NAME: _____

TALENT 100
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# HSC Chemistry.

## CHEMISTRY SUCCESS. SIMPLIFIED.

## Equilibrium and Acid Reactions III

## Theory booklet

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# SYLLABUS OUTCOMES

**Inquiry question:** How can the position of equilibrium be described and what does the equilibrium constant represent?

By the end of the lesson, students should be able to:

- ☐ Deduce the equilibrium expression (in terms of $K_{eq}$) for homogeneous reactions occurring in solution (ACSH079, ACSCH096).
- ☐ Perform calculations to find the value of $K_{eq}$ and concentrations of substances within an equilibrium system and use these values to make predictions on the direction in which a reaction may proceed (ACSCH096).
- ☐ Explore the use of $K_{eq}$ for different types of chemical reactions, including but not limited to:
  - ☐ Dissociation of ionic solutions
  - ☐ Dissociation of acids and bases (ACSCH098, ACSCH099).
- ☐ Qualitatively analyse the effect of temperature on the value of $K_{eq}$ (ACSCH093).

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Name: _____ Class time: _____ Mentor: _____

# QUIZ

**Question 1 (4 marks)**

a) Explain what is meant by the term 'spontaneous reaction'. (1 mark)

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b) Under what conditions (in terms of the change in enthalpy and entropy) will a reaction always be spontaneous. (1 mark)

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c) The following reaction $4KClO_{3\,(s)} \rightarrow 3KClO_{4\,(s)} + KCl_{(s)}$ where $\Delta H = -144kJ$ and $\Delta S = -36.8\,J/K$ . Under what conditions will this reaction be spontaneous? (2 marks)

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d) Explain whether a gas, solid, or liquid has the greatest entropy. (1 mark)

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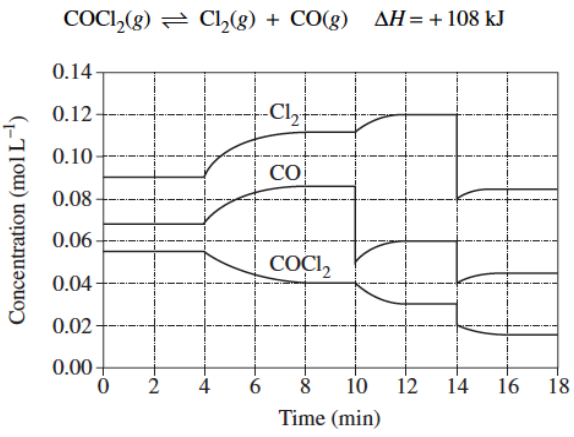
**Question 2 (3 marks)**

The graph shows how concentration of reactant and products vary as a function of time:



Identify and explain each of the changes in conditions that have shaped the curves during the time the system was observed.

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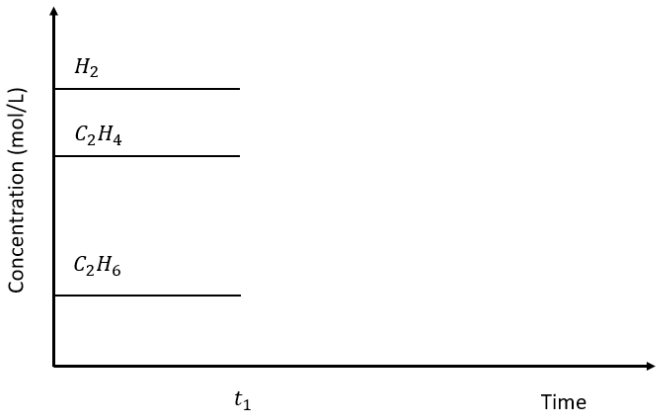
**Question 3**

Consider the cracking of ethene:

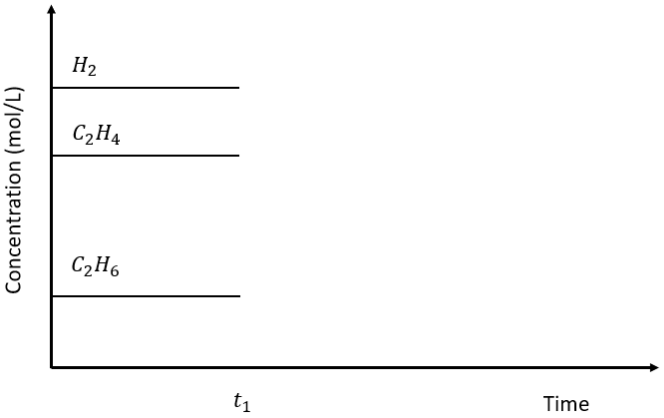
$$C_2H_{6\,(g)} \rightleftharpoons C_2H_{4\,(s)} + H_{2\,(g)}$$

This is an endothermic equilibrium reaction. In the graphs below, sketch the changes you would observe if:

a) Temperature is increased




b) More $H_2$ was added



# THE EQUILIBRIUM CONSTANT

## DEFINITION OF $K_{eq}$

- **The equilibrium constant $K_C$ quantitatively shows the extent at which an equilibrium system is shifted towards products (right) or reactants (left):** Mathematically, the equilibrium constant for the equilibrium reaction $aA + bB \rightleftharpoons cC + dD$ is given by:

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

  Note:

  - **[square brackets]:** the equilibrium concentrations of the substances are denoted [A], [B], [C],[D]
  - **Exponents:** The powers a, b, c and d represent their **stoichiometric coefficients** in the generalised equation. *(To understand why these terms become exponents see the Derivation section)*

- **This formula can be remembered by the acronym "PORK": *Products Over Reactants gives K***

## MAGNITUDE OF $K_{eq}$

$K_{Eq}$ gives us a ratio of products to reactants, and thus the numeric value of $K_{EQ}$ tells us to what extent the reaction favours products:

| Value of $K_C$ | Amount of product/reactant at equilibrium |
|---|---|
| $k > 1000$ | Mostly product |
| $k < 0.001$ | Mostly reactant |
| $0.001 < k < 1000$ | Significant concentration of both products and reactants |

**Question 1**

Write an expression for the equilibrium constants of the following reactions

a) $CH_{4(g)} + H_2O_{(g)} \rightleftharpoons \mathrm{CO}_{(g)} + 3H_{2(g)}$

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b) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

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c) $2SO_{2(g)} + O_{2\,(g)} \rightleftharpoons 2SO_{3\,(g)}$

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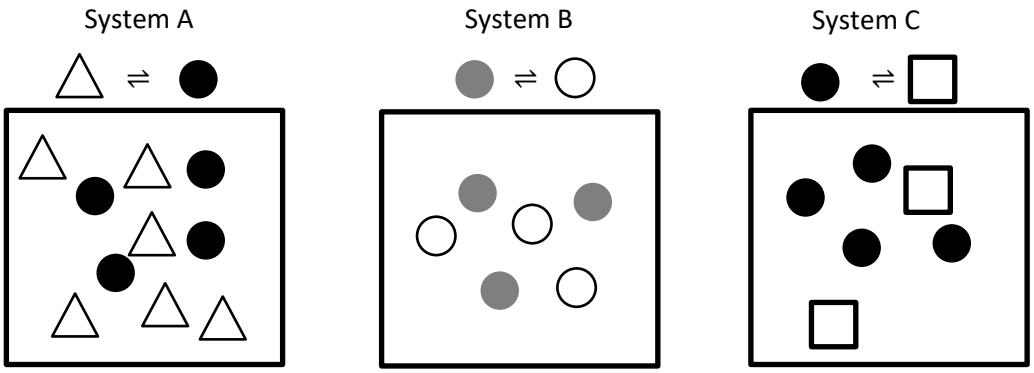
**Question 2**

In the following diagrams, molecules have been represented by shapes. Each box represents a 1L container.




By estimating $K_c$, Rank A, B, C in order of increasing $K_C$.

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**Question 3**

An equilibrium system can be represented by the following equation

$$A + 2B \rightleftharpoons 2C + D$$

The reaction is carried out in a 1L container, and at equilibrium, the moles of A, B,C, D are found to be 0.10, 0.15, 0.20, 0.30 mol respectively.

a) Write an equilibrium constant for this reaction

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b) Calculate the value of the equilibrium constant at this temperature

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c) At equilibrium, do you expect there to be: mostly product, mostly reactant, or a significant amount of both?

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## CALCULATIONS INVOLVING $K_{Eq}$

- **The equilibrium constant is specific to a particular reaction at a particular temperature**. If the temperature changes, or the relative amounts of product or reactants change, the equilibrium constant will not apply to the new reaction

- **Forward and reverse equations have equilibrium constants which are the inverse of each other**

| **Forward Reaction** | **Backward Reaction** |
|---|---|
| $N_2O_{4\,(g)} \rightleftharpoons 2NO_{2\,(g)}$ | $2NO_{2\,(g)} \rightleftharpoons N_2O_{4\,(g)}$ |
| $\mathrm{K_{eq}} = \frac{[NO_{2\,(g)}]^2}{[N_2O_{4\,(g)}]^1}$ | $\mathrm{K_{eq}} = \frac{[N_2O_{4\,(g)}]^1}{[NO_{2\,(g)}]^2}$ |

- **Multiplying or dividing the stoichiometric coefficients of an equation will also affect the equilibrium constant:**

$$2N_2O_{4\,(g)} \rightleftharpoons 4NO_{2\,(g)}$$

$$\mathrm{K_{eq}} = \frac{[NO_{2\,(g)}]^4}{[N_2O_{4\,(g)}]^2}$$

*Note that **doubling** the amount of product and reactant causes $K_{eq}$ to be **squared***

**Question 4**

The reversible reaction below is found to have an equilibrium constant of 0.211.

$$N_2O_{4\,(g)} \rightleftharpoons 2NO_{2\,(g)}$$

Calculate the equilibrium constant of the reverse reaction.

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**Question 5 (2 marks)**

a) Write the equilibrium expression for the following reaction:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

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b) For the same reaction, at equilibrium $[H_2] = 0.0300$ mol $L^{-1}$ , $[I_2] = 0.0150$ mol $L^{-1}$ , $[HI] = 0.1600$ mol $L^{-1}$.

Calculate the value of the equilibrium constant $K_{eq}$ using the equilibrium expression from a).

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**Question 6 (2 marks)**

Consider the following reaction occurring in a 5.0 L reaction vessel:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

a) Write the equilibrium constant $K_{eq}$ for this reaction.

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b) At equilibrium, $n(H_2) = 3.00$ mol, $n(N_2) = 2.45$ mol, $n(NH_3) = 2.00$ mol. Calculate the value of the equilibrium constant $K_{eq}$.

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# EXAMPLES OF $K_{eq}$

## HOMOGENEOUS V. HETEROGENOUS EQUILIBRIA

- **Homogenous equilibria** occur when all products and reactants are in the same phase/state, whilst heterogenous equilibria occurs when species are in different phases
- **The equilibrium constant only includes gaseous and aqueous species, NOT solids or liquids.** Unlike gases or aqueous solutions, solids and liquids cannot be compressed, and so effectively be thought as having a invariant concentration, i.e. you can simply disregard solids and liquids in the equilibrium constant expression
- Two important heterogenous equilibria are:
    - The dissolution of an ionic solution
    - The ionization of an acid in water.

**Question 7**

Consider the following reaction:

$$A(s) \rightleftharpoons B(s) + 2C_{(aq)} \quad \text{with} \quad K_c = 4.5 \times 10^2$$

Find the concentration of C present at equilibrium.

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**Question 8**

At equilibrium, the following reaction takes place:

$$2A_{(aq)} + 3B_{(l)} \rightleftharpoons C_{(aq)}.$$

The concentrations of A and C are 0.30 M and 0.60 M respectively. What is $K_c$ for the reaction?

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## $K_{EQ}$ FOR IONIC SOLUTIONS

For the dissolution of a salt in solution:

$$CaCl_{2\,(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2Cl^{-}_{(aq)}$$

Its corresponding equilibrium constant has the equation:

$$\mathrm{K_{eq}} = \left[Ca^{2+}_{(aq)}\right]\left[Cl^{-}_{(aq)}\right]^2$$

Observe how the solid $CaCl_2$ was not included in the formula.

**Question 9 (4 marks)**

The dissolution of solid lead (II) chloride forms an equilibrium with its constituent ions

a) Write the full equilibrium equation.

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b) What is the $K_{eq}$ expression for this reaction?

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c) Given that 0.016 moles of lead (II) chloride completely dissolve in a 1 L of water, calculate the equilibrium constant.

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## $K_{EQ}$ FOR ACIDS AND BASES

For the ionisation of an acid in water:

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$$

Its corresponding equilibrium constant has the equation:

$$\mathrm{K_{eq}} = \frac{\left[CH_3COO^-_{(aq)}\right]^1\left[H_3O^+_{(aq)}\right]^1}{\left[CH_3COOH_{(aq)}\right]^1}$$

Observe how liquid $H_2O$ was not included in the formula.

**Question 10 (4 marks)**

Ammonia mixed in water acts as a base according to the following equation:

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH^+_{4\,(aq)} + OH^-_{(aq)}$$

a) What is the $K_{eq}$ expression for this reaction?

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b) For a solution of ammonia, the equilibrium concentrations for two species are found to be $[NH_4^+]$ = 0.0020 M and $[OH^-]$ = 0.0025 M, and it is given that $K_{eq} = 1.76 \times 10^{-5}$. Calculate the concentration of $NH_3$.

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# FACTORS AFFECTING $K_{EQ}$ (TEMPERATURE)

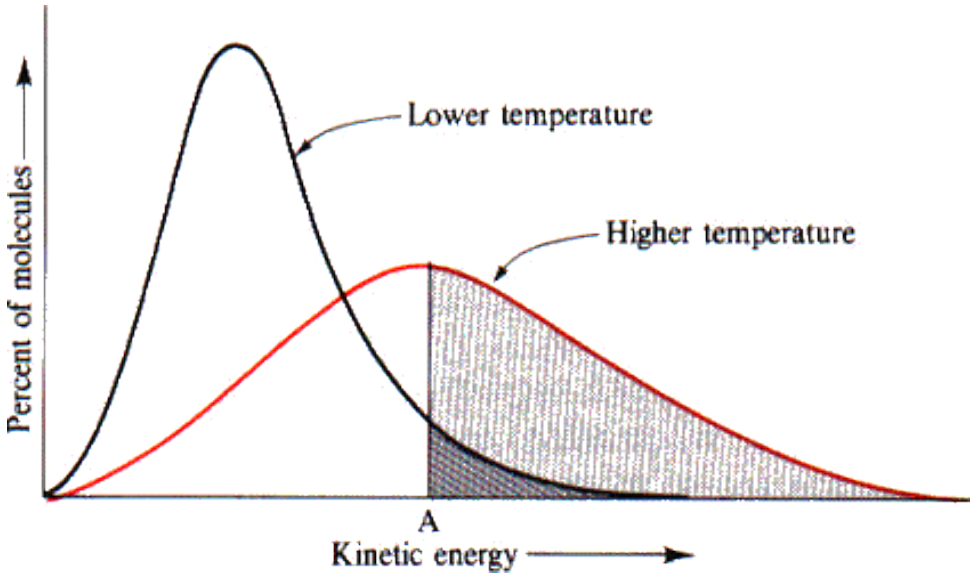
- **Temperature is the only factor that effects the equilibrium constant.** Each equilibrium constant is specified for a given temperature

- **The effect of temperature on an equilibrium system can be determined by LCP.**
  *Consider the following exothermic reaction*

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} + Heat$$

*Adding heat clearly favours the backward reaction, producing a higher concentration of reactants, and thus affecting the equilibrium constant*

***Collision theory explanation:*** *On a particle level, the addition of heat causes the particles to have more kinetic energy. In particular, there will be a greater proportional increase of higher energy particles than lower energy particles (according to the Boltzmann distribution) and hence more particles will have energy in excess of the activation energy needed to successfully negotiate the higher activation energy backward reaction.*



- **$K_{eq}$ is NOT affected by concentration, pressure, volume, catalysts or inert species.**
    - **Concentration:** If the concentrations of species in an equilibrium system change, the value of the equilibrium constant does not change. This is because increasing the concentration of a species does not change the proportion of particles that have sufficient activation energy, and hence will note change the equilibrium constant.
    - **Pressure/Volume:** A change in these variables will always lead to changes concentration. Similarly, the system will adjust itself to reach the $K_{eq}$ value.
    - **Catalysts:** Introduction of a catalyst will increase the rates of the forward **AND** reverse reactions. This may make the system reach equilibrium faster, however it will not affect the position of equilibrium.
    - **Inert species:** These species do not participate in the reaction, and therefore do not affect the equilibrium constant.

**Question 11 (4 marks)**

Fill in the following table to determine the effect of the following temperature changes on the equilibrium constant.

| Forward reaction is | Temperature | ΔH (forward reaction) | $K_{eq}$ |
|---|---|---|---|
| ***Exothermic*** | ***Increases*** | Negative | Decreases |
| ***Exothermic*** | ***Decreases*** | Negative | Increases |
| ***Endothermic*** | ***Increases*** | Positive | Increases |
| ***Endothermic*** | ***Decreases*** | Positive | Decreases |

***Talent Tip:*** The equilibrium constant is the **quantitative** description of equilibrium position, whereas Le Chatelier's principle enables the **qualitative** prediction of equilibrium changes. Both descriptions are equally valid and complement each other.

**Question 12 (3 marks)**

The production of carbon dioxide from its constituent carbon monoxide and oxygen gas forms an equilibrium and has an enthalpy change of $\Delta H = -564$ kJ $mol^{-1}$.

a) What is the equation for this reaction?

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b) Write the $K_{eq}$ expression for this reaction.

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c) If the temperature is increased, how would the value of the equilibrium constant $K_{eq}$ change?

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**Question 13 (4 marks)**

For the following reaction:

$$4HCl_{(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(g)} + 2Cl_{2(g)} \ (\Delta H = -113\ kJ\ mol^{-1})$$

a) Write the equilibrium constant expression.

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b) If the equilibrium concentration of chlorine gas is to be minimised, what temperature change would need to occur, and how would this be reflected in the value of $K_{eq}$?

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***Talent Tip:*** It is a good idea to state Le Chatelier's Principle in any short answer question which asks about the shifting of an equilibrium.

**Question 14 (3 marks)**

a) At 25°C the equilibrium concentrations were initially $[N_2O_4]$ = 0.152 mol $L^{-1}$ and $[NO_2]$ = 0.0300 mol $L^{-1}$ for the reaction

$$2NO_{2(g)} \leftrightharpoons N_2O_{4(g)}$$

Calculate the value of $K_{eq}$.

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b) When the volume of the system is halved, as outlined above, what are the immediate resulting concentrations, before equilibrium readjusts?

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c) After equilibrium readjusts, the new concentrations are $[N_2O_4]$ = 0.500 and $[NO_2]$ = 0.0544. Calculate $K_{eq}$ now.

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As you can see, even when the concentrations changed after the volume change to the system, **$K_{eq}$ was not affected.**

# CALCULATIONS INVOLVING K

## THE ICEBOX METHOD

The "Icebox" method is an effective to solve questions which require you to calculate the equilibrium constant of a reaction given a set of initial conditions, and equilibrium conditions. It decomposes the calculations into:

**I**nitial Conditions

**C**hange

**E**quilibrium

**Question 15**

2.00 mol of phosphorus trichloride gas and 1.50 mol of chlorine gas are pumped into a 1.0 L reaction chamber, resulting in the following equilibrium reaction:

$$PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$$

At equilibrium, there are 0.75 mol of phosphorus pentachloride gas produced.

Using the ICE table, calculate the equilibrium constant of this reaction.

| | $PCl_3$ | $Cl_2$ | $PCl_5$ |
|---|---|---|---|
| **I** | | | |
| **C** | | | |
| **E** | | | |

First, fill the table with all information that is provided by the question.

| | $PCl_3$ | $Cl_2$ | $PCl_5$ |
|---|---|---|---|
| **I** | | | |
| **C** | | | |
| **E** | | | |

Now, include the changes that occur to the initial condition, noting:

- **reactants must be converted into products** – increases in concentration on one side of the equilibrium must be balanced out with decreases in concentration on the other side (in this case, increases on the right of the equilibrium and decreases on the left)
- **the change in concentration must reflect the reaction ratios of the equilibrium (in this case $PCl_3 : Cl_2 : PCl_5 = 1:1:1$)**

| | $PCl_3$ | $Cl_2$ | $PCl_5$ |
|---|---|---|---|
| **I** | | | |
| **C** | | | |
| **E** | | | |

Finally, complete the table:

| | $PCl_3$ | $Cl_2$ | $PCl_5$ |
|---|---|---|---|
| **I** | | | |
| **C** | | | |
| **E** | | | |

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**Question 16 (3 marks)**

Sulfur dioxide and oxygen react to form sulfur trioxide as follows:

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

One mole of sulfur dioxide is mixed with 0.70 moles of oxygen gas in a 2.0 L container. There are 0.80 moles of sulfur trioxide present in the container at equilibrium.

Calculate the value of K for this reaction.

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**Question 17 (3 marks)**

Consider the following reaction occurring in a 1.0 L reaction vessel:

$$\mathrm{N_{2(g)}} + 3\mathrm{H_{2(g)}} \rightleftharpoons 2\mathrm{NH_{3(g)}}$$

Initially, 0.56 mol of ammonia is introduced into the vessel. It was found at equilibrium that the concentration of nitrogen gas was 0.12 mol.

Calculate the value of the equilibrium constant $K_{eq}$.

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**Question 18 (5 marks)**

The equilibrium constant expression for a gaseous reaction is as follows:

$$K = \frac{[N_2][O_2]}{[NO]^2}$$

a) Write the equation for this reaction. (1 mark)

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b) $0.400$ moles of $NO$ was placed in a $1.00\ L$ vessel at $2000℃$. The equilibrium concentration of $N_2$ was found to be $0.198\ \text{mol L}^{-1}$.

Calculate the equilibrium constant for this reaction and use this value to describe the position of the equilibrium. (3 marks)

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c) What could be change that would result in a different value for $K$ for this equilibrium? (1 mark)

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**Question 19 (5 marks)**

Nitrosyl chloride is introduced into an empty container by a kindly soul named Jefferson. It then dissociates into nitric oxide and chlorine gas according to the following equation:

$$2\mathrm{NOCl}_{(g)} \rightleftharpoons 2\mathrm{NO}_{(g)} + \mathrm{Cl}_{(g)}$$

**The reaction is endothermic.**

a) Explain the effect on the equilibrium constant if the temperature is increased. (2 marks)

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b) The equilibrium constant, K, for the reaction is 0.0280. Calculate the equilibrium concentration of $NOCl_{(g)}$ if the equilibrium concentration of $Cl_{2(g)}$ is 0.170 mol $L^{-1}$. (3 marks)

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**Question 20 (6 marks)**

*At a particular temperature, iodine trichloride dissociates into iodine gas and chlorine gas according to the following equation:*

$$2ICl_{3(g)} \leftrightharpoons I_{2(g)} + 3Cl_2 \qquad \Delta H = 240kJ$$

Initially $0.35\ mol$ of $\mathrm{I_{3(g)}}$ was introduced into a $1.0\ L$ container and allowed to come to equilibrium. At equilibrium there was $0.45\ mol\ L^{-1}$ of $Cl_{2(g)}$.

a) Write the equilibrium constant expression for this reaction. (1 mark)

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b) Calculate the value of K at this temperature. (3 marks)

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c) What are TWO consequences of increasing the temperature of the mixture at equilibrium? (2 marks)

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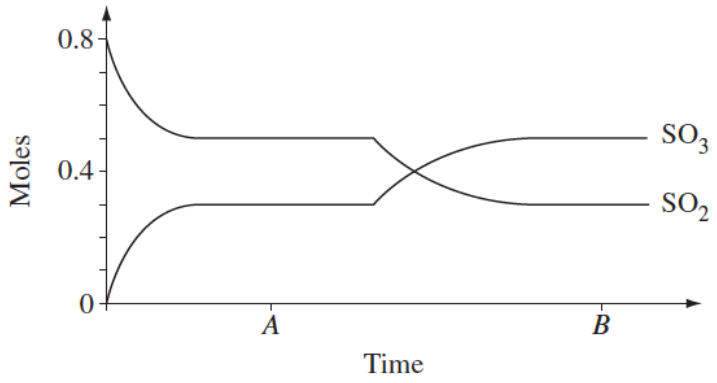
**Question 21* (5 marks)**

At room temperature $0.80$ moles of $SO_2$ and $0.40$ moles of $O_2$ were introduced into a sealed $10L$ vessel and allowed to come to equilibrium.




a) Write the equilibrium constant expression and calculate the value for the equilibrium constant at time A. (3 marks)

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b) Explain why a new equilibrium position was established at time B. (2 marks)

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**Question 22**

Hydrogen Iodide gas decomposes into hydrogen and iodine in an equilibrium reaction. A reaction mixture initially has $[HI] = 0.75\ \text{M}$.

a) Write a chemical equation for this reaction

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b) At equilibrium, the concentration of $I_2$ was found to be 0.300 M. Calculate the equilibrium concentration of HI in the mixture.

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**Question 23***

Consider the following reaction

$$PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$$

The initial concentrations of $[PCl_3]$, $[Cl_2]$ and $[PCl_5]$ are 0.485 M, 0.261 M and 0.399 M respectively. $K_{eq} = 0.50$. Calculate the equilibrium concentration of $[Cl_2]$

*[Hint: Solution involves quadratic formula]*

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## SMALL $x$ APPROXIMATION FOR SMALL AND LARGE $K_C$

When a reaction strongly favours the product or the reactant, we can avoid forming (difficult) quadratic formula by making an approximation for small values of $x$. This works when

- $K_C \geq \sim 10^4$, i.e. Heavily favours product
- $K_c \leq \sim 10^{-4}$, i.e. Heavily favours reactant

To use the small x approximation, follow these steps:

- Assume the reaction goes 100% to products or reactants
- Create an ICE Table
- Solve for $x$, assuming $x$ is small
- **Check answer – this is a critical step in determining whether the approximation is valid.**

**Question 24**

Consider the following reaction:

$$I_{2(g)} \rightleftharpoons 2I_{(g)} \quad K_c = 5.6 \times 10^{-12}$$

Suppose we have 0.45M of $I_2$. Determine the final concentration of $I^-$

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**Question 25**

0.50 moles of $N_2$ gas is mixed with 0.86 moles of $O_2$ gas in a 2.00 L tank at 2000 K. The two gasses react to form nitric oxide gas by the reaction

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)} \quad K_c = 4.1 \times 10^{-4}\ at\ 2000K$$

What are the equilibrium concentrations of each gas?

*[Assume you can use a small x approximation]*

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