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Chemistry
Teach Yourself Series
Topic 10: Equilibrium

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Contents

Equilibrium 3
Reversible reactions 3
As it appears in Unit 4 3
The Equilibrium Law 5
As it appears in Unit 4 5
Significance of K 5
Chemical Equilibrium 6
As it appears in Unit 4 6
Review Questions 6
Calculations involving K 7
As it appears in Unit 4 7
Simple calculations 7
Review Questions 8
More difficult calculations 9
As it appears in Unit 4 9
Review Questions 10
Le Chatelier's Principle 11
As it appears in Unit 4 11
Other changes 12
CARE 13
Review Questions 14
Weak acids 15
As it appears in Units 2 and 4 15
Water self-ionisation 16
As it appears in Unit 4 16
Review Questions 16
Solutions to Review Questions 17

Equilibrium

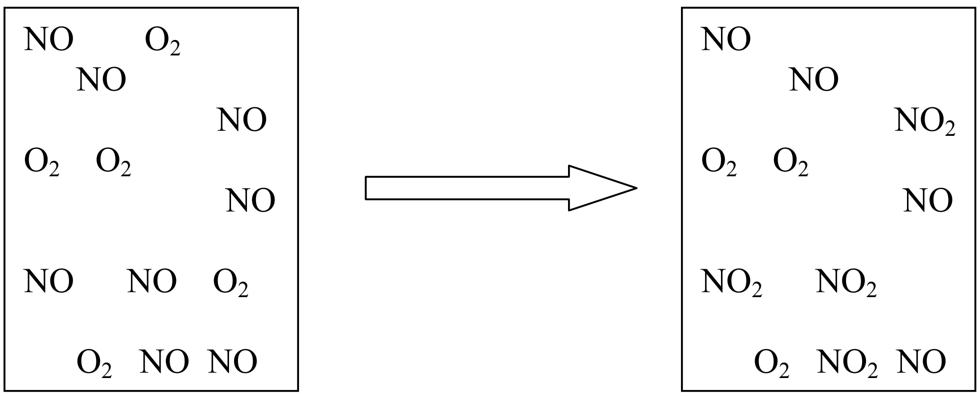
Some chemical reactions are easily reversed. This is very significant for manufacturers. It might be very difficult to produce a chemical if the products are easily returning to reactants. When this is the case, the manufacturer needs to vary the conditions to try and improve the yield of products. The impact of various changes is predictable, once certain principles are understood.

Reversible reactions

As it appears in Unit 4

Nitrogen monoxide, NO, reacts with oxygen to form nitrogen dioxide gas, NO_2.

$$2NO(g) \quad + \quad O_2(g) \rightarrow 2NO_2(g)$$



A mixture of NO and O_2 is added to a reactor.

After considerable time, the reactor contains products and both reactants

This is a **reversible** reaction.
The reactants are never all used up.
The reaction does not stop.
The rate products form = the rate products react back to reactants.
Reversible reactions reach a **point of equilibrium**.

Reversible reactions are indicated through the use of a **double arrow**.

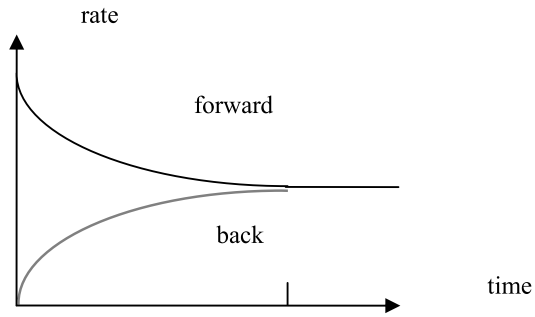
$$2NO(g) \quad + \quad O_2(g) \rightleftharpoons 2\ NO_2(g)$$

Not all reactions are reversible.

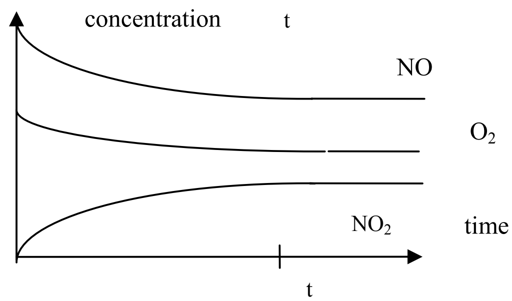
$NaCl(aq) \quad + \quad AgNO_3(aq) \rightarrow NaNO_3(aq) \quad + \quad AgCl(s)$ **irreversible**

$H_2(g) \quad + \quad I_2(g) \rightleftharpoons 2HI(g)$ **reversible**

For $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$ the progress of the reaction can be shown with graphs.



A point of **equilibrium** is reached where:
rate of forward reaction = rate of back reaction

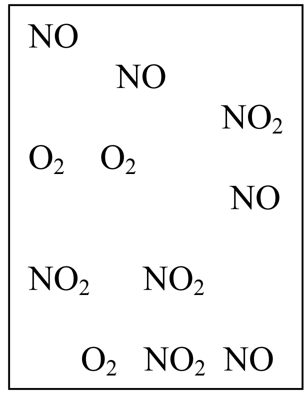


At equilibrium, the concentrations of reactants and products are now constant

The Equilibrium Law

As it appears in Unit 4

The concentrations present at equilibrium are not coincidental. They are governed by an **equilibrium law**.



For the reaction

$$2NO(g) \; + \; O_2(g) \; \rightleftharpoons \; 2NO_2(g)$$

the fraction $K = \dfrac{[NO_2]^2}{[NO]^2[O_2]}$

will always be a constant i.e. 300 °C K = 380
400 °C K= 122

This means that the concentrations in any reactor at 300 °C will eventually settle on a K value of 380. This even applies if NO_2 is the only chemical added to the reactor.

The indices in the equation come from the **coefficients** in the equation

$$2NO(g) \; + \; O_2(g) \; \rightleftharpoons \; 2NO_2(g)$$

$$K = \frac{[NO_2]^2}{[NO]^2[O_2]}$$

K will be different for each reaction.

Significance of K

Reversible reactions are not good for manufacturers as some of the reactants are not being used up.
The **higher** the value of K, the higher the **yield** of a reaction.

Yield refers to the fraction of reactants that is converted to products.

High K value means good yield
Low K value means low yield

Chemical Equilibrium

As it appears in Unit 4

- Reversible reactions will reach a point of equilibrium if conditions are held constant and the system is a closed one.
- At equilibrium, reactants and products will both be present. The concentrations of all reactants and products are constant.
- Equilibrium is a dynamic state – the reactions are still occurring. The rate of the forward reaction equals the rate of the back reaction.
- Equilibrium is a favourable situation from an energy point of view. A system in equilibrium will oppose any change.

Review Questions

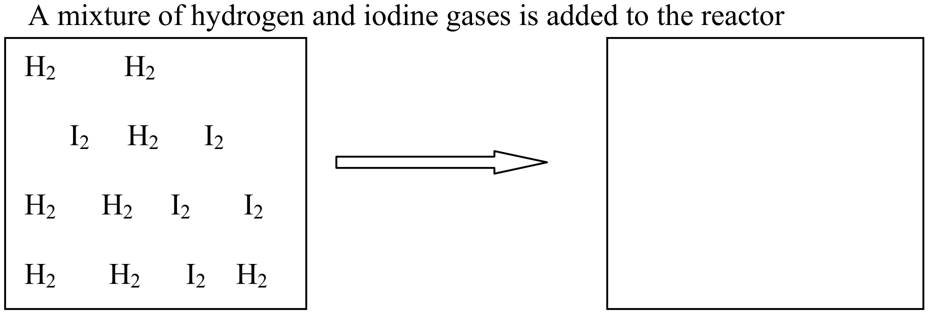
1. Write equilibrium constant expressions for each of the following equations

a. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
b. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
c. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

2. For the reversible reaction between hydrogen and iodine the equation is

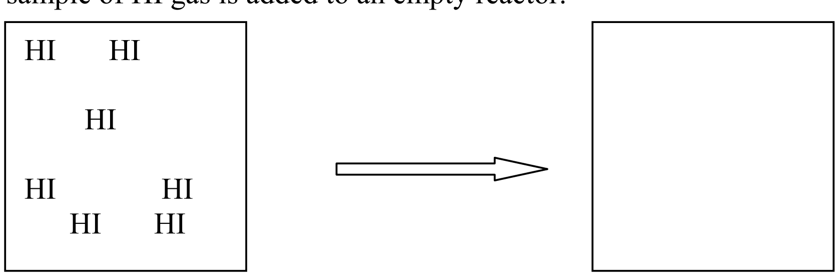
$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

a. A mixture of hydrogen and iodine gases is added to the reactor



Draw and describe what happens.

b. A sample of HI gas is added to an empty reactor.



Draw and describe what will happen.

Calculations involving K

As it appears in Unit 4

Simple calculations

Example 1: Substituting concentrations

Hydrogen and iodine react together to form hydrogen iodide. The equation is;

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

a. In one equilibrium mixture, the concentrations are H_2 = 0.20 M, I_2 = 0.30 M and HI = 0.5 M. Calculate K.

b. At the same temperature, the concentrations in another equilibrium mixture are H_2 = 0.3 M, I_2 = 0.3 M.
Calculate the concentration of HI

Solution

a. $$K = \frac{[HI]^2}{[I_2][H_2]} = \frac{(0.5)^2}{(0.2)(0.3)} = 4.2$$

b. **At the same temperature** means the value of **K is unchanged**.

$$K = \frac{[HI]^2}{[I_2]^2[H_2]} = \frac{(x)^2}{(0.3)(0.3)} = 4.2$$

$$x^2 = 4.2 \text{ x } 0.3 \text{ x } 0.3 = 0.38 \quad => x = 0.61\ M$$

Example 2: Substituting amounts

Another reactor has a volume of 5 litres. An equilibrium mixture is found to contain 2.0 mole of H_2, 2.2 mole of I_2 and 1.6 mole of HI.
Calculate K

Solution

This time the concentrations of each reactant must be determined first.

$$[H_2] = \frac{2}{5} = 0.4M \qquad [I_2] = \frac{2.2}{5} = 0.44M \qquad [HI] = \frac{1.6}{5} = 0.32M$$

$$K = \frac{[HI]^2}{[I_2]^2[H_2]} = \frac{(0.32)^2}{(0.4)(0.44)} = 0.58$$

Review Questions

3. Carbonyl bromide, $COBr_2$, can decompose according to the equation

$$COBr_2(g) \rightleftharpoons CO(g) + Br_2(g)$$

The equilibrium amounts of each chemical in a 4.0 L container are 1.4 mol of $COBr_2$, 1.8 mol CO and 0.82 mol of Br_2
Calculate K

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4. Carbon monoxide reacts with steam to form carbon dioxide and hydrogen gas.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \qquad K = 6.2 \text{ at } 300\ °C$$

The amount of carbon monoxide in a 5.6 L container is 2.8 mol. The amount of H_2 is 1.4 mol and the amount of CO_2 is 1.4 mol. Calculate the amount of steam in this equilibrium mixture

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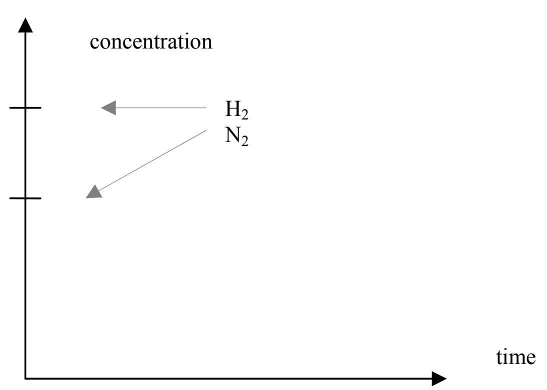
5. Ammonia is formed from the reaction between nitrogen and hydrogen gases

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

Use the axes provided to draw in the possible concentration changes when a sample of N_2 and H_2 gases are added to an empty reactor.



More difficult calculations

As it appears in Unit 4

Example 3: Two unknowns

The equation for the decomposition of phosphorous pentachloride is

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ K = 24.8 at 250 °C

A sample of PCl_5 is added to a 1 L reactor at 250 °C. At equilibrium the concentration of PCl_5 is 0.80 M. Calculate the concentration of Cl_2

Solution

There are two concentrations not given in this example but it can be assumed that their values are equal, since each molecule of PCl_5 reacting forms one PCl_3 and one Cl_2.

$$K = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(x)^2}{(0.8)} = 24.8$$

$$x = 24.8 \ \text{x}\ 0.8 = 19.8 \quad \Rightarrow \quad x = 4.45\ M$$

Example 4: Reactant grids

Carbon monoxide can react with chlorine gas

$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$

0.8 mol of CO and 0.6 mol of Cl are added to a 1.0 L reactor. At equilibrium, the amount of CO remaining is 0.5 mol. Calculate K.

	$CO(g)$	+ $Cl_2(g)$	$\rightleftharpoons COCl_2(g)$
start	0.8	0.6	0
equilibrium	0.5		
change	0.3		

The initial amounts of reactants cannot be used in the expression for K as this is a n equilibrium expression. A grid like the one below should be used to determine the equilibrium amounts

	$CO(g)$	+ $Cl_2(g)$	$\rightleftharpoons COCl_2(g)$
start	0.8	0.6	0
equilibrium	0.5	(0.6-0.3)	0.3
	0.5	0.3	0.3

Review Questions

6. Hydrochloric acid gas can decompose to hydrogen and chlorine gases.
1.2 mol of HCl gas is added to 1.0 L reactor. When equilibrium is reached, 1.1 mol of HCl is present. Calculate K.

7. 0.20 mol of SO_2 gas is added to 0.08 mol of O_2 gas in a 1.0 L reactor. When equilibrium is reached 0.04 mol of SO_3 has formed. Calculate K.

Le Chatelier's Principle

As it appears in Unit 4

Le Chatelier's Principle : A system in equilibrium partially opposes any change.

If the yield is low, change the conditions to improve it.
The usual variables are

1. **Temperature**

Temperature is the only variable that leads to a change in the numerical value of K.

Endothermic reaction ΔH = +ve	T↑, K↑	T ↓, K↓
Exothermic reaction ΔH = - ve	T↑, K ↓	T↓, K↑

$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \quad \Delta H = -92 \text{ kJ mol}^{-1}$

This is an **exothermic reaction**. If the **temperature** of the reactor is **increased**, the value of **K will drop.**

This means the back reaction is favoured and the yield drops. The back reaction is exothermic so this reaction is favoured to oppose the original temperature increase.

2. **Pressure (Volume)**

$$\underbrace{CO(g) + 2H_2(g)}_{\text{3 molecules}} \rightleftharpoons \underbrace{CH_3OH(g)}_{\text{1 molecule}}$$

If the **pressure is increased**, the system will oppose this. In this case **the forward reaction is favoured**.

Three molecules are converted to one molecule, therefore the pressure is reduced.

The yield is improved. The numerical value of K is unchanged because the temperature has not changed.

If the pressure is decreased, the system will oppose this by moving in the reverse direction.

3. **Concentration**

$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

Extra H_2 gas is injected into an equilibrium mixture.

The system opposes this by moving in the **forward dirction** to use up some of the H_2.

The yield of H_2 is increased. The numerical value of K is unchanged because the temperature is held constant.

Example 1
The formation of ethene is an endothermic reaction.

$$C_2H_6(g) \Leftrightarrow C_2H_4(g) + H_2(g) \qquad \Delta H = +135 \text{ kJ mol}$$

For this reaction, describe the impact upon the value of K, the yield of ethene and the position of equilibrium of the following changes

a. An increase in temperature
b. An increase in volume
c. The removal of some of the H_2 gas

Solution

a. Endothermic reaction, T↑, K↑. An increase in temperature favours the forward reaction. Yield increased.
b. Volume increased, the pressure is decreased. System will move in the forward direction to increase the pressure. K unchanged and yield increased.
c. Removal of H_2. The forward reaction is favoured and the yield improved.

Other changes

Addition of catalyst. Catalysts work for either the forward or back direction. They do not affect the final yield, just the reaction rate.
A catalyst will not change the concentrations of a system at equilibrium.
If the system is not at equilibrium, the catalyst will help it reach equilibrium faster.

Addition of an inert gas. An inert gas does not change the volume of the reactor or the amounts of any chemicals. Therefore the system has nothing to oppose so no change occurs.

Dilution of solution. Dilution of a solution works like a gas. The system favours the side with the most particles other than water.

$$Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons FeSCN^{2+}(aq)$$

Reverse reaction is favoured if water is added to the solution. The value of K is unchanged but the amount of $Fe^{3+}(aq)$ present has increased. The concentration of $Fe^{3+}(aq)$ has decreased due to the initial dilution.

Example 2
For the reaction

$$4HCl(aq) + O_2(g) \rightleftharpoons 2H_2O(g) + Cl_2(g) \qquad \Delta H = +ve$$

Explain the effect on the position of equilibrium and on the concentration of Cl gas of the following changes

a. an increase in temperature
b. a decrease in volume
c. the addition of helium gas
d. the addition of a catalyst to an equilibrium mixture of the gases

Solution

a. Endothermic reaction. T↑ then K↑. Forward reaction favoured, Cl_2 concentration increased.
b. Decrease in volume, increase in pressure. Forward reaction favoured, Cl_2 concentration increased.
c. No effect
d. No effect since the reaction was already at equilibrium

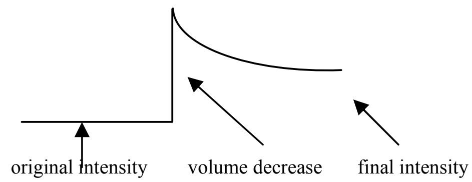
CARE

The reaction between nitrogen tetroxide and ditrogen dioxide is

$$\underset{\text{colourless}}{N_2O_4(g)} \rightleftharpoons \underset{\text{brown}}{2NO_2(g)}$$

An equilibrium mixture will be brown in colour due to the NO_2 present.
The volume of an equilibrium mixture is halved, what will happen to the intensity of the brown colour?

Many students suggest the brown intensity will decrease as the system favours the reverse reaction trying to reduce the number of particles present. However, this is ignoring the fact that the initial change in volume increased the brown intensity significantly.



The final intensity is greater than the original intensity.

Review Questions

8. For the reaction between N_2 and H_2 gases

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = \text{-ve}$$

Explain the impact upon the position of equilibrium and the value of K of the following changes

a. an increase in temperature
b. an increase in pressure
c. removal of ammonia as a liquid
d. addition of helium gas

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9. The reaction for the formation of methanol is

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H = -92 \text{ kJ mol}^{-1}$$

List ways in which the

a. Yield of this reaction could be improved

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b. The rate of this reaction could be improved.

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Weak acids

(covered in more detail in pH unit)

As it appears in Units 2 and 4

CH_3COOH is a **weak acid**. It only **donates a small percentage** of its protons.

$$CH_3COOH(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

$$K = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH][H_2O]} \quad \text{hence} \quad K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

where K_a = acidity constant

$$\boxed{K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}}$$

The action of weak acids is typical of any equilibrium system. Le Chatelier's Principle can be used to explain most changes occurring in solutions of weak acid.

Example

A 0.05 M ethanoic acid solution has a pH of 3.2. Calculate the value of K_a for the ethanoic acid.

Solutions

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

If pH = 3.2, then $[H_3O^+] = 10^{-3.2} = 6.31 \times 10^{-4}$

Since CH_3COOH was the only acid added, $[H_3O^+] = [CH_3COO^-] = 6.31 \times 10^{-4}$

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \frac{6.31 \times 10^{-4} \times 6.31 \times 10^{-4}}{0.05} = 7.96 \times 10^{-6}\ M$$

Water self-ionisation

As it appears in Unit 4

$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \quad H = +ve$

$K = \frac{[H_3O^+][OH^-]}{[H_2O][H_2O]}$ hence $K_w = [H_3O^+][OH^-]$ **K_w = ionisation constant of water**

$$\boxed{K_w = [H_3O^+][OH^-]}$$

At 25 °C, the value of K is found to be 10^{-14}. This explains the origins of the acid/base formula used in Unit 2 chemistry:

$[H_3O^+][OH^-] = 10^{-14}$

At 25 °C $[H_3O^+][OH^-] = 10^{-14}$.
Since pure water is neutral, $[H_3O^+] = [OH^-] = 10^{-7}$ and . The pH of pure water at 25 ^{0}C is 7
Acid solutions, $[H_3O^+] > 10^{-7}$, $[OH^-] < 10^{-7}$
Base solutions $[H_3O^+] < 10^{-7}$, $[OH^-] > 10^{-7}$

The self-ionisation reaction is reversible, therefore it is temperature dependent. Being endothermic, as the temperature increases so does K. The pH of pure water will no longer be 7.

Review Questions

10. Answer True or False to each of the following
At 60 °C:

- the pH of pure water will be 7
- the concentration of H_3O^+ will be higher than at 25 °C
- the pH will be higher than that at 25 °C
- the concentration of $[H_3O^+] = [OH^-]$

11. Calculate the pH of a 0.01 M solution of HCN. (Data book required)

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Solutions to Review Questions

1. **a**. $K = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$

b. $K = \dfrac{[HI]^2}{[H_2][I_2]}$

c. $K = \dfrac{[NO_2]^2}{[N_2O_4]}$

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

a. A mixture of hydrogen and iodine gases is added to the reactor

H_2 H_2 I_2 H_2 I_2 H_2 H_2 I_2 I_2 H_2 H_2 I_2 H_2	$\Longrightarrow$	H_2 H_2 HI I_2 H_2 HI HI I_2 HI H_2 H_2 I_2 H_2

An equilibrium mixture of the gases will form. Some of all 3 gases will be present. The same amounts of H_2 and I_2 will be used up.

b. A sample of all gases will again form. The amounts of formed H_2 and I_2 should be the same.

HI HI HI HI HI HI HI	$\Longrightarrow$	HI H_2 I_2 H_2 I_2 HI HI

3. $[COBr_2] = \dfrac{n}{V} = \dfrac{1.4}{4} = 0.35M$ $\quad [CO] = \dfrac{1.8}{4} = 0.45M$ $\quad [Br_2] = \dfrac{0.82}{4} = 0.21M$

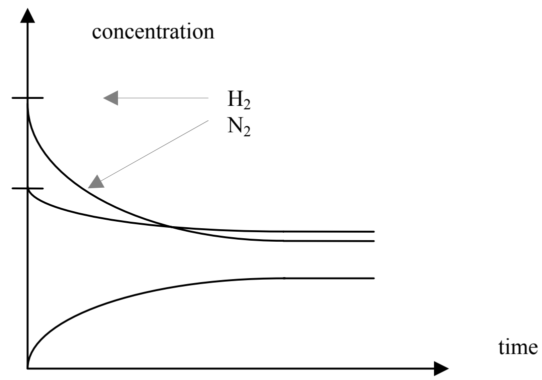
$K = \dfrac{[0.45][0.21]}{[0.35]} = 0.23$ M

4. $[CO] = \frac{n}{V} = \frac{2.8}{5.6} = 0.5M$ $\quad [H_2] = \frac{1.4}{5.6} = 0.25M$ $\quad [CO_2] = \frac{1.4}{5.6} = 0.25M$

$$K = \frac{[CO_2][H_2]}{[CO][H_2O]} \quad \Rightarrow 6.2 = \frac{(0.25)(0.25)}{(0.5)x}$$

$$\Rightarrow x = \frac{0.0625}{6.2 \times 0.5} \quad = 0.020\ M$$

5.



Several possible graphs –look for the gadients to match the balanced equation i.e. hydrogen concentration to drop at three times the rate of the nitrogen

6.

	$2HCl(g)$ $\rightleftharpoons$	$H_2(g)$ +	$Cl_2(g)$
start	1.2	0	0
equilibrium	1.1		
change	0.1	0.05	0.05

$$K = \frac{[0.05][0.05]}{[1.1]} = 0.00227\ M$$

7.

	$2SO_2(g)$ +	$O_2(g)$ $\rightleftharpoons$	$2SO_3(g)$
start	0.2	0.08	0
equilibrium			0.04
change	0.2-0.04	0.08 – 0.02	0.04

$$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

$$K = \frac{(0.04)^2}{(0.16)^2(0.06)} = 1.04\ M^{-1}$$

8. Explain the impact upon the position of equilibrium and the value of K of the following changes

a. an increase in temperature will lower the value of K favouring the back reaction. K is lower

b. K unchanged. Forward reaction favoured

c. K unchanged, forward reaction favoured

d. No change

9. **a**. Yield is improved if the temperature is lowered or the pressure is lowered or the concentration of one of the reactants is increased.

b. The rate will be increased if the temperature is increased or the concentrations are increased.

10. Answer True or False to each of the following

At 60 °C:

a. the pH of pure water will be 7 False

b. the concentration of H_3O^+ will be higher than at 25 °C True

c. the pH will be higher than that at 25 °C False

d. the concentration of $[H_3O^+] = [OH^-]$ True

11. $K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = 6.3 \times 10^{-10}$

$$\frac{X \times X}{0.01} = 6.3 \times 10^{-10}$$

$$X^2 = 6.3 \times 10^{-12}$$

$$X = 2.51 \times 10^{-6}$$

$$pH = -\log(2.51 \times 10^{-6}) = 5.6$$