equilibrium constant is quoted.

### What does an equilibrium constant tell us?

The value of  $K$  is based on equilibrium concentrations of products divided by equilibrium concentrations of reactants.

Therefore, it gives an indication of how far forward the reaction proceeded before equilibrium was reached.

- When  $K$  is between  $10^{-4}$  and  $10^4$ , there will be significant amounts of reactants and products at equilibrium.
- When  $K$  is very large ( $>10^4$ ) the equilibrium mixture consists mainly of products.
- When  $K$  is very small ( $<10^{-4}$ ), the equilibrium mixture consists mainly of reactants.

### Effect of temperature on equilibria

The value of  $K$  depends on temperature. It is not affected by addition of reactants or products, changes in pressure, or the use of catalysts.

The effect of temperature on  $K$  depends on whether the reaction is exothermic or endothermic.

As  $T^\circ$  increases:

For exothermic reactions, the amount of products decreases ( $K$  decreases) or to specify the temperature at which an equilibrium constant has been measured.

| $\Delta H$      | $T$ | $K$ |
|-----------------|-----|-----|
| Exothermic (-)  | ↑   | ↓   |
| Endothermic (+) | ↑   | ↑   |

Figure 16.8  
Effect of temperature on  $K$  for exothermic and endothermic reactions.

### Calculations using equilibrium constants

The following examples deal with equilibrium reactions in which reactants are not completely consumed.

#### Worked example 16.2a

Calculate the value of the equilibrium constant for the reaction represented by the equation:



at  $460^\circ\text{C}$ , if a 2.00 L vessel contains an equilibrium mixture of 0.0860 mol of  $\text{H}_2$ , 0.124 mol of  $\text{I}_2$  and 0.716 mol of HI.

#### Solution

$$[\text{H}_2] = \frac{n(\text{H}_2)}{V(\text{H}_2)} = \frac{0.0860}{2.00} = 0.0430 \text{ M}$$

$$[\text{I}_2] = \frac{0.124}{2.00} = 0.0620 \text{ M}$$

$$[\text{HI}] = \frac{0.716}{2.00} = 0.358 \text{ M}$$

$$K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{0.358^2}{0.0430 \times 0.0620} = 48.1$$

The equilibrium constant has a value of 48.1. (Note that in this example the constant has no units as the number of particles in the numerator and denominator of the concentration fraction are equal.)

#### Worked example 16.2c

At a particular temperature 0.0500 mol of  $\text{SO}_2$ , 0.0100 mol of  $\text{O}_2$  and 0.1500 mol of  $\text{SO}_3$  were mixed in a 2.00 L vessel and allowed to reach equilibrium according to the equation:



Analysis showed that 0.1400 mol of  $\text{SO}_3$  was present in the gas mixture at equilibrium. Calculate the value of the equilibrium constant at this temperature.

#### Solution

Because the amount of  $\text{SO}_3$  has decreased, a net back reaction must have occurred.

The amount of  $\text{SO}_3$  that has reacted is  $0.1500 - 0.1400 = 0.0100$  mol. From the equation, 2 mol of  $\text{SO}_3$  decomposes to 2 mol of  $\text{SO}_2$  and 1 mol of  $\text{O}_2$ . Therefore, 0.0100 mol of  $\text{SO}_3$  will form 0.0100 mol of  $\text{SO}_2$  and 0.005 00 mol of  $\text{O}_2$ .

So at equilibrium:

$$n(\text{SO}_2) = 0.0100 + 0.0500 = 0.0600 \text{ mol}$$

$$n(\text{O}_2) = 0.005 00 + 0.0100 = 0.0150 \text{ mol}$$

$$n(\text{SO}_3) = 0.1400 \text{ mol}$$

$$[\text{SO}_2] = \frac{n(\text{SO}_2)}{V(\text{SO}_2)} = \frac{0.0600}{2.00} = 0.0300 \text{ M}$$

$$[\text{O}_2] = \frac{0.0150}{2.00} = 0.007 50 \text{ M}$$

$$[\text{SO}_3] = \frac{0.1400}{2.00} = 0.0700 \text{ M}$$

$$K = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = \frac{0.0700^2}{0.0300^2 \times 0.007 50} = 726 \text{ M}^{-1}$$

The equilibrium constant has a value of  $726 \text{ M}^{-1}$ .

### Worked example 16.2b

The equilibrium constant for the reaction described by the equation:



is 4.5 M at 80°C. In an equilibrium mixture at this temperature, what is the concentration of  $\text{NO}_2$  if the concentration of  $\text{N}_2\text{O}_4$  is 0.0012 M?

**Solution**

$$K = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = 4.5$$

$$\text{Therefore } \frac{[\text{NO}_2]^2}{0.0012} = 4.5$$

$$[\text{NO}_2]^2 = 4.5 \times 0.0012 = 0.0054$$

Taking the square root of both sides,  $[\text{NO}_2] = \sqrt{0.0054} = 0.073 \text{ M}$

The concentration of  $\text{NO}_2$  in the equilibrium mixture is 0.073 M.

### Worked example 16.2c

The equilibrium constant for the reaction  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$  is 4.5 M at 80°C.

A gas mixture in a 2.0 L vessel at 80°C contained 0.20 mol of  $\text{N}_2\text{O}_4$  and 0.30 mol of  $\text{NO}_2$ . Decide if the reaction is at equilibrium and, if it is not, predict the direction the reaction will shift to reach equilibrium.

**Solution**

$$[\text{N}_2\text{O}_4] = \frac{n(\text{N}_2\text{O}_4)}{V(\text{N}_2\text{O}_4)} = \frac{0.20}{2.0} = 0.10 \text{ mol}$$

$$[\text{NO}_2] = \frac{n(\text{NO}_2)}{V(\text{NO}_2)} = \frac{0.30}{2.0} = 0.15 \text{ mol}$$

$$\text{The reaction quotient } \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{0.0225}{0.10} = 0.23 \text{ M}$$

Since the reaction quotient is not equal to  $K$ , the reaction is not in equilibrium. For an equilibrium to be established and the reaction quotient to equal  $K$ , the concentration of  $\text{NO}_2$  must increase and the concentration of  $\text{N}_2\text{O}_4$  must decrease, i.e. a net forward reaction will occur.

### Changing the equilibrium position of a reaction

This may be changed by

1. Adding or removing a reactant or product
2. Changing the pressure by changing the volume where gases are involved
3. Dilution where solutions are involved
4. Changing the temperature

### 1. Adding or removing a reactant or product

Consider  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

Addition of more nitrogen will cause the mixture to be out of equilibrium momentarily:

As  $\text{N}_2 \uparrow \Rightarrow$  forward reaction  $\uparrow \Rightarrow \uparrow \text{NH}_3$

As  $\text{NH}_3 \uparrow$ ,  $\text{N}_2$  and  $\text{H}_2$  back reaction  $\uparrow$

Ultimately, forward and back reactions become equal again and a new equilibrium is reached where concentrations of all the substances have changed.

The overall effect is a net forward reaction.

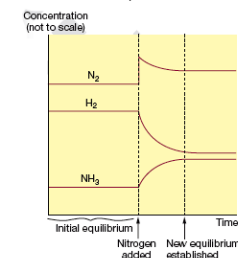


Figure 16.9  
A representation of changes in concentrations that occur when additional nitrogen gas is added to the equilibrium  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ .

## Le Chatelier's Principle

"If a change is imposed on a system at equilibrium, the system will adjust itself to partially oppose the effect of the change."

The equilibrium will never completely return to its original state, but it will tend to oppose the effect.

This principle can be used to predict the consequences of adding substances to, or removing substances from an equilibrium mixture.

Henri Louis Le Chatelier



1850 - 1936

## 2. Changing the pressure

### a. By changing volume

Gas pressure can be changed by increasing or decreasing the volume of the container while keeping temperature constant.

#### Example 16.3a

During sulfuric acid manufacture, one step involves sulfur dioxide reacting with oxygen to form sulfur trioxide gas:



In this equilibrium the forward reaction involves a reduction in the number of particles of gas, causing a reduction in pressure. The back reaction involves an increase in the number of gas particles, causing an increase in pressure. Applying Le Chatelier's principle, an equilibrium will respond to an increase in pressure by adjusting to reduce the pressure. A net forward reaction will occur, increasing the amount of sulfur trioxide present at equilibrium (Figure 16.10). The effect on the pressure change on concentrations is shown in Figure 16.11.

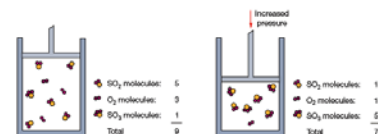


Figure 16.10  
A representation of the effect of increased pressure on the equilibrium  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$ .

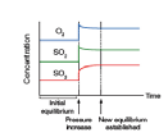


Figure 16.11  
The effect of increased pressure on the equilibrium  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$ .

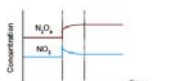


Figure 16.12  
The effect of increased pressure on the equilibrium  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ .

#### Example 16.3b

Colourless dinitrogen tetroxide gas and brown nitrogen dioxide gas exist in equilibrium:



When an equilibrium mixture of the gases is compressed it is observed that, after an initial darkening because of the higher concentration of the brown gas, the colour of the gas mixture fades. Some nitrogen dioxide has converted to dinitrogen tetroxide.

The system adjusts to the increased pressure by undergoing a net back reaction; the equilibrium moves in the direction that produces fewer particles and reduces the pressure (Figure 16.12). Note that the concentration of  $\text{NO}_2$  in the new equilibrium will be higher than in the initial equilibrium, but not as high as it would be if there had not been a net back reaction (Figure 16.13).



In general the effect of a change of pressure by changing the container volume, depends on the relative number of gas particles on both sides of the equation.

### b. By adding an inert gas (without changing container volume)

such as helium, neon or argon. In this case, because the concentration of the reactants does not change, there is no change in the equilibrium (no net forward or back reaction)

## 3. Dilution

Effect of dilution by adding water is the same as changing the volume in gaseous equilibria.

Where possible, a net reaction occurs in the direction that produces the greater number of particles.

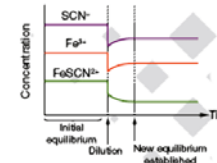
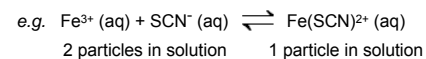
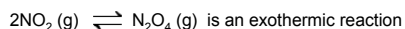


Figure 16.14  
Graph showing the effect of dilution on the equilibrium  $\text{Fe}^{3+}(\text{aq}) + \text{SCN}^{-}(\text{aq}) \rightleftharpoons \text{Fe}(\text{SCN})^{2+}(\text{aq})$ .

#### 4. Changing the temperature



Heating such a reaction will cause it to try to remove energy by a net back reaction.

An increase in temperature in an equilibrium mixture results in:

- A net backward reaction (less products) for exothermic reactions
- A net forward reaction (more products) for endothermic reactions.

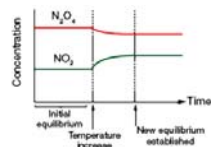
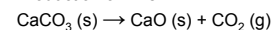


Figure 16.16  
The effect of heating on the equilibrium  
 $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$ .

#### Do all reactions reach equilibrium?

Production of lime



Reactions considered as continuing:

- where products are gases which escape the reaction mixture.
- where reactants are in minute quantities.



Figure 16.17  
Limestone is heated to 1000°C in this kiln to convert it to lime. If the process were performed in a sealed container an equilibrium mixture would form. Instead, the carbon dioxide produced is allowed to escape so that conversion into lime is complete. The limestone takes approximately 30 hours to travel the vertical length of the kiln, before emerging as lime.

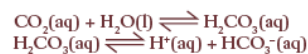
#### Extension

##### Carbon dioxide transport

Carbon dioxide is produced by cells during respiration. An equilibrium between carbon dioxide gas and dissolved carbon dioxide is established.



The relatively high concentration of carbon dioxide gas drives this reaction forward. The forward reaction is assisted by reaction of dissolved carbon dioxide with water:



In this sequence of reactions, carbon dioxide forms carbonic acid, a weak acid, which in turn is in equilibrium with the hydrogen carbonate ion. Almost 95 per cent of carbon dioxide is transported back to the lungs as  $\text{HCO}_3^-$ .

In the lungs, the low concentration of carbon dioxide gas in air causes these reactions to occur in reverse, releasing the carbon dioxide gas, which is exhaled.

##### Carbon monoxide poisoning

Carbon monoxide is a colourless, odourless and tasteless gas present in cigarette smoke and in the exhaust gases from car engines. It forms when carbon or carbon compounds burn in a limited supply of air. It is toxic because, like oxygen, it reacts with haemoglobin:



Carbon monoxide bonds much more strongly to the haemoglobin molecule than does oxygen. The equilibrium constant for this reaction is nearly 20 000 times greater than for the reaction between oxygen and haemoglobin. Even small concentrations of carbon monoxide cause the position of equilibrium to go well to the right.

This has a critical effect on the equilibrium between haemoglobin and oxygen:



When carbon monoxide is available, the formation of carboxyhaemoglobin reduces the concentration of haemoglobin. This in turn causes the back reaction of oxyhaemoglobin. In extreme cases almost no oxyhaemoglobin is left in the blood and 'carbon monoxide poisoning' occurs. Symptoms of carbon monoxide poisoning include drowsiness, dizziness, headaches, shortness of breath and loss of intellectual skills. Loss of consciousness and death can result from carbon monoxide concentrations as low as 200 ppm.

In competing equilibria, the equilibrium with the higher  $K$  has a significant effect on the equilibrium of the other.

**summary**

- The arrows show how the position of an equilibrium will shift in response to changes.
  - indicates a shift 'to the right' (a net forward reaction)
  - ← indicates a shift 'to the left' (a net backward reaction)

|                        | reactants                               | ⇌ | products            |
|------------------------|---|---|---------------------|
| Add reactants:         |   |   | →                   |
| Add products:          |   |   | ←                   |
| Increase pressure:     | e.g. 2 reactant particles               | ⇌ | 1 product particle  |
|                        | e.g. 1 reactant particle                | ⇌ | 2 product particles |
| Increase temperature:  |   |   | →                   |
| exothermic reactions:  |   |   | ←                   |
| endothermic reactions: |   |   | →                   |
| Add a catalyst:        | does not alter the extent of a reaction |   |                     |

- The position of an equilibrium may be changed by adding or removing reactant or product, changing the pressure by changing volume (for equilibria involving gases), dilution (for equilibria in solution) and changing the temperature.
- The position of equilibrium is not affected by catalysts. Catalysts affect the forward and reverse reactions equally.
- If an equilibrium system is subject to change, the system will adjust itself to partly oppose the change. This is known as Le Chatelier's principle and may be used to predict the effect of a change on an equilibrium.

**key questions**

9 Use Le Chatelier's principle to predict the effect of adding more hydrogen gas to the following equilibria:

- $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$
- $2\text{H}_2(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$
- $\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g})$

10 Predict the effect of the following changes on the position of each equilibrium:

- addition of  $\text{SO}_2$  to the equilibrium:
 
$$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$$
- removal of  $\text{CH}_3\text{COO}^-$  from the equilibrium:
 
$$\text{CH}_3\text{COOH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{CH}_3\text{COO}^-(\text{aq})$$
- halving the volume (doubling the pressure) of the equilibrium:
 
$$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$$
- increasing the pressure on the equilibrium:
 
$$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$$
- increasing the temperature of the endothermic equilibrium:
 
$$\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$$

11 Consider the following equilibria.

- $\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g}); \Delta H = +42 \text{ kJ mol}^{-1}$
- $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g}); \Delta H = +58 \text{ kJ mol}^{-1}$
- $\text{H}_2(\text{g}) + \text{F}_2(\text{g}) \rightleftharpoons 2\text{HF}(\text{g}); \Delta H = -536 \text{ kJ mol}^{-1}$

How would you alter:

- the temperature of each equilibrium mixture in order to produce a net forward reaction?
- the volume of each mixture in order to produce a net forward reaction?

12 An equilibrium mixture consists of the gases  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$ :

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

The volume of the container was increased at constant temperature and a new equilibrium was established. Predict how each of the following quantities would change at the new equilibrium compared with the initial equilibrium:

- concentration of  $\text{NO}_2$
- mass of  $\text{NO}_2$

22 Consider the reaction:

$$\text{A} + 3\text{B} \rightleftharpoons 2\text{C} + \text{D}$$

Analysis of an equilibrium mixture in a 2.0 L container shows that 2.0 mol of A, 0.50 mol of B and 3.0 mol of D are present. If the equilibrium constant of the reaction is  $0.024 \text{ M}^{-1}$ , calculate:

- the concentration of A, B and D at equilibrium
- the concentration of C in the equilibrium mixture
- the amount of C, in mol, in the equilibrium mixture

**Changing the equilibrium position**

24 How will the concentration of hydrogen gas in each of the following equilibrium mixtures change when the mixtures are heated and kept at constant volume?

- $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}); \Delta H = -91 \text{ kJ mol}^{-1}$
- $\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + 3\text{H}_2(\text{g}); \Delta H = +208 \text{ kJ mol}^{-1}$

25 The following equations represent reactions that are important in industrial processes. Predict the effect on the equilibrium position if each reaction mixture was compressed at constant temperature.

- $\text{C}_2\text{H}_6\text{O}(\text{g}) \rightleftharpoons \text{C}_2\text{H}_5\text{O}(\text{g}) + \text{H}_2(\text{g})$
- $\text{CO}(\text{g}) + 2\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_3\text{OH}(\text{g})$
- $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$

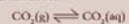
27 Carbon monoxide is used as a fuel in many industries. It reacts according to the equation:

$$2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{CO}_2(\text{g})$$

In a study of this exothermic reaction, an equilibrium system is established in a closed vessel of constant volume at  $1000^\circ\text{C}$ .

- Predict what will happen to the equilibrium position as a result of the following changes:
  - decrease in temperature
  - addition of a catalyst
  - addition of more oxygen
- What will happen to the equilibrium constant as a result of each of the changes above?
- If carbon monoxide can be used as a fuel, comment on the magnitude of the equilibrium constant for the reaction.

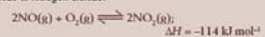
28 Sealed bottles of fizzy drinks, such as lemonade and sparkling wines, contain carbon dioxide gas in equilibrium with dissolved carbon dioxide:



The forward reaction is exothermic.

- Use Le Chatelier's principle to explain why bubbles appear when the bottles are opened.
- Why are the drinks usually cooled before they are carbonated?

29 A step during nitric acid production is the oxidation of nitrogen oxide to nitrogen dioxide.

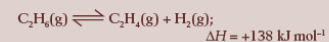


Nitrogen dioxide is a brown coloured gas and nitrogen oxide and oxygen are colourless. An equilibrium mixture was prepared in a 1 L container at 350°C. Copy the table below, and for each of the following changes indicate if the reaction mixture would become darker or lighter, giving a reason for your choice.

| Colour change    | Explanation |
|------------------|-------------|
| lighter / darker |             |

- The temperature is increased to 450°C at constant volume.
- The volume of the container is increased at constant temperature.
- A catalyst is added at constant volume and temperature.
- More oxygen is added at constant volume and temperature.

30 Ethene gas is produced from ethane gas in an endothermic reaction represented by the equation:

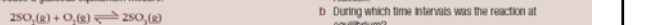


- Copy the table below and place a tick in the appropriate box to indicate what will happen to the equilibrium percentage yield of ethene when each of the following changes is made.

| Increased ethene yield | No change in ethene yield | Decreased ethene yield |
|------------------------|---------------------------|------------------------|
|                        |                           |                        |

- The volume is reduced at constant temperature.
  - More hydrogen gas is added at constant temperature and volume.
  - The temperature is increased at constant volume.
  - A catalyst is added.
  - Argon gas is added at constant temperature and volume.
- How will each of the changes in part a affect the rate at which the reaction achieves equilibrium?

37 Sulfur dioxide gas and oxygen gas were mixed at 600°C to produce a gaseous equilibrium mixture:



A number of changes were then made, including the addition of a catalyst, resulting in the formation of new equilibrium mixtures. Figure 16.23 shows how the concentrations of the three gases changed.

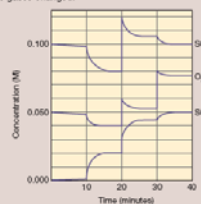


Figure 16.23  
Graph of concentration versus time.

- Write an expression for the equilibrium constant,  $K$ , of the reaction.
- During which time intervals was the reaction at equilibrium?
- Calculate the value of  $K$  at 600°C.
- At what time was the catalyst added? Explain your reasoning.
- What change was made to the system at:  
i 20 minutes?    ii 30 minutes?