Equilibria

This topic illustrates that many chemical reactions are reversible and involve an equilibrium process. The consideration of the many factors that can affect an equilibrium is an important aspect of physical chemistry.

a	explain, in terms of rates of the forward and reverse reactions, what is meant by a reversible reaction and dynamic equilibrium	☐
b	state Le Chatelier's principle and apply it to deduce qualitatively (from appropriate information) the effects of changes in temperature, concentration or pressure on a system at equilibrium	☐
c	state whether changes in temperature, concentration or pressure or the presence of a catalyst affect the value of the equilibrium constant for a reaction	☐
d	deduce expressions for equilibrium constants in terms of concentrations, K_c , and partial pressures, K_p (treatment of the relationship between K_p and K_c is not required)	☐
e	calculate the values of equilibrium constants in terms of concentrations or partial pressures from appropriate data	☐
f	calculate the quantities present at equilibrium, given appropriate data (such calculations will not require the solving of quadratic equations)	☐
g	describe and explain the conditions used in the Haber process and the Contact process, as examples of the importance of an understanding of chemical equilibrium in the chemical industry	☐

EQUILIBRIA

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7 Equilibria

This topic illustrates that many chemical reactions are reversible and involve an equilibrium process. The consideration of the many factors that can affect an equilibrium is an important aspect of physical chemistry.

	Learning outcomes Candidates should be able to:
7.1 Chemical equilibria: reversible reactions; dynamic equilibrium	a) explain, in terms of rates of the forward and reverse reactions, what is meant by a *reversible reaction* and *dynamic equilibrium* b) state Le Chatelier's principle and apply it to deduce qualitatively (from appropriate information) the effects of changes in temperature, concentration or pressure on a system at equilibrium c) state whether changes in temperature, concentration or pressure or the presence of a catalyst affect the value of the equilibrium constant for a reaction d) deduce expressions for equilibrium constants in terms of concentrations, K_c, and partial pressures, K_p (treatment of the relationship between K_p and K_c is not required) e) calculate the values of equilibrium constants in terms of concentrations or partial pressures from appropriate data f) calculate the quantities present at equilibrium, given appropriate data (such calculations will *not* require the solving of quadratic equations) g) describe and explain the conditions used in the Haber process and the Contact process, as examples of the importance of an understanding of chemical equilibrium in the chemical industry

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EQUILIBRIA

REVERSIBLE REACTIONS

In most reactions the reactants are completely converted to products i.e. the reaction proceeds in one direction only. Such reactions are referred to as **irreversible reactions**.

There are some reactions, which can be **reversed** by altering the conditions of the reactions.

For example when gaseous ammonia and hydrogen chloride are brought together at room temperature white dense fumes of ammonium chloride is formed.

However, on heating, ammonium chloride decomposes to give ammonia and hydrogen chloride. Such reactions are described as **reversible reactions**.

2

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REVERSIBLE REACTIONS

If in a reversible reaction the conditions required for the forward reaction and the backward reaction are the same, a stage will be reached when the rate of the forward reaction becomes equal to the rate of the backward reaction.

Then the system is said to be in a state of chemical equilibrium.

The equilibrium is dynamic. i.e. the forward and the backward reactions keep on occurring continually without affecting the concentration of the components.

Thus, at equilibrium the concentration of the constituents do not change with time.

3

CHARACTERISTICS OF THE EQUILIBRIUM STATE

A system is said to be in a state of dynamic equilibrium when in a reversible reaction, the rate of the forward reaction is equal to the rate of the backward reaction.

1. The rate of the forward reaction is equal to the rate of the backward reaction.
2. The concentration of the constituents at equilibrium does not change with time.
3. Equilibrium is a dynamic state – opposing changes at molecular level are continually taking place.
4. The position of equilibrium is sensitive to changes of temperature and pressure or concentration.
5. The equilibrium may be attained from either direction.

4

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EQUILIBRIUM LAW

For an equilibrium reaction of the form:

$$wA + xB \rightleftharpoons yC + zD$$

Then (at a constant temperature) = $\frac{[C]^y . [D]^z}{[A]^w . [B]^x}$ = a constant, (K_c)

Where [ ] denotes the equilibrium concentration in mol dm^{-3}. **K_c** is known as the **Equilibrium Constant.**

Note: Solids are NOT a part of equilibrium expressions because the concentration of solids is ALWAYS constant.

5

EXAMPLE 1

Consider the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

If the equilibrium concentrations are:

SO_2: 0.016 mol dm^{-3} O_2: 0.0083 mol dm^{-3} SO_3: 0.15 mol dm^{-3},

Calculate the value of the equilibrium constant K_c , stating its units.

$$K_c = \frac{[SO_3]^2}{[SO_2]^2 \times [O_2]} = \frac{(0.15)^2}{(0.016)^2 \times 0.0083} = 1.1 \times 10^4 \text{ mol}^{-1} \text{ dm}^3$$

The units can be calculated by realizing:

$$\frac{\text{conc}^2}{\text{conc}^2 \times \text{conc}} = \frac{1}{\text{conc}} \qquad \text{which is} = \frac{1}{\text{mol dm}^{-3}} = \text{mol}^{-1} \text{ dm}^3$$

6

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EXAMPLE 2

What are the units of the equilibrium constant K_c for the following reactions?

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

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

a) Units are $\frac{conc^2}{conc \times conc^3} = \frac{1}{conc^2} = mol^{-2}\ dm^6$

b) Units are $\frac{conc^2}{conc \times conc}$ = no units as all the concentration terms cancel

7

CALCULATING K_C – EXAMPLE 1

Consider the equilibrium **P + 2Q ⇌ R + S** (all species are aqueous)

One mole of P and one mole of Q are mixed in 1 dm^3 water. Once equilibrium has been achieved 0.6 moles of P are present. How many moles of Q, R and S are present at equilibrium? What is the K_c?

	P	Q	R	S
initial moles	1	1	0	0
moles that reacted	_____	_____	_____	_____
moles @ equilibrium	0.6	_____	_____	_____
[conc] @ equilibrium	_____	_____	_____	_____

8

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CALCULATING K_C – EXAMPLE 1

The method is:

1. Construct the balanced equation, including state symbols (aq), (g) etc.
2. Write down the expression for K_c.
3. Calculate the moles of each substance that reacted.
4. Calculate the moles of each substance at equilibrium.
5. Divide these by the volume to get the concentration of each substance, use V if no volume given.
6. Put the equilibrium values into the expression for Kc and calculate the answer and work out the units.

9

CALCULATING K_C – EXAMPLE 1

Consider the equilibrium $P + 2Q \rightleftharpoons R + S$ (all species are aqueous)

One mole of P and one mole of Q are mixed in 1 dm^3 water. Once equilibrium has been achieved 0.6 moles of P are present.

	P	Q	R	S
initial moles	1	1	0	0
moles that reacted	0.4	0.8	0.4	0.4
moles @ equilibrium	0.6	0.2	0.4	0.4
[conc] @ equilibrium	**0.6**	**0.2**	**0.4**	**0.4**

$$K_c = \frac{[R] \times [S]}{[P] \times [Q]^2} = \frac{0.4 \times 0.4}{0.6 \times (0.2)^2} = 6.67$$

- If 0.6 mol of P remain of the original 1 mol, 0.4 mol have reacted.
- The equation states that 2 moles of Q react with every 1 mole of P.
- This means that 0.8 (2 x 0.4) moles of Q have reacted, leaving 0.2 moles.
- One mole of R and S are produced from every mole of P that reacts.
- This means 0.4 moles of R and 0.4 moles of S are present at equilibrium.

10

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CALCULATING K_C – EXAMPLE 2

One mole of ethanoic acid reacts with one mole of ethanol at 298K. When equilibrium is reached it is found that two thirds of the acid has reacted. Calculate the value of K_c.

$$CH_3COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3CO_2CH_2CH_3(l) + H_2O(l)$$

	CH_3COOH	CH_3CH_2OH	$CH_3CO_2CH_2CH_3$	H_2O
initial moles	1	1	0	0
moles that reacted	$^2/_3$	$^2/_3$	$^2/_3$	$^2/_3$
moles @ equilibrium	$1 - {}^2/_3 = {}^1/_3$	$1 - {}^2/_3 = {}^1/_3$	$^2/_3$	$^2/_3$
[conc] @ equilibrium	$^1/_3$ / V	$^1/_3$ / V	$^2/_3$ / V	$^2/_3$ / V

$$K_c = \frac{[CH_3CO_2CH_2CH_3][H_2O]}{[CH_3COOH][CH_3CH_2OH]} = \frac{^2/_3 \text{ / V} \; . \; ^2/_3 \text{ / V}}{^1/_3 \text{ / V} \; . \; ^1/_3 \text{ / V}} = 4$$

11

CALCULATING K_C – EXAMPLE 3

2.6 mol of ethanoic acid, CH_3COOH, was mixed with 1.6 mol of ethan–1,2–diol and allowed to reach equilibrium when 1.1 mol of the ester $CH_3COOCH_2CH_2OCOCH_3$, was present. The total volume was 250cm^3. Calculate the value of the equilibrium constant, K_c.

$$2CH_3COOH(l) + CH_2(OH)CH_2OH(l) \rightleftharpoons CH_3COOCH_2CH_2OCOCH_3(l) + 2H_2O(l)$$

12

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CALCULATING K_C – EXAMPLE 3

	CH_3COOH	$CH_2(OH)CH_2OH$	ester	H_2O
initial moles	2.6	1.6	0	0
moles that reacted	2.2	1.1	1.1	2.2
moles @ equilibrium	0.4	0.5	1.1	2.2
[conc] @ equilibrium	0.4 / 0.25 = 1.6	0.5 / 0.25 = 2.0	1.1 / 0.25 = 4.4	2.2 / 0.25 = 8.8

$$Kc = \frac{[CH_3COOCH_2CH_2OCOCH_3] \times [H_2O]^2}{[CH_3COOH]^2 \times [CH_2(OH)CH_2OH]} = \frac{4.4 \times (8.8)^2}{(1.6)^2 \times 2} = 67 \text{ (no units)}$$

13

CALCULATIONS INVOLVING K_C

Calculate the amount of hydrogen iodide at equilibrium when 1.0 mol of hydrogen and 1.0 mol of iodine are heated at a temperature T until equilibrium is reached in a container of volume $10dm^3$.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \quad K_c = 49 \text{ (no units)}$$

14

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CALCULATIONS INVOLVING K_C

This can be done in some cases where the number of molecules on the two sides are the same:

1. Write down the expression for K_c (there will always be a mark for this).
2. Assume that x moles of the substance(s) on the left have reacted.
3. Calculate the equilibrium moles of each substance and their concentrations in terms on x.
4. Substitute these values into the expression for K_c and solve for x by taking the square root of both sides.

15

CALCULATIONS INVOLVING K_C

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $\quad K_c = \dfrac{[HI]^2}{[H_2][I_2]} = 49$

Let x mol of hydrogen that react.

	H_2	I_2	HI
initial moles	1	1	0
moles that reacted	x	x	2x
moles @ equilibrium	1 − x	1 − x	2x
[conc] @ equilibrium	(1 − x) / 10	(1 − x) / 10	2x / 10

16

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CALCULATIONS INVOLVING K_C

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x/10)}{(1-x)/10 \,.\, (1-x)/10} = \frac{4x^2}{(1-x)^2} = 49$$

$$\frac{2x}{1-x} = \pm 7$$

$\frac{2x}{1-x} = +7$

$2x = 7 - 7x$
$9x = 7$
$x = 7/9 = 0.78$

As the moles of HI at equilibrium is 2x, there are 1.56 moles of HI at equilibrium.

$\frac{2x}{1-x} = -7$

$2x = -7 + 7x$
$-5x = -7$
$x = -7/5 = -1.4$

As the moles of H_2 at equilibrium is 1 – x, that would result in – 0.4 moles of H_2 at equilibrium. **NOT POSSIBLE**

17

EQUILIBRIUM CONSTANT K_P

K_p is the equilibrium constant in terms of the partial pressures of the gases in the equilibrium reaction.

For the reaction: $nA(g) + mB(g) \rightleftharpoons xC(g) + yD(g)$

$$K_p = \frac{pC^x \times pD^y}{pA^n \times pB^m}$$

Partial pressure of gas A:
$p(A)$ = mole fraction of A x total pressure

Mole fraction of A = $\frac{\text{moles of A}}{\text{total moles of gas}}$

1. Use the value of the partial pressure of any gas in the equilibrium mixture.
2. As with K_c, the units of K_p depend on the stoichiometry of the reaction.

18

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EXAMPLE 1

Calculate the partial pressure of sulfur dioxide in a mixture containing 0.016 mol SO_2, 0.0083 mol O_2 and 0.15 mol SO_3 in a vessel at a pressure of 7.0 atm. and hence the K_p of the following reaction:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

Total number of moles = 0.016 + 0.0083 + 0.15 = 0.1743 mol

19

EXAMPLE 1

SO_2: Mole fraction of SO_2 = 0.016 / 0.1743 = 0.0918

Partial Pressure of SO_2 = 0.0918 x 7.0 = 0.643 atm

O_2: Mole fraction of O_2 = 0.0083 / 0.1743 = 0.0476

Partial Pressure of O_2 = 0.0476 x 7.0 = 0.333 atm

SO_3: Partial Pressure of SO_3 = 7 − (0.643 + 0.333) = 6.024

$$K_p = \frac{p(SO_3)^2}{p(SO_2)^2 \times p(O_2)} = \frac{(6.024)^2}{(0.643)^2 \times 0.333} = 264 \text{ atm}^{-1}$$

20

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EXAMPLE 2

When some phosphorous pentachloride PCl_5, was heated to a temperature T in a container, 78% of it decomposed and the pressure in the container was 2.2 atm.

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

Calculate the value of the equilibrium constant Kp.

$$K_p = \frac{p(PCl_3) \times p(Cl_2)}{p(PCl_5)}$$

21

EXAMPLE 2

The method is:

1. Write down the expression for K_p.
2. Calculate the moles of each substance at equilibrium – starting amount is given, assume there was 1 mol of the reactant on the left.
3. Add up all the equilibrium moles to get the total number of moles. Work out the mole fraction of each gas (moles/total moles). Work out the partial pressure of each gas (mole fraction x total pressure).
4. Put these partial pressures into the expression for K_p and calculate its value with units.

22

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EXAMPLE 2

Assume that there was 1 mol of PCl_5 to start with. As 78% reacted, 0.22 mol was present at equilibrium. 0.78 mol of PCl_3 and Cl_2 were formed.

	PCl_5	PCl_3	Cl_2
initial moles	1	0	0
moles that reacted	0.78	0.78	0.78
moles @ equilibrium	0.22	0.78	0.78
mole fraction	0.22/1.78 = 0.124	0.78/1.78 = 0.438	0.78/1.78 = 0.438
partial pressure	0.124 x 2.2 = 0.273	0.438 x 2.2 = 0.964	0.438 x 2.2 = 0.964

$$K_p = \frac{p(PCl_3) \times p(Cl_2)}{p(PCl_5)} = \frac{0.964 \times 0.964}{0.272} = 3.42 \text{ atm}$$

23

CALCULATING K_P

When nitrogen (1 mole) and hydrogen (3 moles) react at constant temperature at a pressure of 8×10^6 Pa, the equilibrium mixture was found to contain 0.7 moles of ammonia. Calculate K_p.

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

	N_2	H_2	NH_3
initial moles	1	3	0
moles that reacted	0.35	1.05	0.7
moles @ equilibrium	0.65	1.95	0.7
partial pressure	$0.65/3.3 \times 8 \times 10^6$	$1.95/3.3 \times 8 \times 10^6$	$0.7/3.3 \times 8 \times 10^6$

24

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CALCULATING K_P

$$K_p = \frac{p(NH_3)^2}{p(N_2) \times p(H_2)^3} = \frac{(1.7 \times 10^6)^2}{(1.58 \times 10^6) \times (4.77 \times 10^6)^3}$$

$$= 1.73 \times 10^{-14}\ Pa^{-2}$$

Note: The ratio of partial pressures is the same as the mole ratio at equilibrium.

25

SKILL CHECK

When nitrogen (1 mole) and hydrogen (3 moles) react at constant temperature at a pressure of 8 x ^{6} Pa, the equilibrium mixture was found to contain 0.7 moles of ammonia. Calculate K_p.

26

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SKILL CHECK

Given that PCl_5 at 700 K and 1.1 atm total pressure dissociated 33%, find K_p.

$$\mathbf{PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)}$$

27

SKILL CHECK

A chemist carries out an investigation on the equilibrium system shown below.

$$2CO(g) + 2NO(g) \rightleftharpoons 2CO_2(g) + N_2(g)$$

The chemist mixes 0.46 mol of CO with 0.45 mol of NO. The mixture is left to reach equilibrium at constant temperature.

The chemist analyses the equilibrium mixture and finds that 0.25 mol NO remains and the total pressure was 5 atm. What is the value of K_p.

28

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SKILL CHECK

1.0 mol of N_2O_4 was allowed to reach equilibrium at 400K. At equilibrium the partial pressure of N_2O_4 was found to be 0.15 atm. Given that the K_p for the reaction is 48 atm, calculate the partial pressure of NO_2 in the equilibrium mixture.

$$\mathbf{N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)}$$

29

VALUE OF K AND THE EXTENT OF A REACTION

If the value of K_c is large it means that the position of the equilibrium is well to the right (towards products).

If the value of K_c is close to 1 it means that the position of the equilibrium is close to being halfway.

If the value of K_c is very small (< 1), the position of equilibrium is well to the left (towards reactants).

Reminder: the concentration of pure solids and pure liquids is a constant and so is not included in the expression for K_c.

e.g. $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$

$$K_c = \frac{[CO][H_2]}{[H_2O]}$$

30

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VALUE OF K AND THE EXTENT OF A REACTION

Only the partial pressures of gases are included in the expression for K*p*; the other substances are ignored.

Example State the expression for Kp for the reaction

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

and calculate the pressure of carbon dioxide when calcium carbonate is heated to 800°C given that K_p = 0.80 atm.

$K_p = p(CO_2) = 0.80$ atm

The two solids must be omitted from the expression for K_p

31

LE CHATELIER'S PRINCIPLE

If a **change in condition** is made to a **closed system** in equilibrium, the system responds to **counteract the change** as much as possible.

Conditions include concentration, pressure and temperature

The system **counteracts the change** by making the **direction** of the reaction move **against** the change.

Note: Catalysts do **not** affect the position of equilibrium! They only speed up the rate of reaching equilibrium – getting there faster!

32

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EFFECT OF CONCENTRATION ON EQUILIBRIUM

TWO GENERAL RULES:

1. If the concentration of a substance is increased, the system will counteract the change by forcing the reaction to go in the direction that uses up the 'extra' substance.
2. If the concentration of a substance is decreased, the system will counteract the change by forcing the reaction to go in the direction that makes more of the substance.

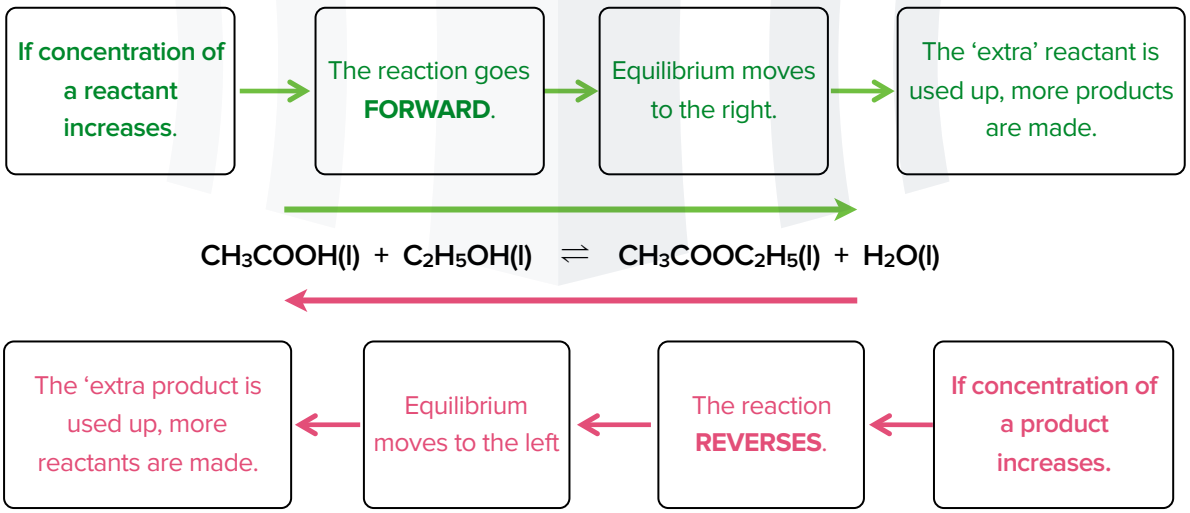
Example

$$A(g) + 2B(g) \rightleftharpoons 2C(g) \quad \Delta H = -200\ kJ\ mol^{-1}$$

If concentration of C is increased, the equilibrium will move in a way so as to oppose the change, that is, decrease C by favoring the backward reaction.

33

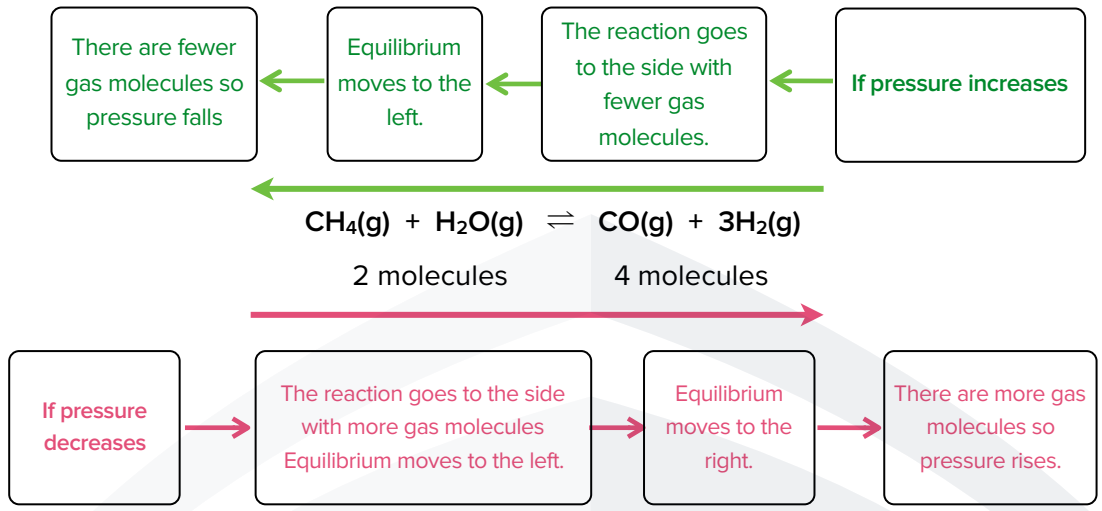
EFFECT OF CONCENTRATION ON EQUILIBRIUM



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EFFECT OF PRESSURE ON EQUILIBRIUM



35

EFFECT OF TEMPERATURE ON EQUILIBRIUM

Le Chatelier's principle also works for temperature changes.

If the **temperature is increased**, the reaction will go in the direction that **reduces** the temperature by **taking in energy** (converting heat energy to chemical energy), i.e. the **endothermic** direction.

If the **temperature is decreased**, the reaction will go in the direction that **increases** the temperature by **giving out energy** (converting chemical energy to heat energy), i.e. the **exothermic** direction.

36

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EFFECT OF TEMPERATURE ON EQUILIBRIUM

Example

$$A(g) + 2B(g) \rightleftharpoons 2C(g) \quad \Delta H = -200 \text{ kJ mol}^{-1}$$

If temperature increases, the equilibrium shifts in a way so as to decrease the temperature of the system. Hence, the backward reaction is favored as it is the endothermic reaction and results in a temperature decrease.

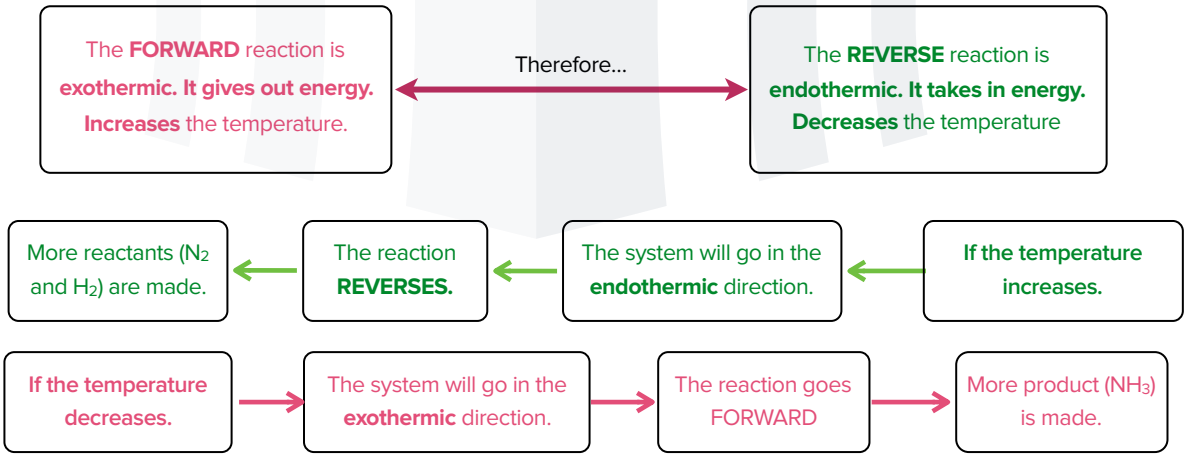
Note:

- Low temperatures favor exothermic reactions.
- High temperatures favor endothermic reactions.

37

EXOTHERMIC CHANGES

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ **$\Delta H = -92$ kJ mol^{-1}**



38

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EXOTHERMIC CHANGES

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ **ΔH = + 57 kJ mol^{-1}**

The **FORWARD** reaction is **endothermic**

Therefore...

The **REVERSE** reaction is **exothermic**

If the temperature increases. → The system will go in the **endothermic** direction. → The reaction goes FORWARD → More product (NO_2) is made.

If the temperature decreases. → The system will go in the **exothermic** direction. → The reaction **REVERSES.** → More reactants (N_2O_4) are made.

39

CONDITIONS AFFECTING EQUILIBRIUM – EXAMPLE 1

Ethanol is made on an industrial scale by reacting ethene with steam at 300°C.

$$C_2H_4(g) + H_2O(g) \rightleftharpoons C_2H_5OH(g)$$

Explain the effect that each of the following changes has on the yield of ethanol.

A. Increasing the pressure.

B. Increasing the concentration of ethene.

C. Using a catalyst.

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CONDITIONS AFFECTING EQUILIBRIUM – EXAMPLE 1

A. Increasing the pressure would increase the yield of ethanol. There are two molecules on the left of the equation and only one on the right. The system would act to reduce the increased pressure by forming fewer gas molecules, moving the equilibrium to the right (forward reaction).

B. Increasing the concentration of ethene would increase the yield of ethanol. The system would act to reduce the increased concentration by moving to the right (forward reaction) and forming more products.

C. Catalyst have no effect on yield – they only affect the rate.

41

CHOOSING THE CONDITIONS

For industrial processes, the best conditions give high yields (more products) at a fast rate.

Changing conditions affects both rate and position of equilibrium.

'Compromise conditions' of pressure and temperature are used to give reasonable yields at fast rates.

42

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CHOOSING THE CONDITIONS

CHANGES	RATE	EQUILIBRIUM POSITION (YIELD)
Increased concentration of reactants	**Faster**	Moves to the right More products = **higher yield**
Increased pressure (gases)	**Faster**	Moves to the side of the reaction with **fewer gas molecules** For some reactions this decreases yield
Increased temperature	**Faster**	Moves in the **endothermic** direction For exothermic reactions this **decreases** yield
Use of a **catalyst**	**Faster**	**No effect**

43

CONDITIONS AFFECTING EQUILIBRIUM – EXAMPLE 2

Explain whether the yield of the following reactions would increase or decrease if the temperature was increased.

A. $C_2H_4(g) + H_2O(g) \rightleftharpoons C_2H_5OH(g)$ $\quad \Delta H = -46\ kJ\ mol^{-3}$

B. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $\quad \Delta H = +90\ kJ\ mol^{-3}$

C. $H_2O(g) + C(s) \rightleftharpoons CO(g) + H_2(g)$ $\quad \Delta H = +13\ kJ\ mol^{-3}$

44

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CONDITIONS AFFECTING EQUILIBRIUM – EXAMPLE 2

A. The reaction is **exothermic** in the forward direction. An increase in the temperature moves the reaction in the **endothermic** direction, so it **reverses** and **less yield** of C_2H_5OH is formed.

B. The reaction is **endothermic** in the forward direction. An increase in the temperature moves the reaction in the **endothermic** direction, so it **goes forward** and **more yield** of NO is formed.

C. The reaction is **endothermic** in the forward direction. An increase in the temperature moves the reaction in the **endothermic** direction, so it **goes forward** and **more yield** of CO and H_2 is formed.

45

EFFECT OF TEMPERATURE ON K

In the following case:

$$\mathbf{A(g) + 2B(g) \rightleftharpoons 2C(g)\ \Delta H = -200\ kJ\ mol^{-1}}$$

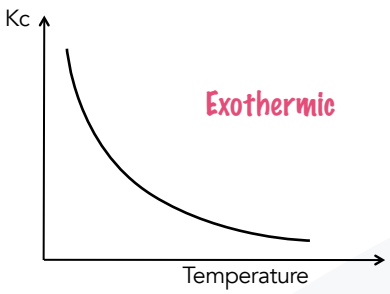
Only temperature affects K_c and K_p. If temperature increases, K_c decreases. This is because increasing temperature will make the reaction move backwards, increasing the value of the denominator and lowering the value of numerator.

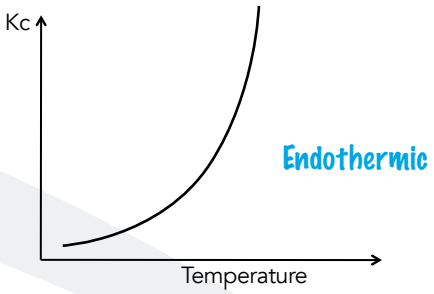
Note: Always write the effect on equilibrium and rate. For example, for an exothermic reaction, a **low temperature** would **slow down** the rate and **increase** the yield.

46

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EFFECT OF TEMPERATURE ON K





47

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ACID AND BASES

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ACIDS AND BASES

ARRHENIUS THEORY

Acids are substances that produce **H^+ ions** when they dissolve in water.

Bases are substances that react with H^{+}+ ions to produce water.

Alkalis are bases which dissolve in water to produce OH^- ions.

Hence, the stronger the dissociation, the stronger the acid.

However, H^+ ions exist as Hydronium H_3O^+ ions, associating with water molecules by coordinate bonds.

2

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ARRHENIUS THEORY

Arrhenius theory limits itself to the concentration of H^+ and OH^- ions determining the strength of acids and bases.

Hence, this theory is restricted to polar solvents like water.

However, this is also why Hydrochloric and Ethanoic acid show acidity.

strong acid: $HCl \rightarrow H^+ + Cl^-$

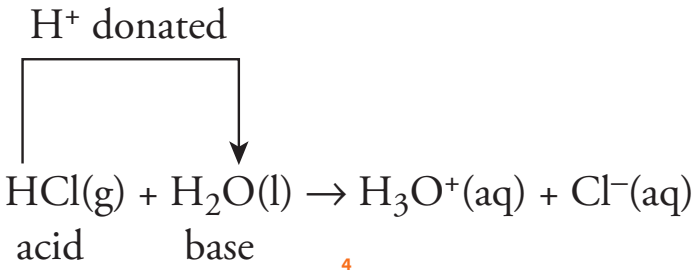
weak acid: $CH_3CO_2H \rightleftharpoons H^+ + CH_3CO_2^-$

3

BRONSTED-LOWRY THEORY

According to this, an acid is a proton (H+) **donor**, and bases are proton **acceptors**.

In the following reaction HCl is an acid because it donates a proton to water. This means that water is acting as a Brønsted– Lowry base. The water is accepting a proton.



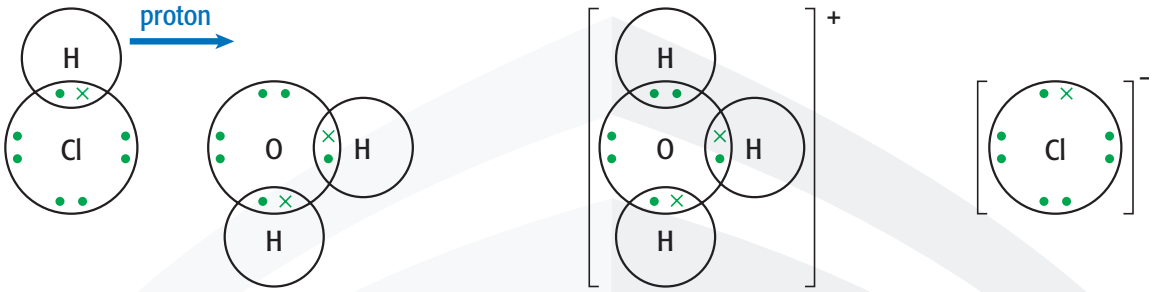
4

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BRONSTED-LOWRY THEORY

Also, a base has to be a substance with a lone pair, to coordinate with the proton.

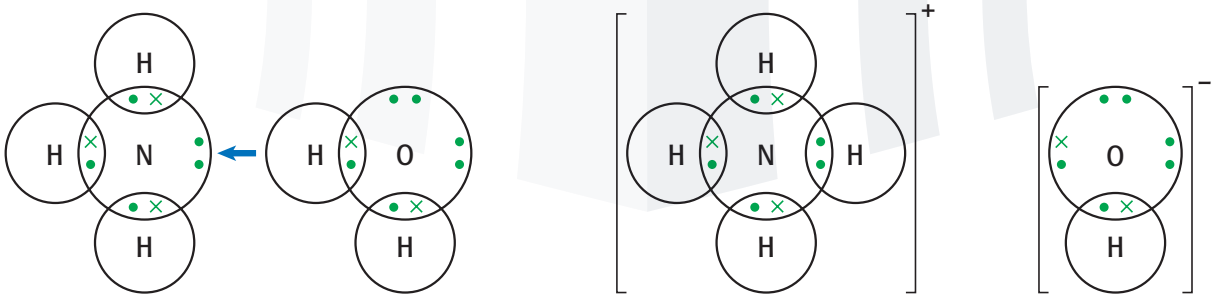
$HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$



5

BRONSTED-LOWRY THEORY

$NH_3(g) + H_2O(l) \longrightarrow NH_4^+(aq) + OH^-(aq)$



The proton, H^+, is donated by the water and accepted by the ammonia…

…forming the positive ammonium ion…

…and the negative hydroxide ion.

6

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BRONSTED-LOWRY THEORY

$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$

A conjugate acid is a base that has accepted a proton.

A conjugate base is an acid that has donated a proton.

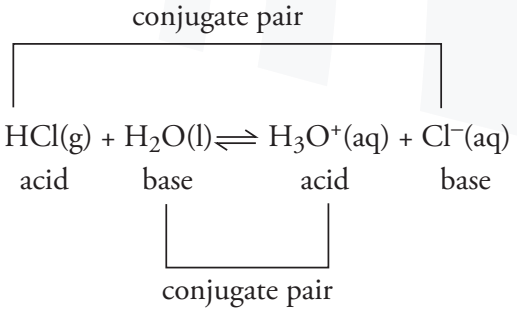
Hence, the NH_4^+ ion is said to be the conjugate acid of NH_3, and likewise, NH_3 is the conjugate base of NH_4^+ ion.

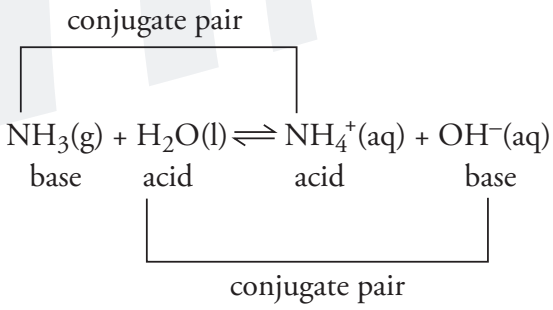
H_2O is the conjugate acid of the OH^- ion, and the OH^- ion is the conjugate base of H_2O.

7

BRONSTED-LOWRY THEORY

This suggests that a substance can both be an acid and a base depending on the situation.





8

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STRENGTH OF ACIDS

The strength of acids is judged by their tendency to donate protons.

The strength of bases is judged by their tendency to accept protons.

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

The above reaction proceeds to completion, therefore, HCl is a stronger acid than H_3O^+, and H_2O is a stronger base than Cl^-.

9

STRENGTH OF ACIDS

$$CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-$$

Th above reaction however is a reversible reaction, with the equilibrium position well towards the left.

H_3O^+ is a stronger acid than CH_3CO_2H, and $CH_3CO_2^-$ is a stronger base than H_2O.

Hence, strong acids have weak conjugate bases, and vice versa.

10

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SKILL CHECK 1

Identify which reactants are acids and which are bases:

(a) $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

(b) $HCOOH + HClO_2 \rightleftharpoons HCOOH_2^+ + ClO_2^-$

(c) $HClO_4 + CH_3COOH \rightleftharpoons ClO_4^- + CH_3COOH_2^+$

(d) $H_2SO_4 + HNO_3 \rightleftharpoons HSO_4^- + H_2NO_3^+$

(e) $H_2S + H_2O \rightleftharpoons HS^- + H_3O^+$

11

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EQUILIBRIA WS 1

SECTION A

1 In an experiment, 2.00 mol of hydrogen and 3.00 mol of iodine were heated together in a sealed container and allowed to reach equilibrium at a fixed temperature. The container had a fixed volume of 1.00 dm^3. At equilibrium, there were 2.40 mol of iodine present in the mixture.

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

What is the value of the equilibrium constant, K_c?

A 0.107 **B** 0.357 **C** 0.429 **D** 2.33

2 An aqueous solution was prepared containing a mixture of 1.0 mol of $AgNO_3$ and 1.0 mol of $FeSO_4$ in 1.00 dm^3 of water. When equilibrium was established, there was 0.44 mol of $Ag^+(aq)$ in the mixture.

$$Ag^+(aq) + Fe^{2+}(aq) \rightleftharpoons Ag(s) + Fe^{3+}(aq)$$

What is the numerical value of K_c?

A 0.62 **B** 1.40 **C** 1.62 **D** 2.89

3 The equation for the reaction between carbon monoxide and hydrogen is shown.

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

What are the units of K_p for this reaction?

A kPa **B** kPa^{-1} **C** kPa^2 **D** kPa^{-2}

4 When solid ammonium chloride dissociates at a certain temperature in a 0.500 dm^3 container, ammonia and hydrogen chloride are formed.

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$

The initial amount of ammonium chloride was 1.00 mol, and when the system had reached equilibrium there was 0.300 mol of ammonium chloride.

What is the numerical value of K_c for this reaction under these conditions?

A 0.490 **B** 1.63 **C** 1.96 **D** 3.27

5 The equilibrium constant, K_c, for the reaction shown is 2 $mol^{-2}\,dm^6$, at 600 K.

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

What is the concentration of NH_3 at equilibrium, at 600 K, when the equilibrium concentrations of N_2 and H_2 are both 2 $mol\,dm^{-3}$?

A $\sqrt{8}$ $mol\,dm^{-3}$ **B** $\sqrt{16}$ $mol\,dm^{-3}$ **C** $\sqrt{32}$ $mol\,dm^{-3}$ **D** 32 $mol\,dm^{-3}$

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6 Catalysts are an important feature of many industrial processes and biochemical reactions.

Which row correctly describes the effect of a catalyst on a reversible chemical reaction?

	position of equilibrium	effect on value of ΔH
A	moved to right	decreased
B	unaffected	decreased
C	unaffected	increased
D	unaffected	unaffected

7 The table shows the partial pressures in an equilibrium mixture formed by the Haber process.

substance	partial pressure / kPa
nitrogen	7000
hydrogen	8000
ammonia	4000

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

What is the numerical value of the equilibrium constant, K_p, for this reaction?

A 4.46×10^{-9}

B 4.76×10^{-5}

C 7.14×10^{-5}

D 2.24×10^{8}

8 Nitrogen reacts with hydrogen to produce ammonia.

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

A mixture of 2.00 mol of nitrogen, 6.00 mol of hydrogen and 2.40 mol of ammonia is allowed to reach equilibrium in a sealed vessel of volume 1 dm^3. It was found that 2.32 mol of nitrogen were present in the equilibrium mixture.

What is the value of K_c?

A $\dfrac{(1.76)^2}{(2.32)(6.96)^3}$

B $\dfrac{(1.76)^2}{(2.32)(6.32)^3}$

C $\dfrac{(2.08)^2}{(2.32)(6.32)^3}$

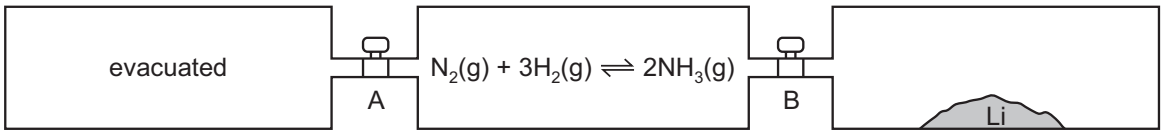
D $\dfrac{(2.40)^2}{(2.32)(6.00)^3}$

9 Lithium reacts with nitrogen at room temperature to form solid Li_3N.

Three vessels of equal volume are connected by taps, A and B, as shown.

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10



At the start, A and B are closed, the left-hand vessel is evacuated, the middle vessel has the indicated reaction at equilibrium and the right-hand vessel contains lithium only.

Which action would allow the equilibrium mixture to contain the **most** ammonia?

A Keep both A and B closed.

B Open both A and B.

C Open A only.

D Open B only.

11 The table shows the partial pressures in an equilibrium mixture formed by the Haber process.

substance	partial pressure / kPa
nitrogen	7000
hydrogen	8000
ammonia	4000

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

What is the numerical value of the equilibrium constant, K_p, for this reaction?

A 4.46×10^{-9}

B 4.76×10^{-5}

C 7.14×10^{-5}

D 2.24×10^{8}

12 Hydrogen iodide dissociates into hydrogen and iodine.

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

In an experiment, b mol of hydrogen iodide were put into a sealed vessel at pressure p. At equilibrium, x mol of the hydrogen iodide had dissociated.

Which expression for K_p is correct?

A $\dfrac{x^2}{(b-x)^2}$ **B** $\dfrac{x^2p^2}{(b-x)^2}$ **C** $\dfrac{x^2p^2}{4b(b-x)}$ **D** $\dfrac{x^2}{4(b-x)^2}$

13 For the reaction shown, an equilibrium is established at a temperature of 700 K.

The equilibrium constant, K_p, for the reaction is 9.80 kPa. The partial pressure of N_2O_4 at equilibrium is 80.0 kPa.

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

What is the partial pressure of NO_2 at equilibrium?

A 8.16 kPa **B** 28.0 kPa **C** 66.6 kPa **D** 784 kPa

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14 Ammonia is produced by the Haber process.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad \Delta H^{\ominus} = -92\,kJ\,mol^{-1}$$

A fault in the temperature control during the process resulted in the temperature changing to 600 °C for two hours.

What effect did this have on the ammonia production during this time?

A Ammonia was formed faster. The equilibrium yield decreased.

B Ammonia was formed faster. The equilibrium yield increased.

C Ammonia was formed slower. The equilibrium yield decreased.

D Ammonia was formed slower. The equilibrium yield increased.

15 Ammonia is manufactured from nitrogen and hydrogen using the Haber process.

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

What is the expression for K_c for this equilibrium?

A $\dfrac{2[NH_3(g)]}{[N_2(g)] + 3[H_2(g)]}$

B $\dfrac{2[NH_3(g)]}{[N_2(g)] \times 3[H_2(g)]}$

C $\dfrac{[NH_3(g)]^2}{[N_2(g)] + [H_2(g)]^3}$

D $\dfrac{[NH_3(g)]^2}{[N_2(g)] \times [H_2(g)]^3}$

16 Two moles of compound P were placed in a sealed container. The container was heated and P was partially decomposed to produce Q and R only. A dynamic equilibrium between P, Q and R was established.

At equilibrium x moles of R were present and the total number of moles present was $\left(2 + \frac{x}{2}\right)$.

What is the equation for this reversible reaction?

A $P \rightleftharpoons 2Q + R$

B $2P \rightleftharpoons 2Q + R$

C $2P \rightleftharpoons Q + R$

D $2P \rightleftharpoons Q + 2R$

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17 A reaction involved in the Contact process is shown.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H^{\ominus} = -197\,kJ\,mol^{-1}$$

The reaction is investigated at 200 kPa and 700 K and the value of the equilibrium constant, K_p, is found to be Y. The reaction is then investigated at 1000 kPa and 700 K and the value of K_p is found to be Z.

Which statement comparing Y and Z is correct?

A Y and Z are the same.

B Y is greater than Z.

C Z is 2.2 times greater than Y.

D Z is 5.0 times greater than Y.

18 Nitrogen dioxide, NO_2, is a brown gas.

Dinitrogen tetroxide, N_2O_4, is a colourless gas.

An equilibrium is established between NO_2 and N_2O_4 in a closed vessel.

$$\underset{\text{brown}}{2NO_2(g)} \rightleftharpoons \underset{\text{colourless}}{N_2O_4(g)} \qquad \Delta H = -57\,kJ\,mol^{-1}$$

Which row describes the effects of changing conditions on the colour of an equilibrium mixture of NO_2 and N_2O_4?

	increasing the pressure	increasing the temperature
A	colour becomes darker	colour becomes darker
B	colour becomes darker	colour becomes lighter
C	colour becomes lighter	colour becomes darker
D	colour becomes lighter	colour becomes lighter

[W'17 2 Q9]

19 The reaction between sulfur dioxide and oxygen is reversible.

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 \qquad \Delta H^{\ominus} = -196\,kJ\,mol^{-1}$$

Which conditions of pressure and temperature favour the **reverse** reaction?

	pressure	temperature
A	high	high
B	high	low
C	low	high
D	low	low

[M'18 P12 Q11]

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20 In a particular reversible reaction the yield of product is increased

- if the temperature is increased;
- if the pressure is decreased.

Which equation could describe this reversible reaction?

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

B $4NH_3(g) + 3O_2(g) \rightleftharpoons 2N_2(g) + 6H_2O(g)$ $\Delta H = -227\,kJ\,mol^{-1}$

C $2NO_2(g) \rightleftharpoons N_2O_4(g)$ $\Delta H = -58\,kJ\,mol^{-1}$

D $3O_2(g) \rightleftharpoons 2O_3(g)$ $\Delta H = +143\,kJ\,mol^{-1}$

[J'18 P12 Q10]

21 Hydrogen is produced industrially from methane as shown in the equation.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \qquad \Delta H^{\ominus} = +205\,kJ\,mol^{-1}$$

Which conditions would most favour the formation of hydrogen?

	pressure	temperature
A	high	high
B	high	low
C	low	high
D	low	low

[J'18 P13 Q9]

22 The chemical equilibrium shown is formed when ammonia is produced in the Haber process.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

The following concentrations are found to be present at equilibrium under certain conditions.

N_2	H_2	NH_3
$0.200\,mol\,dm^{-3}$	$0.300\,mol\,dm^{-3}$	$0.600\,mol\,dm^{-3}$

What is the numerical value of K_c under these conditions?

A 0.0150 **B** 6.0 **C** 10.0 **D** 66.7

[J'18 P13 Q10]

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23 Silver chloride and silver iodide form equilibria when added to water.

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \qquad K_c = K_1$$

$$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq) \qquad K_c = K_2$$

Each equilibrium position lies well to the **left**.

Silver iodide will not dissolve in aqueous ammonia. Silver chloride will dissolve in aqueous ammonia. Another equilibrium is formed.

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) \qquad K_c = K_3$$

The position of this equilibrium lies to the **right**.

What is the order of magnitude for these three equilibrium constants?

A $K_1 > K_2 > K_3$

B $K_2 > K_1 > K_3$

C $K_3 > K_1 > K_2$

D $K_3 > K_2 > K_1$

[J'18 P13 Q17]

24 In this question you should assume that all gases behave ideally.

Hydrogen and iodine react reversibly in the following reaction. The system reaches dynamic equilibrium.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \qquad \Delta H = -9.5\,kJ\,mol^{-1}$$

Which statement **must** be true for the K_p of this equilibrium to be constant?

A The partial pressures of H_2, I_2 and HI are equal.

B The external pressure is constant.

C The forward and reverse reactions have stopped.

D The temperature is constant.

[N'18 P11 Q9]

25 0.200 mol of sulfur dioxide and 0.200 mol of oxygen are placed in a 1.00 dm^3 sealed container. The gases are allowed to react until equilibrium is reached.

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

At equilibrium there is 0.100 mol of SO_3 in the container.

What is the value of K_c?

A 0.150 $mol\,dm^{-3}$

B 0.800 $mol\,dm^{-3}$

C 1.25 $mol^{-1}\,dm^3$

D 6.67 $mol^{-1}\,dm^3$

[N'18 P11 Q10]

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SECTION B

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

1 Methanoic acid molecules, HCO_2H, and hydrogen carbonate ions, HCO_3^-, can both behave as acids.

Why does a solution of methanoic acid have a lower pH than a solution of sodium hydrogen carbonate of the same concentration?

1 HCO_2H molecules dissociate more fully than HCO_3^- ions do.

2 Each HCO_2H molecule has two hydrogen atoms; each HCO_3^- ion only has one.

3 Methanoic acid is a weaker acid than sodium hydrogen carbonate.

2 The following equilibrium is an exothermic reaction in the forward direction.

$$2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$$

What happens when the concentration of CrO_4^{2-} ions **increases and** the temperature **decreases**?

1 The concentration of $Cr_2O_7^{2-}$ ions increases.

2 The equilibrium constant increases.

3 The activation energy decreases.

3 R and S react together.

$$R + S \rightleftharpoons T$$

Which factors affect the rate of the forward reaction?

1 the activation energy of the reaction

2 the enthalpy change of the reaction

3 the equilibrium constant of the reaction

4 The Brønsted-Lowry theory describes acid and base character.

When concentrated sulfuric acid and concentrated nitric acid are mixed, the following reactions occur.

$$H_2SO_4 + HNO_3 \rightleftharpoons HSO_4^- + H_2NO_3^+$$

$$H_2NO_3^+ \rightleftharpoons H_2O + NO_2^+$$

$$H_2O + H_2SO_4 \rightleftharpoons HSO_4^- + H_3O^+$$

Which species are bases in these reactions?

1 HSO_4^-

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5 Which statements about reversible reactions are correct?

1 An increase in concentration of a reactant always increases the concentration of the product.

2 An increase in temperature always increases the rate at which the equilibrium is established.

3 An increase in temperature always increases the concentration of the product at equilibrium.

6 In this question, all gases can be assumed to behave ideally.

A chemist heats a mixture of nitrogen and oxygen gases in a sealed container at a constant temperature until the mixture reaches a dynamic equilibrium containing $N_2(g)$, $O_2(g)$ and NO(g).

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

The chemist repeats the experiment at the same temperature using the same initial amounts of $N_2(g)$ and $O_2(g)$, but at a much higher pressure.

Which statements about the second experiment at higher pressure are correct?

1 At higher pressure, there are more particles per unit volume.

2 The composition of the equilibrium mixture does not change.

3 There are more collisions per second so equilibrium is reached faster.

7 In the manufacture of sulfuric acid, the following exothermic reaction occurs.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

Which changes will move the position of the equilibrium to the right?

1 increasing the pressure

2 increasing the temperature

3 using twice as much catalyst

8 Methanol, CH_3OH, can be produced industrially by reacting CO with H_2.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H = -91\,kJ\,mol^{-1}$$

The process can be carried out at 4×10^3 kPa and 1150 K.

Which statements about this reaction are correct?

1 Increasing the temperature will increase the rate of reaction because more effective collisions will occur.

2 Lowering the temperature will reduce the rate of reaction because the forward reaction is exothermic.

3 Increasing the pressure will reduce the rate of reaction because there are a larger number of moles on the left-hand side of the equation.

9 In the manufacture of sulfuric acid, the following exothermic reaction occurs.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

Which changes will move the position of the equilibrium to the right?

1 increasing the pressure

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10 Ammonia and chlorine react together in the gas phase.

$$8NH_3 + 3Cl_2 \rightarrow N_2 + 6NH_4Cl$$

Which statements are correct?

1 Ammonia behaves as a reducing agent.

2 Ammonia behaves as a base.

3 The oxidation number of hydrogen changes.

[M'18 P12 Q33]

11 In which reactions does NH_3 behave as a Brønsted-Lowry acid?

1 $2NH_3 \rightarrow NH_2^- + NH_4^+$

2 $HSO_4^- + NH_3 \rightarrow SO_4^{2-} + NH_4^+$

3 $Ag^+ + 2NH_3 \rightarrow [Ag(NH_3)_2]^+$

[M'18 P12 Q34]

12 Which statements are correct when a reversible reaction is at equilibrium?

1 All species are at equal concentration.

2 The concentrations of all species remain constant.

3 The rate of the forward reaction equals the rate of the reverse reaction.

[J'18 P11 Q34]

13 Ammonia and chlorine react as shown.

$$8NH_3 + 3Cl_2 \rightarrow N_2 + 6NH_4Cl$$

Which statements are correct?

1 Each nitrogen atom is oxidised.

2 Each chlorine atom is reduced.

3 Ammonia behaves as a base.

[J'18 P13 Q33]

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EQUILIBRIA WS 2

1 **(c)** At temperatures above 1500 K, HCl will decompose.

A sample of 0.300 mol of HCl decomposed in a sealed container.

The resulting equilibrium mixture was found to contain 1.50×10^{-2} mol of Cl_2.

(i) Calculate the amounts, in mol, of H_2 and HCl present in the equilibrium mixture.

H_2 = ... mol

HCl = ... mol
[2]

(ii) Calculate the mole fraction of each gas in the equilibrium mixture.

mole fraction of HCl = ...

mole fraction of H_2 = ...

mole fraction of Cl_2 = ...
[1]

(d) In another experiment under different conditions, an equilibrium mixture was produced with mole fractions for each species as shown.

species	mole fraction
HCl	0.88
H_2	0.06
Cl_2	0.06

(i) Write the expression for the equilibrium constant, K_p, for the decomposition of HCl.

$$2HCl(g) \rightleftharpoons H_2(g) + Cl_2(g)$$

K_p =

[1]

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(ii) Explain why the total pressure of the system does **not** need to be known for K_p to be calculated for this experiment.

.....

..... [1]

(iii) Calculate the value of K_p for this experiment.

K_p = ... [1]

20 **(b)** The equation for the preparation of hydrogen chloride using concentrated sulfuric acid is shown.

$$H_2SO_4 + NaCl \rightarrow NaHSO_4 + HCl$$

(i) Use the Brønsted-Lowry theory of acids and bases to identify the base and its conjugate acid in this reaction. Explain your answer.

Brønsted-Lowry base (base-I) = ...

conjugate acid (acid-II) = ...

.....

.....

.....

[2]

(ii) Explain why the reaction of concentrated sulfuric acid and sodium iodide is **not** suitable for the preparation of hydrogen iodide.

.....

.....

.....

..... [2]

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2 **(c)** Hydrogen chloride undergoes a reversible reaction with oxygen.

$$4HCl(g) + O_2(g) \rightleftharpoons 2Cl_2(g) + 2H_2O(g)$$

The reaction is carried out at 400 °C in the presence of a copper(II) chloride catalyst.

(i) Use the data in the table to calculate the overall enthalpy change of reaction.

compound	enthalpy change of formation / kJ mol^{-1}
$HCl(g)$	–92
$H_2O(g)$	–242

enthalpy change of reaction = ... kJ mol^{-1} [2]

(ii) State the **type** of catalyst used in this reaction. Explain how a catalyst is able to increase the rate of a chemical reaction.

.....

.....

.....

..... [2]

(iii) The reaction exists in dynamic equilibrium.

The reaction was repeated at 1000 °C and the same pressure.

State and explain the effect on the composition of the equilibrium mixture of the change in temperature.

.....

.....

.....

..... [2]

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(iv) When 1.60 mol of HCl are mixed in a sealed container with 0.500 mol of O_2 at 400 °C, 0.600 mol of Cl_2 and 0.600 mol of H_2O are formed.

The total pressure inside the container is 1.50×10^5 Pa.

- Calculate the amounts, in mol, of HCl and O_2 in the equilibrium mixture.

HCl = ... mol

O_2 = ... mol

- Calculate the mole fraction of Cl_2 and hence the partial pressure of Cl_2 in the equilibrium mixture.

mole fraction of Cl_2 = ...

p_{Cl_2} = ... Pa
[3]

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(v) In a separate experiment, an equilibrium reaction mixture was found to contain the four gases at the partial pressures shown in the table.

gas	HCl	O_2	Cl_2	H_2O
partial pressure / Pa	4.8×10^4	3.0×10^4	3.6×10^4	3.6×10^4

$$K_p = \frac{(p_{Cl_2})^2 \times (p_{H_2O})^2}{(p_{HCl})^4 \times p_{O_2}}$$

Use this information and the expression given for K_p to calculate a value for K_p. State the units of K_p.

K_p = ...

units = ...
[2]

(vi) The reaction is repeated without a catalyst.

State the effect of this on K_p.

..... [1]

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3 Ammonia, NH_3, is manufactured from nitrogen and hydrogen by the Haber process.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92\,kJ\,mol^{-1}$$

(c) At a pressure of 2.00×10^7 Pa, 1.00 mol of nitrogen, $N_2(g)$, was mixed with 3.00 mol of hydrogen, $H_2(g)$. The final equilibrium mixture formed contained 0.300 mol of ammonia, $NH_3(g)$.

(i) Calculate the amounts, in mol, of $N_2(g)$ and $H_2(g)$ in the equilibrium mixture.

$N_2(g)$ = ... mol

$H_2(g)$ = ... mol
[2]

(ii) Calculate the partial pressure of ammonia, pNH_3, in the equilibrium mixture.

Give your answer to **three** significant figures.

pNH_3 = ... Pa [3]

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(d) In another equilibrium mixture the partial pressures are as shown.

substance	partial pressure / Pa
$N_2(g)$	2.20×10^6
$H_2(g)$	9.62×10^5
$NH_3(g)$	1.40×10^4

(i) Write the expression for the equilibrium constant, K_p, for the production of ammonia from nitrogen and hydrogen.

K_p =

[1]

(ii) Calculate the value of K_p for this reaction.

State the units.

K_p = ...

units = ...

[2]

(iii) This reaction is repeated with the same starting amounts of nitrogen and hydrogen. The same temperature is used but the container has a smaller volume.

State the effects, if any, of this change on the yield of ammonia and on the value of K_p.

effect on yield of ammonia .....

effect on value of K_p .....

[2]

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4 At 450 K phosphorus(V) chloride, $PCl_5(g)$, decomposes to form phosphorus(III) chloride, $PCl_3(g)$, and chlorine, $Cl_2(g)$. A dynamic equilibrium is established as shown.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \qquad \Delta H = +124\,kJ\,mol^{-1}$$

(a) The enthalpy change of formation of $PCl_3(g)$ under these conditions is given.

$$\Delta H_f\, PCl_3(g) = -320\,kJ\,mol^{-1}$$

Calculate the enthalpy change of formation of $PCl_5(g)$ under these conditions.

Include a sign with your answer.

enthalpy change = ... $kJ\,mol^{-1}$ [1]

(b) **(i)** State and explain the effect of increasing temperature on the rate of decomposition of $PCl_5(g)$.

.....

.....

..... [2]

(ii) State and explain the effect of increasing temperature on the percentage of $PCl_5(g)$ that decomposes.

.....

.....

..... [2]

(c) Explain the meaning of the term *dynamic equilibrium* and the conditions necessary for it to become established.

.....

.....

.....

..... [2]

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(d) When 2.00 mol of $PCl_5(g)$ are decomposed at 450 K and 1.00×10^5 Pa the resulting equilibrium mixture contains 0.800 mol of $Cl_2(g)$.

(i) Calculate the partial pressure of phosphorus(V) chloride, $p PCl_5$, in this equilibrium mixture.

$p PCl_5$ = ... Pa [2]

(ii) Write the expression for the equilibrium constant, K_p, for the decomposition of $PCl_5(g)$.

K_p =

[1]

(iii) The partial pressures of $PCl_3(g)$ and of $Cl_2(g)$ in this equilibrium mixture are both 2.86×10^4 Pa.

Calculate the value of K_p and state its units.

K_p = ...

units = ...
[2]

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5 **(c)** Hydrogen chloride undergoes a reversible reaction with oxygen.

$$4HCl(g) + O_2(g) \rightleftharpoons 2Cl_2(g) + 2H_2O(g)$$

The reaction is carried out at 400 °C in the presence of a copper(II) chloride catalyst.

(ii) State the **type** of catalyst used in this reaction. Explain how a catalyst is able to increase the rate of a chemical reaction.

.....

.....

.....

..... [2]

(iii) The reaction exists in dynamic equilibrium.

The reaction was repeated at 1000 °C and the same pressure.

State and explain the effect on the composition of the equilibrium mixture of the change in temperature.

.....

.....

.....

..... [2]

[M'17 2 Q2]

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The equation for this stage of the Contact Process is shown.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -196\,kJ\,mol^{-1}$$

(d) (i) State and explain the effect of increasing temperature on the rate of production of SO_3.

.....

.....

.....

..... [3]

(ii) State and explain the effect of increasing temperature on the yield of SO_3.

.....

.....

.....

..... [3]

(e) The SO_3 produced is converted to sulfuric acid in two stages. In the first stage the SO_3 is reacted with concentrated sulfuric acid to produce oleum, $H_2S_2O_7$.
The oleum is then reacted with water to form sulfuric acid.

Suggest an equation for the reaction of oleum, $H_2S_2O_7$, with water to form sulfuric acid.

..... [1]

[J'18 P11 Q1]

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6 **(d)** 2.00 moles of $SO_2(g)$ and 2.00 moles of $O_2(g)$ are sealed in a container with a suitable catalyst, at constant temperature and pressure. The resulting equilibrium mixture contains 1.98 moles of $SO_3(g)$.
The total volume of the equilibrium mixture is 40.0 dm^3.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

(i) Write the expression for the equilibrium constant, K_c, for the reaction between $SO_2(g)$ and $O_2(g)$ to produce $SO_3(g)$.

K_c =

[1]

(ii) Calculate the amount, in moles, of $SO_2(g)$ and $O_2(g)$ in the equilibrium mixture.

$SO_2(g)$ = ... mol

$O_2(g)$ = ... mol
[2]

(iii) Use your answers to **(d)(i)** and **(d)(ii)** to calculate the value of K_c for this equilibrium mixture. Give the units of K_c.

K_c = ...

units = ...
[3]

[J'18 P23 Q1]

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7 **(c)** At a pressure of 2.00×10^7 Pa, 1.00 mol of nitrogen, $N_2(g)$, was mixed with 3.00 mol of hydrogen, $H_2(g)$. The final equilibrium mixture formed contained 0.300 mol of ammonia, $NH_3(g)$.

(i) Calculate the amounts, in mol, of $N_2(g)$ and $H_2(g)$ in the equilibrium mixture.

$N_2(g)$ = ... mol

$H_2(g)$ = ... mol
[2]

(ii) Calculate the partial pressure of ammonia, pNH_3, in the equilibrium mixture.

Give your answer to **three** significant figures.

pNH_3 = ... Pa [3]

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(d) In another equilibrium mixture the partial pressures are as shown.

substance	partial pressure / Pa
$N_2(g)$	2.20×10^6
$H_2(g)$	9.62×10^5
$NH_3(g)$	1.40×10^4

(i) Write the expression for the equilibrium constant, K_p, for the production of ammonia from nitrogen and hydrogen.

K_p =

[1]

(ii) Calculate the value of K_p for this reaction.

State the units.

K_p = ...

units = ...

[2]

(iii) This reaction is repeated with the same starting amounts of nitrogen and hydrogen. The same temperature is used but the container has a smaller volume.

State the effects, if any, of this change on the yield of ammonia and on the value of K_p.

effect on yield of ammonia .....

effect on value of K_p .....

[2]

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8 At 450 K phosphorus(V) chloride, $PCl_5(g)$, decomposes to form phosphorus(III) chloride, $PCl_3(g)$, and chlorine, $Cl_2(g)$. A dynamic equilibrium is established as shown.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \qquad \Delta H = +124\,kJ\,mol^{-1}$$

(a) The enthalpy change of formation of $PCl_3(g)$ under these conditions is given.

$$\Delta H_f\ PCl_3(g) = -320\,kJ\,mol^{-1}$$

Calculate the enthalpy change of formation of $PCl_5(g)$ under these conditions.

Include a sign with your answer.

enthalpy change = ... $kJ\,mol^{-1}$ [1]

(b) **(i)** State and explain the effect of increasing temperature on the rate of decomposition of $PCl_5(g)$.

.....

.....

..... [2]

(ii) State and explain the effect of increasing temperature on the percentage of $PCl_5(g)$ that decomposes.

.....

.....

..... [2]

(c) Explain the meaning of the term *dynamic equilibrium* and the conditions necessary for it to become established.

.....

.....

.....

..... [2]

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(d) When 2.00 mol of $PCl_5(g)$ are decomposed at 450 K and 1.00×10^5 Pa the resulting equilibrium mixture contains 0.800 mol of $Cl_2(g)$.

(i) Calculate the partial pressure of phosphorus(V) chloride, $p PCl_5$, in this equilibrium mixture.

$p PCl_5$ = ... Pa [2]

(ii) Write the expression for the equilibrium constant, K_p, for the decomposition of $PCl_5(g)$.

K_p =

[1]

(iii) The partial pressures of $PCl_3(g)$ and of $Cl_2(g)$ in this equilibrium mixture are both 2.86×10^4 Pa.

Calculate the value of K_p and state its units.

K_p = ...

units = ...

[2]

[W'17 P22 Q2]

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EQUILIBRIA WS 3

SECTION A

1 For which equilibrium does K_c have *no units*?

A $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$

B $CH_3OH(l) + CH_3CO_2H(l) \rightleftharpoons CH_3CO_2CH_3(l) + H_2O(l)$

C $Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq)$

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

2 When 0.20 mol of hydrogen gas and 0.15 mol of iodine gas are heated at 723 K until equilibrium is established, the equilibrium mixture is found to contain 0.26 mol of hydrogen iodide.

The equation for the reaction is as follows.

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

What is the correct expression for the equilibrium constant K_c?

A $\dfrac{2 \times 0.26}{0.20 \times 0.15}$

B $\dfrac{(2 \times 0.26)^2}{0.20 \times 0.15}$

C $\dfrac{(0.26)^2}{0.07 \times 0.02}$

D $\dfrac{(0.26)^2}{0.13 \times 0.13}$

3 Two equilibria are shown below.

reaction I $\quad 2X_2(g) + Y_2(g) \rightleftharpoons 2X_2Y(g)$

reaction II $\quad X_2Y(g) \rightleftharpoons X_2(g) + \frac{1}{2}Y_2(g)$

The numerical value of K_c for reaction I is 2.

Under the same conditions, what is the numerical value of K_c for reaction II?

A $\dfrac{1}{\sqrt{2}}$ **B** $\dfrac{1}{2}$ **C** $\dfrac{1}{4}$ **D** -2

4 For the reaction

$$W(aq) + 2X(aq) \rightleftharpoons 2Y(aq) + 3Z(aq)$$

what are the correct units for the equilibrium constant K_c?

A $mol\,dm^{-3}$ **B** $mol^2\,dm^{-6}$ **C** $mol^{-1}\,dm^3$ **D** $mol^{-2}\,dm^6$

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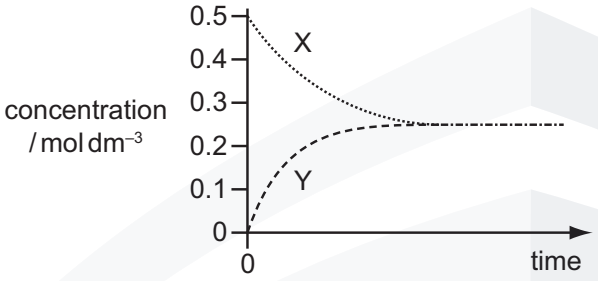
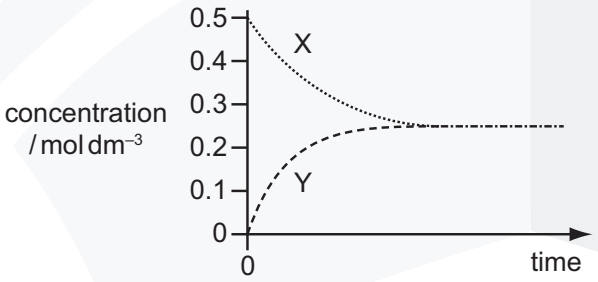
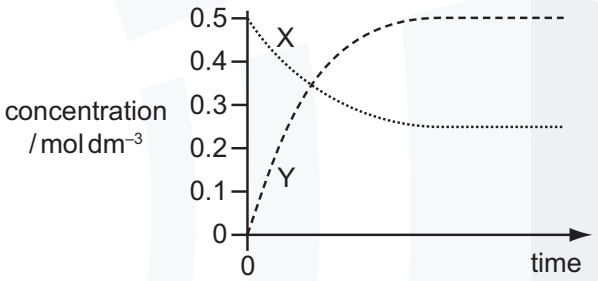
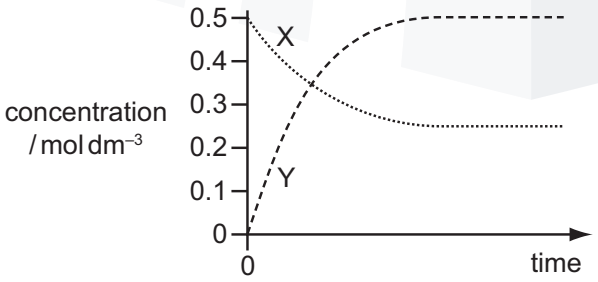
5 A dimer, X, is stable when solid but a dynamic equilibrium is set up in solution.

$$X(aq) \rightleftharpoons 2Y(aq)$$

A solution of X has an initial concentration of 0.50 mol dm^{-3}. When equilibrium has been reached [X(aq)] has fallen to 0.25 mol dm^{-3}.

The changes in [X(aq)] and [Y(aq)] are plotted against time until equilibrium is reached. The value of K_c is then calculated.

Which graph and value for K_c are correct?

	graph	K_c / mol dm^{-3}
A		1
B		2
C		1
D		2

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6 In an experiment, *b* mol of hydrogen iodide were put into a sealed vessel under pressure p. At equilibrium, *x* mol of the hydrogen iodide had dissociated, the reaction being represented by the following equation.

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

Which expression for K_p is correct?

A $\dfrac{x^2}{(b-x)^2}$

B $\dfrac{x^2p^2}{(b-x)^2}$

C $\dfrac{x^2p^2}{4b(b-x)}$

D $\dfrac{x^2}{4(b-x)^2}$

7 The value of the equilibrium constant, K_c, for the reaction to form ethyl ethanoate from ethanol and ethanoic acid is 4.0 at 60 °C.

$$C_2H_5OH + CH_3CO_2H \rightleftharpoons CH_3CO_2C_2H_5 + H_2O$$

When 1.0 mol of ethanol and 1.0 mol of ethanoic acid are allowed to reach equilibrium at 60 °C, what is the number of moles of ethyl ethanoate formed?

A $\frac{1}{3}$ **B** $\frac{2}{3}$ **C** $\frac{1}{4}$ **D** $\frac{3}{4}$

8 Nitrogen dioxide decomposes on heating according to the following equation.

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

When 4 mol of nitrogen dioxide were put into a 1 dm^3 container and heated to a constant temperature, the equilibrium mixture contained 0.8 mol of oxygen.

What is the value of the equilibrium constant, K_c, at the temperature of the experiment?

A $\dfrac{0.8^2 \times 0.8}{4^2}$ **B** $\dfrac{1.6 \times 0.8}{2.4^2}$ **C** $\dfrac{1.6^2 \times 0.8}{4^2}$ **D** $\dfrac{1.6^2 \times 0.8}{2.4^2}$

9 Dinitrogen tetroxide dissociates into nitrogen dioxide on heating.

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

In an experiment the partial pressures of the gases at equilibrium were found to be NO_2, 0.33 atm; N_2O_4, 0.67 atm.

What is the numerical value of K_p at the temperature of the experiment?

A 0.16 **B** 0.49 **C** 0.65 **D** 2.03

10 At a total pressure of 1.0 atm, dinitrogen tetraoxide is 50 % dissociated at a temperature of 60 °C, according to the following equation.

$$N_2O_4 \rightleftharpoons 2NO_2$$

stant, K_p, for this reaction at 60 °C?

C $^4/_3$ atm **D** 2 atm

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11 At high temperatures, steam decomposes into its elements according to the following equation.

$$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$$

In one experiment at 1 atm pressure, it was found that 20 % of the steam had been converted into hydrogen and oxygen.

What are the values of the equilibrium partial pressures, in atm, of the components of this equilibrium?

	partial pressure of steam	partial pressure of hydrogen	partial pressure of oxygen
A	$\frac{0.80 \times 1}{1.0}$	$\frac{0.10 \times 1}{1.0}$	$\frac{0.10 \times 1}{1.0}$
B	$\frac{0.80 \times 1}{1.0}$	$\frac{0.133 \times 1}{1.0}$	$\frac{0.067 \times 1}{1.0}$
C	$\frac{0.80 \times 1}{1.0}$	$\frac{0.20 \times 1}{1.0}$	$\frac{0.10 \times 1}{1.0}$
D	$\frac{0.80 \times 1}{1.1}$	$\frac{0.20 \times 1}{1.1}$	$\frac{0.10 \times 1}{1.1}$

12 When vanadium(II) compounds are dissolved in water, the following equilibrium is established.

$$V^{2+} + H_2O \rightleftharpoons V^{3+} + \tfrac{1}{2}H_2 + OH^-$$

What would alter the composition of the equilibrium mixture in favour of the V^{2+} ions?

A adding an acid

B adding a reagent that selectively precipitates V^{3+} ions

C allowing the hydrogen to escape as it forms

D making the solution more alkaline

13 Which statement concerning the equilibrium reaction below is true?

$$2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$$

A An increase in acid concentration will result in an increase in the concentration of $Cr_2O_7^{2-}(aq)$.

B A redox reaction is taking place.

C The addition of a catalyst will result in an increase in the concentration of $Cr_2O_7^{2-}(aq)$.

D The equilibrium constant, K_c, has no units.

14 For the equilibrium $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, what will change the value of K_p?

A adding a catalyst

B adding more O_2

C increasing the pressure

D increasing the temperature

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15 An experiment is set up to measure the rate of hydrolysis of methyl ethanoate.

$$CH_3CO_2CH_3 + H_2O \rightleftharpoons CH_3CO_2H + CH_3OH$$

The hydrolysis is found to be slow in neutral aqueous solution but it proceeds at a measurable rate when the solution is acidified with hydrochloric acid.

What is the function of the hydrochloric acid?

A to dissolve the methyl ethanoate

B to ensure that the reaction reaches equilibrium

C to increase the reaction rate by catalytic action

D to suppress ionisation of the ethanoic acid formed

16 The equilibrium

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad \Delta H = +180\,kJ\,mol^{-1}$$

contributes to a series of reactions producing photochemical smog.

Which factors would affect the value of K_p of the above equilibrium?

	change in pressure	change in temperature	presence or absence of a catalyst
A	✓	✓	✗
B	✓	✗	✓
C	✗	✓	✓
D	✗	✓	✗

17 When sulfur trioxide is manufactured from sulfur dioxide and oxygen, using the Contact process, which condition affects the value of the equilibrium constant, K_c?

A adjusting the temperature

B adjusting the pressure

C using a catalyst

D removing SO_3 from the equilibrium mixture

18 The Haber process for the manufacture of ammonia is represented by the following equation.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92\,kJ\,mol^{-1}$$

Which statement is correct about this reaction when the temperature is increased?

A Both forward and backward rates increase.

B The backward rate only increases.

C The forward rate only increases.

D There is no effect on the backward or forward rate.

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19 Swimming pool water can be kept free of harmful bacteria by adding aqueous sodium chlorate(I), NaOC*l*. This reacts with water to produce HOC*l* molecules which kill bacteria.

$$OCl^-(aq) + H_2O \rightleftharpoons OH^-(aq) + HOCl(aq)$$

In bright sunshine, the OCl^- ion is broken down by ultra-violet light.

$$OCl^-(aq) + \text{uv light} \rightarrow Cl^-(aq) + \tfrac{1}{2}O_2(g)$$

Which method would maintain the highest concentration of HOC*l*(aq)?

A acidify the pool water

B add a solution of chloride ions

C add a solution of hydroxide ions

D bubble air through the water

20 The dissociation of dinitrogen tetraoxide into nitrogen dioxide is represented by the equation below.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g); \qquad \Delta H^{\ominus} = +57\,kJ\,mol^{-1}$$

If the temperature of an equilibrium mixture of the gases is increased at constant pressure, will the volume of the mixture increase or decrease and why?

A The volume will increase, but only because of a shift of equilibrium towards the right.

B The volume will increase, both because of a shift of equilibrium towards the right and also because of thermal expansion.

C The volume will stay the same, because any thermal expansion could be exactly counteracted by a shift of equilibrium towards the left.

D The volume will decrease, because a shift of equilibrium towards the left would more than counteract any thermal expansion.

21 PCl_5 dissociates as follows.

$$PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$$

The extent of dissociation is 13 % at 160 °C and 100 % at 300 °C.

Which pair of statements about this formation of PCl_3 is correct?

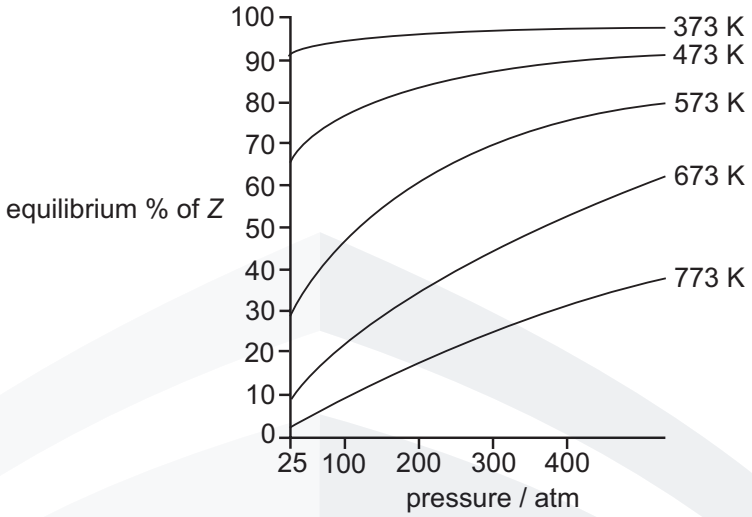
	shape of PCl_3 molecule	the reaction is
A	pyramidal	endothermic
B	pyramidal	exothermic
C	trigonal	endothermic
D	trigonal	exothermic

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22 In an industrial process, two gases *X* and *Y* react together to form a single gaseous product *Z*.

$$X(g) + Y(g) \rightleftharpoons Z(g)$$

The percentage yield of product *Z* varies according to the pressure and the temperature as shown in the graphs.



Which statement about this equilibrium reaction is correct?

A Decreasing the temperature decreases the value of the equilibrium constant.

B Decreasing the temperature increases the rate of this reaction.

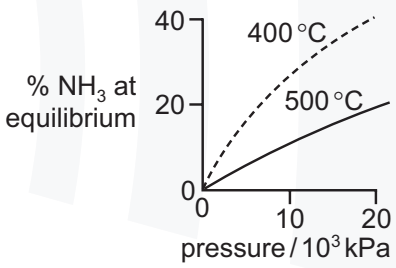
C Increasing the pressure increases the value of the equilibrium constant.

D The reaction is exothermic in the forward direction.

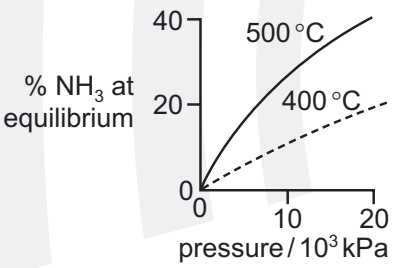
23 The percentage of ammonia obtainable, if equilibrium were established during the Haber process, is plotted against the operating pressure for two temperatures, 400 °C and 500 °C.

Which diagram correctly represents the two graphs?

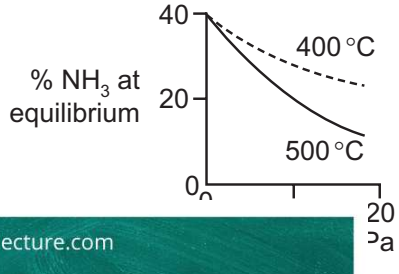
A



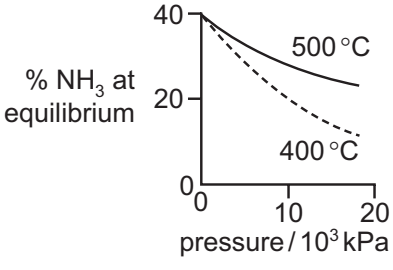
B



C



D



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24 The table gives the concentrations and pH values of the aqueous solutions of two compounds, X and Y. Either compound could be an acid or a base.

	X	Y
concentration	$2\,\text{mol}\,\text{dm}^{-3}$	$2\,\text{mol}\,\text{dm}^{-3}$
pH	6	9

Student P concluded that X is a strong acid.

Student Q concluded that the extent of dissociation is lower in X(aq) than in Y(aq).

Which of the students are correct?

A both P and Q

B neither P nor Q

C P only

D Q only

25 Which substance, in 1 mol dm^{-3} aqueous solution, would have the same hydrogen ion concentration as $1\,\text{mol}\,\text{dm}^{-3}$ of hydrochloric acid?

A ethanoic acid

B nitric acid

C sodium hydroxide

D sulphuric acid

26 Why is ethanoic acid a stronger acid in liquid ammonia than in aqueous solution?

A Ammonia is a stronger base than water.

B Ammonium ethanoate is completely ionised in aqueous solution.

C Ammonium ethanoate is strongly acidic in aqueous solution.

D Liquid ammonia is a more polar solvent than water.

27 The following equilibrium is set up in a mixture of concentrated nitric and sulfuric acids.

$$HNO_3 + H_2SO_4 \rightleftharpoons H_2NO_3^+ + HSO_4^-$$

Which row correctly describes the behaviour of each substance in the equilibrium mixture?

	HNO_3	H_2SO_4	$H_2NO_3^+$	HSO_4^-
A	acid	acid	base	base
B	acid	base	base	acid
C	base	acid	acid	base
D	base	acid	base	acid

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28 The table shows the enthalpy change of neutralisation per mole of water formed, ΔH, for various acids and bases.

acid	base	ΔH / kJ mol^{-1}
hydrochloric acid	sodium hydroxide	–57.0
P	sodium hydroxide	–54.0
hydrochloric acid	**Q**	–52.0
nitric acid	**R**	–57.0

What are **P**, **Q** and **R**?

	P	Q	R
A	ethanoic acid	ammonia	potassium hydroxide
B	ethanoic acid	sodium hydroxide	ammonia
C	sulphuric acid	ammonia	potassium hydroxide
D	sulphuric acid	sodium hydroxide	ammonia

29 The esterification reaction

$$\text{ethanol + ethanoic acid} \rightleftharpoons \text{ethyl ethanoate + water}$$

is an equilibrium. The forward reaction is exothermic.

How can the value of the equilibrium constant K_C be increased?

A by adding a little concentrated sulfuric acid as a catalyst

B by increasing the initial concentration of ethanol

C by lowering the temperature

D by raising the temperature

30 An aqueous solution was prepared containing 1.0 mol of $AgNO_3$ and 1.0 mol of $FeSO_4$ in 1.00 dm^3 of water. When equilibrium was established, there was 0.44 mol of $Ag^+(aq)$ in the mixture.

$$Ag^+(aq) + Fe^{2+}(aq) \rightleftharpoons Ag(s) + Fe^{3+}(aq)$$

What is the numerical value of K_c?

A 0.35 **B** 0.62 **C** 1.62 **D** 2.89

31 For the equilibrium $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, what will change the value of K_p?

A adding a catalyst

B adding more O_2

C increasing the pressure

D increasing the temperature

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32 When gaseous iodine is heated with hydrogen at 450 °C, an equilibrium is established.

$$\underset{\text{colourless}}{H_2(g)} + \underset{\text{purple}}{I_2(g)} \rightleftharpoons \underset{\text{colourless}}{2HI(g)} \qquad \Delta H = +53\,\text{kJ mol}^{-1}$$

Which change of conditions will cause the purple colour of the equilibrium mixture to become paler?

A decrease in pressure

B decrease in temperature

C increase in pressure

D increase in temperature

33 For the reaction

$$W(aq) + 2X(aq) \rightleftharpoons 2Y(aq) + 3Z(aq)$$

what are the correct units for the equilibrium constant K_c?

A mol dm^{-3} **B** $\text{mol}^2\,\text{dm}^{-6}$ **C** $\text{mol}^{-1}\,\text{dm}^3$ **D** $\text{mol}^{-2}\,\text{dm}^6$

34 Two moles of compound P were placed in a vessel. The compound P was partly decomposed by heating. A dynamic equilibrium between chemicals P, Q and R was established.

At equilibrium, x mol of R were present and the total number of moles present was $(2 + x)$.

What is the equation for this equilibrium?

A $P \rightleftharpoons 2Q + R$

B $2P \rightleftharpoons 2Q + R$

C $2P \rightleftharpoons Q + R$

D $2P \rightleftharpoons Q + 2R$

35 Methanol is manufactured by reacting carbon dioxide and hydrogen.

$$CO_2(g) + 3H_2(g) \rightleftharpoons CH_3OH(g) + H_2O(g) \qquad \Delta H = -49\,\text{kJ mol}^{-1}$$

What would increase the equilibrium yield of methanol in this process?

A adding a catalyst

B adding an excess of steam

C increasing the pressure

D increasing the temperature

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36 An experiment is set up to measure the rate of hydrolysis of ethyl ethanoate.

$$CH_3CO_2C_2H_5 + H_2O \rightleftharpoons CH_3CO_2H + C_2H_5OH$$

The hydrolysis is found to be slow in neutral aqueous solution but it proceeds at a measurable rate when the solution is acidified with hydrochloric acid.

What is the function of the hydrochloric acid?

A to dissolve the ethyl ethanoate

B to ensure that the reaction reaches equilibrium

C to increase the reaction rate by catalytic action

D to suppress ionisation of the ethanoic acid formed

37 The reaction between sulfur dioxide and oxygen is a dynamic equilibrium.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

What happens when the pressure of the system is increased?

A The rate of reaction will decrease and the position of the equilibrium will move to the left.

B The rate of reaction will decrease and the position of the equilibrium will move to the right.

C The rate of reaction will increase and the position of the equilibrium will move to the left.

D The rate of reaction will increase and the position of the equilibrium will move to the right.

38 Nitrogen reacts with hydrogen to produce ammonia.

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

A mixture of 2.00 mol of nitrogen, 6.00 mol of hydrogen, and 2.40 mol of ammonia is allowed to reach equilibrium in a sealed vessel of volume 1 dm^3 under certain conditions. It was found that 2.32 mol of nitrogen were present in the equilibrium mixture.

What is the value of K_c under these conditions?

A $\dfrac{(1.76)^2}{(2.32)(6.96)^3}$

B $\dfrac{(1.76)^2}{(2.32)(6.32)^3}$

C $\dfrac{(2.08)^2}{(2.32)(6.32)^3}$

D $\dfrac{(2.40)^2}{(2.32)(6.00)^3}$

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39 Nitrogen reacts with hydrogen to produce ammonia.

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

A mixture of 1.00 mol of nitrogen, 3.00 mol of hydrogen and 1.98 mol of ammonia is allowed to reach equilibrium in a sealed vessel under certain conditions. It was found that 1.64 mol of nitrogen were present in the equilibrium mixture.

What is the value of K_c under these conditions?

A $\dfrac{(0.70)^2}{(1.64)(4.92)^3}$

B $\dfrac{(1.34)^2}{(1.64)(3.64)^3}$

C $\dfrac{(1.64)(4.92)^3}{(0.70)^2}$

D $\dfrac{(1.64)(3.64)^3}{(1.34)^2}$

40 The equilibrium constant, K_c, for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, is 60 at 450 °C.

What is the number of moles of hydrogen iodide in equilibrium with 2 mol of hydrogen and 0.3 mol of iodine at 450 °C?

A $\dfrac{1}{100}$ **B** $\dfrac{1}{10}$ **C** 6 **D** 36

41 Hydrogen and carbon dioxide gases are mixed in equal molar amounts at 800 K. A reversible reaction takes place.

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$$

At equilibrium, the partial pressures of H_2 and CO_2 are both 10.0 kPa. K_p is 0.288 at 800 K.

What is the partial pressure of CO in the equilibrium mixture?

A 5.37 kPa **B** 18.6 kPa **C** 28.8 kPa **D** 347 kPa

42 The formation of hydrogen and ethyne, C_2H_2, from methane reaches dynamic equilibrium.

$$2CH_4(g) \rightleftharpoons 3H_2(g) + C_2H_2(g)$$

What are the units of K_c?

A $mol\,dm^{-3}$ **B** $mol^2\,dm^{-6}$ **C** $mol^3\,dm^{-9}$ **D** $mol^4\,dm^{-12}$

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43 One mole of phosphorus(V) chloride, PCl_5, is heated to 600 K in a sealed flask of volume 1 dm^3. Equilibrium is established and measurements are taken.

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

The experiment is repeated with one mole of phosphorus(V) chloride heated to 600 K in a sealed flask of volume 2 dm^3.

How will the measurements vary?

A The equilibrium concentrations of $PCl_3(g)$ and $Cl_2(g)$ are higher in the second experiment.

B The equilibrium concentration of $PCl_5(g)$ is lower in the second experiment.

C The equilibrium concentrations of all three gases are the same in both experiments.

D The value of the equilibrium constant is higher in the second experiment.

44 In which reaction is the underlined substance acting as a base?

A $HNO_3 + \underline{H_2SO_4} \rightarrow H_2NO_3^+ + HSO_4^-$

B $HSiO_3^- + \underline{HCN} \rightarrow CN^- + H_2O + SiO_2$

C $HNO_2 + \underline{HCO_3^-} \rightarrow H_2O + CO_2 + NO_2^-$

D $C_6H_5O^- + \underline{CH_2ClCO_2H} \rightarrow C_6H_5OH + CH_2ClCO_2^-$

45 One molecule of haemoglobin, Hb, can bind with four molecules of oxygen according to the following equation.

$$Hb(aq) + 4O_2(aq) \rightleftharpoons Hb(O_2)_4(aq)$$

When the equilibrium concentration of O_2 is 7.6×10^{-6} mol dm^{-3}, the equilibrium concentrations of Hb and $Hb(O_2)_4$ are equal.

What is the value of K_c for this equilibrium?

A 3.0×10^{20} **B** 1.3×10^{5} **C** 7.6×10^{-6} **D** 3.3×10^{-21}

46 Nitrogen dioxide, NO_2, exists in equilibrium with dinitrogen tetroxide, N_2O_4.

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad \Delta H = -57\ kJ\ mol^{-1}$$

Which conditions give the greatest percentage of $N_2O_4(g)$ at equilibrium?

	pressure	temperature
A	high	high
B	high	low
C	low	high
D	low	low

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47 When a sample of HI is warmed to a particular temperature the equilibrium below is established.

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

At this temperature, it is found that the partial pressure of HI(g) is 28 times the partial pressure of $H_2(g)$.

What is the value of K_p at this temperature?

A 1.28×10^{-3} **B** 0.035 **C** 28 **D** 784

48 A mixture of nitrogen and hydrogen gases, at a temperature of 500 K, was put into an evacuated vessel of volume 6.0 dm^3. The vessel was then sealed.

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

The mixture was allowed to reach equilibrium. It was found that 7.2 mol of N_2 and 12.0 mol of H_2 were present in the equilibrium mixture. The value of the equilibrium constant, K_c, for this equilibrium is 6.0×10^{-2} at 500 K.

What is the concentration of ammonia present in the equilibrium mixture at 500 K?

A 0.58 mol dm^{-3}

B 0.76 mol dm^{-3}

C 3.5 mol dm^{-3}

D 27 mol dm^{-3}

49 Ammonia is made by the Haber process. The reactants are nitrogen and hydrogen.

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

What will increase the rate of the forward reaction?

A adding argon to the mixture but keeping the total volume constant

B decreasing the temperature

C increasing the total pressure by reducing the total volume at constant temperature

D removing ammonia as it is made but keeping the total volume of the mixture the same

50 Nitrogen monoxide reacts with oxygen in a reversible reaction according to the equation shown below.

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

The partial pressures of each of the components in an equilibrium mixture are shown in the table.

partial pressure NO / kPa	partial pressure O_2 / kPa	partial pressure NO_2 / kPa
10	30	20

What is the numerical value of the equilibrium constant, K_p, for this equilibrium?

A 6.67×10^{-2} **B** 1.33×10^{-1} **C** 7.50 **D** 15.0

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SECTION B

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, **2** and **3** are correct	**1** and **2** only are correct	**2** and **3** only are correct	**1** only is correct

1 A reversible reaction is catalysed.

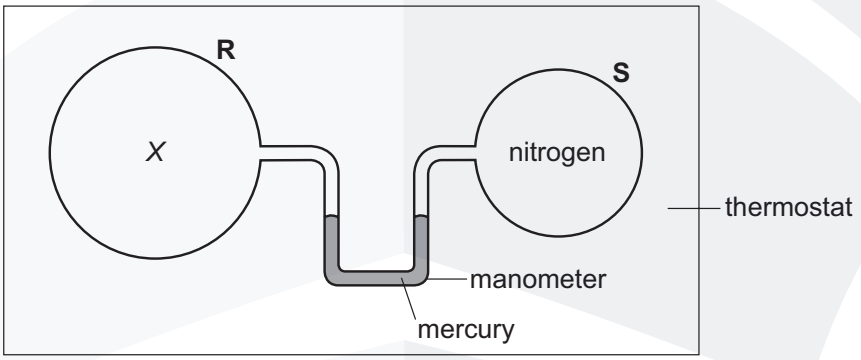
Which statements about the effects of the catalyst on this system are correct?

1 The catalyst alters the mechanism of the reaction.

2 The catalyst reduces the energy of activation (the energy barrier) for both the forward and the backward reaction.

3 The catalyst alters the composition of the equilibrium mixture.

2 Two bulbs **R** and **S**, connected by a mercury manometer, are held in a thermostat, as shown. The volume of **R** is twice that of **S**. **R** contains gas, *X*, at the same pressure as the nitrogen in **S**.



When the temperature is increased, which gases in bulb **R** would cause the mercury level in the right-hand limb of the manometer to rise?

1 an equilibrium mixture $N_2F_4(g) \rightleftharpoons 2NF_2(g)$; ΔH positive

2 an equilibrium mixture $CH_3NC(g) \rightleftharpoons CH_3CN(g)$; ΔH negative

3 nitrogen

3 Hydroxyapatite, $Ca_5(PO_4)_3OH$, is the main constituent of tooth enamel. In the presence of saliva, the following equilibria exist.

$$Ca_5(PO_4)_3OH(s) \rightleftharpoons 5Ca^{2+}(aq) + 3PO_4^{3-}(aq) + OH^-(aq)$$

$$HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq)$$

Which of the following statements help to explain why tooth enamel is dissolved more readily when saliva is acidic?

1 The hydroxide ions are neutralised by the acid.

2 The phosphate ion $PO_4^{3-}(aq)$ accepts $H^+(aq)$

3 Calcium ions react with acids.

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4 Under given conditions, what governs the rate of a forward reaction?

1 the activation energy of the reaction

2 the enthalpy change of the reaction

3 the equilibrium constant of the reaction

5 Carbon monoxide burns readily in oxygen to form carbon dioxide.

What can be deduced from this information?

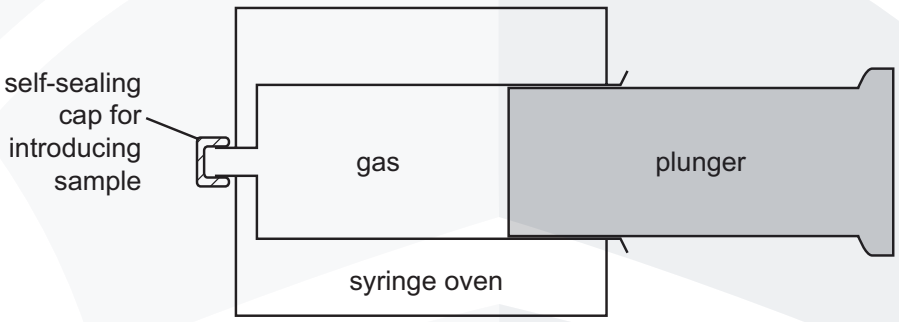
1 The +4 oxidation state of carbon is more stable than the +2 state.

2 The standard enthalpy change of formation of carbon dioxide is more negative than that of carbon monoxide.

3 The value of the equilibrium constant for the reaction, $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$, is likely to be high.

6 Phosphorus pentachloride is introduced into an empty gas syringe which has a movable, tightly-fitting plunger. The gas is allowed to expand until equilibrium is reached at a temperature at which the phosphorus pentachloride partially dissociates.

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



Which statements are correct?

1 The equilibrium pressure inside the syringe will be greater than atmospheric pressure.

2 When the plunger is pushed in the equilibrium adjusts to produce more $PCl_5(g)$.

3 The volume of gas in the syringe at equilibrium will be greater than if no dissociation had occurred.

7 Catalysts are used in many reversible reactions in the chemical industry. Vanadium(V) oxide is used in this way in the Contact process for the formation of SO_3.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

What effect does vanadium(V) oxide have on this equilibrium?

1 It speeds up the forward reaction.

2 It increases the value of K_p.

3 It increases the value of E_a for the reverse reaction.

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8 Which statements about the Haber process for the industrial production of ammonia are correct?

1 The equilibrium constant K_p increases with pressure.

2 As the temperature increases, the equilibrium constant for the forward reaction becomes smaller.

3 The process is usually carried out at between 450 °C and 550 °C at a pressure of at least 150 atm.

9 Which equilibria, in which all species are gaseous, would have equilibrium constants, K_p, with no units?

1 sulfur dioxide and oxygen in equilibrium with sulfur trioxide

2 hydrogen and iodine in equilibrium with hydrogen iodide

3 carbon monoxide and steam in equilibrium with carbon dioxide and hydrogen

10 Which of the following can act as a Bronsted-Lowry acid?

1 H_3O^+

2 NH_4^+

3 H_2O

11 Which statements are correct in terms of the Brønsted-Lowry theory of acids and bases?

1 Water can act as either an acid or a base.

2 Sulfuric acid, H_2SO_4, does not behave as an acid when dissolved in ethanol, C_2H_5OH.

3 The ammonium ion acts as a base when dissolved in liquid ammonia.

12 Concentrated sulphuric acid behaves as a strong acid when it reacts with water.

$$H_2SO_4(l) + aq \rightarrow H^+(aq) + HSO_4^-(aq)$$

The HSO_4^- ion formed behaves as a weak acid.

$$HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq)$$

Which statements are true for 1.0 mol dm^{-3} sulphuric acid?

1 $[H^+(aq)]$ is high

2 $[SO_4^{2-}(aq)]$ is high

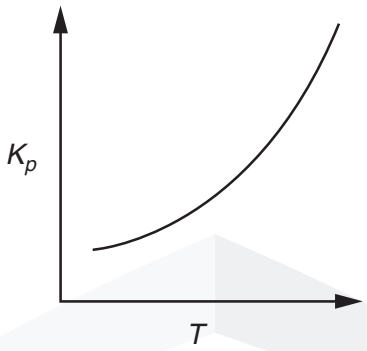
3 $[HSO_4^-(aq)] = [SO_4^{2-}(aq)]$

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13 The equilibrium constant K_p for the reaction

$$X(g) + Y(g) \rightleftharpoons Z(g)$$

varies with temperature as shown in the diagram below.



Which conclusions can be drawn from this information?

1 The reaction is exothermic in the forward direction.

2 The equilibrium mixture contains a greater proportion of Z at higher pressures.

3 The equilibrium mixture contains a greater proportion of Z at higher temperatures.

14 What are necessary properties of a dynamic equilibrium?

1 Equal amounts of reactants and products are present.

2 Concentrations of reactants and products remain constant.

3 The rate of the forward reaction is the same as the rate of the reverse reaction.

15 If N_2O_4 gas is placed in a sealed vessel the following equilibrium is established.

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

The forward reaction is endothermic.

What happens when the temperature is increased?

1 The equilibrium constant increases.

2 The partial pressure of NO_2 increases.

3 The activation energy is unchanged.

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EQUILIBRIA WS 4

1 Hydrogen iodide dissociates into its elements according to the equation below.

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

(a) Write the expression for the equilibrium constant, K_c.

[1]

(b) At 120 °C the equilibrium mixture contains 1.47 mol dm^{-3} of HI(g), 0.274 mol dm^{-3} each of $H_2(g)$ and $I_2(g)$.

Calculate the value of K_c for the equilibrium at 120 °C.

[1]

(c) Suggest and explain why it would be more difficult to determine K_c for this equilibrium at room temperature.

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.....[2]

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2 NO is also formed when nitrosyl chloride, NOC*l*, dissociates according to the following equation.

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

Different amounts of the three gases were placed in a closed container and allowed to come to equilibrium at 230 °C. The experiment was repeated at 465 °C.

The equilibrium concentrations of the three gases at each temperature are given in the table below.

	concentration / mol dm^{-3}		
temperature / °C	NOC*l*	NO	Cl_2
230	2.33×10^{-3}	1.46×10^{-3}	1.15×10^{-2}
465	3.68×10^{-4}	7.63×10^{-3}	2.14×10^{-4}

(c) (i) Write the expression for the equilibrium constant, K_c, for this reaction. Give the units.

(ii) Calculate the value of K_c at each of the temperatures given.

230 °C

465 °C

(iii) Is the forward reaction endothermic or exothermic? Explain your answer.

.....

.....

[5]

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3 **(b)** Ethanoic acid, CH_3CO_2H, reacts with ethanol, C_2H_5OH, to produce ethyl ethanoate and water. The reaction is an example of dynamic equilibrium.

$$CH_3CO_2H + C_2H_5OH \rightleftharpoons CH_3CO_2C_2H_5 + H_2O$$

(i) Explain what is meant by *dynamic equilibrium*.

.....

.....

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

[2]

(c) A mixture of 6.0 g of ethanoic acid and 6.0 g of ethanol was added to 4.4 g of ethyl ethanoate and the overall mixture allowed to reach equilibrium. It was found that 0.040 mol of ethanoic acid was present in the equilibrium mixture.

(i) Calculate the number of moles of each compound, both initially and at equilibrium. Place the results in the spaces provided.

	CH_3CO_2H	+ C_2H_5OH $\rightleftharpoons$	$CH_3CO_2C_2H_5$	+ H_2O
initially	.....	.....	.....	0.00
at equilibrium	0.040	.....	.....	.....

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(ii) Calculate the equilibrium constant, K_c, for the reaction.

(iii) Explain why K_c in this reaction has no units.

.....[4]

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4 The reaction of ethanoic acid with ethanol to form ethyl ethanoate and water is an example of dynamic equilibrium. It is catalysed by the presence of H^+ ions.

$$CH_3CO_2H(l) + C_2H_5OH(l) \rightleftharpoons CH_3CO_2C_2H_5(l) + H_2O(l)$$

$$\Delta H = +14\,kJ\,mol^{-1}$$

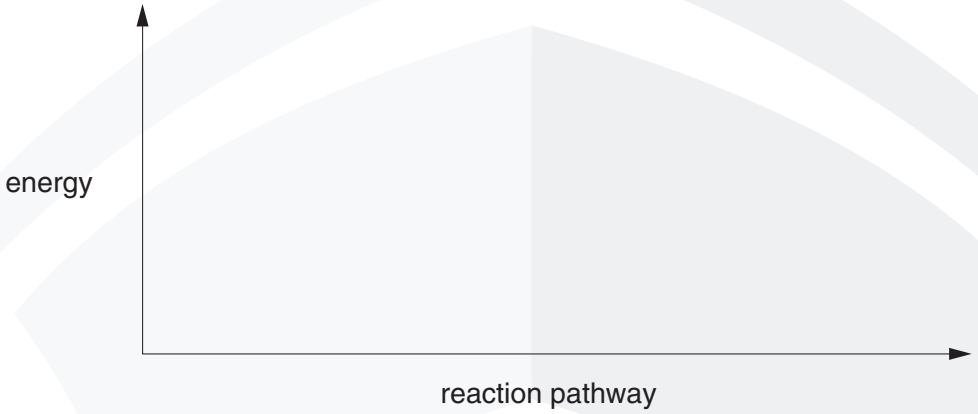
(a) (i) Explain what is meant by *dynamic equilibrium*.

.....

.....

(ii) On the axes below, draw and label a reaction pathway/energy diagram for both the catalysed and uncatalysed reaction.

Also label your diagram with the ΔH value given.



[5]

(b) (i) State the expression for the equilibrium constant, K_c, for this reaction.

(ii) State why, in determining the value of K_c for this reaction, it is only necessary to know the number of moles rather than the concentrations of each substance.

.....

.....

[2]

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(c) In an experiment to determine K_c, 1.00 mol of ethanoic acid was allowed to reach equilibrium at 60 °C with 1.00 mol of ethanol in the presence of 0.100 mol of H^+ dissolved in 1.00 mol of water. It forms an homogeneous mixture.

(i) At equilibrium, it was found that 0.43 mol of ethanoic acid was present.

How many moles of each of the following are present at equilibrium?

ethanol .....

ethyl ethanoate .....

water .....

(ii) Use these values to calculate the equilibrium constant, K_c.

[4]

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5 Alcohols and esters are important organic compounds which are widely used as solvents.

Esters such as ethyl ethanoate can be formed by reacting carboxylic acids with alcohols.

$$CH_3CO_2H + C_2H_5OH \rightleftharpoons CH_3CO_2C_2H_5 + H_2O$$

This reaction is an example of a dynamic equilibrium.

(a) Explain what is meant by the term *dynamic equilibrium*.

.....

.....[1]

(b) Write the expression for the equilibrium constant for this reaction, K_c.

[1]

(c) For this equilibrium, the value of K_c is 4.0 at 298 K.
A mixture containing 0.5 mol of ethanoic acid, 0.5 mol ethanol, 0.1 mol ethyl ethanoate and 0.1 mol water was set up and allowed to come to equilibrium at 298 K. The final volume of solution was V dm^3.

Calculate the amount, in moles, of each substance present at equilibrium.

[4]

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6 Ethanoic acid can be reacted with alcohols to form esters, an equilibrium mixture being formed.

$$CH_3CO_2H + ROH \rightleftharpoons CH_3CO_2R + H_2O$$

The reaction is usually carried out in the presence of an acid catalyst.

(a) Write an expression for the equilibrium constant, K_c, for this reaction, clearly stating the units.

K_c =

units ..... [2]

In an experiment to determine K_c a student placed together in a conical flask 0.10 mol of ethanoic acid, 0.10 mol of an alcohol ROH, and 0.005 mol of hydrogen chloride catalyst.
The flask was sealed and kept at 25 °C for seven days.
After this time, the student titrated all of the contents of the flask with 2.00 mol dm^{-3} NaOH using phenolphthalein indicator.
At the end-point, 22.5 cm^3 of NaOH had been used.

(b) **(i)** Calculate the amount, in moles, of NaOH used in the titration.

(ii) What amount, in moles, of this NaOH reacted with the hydrogen chloride?

(iii) Write a balanced equation for the reaction between ethanoic acid and NaOH.

(iv) Hence calculate the amount, in moles, of NaOH that reacted with the ethanoic acid.

[4]

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(c) **(i)** Use your results from **(b)** to calculate the amount, in moles, of ethanoic acid present at equilibrium. Hence complete the table below.

	CH_3CO_2H	ROH	CH_3CO_2R	H_2O
initial amount / mol	0.10	0.10	0	0
equilibrium amount / mol				

(ii) Use your results to calculate a value for K_c for this reaction.

[3]

(d) Esters are hydrolysed by sodium hydroxide. During the titration, sodium hydroxide reacts with ethanoic acid and the hydrogen chloride, but not with the ester.

Suggest a reason for this.

.....

..... [1]

(e) What would be the effect, if any, on the amount of ester present if all of the water were removed from the flask and the flask kept for a further week at 25 °C?

Explain your answer.

.....

.....

..... [2]

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7 Under certain conditions the equilibrium pressures of the three gases are

nitrogen	44.8 atm,
hydrogen	105.6 atm,
ammonia	37.2 atm.

(i) Write an expression for the equilibrium constant, K_p, for the Haber Process.

(ii) Calculate K_p from these data, giving the units.

[4]

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8 Concern over the ever-increasing use of fossil fuels has led to many suggestions for alternative sources of energy. One of these, suggested by Professor George Olah, winner of a Nobel Prize in chemistry, is to use methanol, CH_3OH, which can be obtained in a number of different ways.

Methanol could be used instead of petrol in a conventional internal combustion engine or used to produce electricity in a fuel cell.

(a) Construct a balanced equation for the **complete** combustion of methanol.

..... [1]

When hydrocarbon fuels are completely burned in an internal combustion engine, several toxic pollutants may be formed.

(b) State **two toxic** pollutants that can be produced after **complete** combustion of a hydrocarbon fuel in an internal combustion engine.

.....

..... [2]

Methanol may be manufactured catalytically from *synthesis gas*, a mixture of CO, CO_2 and H_2. The CO is reacted with H_2 to form methanol, CH_3OH.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H = -91 \text{ kJ mol}^{-1}$$

(c) From your understanding of Le Chatelier's principle, state **two** conditions that could be used in order to produce a high yield of methanol.

In **each** case, explain why the yield would increase.

condition 1 .....

explanation .....

.....

condition 2 .....

explanation .....

..... [4]

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Carbon monoxide, which can be used to make methanol, may be formed by reacting carbon dioxide with hydrogen.

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g) \qquad K_c = 1.44 \text{ at } 1200 \text{ K}$$

(d) (i) It has been suggested that, on a large scale, this reaction could be helpful to the environment.

Explain, with reasons, why this would be the case.

.....

.....

(ii) A mixture containing 0.50 mol of CO_2, 0.50 mol of H_2, 0.20 mol of CO and 0.20 mol of H_2O was placed in a 1.0 dm^3 flask and allowed to come to equilibrium at 1200 K.

Calculate the amount, in moles, of each substance present in the equilibrium mixture at 1200 K.

	CO_2	+	H_2	$\rightleftharpoons$	CO	+	H_2O
initial moles	0.50		0.50		0.20		0.20

[6]

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9 Methanol, CH_3OH, is considered to be a possible alternative to fossil fuels, particularly for use in vehicles.

Methanol can be produced from fossil fuels and from agricultural waste. It can also be synthesised from carbon dioxide and hydrogen.

$$CO_2(g) + 3H_2(g) \rightleftharpoons CH_3OH(g) + H_2O(g)$$

The synthesis of methanol is carried out at about 500 K with a pressure of between 40 and 100 atmospheres (between 4×10^6 Pa and 10×10^7 Pa) and using a catalyst. The use of such conditions will affect both the rate of reaction and the equilibrium yield.

In the spaces below, explain the effects of higher temperature, higher pressure, and the use of a catalyst on the **equilibrium yield** of methanol.

higher temperature

effect .....

explanation .....

.....

higher pressure

effect .....

explanation .....

.....

use of catalyst

effect .....

explanation .....

.....

[6]

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10 Methanol may be synthesised from carbon monoxide and hydrogen.

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

The operating conditions for this reaction are as follows.

pressure	200 atmospheres (2×10^7 Pa)
temperature	600 K
catalyst	oxides of Cr, Cu, and Zn

In the spaces below, explain how **each** of these conditions affects the **rate of formation** of methanol.

pressure

.....

.....

.....

temperature

.....

.....

.....

catalyst

.....

.....

.....

[6]

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11 Hydrogen iodide can be made by heating together hydrogen gas and iodine vapour. The reaction is incomplete.

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

(b) Write an expression for K_c and state the units.

K_c = ... units ..... [2]

(c) For this equilibrium, the numerical value of the equilibrium constant K_c is 140 at 500 K and 59 at 650 K.

Use this information to state and explain the effect of the following changes on the equilibrium position.

(i) increasing the pressure applied to the equilibrium

.....

.....

(ii) decreasing the temperature of the equilibrium

.....

.....

[4]

(d) A mixture of 0.02 mol of hydrogen and 0.02 mol of iodine was placed in a 1 dm^3 flask and allowed to come to equilibrium at 650 K.

Calculate the amount, in moles, of each substance present in the equilibrium mixture at 650 K.

	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	2HI(g)
initial moles	0.02		0.02		0

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12 Hydrogen is the most abundant element in the Universe, although on Earth only very small quantities of molecular hydrogen have been found to occur naturally.

Hydrogen is manufactured on a large scale for use in the chemical industry and is also regarded as a possible fuel to replace fossil fuels in internal combustion engines.

(a) State **one** large scale use of hydrogen in the chemical industry.

..... [1]

One common way of producing hydrogen on a large scale for use in the chemical industry is by the steam 'reforming' of methane (natural gas), in which steam and methane are passed over a catalyst at 1000–1400 K to produce carbon monoxide and hydrogen.

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

(b) Use the information above to state and explain the effect on the equilibrium position of the following changes.

(i) increasing the pressure applied to the equilibrium

.....

.....

(ii) decreasing the temperature of the equilibrium

.....

.....

[4]

(c) What will be the effect on the rate of the reaction of increasing the pressure at which it is carried out? Explain your answer.

.....

.....

..... [2]

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(d) Further hydrogen can be obtained by the 'water-gas shift' reaction in which the carbon monoxide produced is reacted with steam.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \qquad K_c = 6.40 \times 10^{-1} \text{ at } 1100\,K$$

A mixture containing 0.40 mol of CO, 0.40 mol of H_2O, 0.20 mol of CO_2 and 0.20 mol of H_2 was placed in a 1 dm^3 flask and allowed to come to equilibrium at 1100 K

(i) Give an expression for K_c for this reaction.

(ii) Calculate the amount, in moles, of each substance present in the equilibrium mixture at 1100 K.

	$CO(g)$	+	$H_2O(g)$	$\rightleftharpoons$	$CO_2(g)$	+	$H_2(g)$
initial moles	0.40		0.40		0.20		0.20

[5]

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13 Ammonium nitrate fertiliser is manufactured from ammonia. The first reaction in the manufacture of the fertiliser is the catalytic oxidation of ammonia to form nitrogen monoxide, NO. This is carried out at about 1×10^3 kPa (10 atmospheres) pressure and a temperature of 700 to 850 °C.

$$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g) \qquad \Delta H^{\ominus} = -906\,kJ\,mol^{-1}$$

(a) Write the expression for the equilibrium constant, K_p, stating the units.

K_p =

units ..... [2]

(b) What will be the effect on the yield of NO of **each** of the following?
In each case, explain your answer.

(i) increasing the temperature

.....

.....

.....

(ii) decreasing the applied pressure

.....

.....

.....

[4]

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14 Methanol, CH_3OH, can be produced industrially by reacting carbon monoxide, CO, with hydrogen, H_2.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H = -91\,kJ\,mol^{-1}$$

The process is carried out at 4×10^3 kPa (40 atmospheres) and 1150 K.

(a) (i) State Le Chatelier's Principle.

.....

.....

..... [2]

(ii) From your understanding of Le Chatelier's Principle, state the conditions of temperature and pressure that could be used in order to produce an increased yield of methanol in this process.
In **each** case, explain why the yield would increase.

temperature .....

explanation .....

.....

pressure .....

explanation .....

.....
[4]

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(b) The carbon monoxide for use in the production of methanol may be formed by reacting carbon dioxide with hydrogen.

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g) \qquad K_c = 1.44 \text{ at } 1200\,K$$

A mixture containing 0.70 mol of CO_2, 0.70 mol of H_2, 0.30 mol of CO and 0.30 mol of H_2O was placed in a 1 dm^3 flask and allowed to come to equilibrium at 1200 K.

Calculate the amount, in moles, of each substance present in the equilibrium mixture at 1200 K.

	CO_2	+	H_2	$\rightleftharpoons$	CO	+	H_2O
initial moles	0.70		0.70		0.30		0.30

[4]

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15 Nitrogen dioxide, NO_2, can enter the atmosphere in a variety of ways.

(a) **(i)** State one natural and one man-made source of atmospheric NO_2.

natural .....

man-made .....
[1]

(ii) Write an equation to show how NO_2 leads to the formation of nitric acid in acid rain.

..... [1]

(iii) Use equations to illustrate the catalytic role of NO_2 in the formation of sulfuric acid in acid rain.

.....

.....

..... [3]

(b) Nitrogen dioxide exists in equilibrium with dinitrogen tetroxide, N_2O_4.

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

2.00 mol of dinitrogen tetroxide was sealed in a container at 350 K. After equilibrium had been established the total pressure was 140 kPa and the mixture of gases contained 1.84 mol of dinitrogen tetroxide.

(i) Give the expression for the equilibrium constant, K_p, for this equilibrium.

K_p =

[1]

(ii) Calculate the number of moles of NO_2 present at equilibrium.

[1]

(iii) Calculate the total number of moles of gas present at equilibrium and hence the mole fraction of each gas present at equilibrium.

[2]

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(iv) Calculate the partial pressure of each gas present at equilibrium.

[2]

(v) Calculate the value of the equilibrium constant, K_p, at 350 K.
Give your answer to **three** significant figures and include the units.

K_p = ...

units = ...

[2]

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16 The Contact process for the manufacture of sulfuric acid was originally patented in the 19th century and is still in use today.

The key step in the overall process is the reversible conversion of sulfur dioxide to sulfur trioxide in the presence of a vanadium(V) oxide catalyst.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -196\,kJ\,mol^{-1}$$

(a) One way in which the sulfur dioxide for this reaction is produced is by heating the sulfide ore iron pyrites, FeS_2, in air. Iron(III) oxide is also produced. Write an equation for this reaction.

..... [2]

(d) The conversion of sulfur dioxide into sulfur trioxide is carried out at a temperature of 400 °C.

(i) With reference to Le Chatelier's Principle and reaction kinetics, state and explain one advantage and one disadvantage of using a higher temperature.

.....

.....

.....

.....

.....

..... [4]

(ii) State the expression for the equilibrium constant, K_p, for the formation of sulfur trioxide from sulfur dioxide.

K_p =

[1]

(iii) 2.00 moles of sulfur dioxide and 2.00 moles of oxygen were put in a flask and left to reach equilibrium.
At equilibrium, the pressure in the flask was 2.00×10^5 Pa and the mixture contained 1.80 moles of sulfur trioxide.

Calculate K_p. Include the units.

K_p = ...

units = ...
[5]

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17 The Haber process for the manufacture of ammonia, NH_3, was originally devised at the start of the 20th century and was developed into a full-scale industrial process by Carl Bosch in 1913.

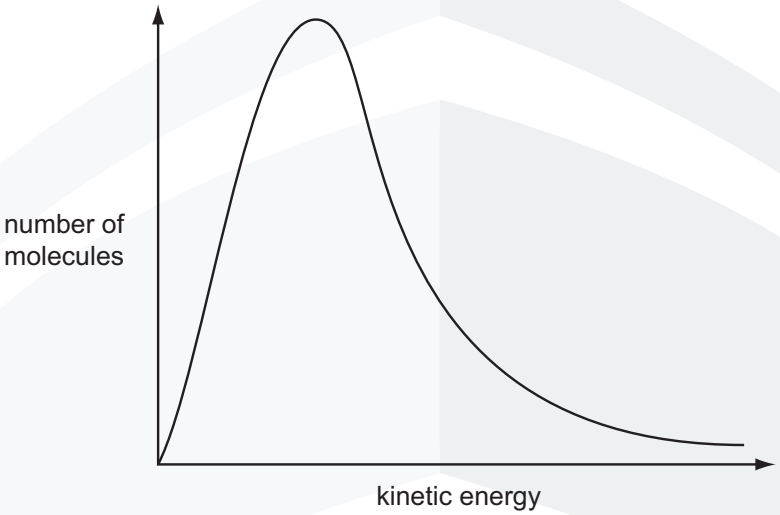
The key step in the process is the reversible reaction of nitrogen and hydrogen in the presence of an iron catalyst.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92\,kJ\,mol^{-1}$$

(a) The hydrogen for this reaction can be formed by reacting methane with steam, during which carbon monoxide is also produced. Write an equation for this reaction.

..... [1]

(b) Use the Boltzmann distribution shown to explain why a catalyst increases the rate of this reaction.



.....

.....

.....

..... [4]

(c) Draw a three-dimensional diagram to show the shape of an ammonia molecule. Name this shape and state the bond angle.

shape ..... bond angle ..... [3]

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(d) The Haber process is typically carried out at a temperature of 400 °C.

(i) With reference to Le Chatelier's Principle and reaction kinetics, state and explain one advantage and one disadvantage of using a higher temperature.

.....

.....

.....

.....

.....

..... [4]

(ii) State the expression for the equilibrium constant, K_p, for the formation of ammonia from nitrogen and hydrogen in the Haber process.

K_p =

[1]

(iii) 2.00 moles of nitrogen and 3.00 moles of hydrogen were put in a vessel and left to reach equilibrium.

At equilibrium, the pressure was 2.00×10^7 Pa and the mixture contained 1.60 moles of ammonia.

Calculate K_p. Include the units.

K_p = ...

units = ...

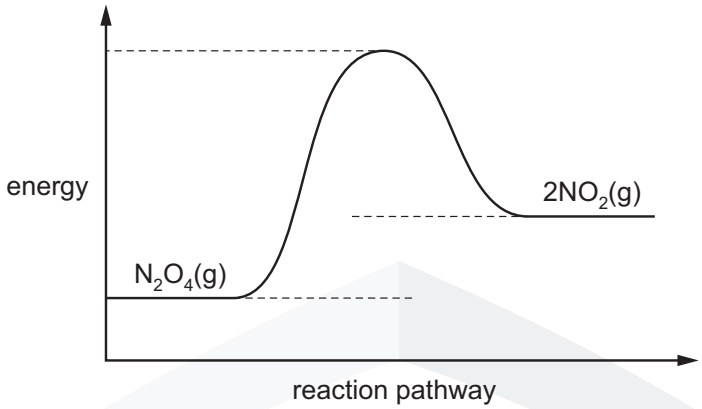
[5]

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18 Dinitrogen tetraoxide, N_2O_4, and nitrogen dioxide, NO_2, exist in dynamic equilibrium with each other.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad \Delta H = +54\,kJ\,mol^{-1}$$

The energy profile for this reaction is shown.



(a) Add labelled arrows to the energy profile to indicate

- the enthalpy change of the reaction, ΔH,
- the activation energy of the forward reaction, E_a.

[2]

(b) 0.0500 mol of N_2O_4 was placed in a sealed vessel of volume 1.00 dm^3, at a temperature of 50 °C and a pressure of 1.68×10^5 Pa. The mass of the resulting equilibrium mixture was 4.606 g.

(i) Calculate the average molecular mass, M_r, of the resulting equilibrium mixture. Give your answer to **three** significant figures.

M_r = ... [2]

(ii) The number of moles of N_2O_4 that dissociated can be represented by n.

State, in terms of n, the amount, in moles, of NO_2 in the equilibrium mixture.

moles of NO_2 = ... [1]

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The number of moles of N_2O_4 remaining at equilibrium is $(0.05 - n)$.

(iii) State, in terms of n, the total amount, in moles, of gas in the equilibrium mixture.

[1]

(iv) State, in terms of n, the mole fraction of NO_2 in the equilibrium mixture.

[1]

In this equilibrium mixture, the mole fraction of NO_2 is 0.400.

(v) Use your answers to **(ii)** and **(iv)** to calculate the amount in moles of each gas in the equilibrium mixture. Give your answers to **three** significant figures.

amount of N_2O_4 = ... mol

amount of NO_2 = ... mol
[2]

(vi) Write the expression for the equilibrium constant, K_p, for this equilibrium.

K_p =

[1]

(vii) Use the total pressure of the mixture, 1.68×10^5 Pa, to calculate the value of the equilibrium constant, K_p, and give its units.

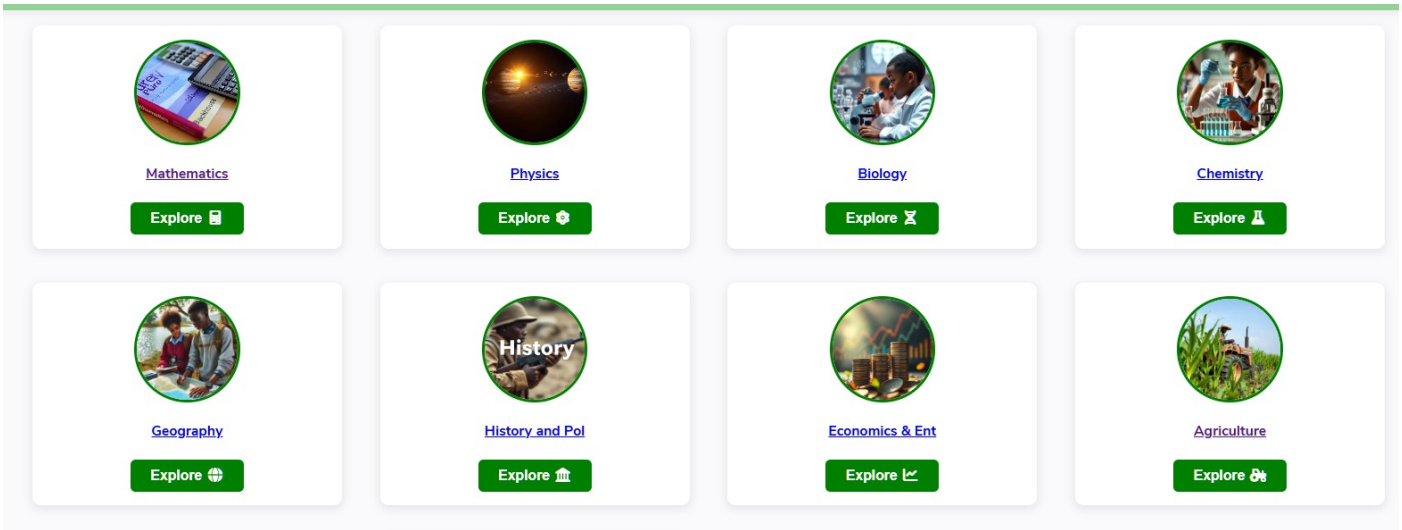
K_p = ...

units = ...
[3]

[Total: 13]

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