

PART A QUESTION 1

Given: Reaction studied: $\text{NO}_2(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{O}(\text{g})$
Arrhenius equation:

$$k = 2.6 \times 10^{12} e^{-\frac{8900}{T}} \text{ L mol}^{-1} \text{ s}^{-1}$$

(a) E_a

$$k = A \times e^{-\frac{E_a}{RT}}$$

where $A = 2.6 \times 10^{12}$
 $-E_a/R = -8900 \text{ mol K}$

$$\therefore E_a = (8900 \text{ mol K})(8.314 \text{ J mol}^{-1} \text{ K}^{-1}) = 7.399 \times 10^4 \text{ J} = \underline{\underline{74 \text{ kJ}}}$$

(b) the rate constant (k) at 298 K

$$k = A \times e^{-\frac{E_a}{RT}}$$

$$k = 2.6 \times 10^{12} e^{-\frac{8900}{298}}$$

$$\begin{aligned} \therefore k &= 0.2782 \\ &\text{L mol}^{-1} \text{ s}^{-1} \\ &= \underline{\underline{0.28}} \\ &\underline{\underline{\text{L mol}^{-1} \text{ s}^{-1}}} \end{aligned}$$

(c) $[\text{NO}_2]$ after 10 minutes

Given: $[\text{A}_0] = [\text{NO}_2] = 3.5 \times 10^{-2} \text{ mol L}^{-1}$
 $t = 10 \text{ min} = 10 \times 60 \text{ s} = 600 \text{ s}$
units: $\text{L mol}^{-1} \text{ s}^{-1}$ indicating *second-order* kinetics

To find: $[\text{A}]$ at $t = 10 \text{ min}$

$$\boxed{\frac{1}{[A]} = k t + \frac{1}{[A_0]}} \quad (\text{second-order kinetics})$$

$$\frac{1}{[A]} = (0.2782 \text{ L mol}^{-1} \text{ s}^{-1}) (600 \text{ s}) + \frac{1}{3.5 \times 10^{-2} \text{ mol L}^{-1}} = 195.49 \text{ L mol}^{-1}$$

$$\therefore [A] \text{ after 10 min} = (195.49 \text{ L mol}^{-1})^{-1} = 5.115 \times 10^{-3} \text{ mol L}^{-1} = \underline{\underline{5.1 \times 10^{-3} \text{ mol L}^{-1}}}$$

**PART A
QUESTION 2**

Given: Reaction studied: $\text{S}_2\text{O}_8^{2-}(\text{aq}) + 3 \text{I}^-(\text{aq}) \rightarrow \text{I}_3^-(\text{aq}) + 2 \text{SO}_4^{2-}(\text{aq})$
 a plot of $\ln k$ versus $1/T$
 slope from a straight line = -5758 K
 $R = 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$

To find: activation energy (E_a) for the reaction

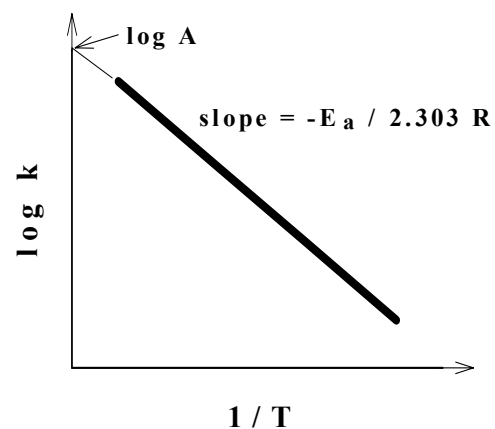
$$\boxed{\ln k = - \frac{E_a}{R} \frac{1}{T} + \ln A}$$

Compare to a straight-line linear equation:

$$y = m x + b$$

where

y	=	$\ln k$
x	=	$1 / T$
m	=	slope = $- E_a / 2.303 R$
b	=	y -intercept = $\ln A$



$$\text{slope} = - \frac{E_a}{2.303 R}$$

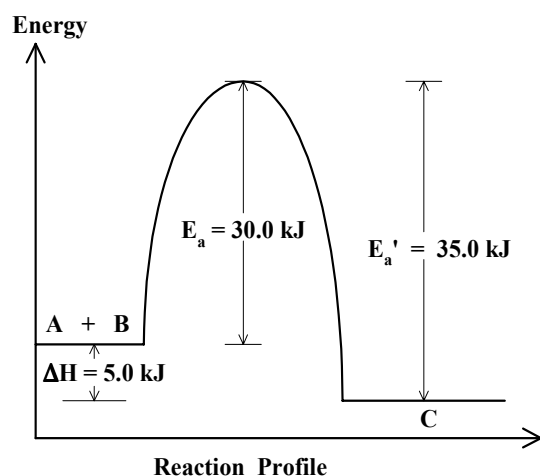
$$- 5758 \text{ K} = - \frac{E_a}{(8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1})}$$

$$\therefore E_a = 47.87 \text{ kJ mol}^{-1} = \underline{\underline{48 \text{ kJ mol}^{-1}}}$$

PART A QUESTION 3

Given: Elementary reaction: $A + B \rightarrow C$
 $E_a = 30.0 \text{ kJ mol}^{-1}$
 $\Delta H = -5.0 \text{ kJ mol}^{-1}$ (\therefore *exothermic* reaction)

To find: E_a for the reverse reaction (E_a')



As shown in the diagram,

The reverse reaction is:

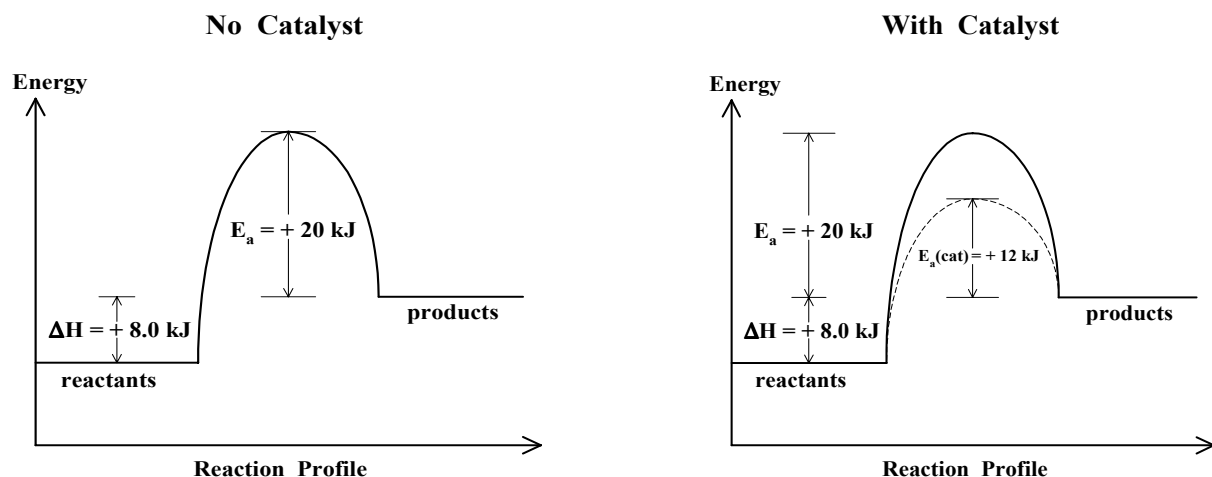


$$E_a' = \underline{\underline{35.0 \text{ kJ mol}^{-1}}}$$

PART A QUESTION 4

Given: $E_a = 20 \text{ kJ}$
 $\Delta H = +8 \text{ kJ}$ (\therefore *endothermic* reaction)
 $E_a(\text{cat}) = 12 \text{ kJ}$

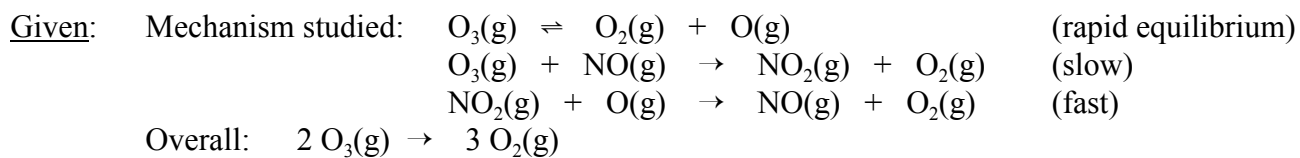
To sketch: the reaction profile with and without a catalyst
 including (1) activation energy (E_a)
 (2) enthalpy change (ΔH) for the reaction



In the presence of a **catalyst**,

- ① the reaction rate *increases*
- ② the rate constant (*k*) *increases*
- ③ $t_{1/2}$ *decreases* because *k* *increases*
- ④ E_a *usually decreases* (\because *k* depends on both *A* and E_a)
- ⑤ The enthalpy difference between reactants and products remains *unchanged* (\because this is not a kinetic property)

PART A QUESTION 5

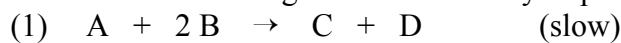


To find: the intermediate(s) and the catalyst

- (1) **intermediates:** $O(g)$ and $NO_2(g)$ (\because *do not appear in the overall reaction*)
- (2) **catalyst:** $NO(g)$ (\because *regenerate at the end of the reaction*)

PART A
QUESTION 6

Given: Mechanism consisting of two elementary steps:



To find: Which of the following statements is **incorrect**?

- (a) The species D is an intermediate. **TRUE**
 (:: The species D does not appear in the overall reaction: $2 A + 2 B \rightarrow 2 C + E$.)
- (b) The first step is the rate-determining step. **TRUE**
 (:: The **slow** elementary step is always the rate-determining step.)
- (c) The second step is a bimolecular elementary step. **TRUE**
 (:: This elementary step involves two molecules: D and A.)
- (d) The rate law for the first step is: $\text{rate} = k [A] [B]^2$. **TRUE**
 (:: The rate law follows the stoichiometry in the rate-determining reaction.)
- (e) If the concentration of B is tripled, the rate of reaction increases 6-fold. **INCORRECT**
 (The rate of reaction should increase **9-fold**.)

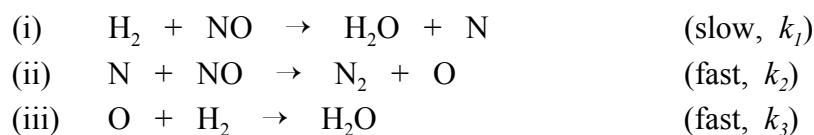
PART A
QUESTION 7

Given: Reaction studied: $2 \text{H}_2(\text{g}) + 2 \text{NO}(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g})$

$$\text{rate} = k_{\text{exp}} [\text{H}_2][\text{NO}]^2$$

To show: Mechanism (a) or Mechanism (b) is consistent with the experimental rate law

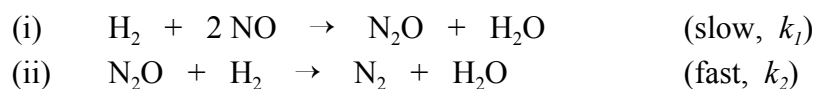
The **slow** elementary step is always the **rate-determining step**.
 ∴ rate law for the overall reaction = rate law of the **slow** step

Mechanism (a):

From (i): $\text{H}_2 + \text{NO} \rightarrow \text{H}_2\text{O} + \text{N}$ (slow, k_1) (i.e. **rate-determining step**)

$$\text{rate} = k_1 [\text{H}_2] [\text{NO}]$$

\therefore Mechanism (a) is not consistent with the experimental data.

Mechanism (b):

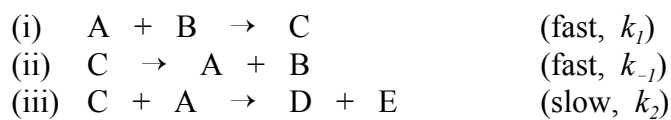
From (i): $\text{H}_2 + 2\text{NO} \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$ (slow, k_1) (i.e. **rate-determining step**)

$$\text{rate} = k_1 [\text{H}_2] [\text{NO}]^2$$

\therefore **Mechanism (b)** is consistent with the experimental data (where $k_1 = k_{exp}$).

**PART A
QUESTION 8**

Given: Reaction: $2\text{A} + \text{B} \rightarrow \text{D} + \text{E}$



(1) The *slow* elementary step is the **rate-determining step**.

From (iii): $\text{C} + \text{A} \rightarrow \text{D} + \text{E}$ (slow, k_2)

$$\text{rate} = k_2 [\text{C}] [\text{A}] \quad \textcircled{1}$$

- (2) C is the *intermediate*, [C] must be eliminated from the rate law equation and substituted by [reactants] and/or [products].

- (a) **use steady-state approach to deduce the rate law for the reaction**

rate of intermediate C <i>formation</i> = rate of intermediate C <i>disappearance</i>	
A + B → C (fast, k_1)	C → A + B (fast, k_{-1}) C + A → D + E (slow, k_2)
rate = $k_1 [\text{A}] [\text{B}]$	rate = $k_{-1} [\text{C}]$ rate = $k_2 [\text{C}] [\text{A}]$

$$k_1 [\text{A}] [\text{B}] = k_{-1} [\text{C}] + k_2 [\text{C}] [\text{A}]$$

$$k_1 [\text{A}] [\text{B}] = [\text{C}] (k_{-1} + k_2 [\text{A}])$$

$$\therefore [\text{C}] = \frac{k_1 [\text{A}] [\text{B}]}{k_{-1} + k_2 [\text{A}]} \quad \textcircled{2}$$

Substitute ② into ①:

$$\text{rate} = k_2 [\text{C}] [\text{A}] = k_2 \left(\frac{k_1 [\text{A}] [\text{B}]}{k_{-1} + k_2 [\text{A}]} \right) [\text{A}] = \frac{k_1 k_2 [\text{A}]^2 [\text{B}]}{k_{-1} + k_2 [\text{A}]}$$

- (b) **conditions the rate law would be simplified to rate = $k_{\text{exp}} [\text{A}]^2 [\text{B}]$**

$$\text{when } k_{-1} \gg k_2 [\text{A}], \quad \text{rate} = \left(\frac{k_1 k_2}{k_{-1}} \right) [\text{A}]^2 [\text{B}]$$

$$\text{if } k_{\text{exp}} = \left(\frac{k_1 k_2}{k_{-1}} \right), \quad \text{rate} = k_{\text{exp}} [\text{A}]^2 [\text{B}]$$

PART A
QUESTION 9

Given: Reaction studied: $\text{COCl}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{Cl}_2(\text{g})$

$$\text{rate} = k_{\text{exp}} [\text{COCl}_2][\text{Cl}_2]^{1/2}$$

- (i) $\text{Cl}_2(\text{g}) \rightleftharpoons 2 \text{Cl}(\text{g})$ (rapid equilibrium, K)
 (ii) $\text{COCl}_2(\text{g}) + \text{Cl}(\text{g}) \rightarrow \text{COCl}(\text{g}) + \text{Cl}_2(\text{g})$ (**slow**, k_2)
 (iii) $\text{COCl}(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{Cl}(\text{g})$ (fast, k_3)

To show: the mechanism is consistent with the rate law ($\text{rate} = k_{\text{exp}} [\text{COCl}_2][\text{Cl}_2]^{1/2}$)

- (1) Elementary step (ii) is the **slow** reaction and is the **rate-determining step**.

$$\text{rate} = k_2 [\text{COCl}_2] [\text{Cl}] \quad \textcircled{1}$$

- (2) $\text{Cl}(\text{g})$ is the **intermediate** and must be substituted by [reactants] and [products].

(a) use Equilibrium Constant (K) to eliminate concentration of an intermediate

From (i): $\text{Cl}_2(\text{g}) \rightleftharpoons 2 \text{Cl}(\text{g})$ (rapid equilibrium, K)

$$K = \frac{[\text{Cl}]^2}{[\text{Cl}_2]}$$

$$\therefore [\text{Cl}] = (K [\text{Cl}_2])^{1/2} \quad \textcircled{2}$$

Substitute $\textcircled{2}$ into $\textcircled{1}$:

$$\begin{aligned} \text{rate} &= k_2 [\text{COCl}_2] [\text{Cl}] \\ &= k_2 [\text{COCl}_2] (K [\text{Cl}_2])^{1/2} \\ &= k_2 K^{1/2} [\text{COCl}_2] [\text{Cl}_2]^{1/2} \\ &= k_{\text{exp}} [\text{COCl}_2] [\text{Cl}_2]^{1/2} \end{aligned}$$

$$\text{where } k_{\text{exp}} = k_2 K^{1/2}$$

(b) k_{exp} expressed in terms of K and k 's

$$k_{exp} = k_2 K^{1/2}$$

PART A
QUESTION 10

Given: Reaction studied: $2 \text{H}_2(\text{g}) + 2 \text{NO}(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g})$

$$\text{rate} = k_{exp} [\text{H}_2][\text{NO}]^2$$

- (i) $2 \text{NO} \rightleftharpoons \text{N}_2\text{O}_2$ (fast equilibrium, K)
 (ii) $\text{N}_2\text{O}_2 + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$ (slow, k_2)
 (iii) $\text{N}_2\text{O} + \text{H}_2 \rightarrow \text{N}_2 + \text{H}_2$ (fast, k_3)

To show: the proposed mechanism is consistent with the experimental rate law

$$\text{rate} = k_{exp} [\text{H}_2][\text{NO}]^2$$

- (1) Elementary step (ii) is the *slow* reaction and is the *rate-determining step*.

$$\text{rate} = k_2 [\text{N}_2\text{O}_2] [\text{H}_2] \quad \textcircled{1}$$

- (2) N_2O_2 is the *intermediate* and must be substituted by [reactants] and [products].

Use Equilibrium Constant (K) to eliminate concentration of intermediate

From (i): $2 \text{NO} \rightleftharpoons \text{N}_2\text{O}_2$ (fast equilibrium, K)

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

$$\therefore [\text{N}_2\text{O}_2] = K [\text{NO}]^2 \quad \textcircled{2}$$

Substitute $\textcircled{2}$ into $\textcircled{1}$:

$$\begin{aligned} \text{rate} &= k_2 [\text{N}_2\text{O}_2] [\text{H}_2] \\ &= k_2 (K [\text{NO}]^2) [\text{H}_2] \end{aligned}$$

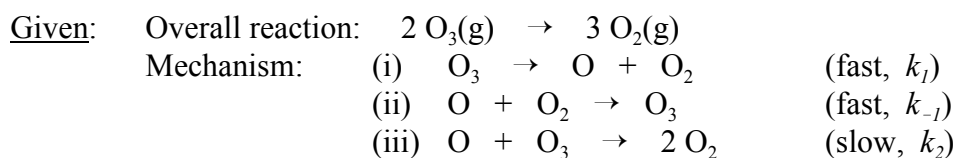
$$= k_2 K [\text{H}_2] [\text{NO}]^2$$

$$= k_{\text{exp}} [\text{H}_2] [\text{NO}]^2$$

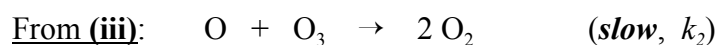
where $k_{\text{exp}} = k_2 K$

∴ **YES**, the proposed mechanism is consistent with the experimental rate law.

**PART A
QUESTION 11**



(1) Elementary step (iii) is the *slow* reaction and is the *rate-determining step*.



$\text{rate} = k_2 [\text{O}] [\text{O}_3]$ ①

(2) **O** is the *intermediate* and must be substituted by [reactants] and [products].

(a) using Steady-State approach to eliminate an intermediate

rate of appearance of intermediate O = rate of disappearance of intermediate O	
$\text{O}_3 \rightarrow \text{O} + \text{O}_2$ (fast, k_1)	$\text{O} + \text{O}_2 \rightarrow \text{O}_3$ (fast, k_{-1}) $\text{O} + \text{O}_3 \rightarrow 2 \text{O}_2$ (slow, k_2)
rate = $k_1 [\text{O}_3]$	rate = $k_{-1} [\text{O}] [\text{O}_2]$ rate = $k_2 [\text{O}] [\text{O}_3]$

$$k_1 [\text{O}_3] = k_{-1} [\text{O}] [\text{O}_2] + k_2 [\text{O}] [\text{O}_3]$$

$$k_1 [\text{O}_3] = [\text{O}] (k_{-1} [\text{O}_2] + k_2 [\text{O}_3])$$

$$\therefore [\text{O}] = \frac{k_1 [\text{O}_3]}{k_{-1} [\text{O}_2] + k_2 [\text{O}_3]}$$
 ②

Substitute ② into ①:

$$\begin{aligned}
 \text{rate} &= k_2 [\text{O}] [\text{O}_3] \\
 &= k_2 \left(\frac{k_1 [\text{O}_3]}{k_{-1} [\text{O}_2] + k_2 [\text{O}_3]} \right) [\text{O}_3] \\
 &= \frac{k_1 k_2 [\text{O}_3]^2}{k_{-1} [\text{O}_2] + k_2 [\text{O}_3]}
 \end{aligned}$$

(b) using Equilibrium Constant (K) method to eliminate an intermediate

(Note that $K = k_1 / k_{-1}$)

Recall the rate-determining step:

$$\text{rate} = k_2 [\text{O}] [\text{O}_3] \quad \textcircled{1}$$

From (i): $\text{O}_3 \rightarrow \text{O} + \text{O}_2$ (fast, k_1)

$$K = \frac{[\text{O}] [\text{O}_2]}{[\text{O}_3]} = \frac{k_1}{k_{-1}}$$

$$\therefore [\text{O}] = \frac{k_1}{k_{-1}} \times \frac{[\text{O}_3]}{[\text{O}_2]} \quad \textcircled{2}$$

Substitute ② into ①:

$$\begin{aligned}
 \text{rate} &= k_2 [\text{O}] [\text{O}_3] \\
 &= k_2 \left(\frac{k_1}{k_{-1}} \times \frac{[\text{O}_3]}{[\text{O}_2]} \right) [\text{O}_3] = \frac{k_1 k_2 [\text{O}_3]^2}{k_{-1} [\text{O}_2]}
 \end{aligned}$$

(c) conditions of the rate laws derived by the methods (a) the same as (b)

From Steady-State Approach:

$$\text{rate} = \frac{k_1 k_2 [\text{O}_3]^2}{k_{-1} [\text{O}_2] + k_2 [\text{O}_3]}$$

From Equilibrium Constant Method:

$$\text{rate} = \frac{k_1 k_2 [\text{O}_3]^2}{k_{-1} [\text{O}_2]}$$

If $k_{-1} [\text{O}_2] \gg k_2 [\text{O}_3]$
then the Steady-State rate law will become

$$\text{rate} = \frac{k_1 k_2 [\text{O}_3]^2}{k_{-1} [\text{O}_2]}$$

which is the same as the rate law derived by Equilibrium Constant method

- (d) if the experimentally found rate law is: $\text{rate} = k_{\text{exp}} [\text{O}_3]^2 / [\text{O}_2]$,
conditions when the proposed mechanism is consistent with the experimental data

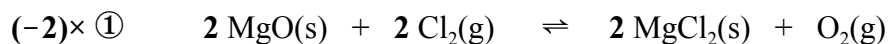
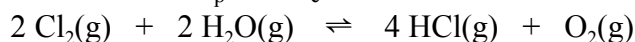
when

$$k_{\text{exp}} = \frac{k_1 k_2}{k_{-1}} = k_2 K$$

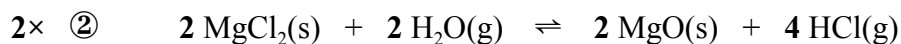
PART B QUESTION 1

Given: ① $\text{MgCl}_2(\text{s}) + \frac{1}{2} \text{O}_2(\text{g}) \rightleftharpoons \text{MgO}(\text{s}) + \text{Cl}_2(\text{g})$ $K_p = 2.95 \text{ atm}^{1/2}$ (at 1000 K)
 ② $\text{MgCl}_2(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{MgO}(\text{s}) + 2 \text{HCl}(\text{g})$ $K_p = 8.40 \text{ atm}$ (at 1000 K)
 $T = 1000 \text{ K}$
 $R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$

To find: the equilibrium constants K_p and K_c at 1000 K for the reaction:



$$K_1 = \left(\frac{1}{2.95 \text{ atm}^{1/2}} \right)^2$$



$$K_2 = (8.40 \text{ atm})^2$$



$$K_p = K_1 \times K_2$$

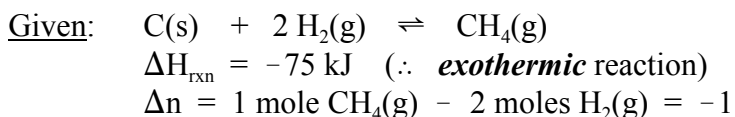
$$K_p = K_1 \times K_2 = \left(\frac{1}{2.95 \text{ atm}^{1/2}} \right)^2 (8.40 \text{ atm})^2 = \underline{8.108 \text{ atm}} = 8.11 \text{ atm}$$

$$\begin{aligned}
 \Delta n &= \sum n(\text{gaseous products}) - \sum n(\text{gaseous reactants}) \\
 &= \{(4 + 1) \text{ moles}\} - \{(2 + 2) \text{ moles}\} \\
 &= 5 \text{ moles} - 4 \text{ moles} \\
 &= 1
 \end{aligned}$$

$$K_p = K_c (R T)^{\Delta n}$$

$$\begin{aligned}
 \therefore \frac{8.108 \text{ atm}}{K_c} &= K_c \{(0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}) (1000 \text{ K})\}^1 \\
 K_c &= \frac{9.8758 \times 10^{-2} \text{ mol L}^{-1}}{9.88 \times 10^{-2} \text{ M}}
 \end{aligned}$$

PART B QUESTION 2



(a) decrease in temperature

For *exothermic* reaction ($\Delta H = -ve$), a *decrease* in temperature shifts the equilibrium **forward**.
 For *endothermic* reaction ($\Delta H = +ve$), an *increase* in temperature shifts the equilibrium **forward**.

Since a *decrease* in temperature favours the *exothermic* reaction, the equilibrium will shift from **LEFT → RIGHT**.

(b) decrease in volume

A *decrease* in the **volume** of a gaseous system (or an *increase* in external **pressure**) favours a *decrease* in the **moles of gas** present (*i.e.* $\Delta n = -ve$) and the equilibrium shifts to the **product** side.
 (where $\Delta n = \sum n(\text{gaseous products}) - \sum n(\text{gaseous reactants})$)

An *increase* in the **volume** of a gaseous system (or a *decrease* in external **pressure**) favours an *increase* in the **moles of gas** present (*i.e.* $\Delta n = +ve$) and the equilibrium shifts to the **product** side.

Since there are **two moles** of $\text{H}_2(\text{g})$ *gaseous* reactant converting into **one mole** of $\text{CH}_4(\text{g})$ *gaseous* product (*i.e.* $\Delta n = -1$), a *decrease* in volume favours a net *decrease* in the number of **moles** of gas. Thus, the equilibrium will shift from **LEFT → RIGHT**.

(c) decrease in pressure of $\text{H}_2(\text{g})$

$$K_p = \frac{p(\text{CH}_4)}{p(\text{H}_2)^2}$$

If $Q < K_{\text{eq}}$, then the reaction proceeds toward products
(i.e. to the **right**).
 If $Q > K_{\text{eq}}$, then the reaction proceeds to form reactants
(i.e. to the **left**).
 If $Q = K_{\text{eq}}$, then the system reaches equilibrium.

If $p(\text{H}_2)$, a reactant, is removed (or decreased) from the system,
 then Q_p becomes *larger than* K_p (\because denominator becomes *smaller*),
 and the equilibrium will shift from **RIGHT** \rightarrow **LEFT**.

(d) increase in pressure of $\text{CH}_4(\text{g})$

If $p(\text{CH}_4)$, a product, is added to the system,
 then Q_p becomes *larger than* K_p (\because numerator becomes *larger*),
 and the equilibrium will shift from **RIGHT** \rightarrow **LEFT**.

(e) addition of $\text{C}(\text{s})$

The position of a heterogeneous equilibrium does not depend on the amounts of pure solids (e.g. $\text{C}(\text{s})$) or liquids present. Because $\text{C}(\text{s})$ does not appear in the K_p expression, there is ***no effect*** on the position of equilibrium.

(f) addition of catalyst

A catalyst lowers the activation energy of a reaction by increasing the rate of reaction. Since the catalyst does not appear in the K_p expression, the equilibrium ***remains unchanged***.

What are the optimal conditions to get a high yield of $\text{CH}_4(\text{g})$?

Factors affecting the equilibrium for the **forward** reaction:

- ① **temperature** An *increase* in temperature favours the **endothermic** reaction.
 A *decrease* in temperature favours the **exothermic** reaction.
- ② **pressure** An *increase* in external pressure (i.e. a *decrease* in volume)
 favours a net *decrease* in the number of **moles of gas** (i.e. $\Delta n = -\text{ve}$).
 A *decrease* in external pressure (i.e. an *increase* in volume)
 favours a net *increase* in the number of **moles of gas** (i.e. $\Delta n = +\text{ve}$).

- (1) **exothermic** reaction ($\Delta H = -\text{ve}$)
 - favours **low temperature**
- (2) **2 moles** gaseous reactants \rightarrow **1 mole** gaseous product

$\therefore \Delta n = (1 \text{ mole} - 2 \text{ moles}) = \underline{\underline{-1}}$

 - favours **high pressure**

**PART B
QUESTION 3**

Given: $\text{SO}_3(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$
endothermic reaction (*i.e.* $\Delta H = +ve$)

To find: conditions favoured by maximum formation of $\text{SO}_2(\text{g})$ and $\text{O}_2(\text{g})$

(1) **1 mole** gaseous reactant \rightarrow **1.5 moles** gaseous products

$$\Delta n = (1.5 \text{ moles} - 1 \text{ mole}) = \underline{+0.5}$$

- The forward reaction is favoured by **lowering the pressure**.

(*i.e.* If $\Delta n = +ve$,

then the reaction is favoured by an **increase** in **volume**, thus a **decrease** in external **pressure**.)

(2) *endothermic* reaction ($\Delta H = +ve$)

- The forward *endothermic* reaction is favoured by **higher temperature**.

**PART B
QUESTION 4**

Given: $2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{SO}_3(\text{g})$

In an 1.0 L vessel,

Initial: $\text{SO}_2(\text{g}) = 0.80 \text{ mol}$ $\therefore [\text{SO}_2] = (0.80 \text{ mol} \div 1.0 \text{ L}) = 0.80 \text{ mol L}^{-1}$

$\text{O}_2(\text{g}) = 0.60 \text{ mol}$ $\therefore [\text{O}_2] = (0.60 \text{ mol} \div 1.0 \text{ L}) = 0.60 \text{ mol L}^{-1}$

At Equilibrium: $\text{SO}_3(\text{g}) = 0.60 \text{ mol}$ $\therefore [\text{SO}_3] = (0.60 \text{ mol} \div 1.0 \text{ L}) = 0.60 \text{ mol L}^{-1}$

To find: K_c for the reaction

In an 1.0 L vessel,

	$2 \text{SO}_2(\text{g})$	+	$\text{O}_2(\text{g})$	\rightleftharpoons	$2 \text{SO}_3(\text{g})$
I:	0.80 mol L^{-1}		0.60 mol L^{-1}		-
C:	$\ominus 0.60 \text{ mol L}^{-1}$		$\ominus \frac{1}{2}(0.60 \text{ mol L}^{-1})$		$\oplus 0.60 \text{ mol L}^{-1}$
E:	<u>0.20 mol L^{-1}</u>		<u>0.30 mol L^{-1}</u>		0.60 mol L^{-1}

(1) $[\text{SO}_3]$ produced *at equilibrium* = 0.60 mol L^{-1} (given)

$$\begin{aligned}
 (2) \quad [\text{SO}_2] \text{ reacted (changed)} &= [\text{SO}_3] \text{ produced} \times (2 \text{ moles SO}_2 \div 2 \text{ moles SO}_3) \\
 &= (0.60 \text{ mol L}^{-1}) (2/2) \\
 &= 0.60 \text{ mol L}^{-1} \\
 \therefore [\text{SO}_2] \text{ leftover at equilibrium} &= (0.80 \text{ mol L}^{-1} - 0.60 \text{ mol L}^{-1}) = \underline{\underline{0.20 \text{ mol L}^{-1}}}
 \end{aligned}$$

$$\begin{aligned}
 (3) \quad [\text{O}_2] \text{ reacted (changed)} &= [\text{SO}_3] \text{ produced} \times (1 \text{ mole O}_2 \div 2 \text{ moles SO}_3) \\
 &= (0.60 \text{ mol L}^{-1}) (1/2) \\
 &= 0.30 \text{ mol L}^{-1} \\
 \therefore [\text{O}_2] \text{ remained at equilibrium} &= (0.60 \text{ mol L}^{-1} - 0.30 \text{ mol L}^{-1}) = \underline{\underline{0.30 \text{ mol L}^{-1}}}
 \end{aligned}$$

$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]}$$

$$K_c = \frac{(0.60 \text{ mol L}^{-1})^2}{(0.20 \text{ mol L}^{-1})^2 (0.30 \text{ mol L}^{-1})} = 30 \left(\frac{\text{mol}}{\text{L}}\right)^{-1} = 30 \text{ M}^{-1}$$

PART B QUESTION 5

Given: $\text{SO}_2(\text{g}) + \text{NO}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g}) + \text{NO}(\text{g})$ ($K_c = 3.0$ at 400°C)

In a 500 mL (0.500 L) flask,

Initial: $\text{SO}_2(\text{g}) = 1.0 \text{ mol}$ $\therefore [\text{SO}_2] = (1.0 \text{ mol} \div 0.500 \text{ L}) = 2.0 \text{ M}$
 $\text{NO}_2(\text{g}) = 1.0 \text{ mol}$ $\therefore [\text{NO}_2] = (1.0 \text{ mol} \div 0.500 \text{ L}) = 2.0 \text{ M}$

To find: $n(\text{SO}_3)$ and $n(\text{NO})$ present *at equilibrium*

In a 500 mL flask,

let $x = [\text{SO}_2] \text{ consumed} = [\text{NO}_2] \text{ consumed} = [\text{SO}_3] \text{ produced} = [\text{NO}] \text{ produced}$

	$\text{SO}_2(\text{g})$	+	$\text{NO}_2(\text{g})$	\rightleftharpoons	$\text{SO}_3(\text{g})$	+	$\text{NO}(\text{g})$
I:	2.0 M		2.0 M		-		-
C:	$\ominus x$		$\ominus x$		$\oplus x$		$\oplus x$
E:	<u>2.0 - x</u>		<u>2.0 - x</u>		<u>x</u>		<u>x</u>

$$K_c = \frac{[\text{SO}_3] [\text{NO}]}{[\text{SO}_2] [\text{NO}_2]}$$

$$3.0 = \frac{(x)(x)}{(2.0 - x)(2.0 - x)}$$

$$3.0 = \frac{(x)^2}{(2.0 - x)^2}$$

$$\sqrt{3.0} = \frac{(x)}{(2.0 - x)}$$

$$x = \frac{1.268}{M}$$

At equilibrium in 500 mL flask,

$$(1) \quad x = [\text{SO}_3] \text{ produced} = [\text{NO}] \text{ produced} = \underline{1.268 \text{ M}}$$

$$\therefore n(\text{SO}_3) = n(\text{NO}) = (1.268 \text{ mol L}^{-1})(500 \times 10^{-3} \text{ L}) = 0.634 \text{ mol} = \underline{\underline{0.63 \text{ mol}}}$$

$$(2) \quad [\text{SO}_2] \text{ remained} = [\text{NO}_2] \text{ remained} = (2.0 \text{ M} - x) = (2.0 \text{ M} - 1.268 \text{ M}) = \underline{0.732 \text{ M}}$$

$$\therefore n(\text{SO}_2) = n(\text{NO}_2) = (0.732 \text{ mol L}^{-1})(500 \times 10^{-3} \text{ L}) = 0.366 \text{ mol}$$

**PART B
QUESTION 6**



(a) $[\text{Cl}_2(\text{g})]$ when 2.00 moles of $\text{NCl}_5(\text{g})$ introduced to 1.00 L container

(i.e. $[\text{NCl}_5] = (2.00 \text{ moles} \div 1.00 \text{ L}) = 2.00 \text{ M}$)

Let $x = [\text{Cl}_2]$ produced = $[\text{NCl}_3]$ produced = $[\text{NCl}_5]$ consumed

	$\text{NCl}_5(\text{g})$	\rightleftharpoons	$\text{NCl}_3(\text{g})$	$+\text{Cl}_2(\text{g})$
<i>I:</i>	2.00 M		-	-
<i>C:</i>	$\ominus x$		$\oplus x$	$\oplus x$
<i>E:</i>	$2.00 - x$		x	x

$$K_c = \frac{[\text{NCl}_3][\text{Cl}_2]}{[\text{NCl}_5]}$$

$$1.30 \times 10^{-3} \text{ M} = \frac{(x)(x)}{(2.00 - x)}$$

$$1^{\text{st}} \text{ approximation: } x = 5.099 \times 10^{-2} \text{ M}$$

$$2^{\text{nd}} \text{ approximation: } x = 5.033 \times 10^{-2} \text{ M}$$

$$3^{\text{rd}} \text{ approximation: } x = 5.033 \times 10^{-2} \text{ M}$$

$$\therefore x = [\text{Cl}_2] \text{ produced} = 5.033 \times 10^{-2} \text{ M} = \underline{\underline{5.03 \times 10^{-2} \text{ M}}}$$

- (b) $[\text{Cl}_2(\text{g})]$ when 0.100 moles of $\text{NCl}_5(\text{g})$ introduced to 1.00 L container
(i.e. $[\text{NCl}_5] = (0.100 \text{ moles} \div 1.00 \text{ L}) = 0.100 \text{ M}$)

Let $x = [\text{Cl}_2]$ produced = $[\text{NCl}_3]$ produced = $[\text{NCl}_5]$ consumed

	$\text{NCl}_5(\text{g})$	\rightleftharpoons	$\text{NCl}_3(\text{g})$	+	$\text{Cl}_2(\text{g})$
I:	0.100 M		-		-
C:	$\ominus x$		$\oplus x$		$\oplus x$
E:	$0.100 - x$		x		x

$$K_c = \frac{[\text{NCl}_3][\text{Cl}_2]}{[\text{NCl}_5]} \quad 1.30 \times 10^{-3} \text{ M} = \frac{(x)(x)}{(0.100 - x)}$$

1st approximation: $x = 1.1402 \times 10^{-2} \text{ M}$

2nd approximation: $x = 1.0732 \times 10^{-2} \text{ M}$

3rd approximation: $x = 1.0772 \times 10^{-2} \text{ M}$

$\therefore x = [\text{Cl}_2]$ produced = $1.077 \times 10^{-2} \text{ M} = \underline{\underline{1.08 \times 10^{-2} \text{ M}}}$

PART B QUESTION 7

Given: $\text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{PCl}_5(\text{g})$ ($K_c = 1.60$ at 544 K)
In a 3.00 L container,
initial: $\text{PCl}_3(\text{g}) = 6.00 \text{ moles}$ $\therefore [\text{PCl}_3] = (6.00 \text{ mol} \div 3.00 \text{ L}) = 2.00 \text{ M}$
 $\text{Cl}_2(\text{g}) = 3.00 \text{ moles}$ $\therefore [\text{Cl}_2] = (3.00 \text{ mol} \div 3.00 \text{ L}) = 1.00 \text{ M}$

To find: $[\text{Cl}_2]$ leftover *at equilibrium*

Let $x = [\text{Cl}_2]$ consumed = $[\text{PCl}_3]$ consumed = $[\text{PCl}_5]$ produced

$\therefore [\text{Cl}_2]$ **leftover at equilibrium** = $(1.00 \text{ M} - x)$

	$\text{PCl}_3(\text{g})$	+	$\text{Cl}_2(\text{g})$	\rightleftharpoons	$\text{PCl}_5(\text{g})$
I:	2.00 M		1.00 M		-
C:	$\ominus x$		$\ominus x$		$\oplus x$
E:	$2.00 - x$		$1.00 - x$		x

$$K_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3] [\text{Cl}_2]}$$

$$1.60 = \frac{(x)}{(2.00 - x)(1.00 - x)}$$

$$1.60x^2 - 5.80x + 3.20 = 0$$

(quadratic equation)

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$\begin{aligned} a &= 1.6 \\ b &= -5.80 \\ c &= 3.20 \end{aligned}$$

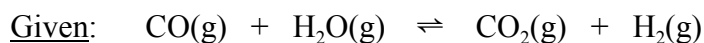
$$x = \frac{-(-5.80) \pm \sqrt{(-5.80)^2 - 4(1.60)(3.20)}}{2(1.60)}$$

$$x = 0.679 \text{ M} \quad \text{OR} \quad 2.946 \text{ M (neglected)}$$

∴ *At equilibrium,*

$$[\text{Cl}_2]_{\text{leftover}} = (1.00 \text{ M} - x) = (1.00 \text{ M} - 0.679 \text{ M}) = 0.321 \text{ M} = \underline{\underline{0.32 \text{ M}}}$$

PART B QUESTION 8



(a) K_c

$$K_c = \frac{[\text{CO}_2] [\text{H}_2]}{[\text{CO}] [\text{H}_2\text{O}]}$$

$$K_c = \frac{(0.900 \text{ M})(0.900 \text{ M})}{(4.00 \text{ M})(4.00 \text{ M})} = \underline{\underline{0.050625}} = 0.0506$$

(b) Q_c when an additional 1.00 M of CO(g) and $\text{H}_2\text{O(g)}$ are added to the container

$$[\text{CO}] = [\text{H}_2\text{O}] = (4.00 \text{ M} + 1.00 \text{ M}) = 5.00 \text{ M}$$

$$Q_c = \frac{[\text{CO}_2] [\text{H}_2]}{[\text{CO}] [\text{H}_2\text{O}]}$$

$$Q_c = \frac{(0.900 \text{ M}) (0.900 \text{ M})}{(5.00 \text{ M}) (5.00 \text{ M})} = 0.0324$$

(c) In which direction will reaction go?

Since $Q_c < K_c$,
(i.e. $0.0324 < 0.0506$)

\therefore The reaction will proceed
from **LEFT** \rightarrow **RIGHT**.

If $Q < K_{eq}$,	then the reaction proceeds toward products (i.e. to the right).
If $Q > K_{eq}$,	then the reaction proceeds to form reactants (i.e. to the left).
If $Q = K_{eq}$,	then the system reaches equilibrium.

PART B QUESTION 9

Given: $2 \text{N}_2\text{O}_4(\text{g}) + 6 \text{H}_2\text{O}(\text{g}) \rightleftharpoons 4 \text{NH}_3(\text{g}) + 7 \text{O}_2(\text{g})$

Initial: $[\text{N}_2\text{O}_4] = 2.20 \text{ M}$
 $[\text{H}_2\text{O}] = 4.20 \text{ M}$

At equilibrium: $[\text{O}_2] = 1.96 \text{ M}$
(i.e. $(1.96 \text{ M} \div 7 \text{ moles O}_2) = \mathbf{0.280 \text{ M}}$ per mole of O_2 produced)

To find: $[\text{N}_2\text{O}_4]$, $[\text{H}_2\text{O}]$ and $[\text{NH}_3]$ at equilibrium

	$2 \text{N}_2\text{O}_4(\text{g})$	$+ 6 \text{H}_2\text{O}(\text{g})$	$\rightleftharpoons 4 \text{NH}_3(\text{g})$	$+ 7 \text{O}_2(\text{g})$
I:	2.20 M	4.20 M	-	-
C:	$\ominus 2 \times (0.280 \text{ M})$ $= 0.560 \text{ M}$	$\ominus 6 \times (0.280 \text{ M})$ $= 1.68 \text{ M}$	$\oplus 4 \times (0.280 \text{ M})$ $= 1.12 \text{ M}$	$\oplus 7 \times (0.280 \text{ M})$ $= 1.96 \text{ M}$
E:	<u>1.64 M</u>	<u>2.52 M</u>	<u>1.12 M</u>	<u>1.96 M</u>

$$\begin{aligned}
 (1) \quad [\text{N}_2\text{O}_4] \text{ reacted} &= [\text{O}_2] \text{ formed} \times (2 \text{ moles } \text{N}_2\text{O}_4 \div 7 \text{ moles } \text{O}_2) \\
 &= (1.96 \text{ M}) (2/7) \\
 &= 0.560 \text{ M}
 \end{aligned}$$

$$\therefore [\text{N}_2\text{O}_4] \text{ remained at equilibrium} = (2.20 \text{ M} - 0.560 \text{ M}) = \underline{\underline{1.64 \text{ M}}}$$

$$\begin{aligned}
 (2) \quad [\text{H}_2\text{O}] \text{ reacted} &= [\text{O}_2] \text{ formed} \times (6 \text{ mole } \text{H}_2\text{O} \div 7 \text{ moles } \text{O}_2) \\
 &= (1.96 \text{ M}) (6/7) \\
 &= 1.68 \text{ M}
 \end{aligned}$$

$$\therefore [\text{H}_2\text{O}] \text{ remained at equilibrium} = (4.20 \text{ M} - 1.68 \text{ M}) = \underline{\underline{2.52 \text{ M}}}$$

$$\begin{aligned}
 (3) \quad [\text{NH}_3] \text{ produced} &= [\text{O}_2] \text{ formed} \times (4 \text{ mole } \text{NH}_3 \div 7 \text{ moles } \text{O}_2) \\
 &= (1.96 \text{ M}) (4/7) \\
 &= \underline{\underline{1.12 \text{ M}}}
 \end{aligned}$$

PART B
QUESTION 10

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

In a 2.00 L container,

Initial: $\text{NH}_3(\text{g}) = 5.00 \text{ moles} \quad \therefore [\text{NH}_3] = (5.00 \text{ moles} \div 2.00 \text{ L}) = 2.50 \text{ M}$

At equilibrium: 30% of $\text{NH}_3(\text{g})$ dissociated

(i.e. $[\text{NH}_3] \text{ dissociated (changed)} = 2.50 \text{ M} \times 30\% = \mathbf{0.750 \text{ M}}$)

(a) the equilibrium concentrations of $\text{NH}_3(\text{g})$, $\text{N}_2(\text{g})$ and $\text{H}_2(\text{g})$

2 moles of $\text{NH}_3(\text{g})$ dissociates into 1 mole of $\text{N}_2(\text{g})$ and 3 moles of $\text{H}_2(\text{g})$

	$2 \text{ NH}_3(\text{g})$	\rightleftharpoons	$\text{N}_2(\text{g})$	+	$3 \text{ H}_2(\text{g})$
<i>I:</i>	2.50 M		-		-
<i>C:</i>	$\ominus 0.750 \text{ M}$		$\oplus \frac{1}{2} (0.750 \text{ M})$		$\oplus \frac{3}{2} (0.750 \text{ M})$
<i>E:</i>	<u>1.75 M</u>		<u>0.375 M</u>		<u>1.125 M</u>

$$\begin{aligned}
 \text{At equilibrium, } [\text{NH}_3] \text{ remained} &= (\text{initial } [\text{NH}_3] - [\text{NH}_3] \text{ dissociated}) \\
 &= (2.50 \text{ M} - 0.750 \text{ M}) \\
 &= \underline{\underline{1.75 \text{ M}}} \\
 \\
 [\text{N}_2] \text{ produced} &= ([\text{NH}_3] \text{ dissociated}) \times (1 \text{ mole N}_2 \div 2 \text{ moles NH}_3) \\
 &= (0.750 \text{ M}) (1/2) \\
 &= \underline{\underline{0.375 \text{ M}}} \\
 \\
 [\text{H}_2] \text{ produced} &= ([\text{NH}_3] \text{ dissociated}) \times (3 \text{ mole H}_2 \div 2 \text{ moles NH}_3) \\
 &= (0.750 \text{ M}) (3/2) \\
 &= \underline{\underline{1.125 \text{ M}}}
 \end{aligned}$$

(b) K_c of the reaction at 500 K

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

$$\begin{aligned}
 \text{At equilibrium, } [\text{NH}_3] &= 1.75 \text{ M} \\
 [\text{N}_2] &= 0.375 \text{ M} \\
 [\text{H}_2] &= 1.125 \text{ M}
 \end{aligned}$$

$$K_c = \frac{(0.375 \text{ M}) (1.125 \text{ M})^3}{(1.75 \text{ M})^2} = \underline{\underline{0.17435 \text{ M}^2}} = \underline{\underline{0.174 \text{ M}^2}}$$

PART D
QUESTION 1

$$\begin{aligned}
 \Delta T &= \text{freezing-point depression } (^\circ\text{C}) \\
 k_f &= \text{molal freezing-point depression constant } (^\circ\text{C kg mol}^{-1}) \\
 m &= \text{molality } (\text{mol kg}^{-1})
 \end{aligned}$$

$$\Delta T = k_f m$$

(a) 45.0 g sucrose $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ in 100 g water

$$M(\text{C}_{12}\text{H}_{22}\text{O}_{11}) = 342 \text{ g mol}^{-1}$$

$$n(\text{C}_{12}\text{H}_{22}\text{O}_{11}) = \text{mass}(\text{C}_{12}\text{H}_{22}\text{O}_{11}) \div M(\text{C}_{12}\text{H}_{22}\text{O}_{11}) = 45.0 \text{ g} \div 342 \text{ g mol}^{-1} = \underline{\underline{0.13158 \text{ mol}}}$$

$$m(\text{C}_{12}\text{H}_{22}\text{O}_{11}) = n(\text{C}_{12}\text{H}_{22}\text{O}_{11}) \div \text{mass}(\text{water}) = \underline{\underline{0.13158 \text{ mol}}} \div 100 \times 10^{-3} \text{ kg} = \underline{\underline{1.3158 \text{ mol kg}^{-1}}}$$

$$\Delta T = k_f m = (1.86^\circ\text{C kg mol}^{-1}) \times (\underline{\underline{1.3158 \text{ mol kg}^{-1}}}) = \underline{\underline{2.4474^\circ\text{C}}}$$

\therefore Freezing point of 45.0 g sucrose $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ in 100 g water is -2.45°C.

(b) 0.100 mol FeCl₃ in 1 kg water

FeCl₃ dissociates into *four ions* per formula unit.

$$n(\text{FeCl}_3) = 0.100 \text{ mol}$$

$$n(\text{ions}) = n(\text{FeCl}_3) \times (4 \text{ moles ions} \div 1 \text{ mole FeCl}_3) = (0.100 \text{ mol}) \times (4) = 0.400 \text{ mol}$$

$$m(\text{ions}) = n(\text{ions}) \div \text{mass}(\text{water}) = (0.400 \text{ mol}) \div (1 \text{ kg water}) = 0.400 \text{ mol kg}^{-1}$$

$$\Delta T = k_f m = (1.86^\circ\text{C kg mol}^{-1}) \times (0.400 \text{ mol kg}^{-1}) = 0.744^\circ\text{C}$$

\therefore Freezing point of 0.100 mol FeCl₃ in 1 kg water is **-0.744°C**.

(c) 0.0200 mol BaCl₂·2H₂O dissolved in 52.2 g water

BaCl₂ dissociates into *three ions* per formula unit.

$$n(\text{ions}) = n(\text{BaCl}_2) \times (3 \text{ moles ions} \div 1 \text{ mole BaCl}_2) = (0.0200 \text{ mol}) \times (3) = 0.0600 \text{ mol}$$

$$n(\text{H}_2\text{O}) = n(\text{BaCl}_2 \cdot 2\text{H}_2\text{O}) \times (2 \text{ moles H}_2\text{O} \div 1 \text{ mole BaCl}_2 \cdot 2\text{H}_2\text{O}) = (0.0200 \text{ mol}) \times (2)$$

$$\text{mass}(\text{H}_2\text{O}) = (0.0200 \text{ mol} \times 2) \times (18.02 \text{ g mol}^{-1}) = 0.7208 \text{ g}$$

$$\text{total mass}(\text{H}_2\text{O}) = 52.2 \text{ g} + 0.7208 \text{ g} = 52.9208 \text{ g} = 52.9208 \times 10^{-3} \text{ kg}$$

$$\begin{aligned} m(\text{ions}) &= n(\text{ions}) \div \text{total mass}(\text{water}) \\ &= (0.0600 \text{ mol}) \div (52.9208 \times 10^{-3} \text{ kg}) \\ &= 1.13377 \text{ mol kg}^{-1} \end{aligned}$$

$$\Delta T = k_f m = (1.86^\circ\text{C kg mol}^{-1}) \times (1.13377 \text{ mol kg}^{-1}) = 2.1088^\circ\text{C}$$

\therefore Freezing point of 0.0200 mol BaCl₂·2H₂O dissolved in 52.2 g water is **-2.11°C**.

**PART D
QUESTION 2**

Given: 500 g (500×10^{-3} kg) of water
freezing point = -2.14°C (*i.e.* $\Delta T = 2.14^\circ\text{C}$)

To find: mass of CaCl₂ required

$$\begin{aligned} \Delta T &= \text{freezing-point depression } (^{\circ}\text{C}) \\ k_f &= \text{molal freezing-point depression constant } (^{\circ}\text{C kg mol}^{-1}) \\ m &= \text{molality } (\text{mol kg}^{-1}) \end{aligned}$$

$$\Delta T = k_f m$$

Let $x = n(\text{CaCl}_2)$

CaCl_2 dissociates into *three ions* per formula unit.

$$n(\text{ions}) = n(\text{CaCl}_2) \times (3 \text{ moles ions} \div 1 \text{ mole CaCl}_2) = 3x$$

$$\begin{aligned} m(\text{ions}) &= n(\text{ions}) \div \text{mass}(\text{water}) \\ &= (3x) \div (500 \times 10^{-3} \text{ kg}) \\ &= \underline{6.00x} \text{ kg}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta T &= k_f m \\ 2.14^{\circ}\text{C} &= (1.86^{\circ}\text{C kg mol}^{-1}) \times (\underline{6.00x} \text{ kg}^{-1}) \\ x &= \underline{0.19175} \text{ mol} = n(\text{CaCl}_2) \end{aligned}$$

$$M(\text{CaCl}_2) = [40.08 + 2(35.453)] \text{ g mol}^{-1} = 110.986 \text{ g mol}^{-1}$$

$$\begin{aligned} \therefore \text{mass of CaCl}_2 \text{ required} &= n(\text{CaCl}_2) \times M(\text{CaCl}_2) \\ &= (0.19175 \text{ mol}) (110.986 \text{ g mol}^{-1}) \\ &= \underline{21.281} \text{ g} \\ &= \underline{\underline{21.3}} \text{ g} \end{aligned}$$

PART D QUESTION 3

Given: osmotic pressure (π) = 7.6 atm
 $T = 37^{\circ}\text{C} = (273 + 37) \text{ K} = 310 \text{ K}$
 $R = 0.0821 \text{ atm L K}^{-1} \text{ mol}^{-1}$

To find: the concentration of NaCl solution in mol L^{-1}

$$\pi = c R T$$

π = osmotic pressure (atm)
 c = molar concentration (mol L⁻¹)
 R = 0.0821 L atm K⁻¹ mol⁻¹
 T = absolute temperature (K)

$$\begin{aligned}
 \pi &= c(\text{ions}) R T \\
 7.6 \text{ atm} &= c(\text{ions}) (0.0821 \text{ atm L mol}^{-1} \text{ K}^{-1}) (310 \text{ K}) \\
 c(\text{ions}) &= \underline{0.2986 \text{ mol L}^{-1}}
 \end{aligned}$$

NaCl dissociates into *two ions* (Na⁺ and Cl⁻) per formula unit.

$$\begin{aligned}
 \therefore c(\text{NaCl}) &= c(\text{ions}) \times (1 \text{ mole NaCl} \div 2 \text{ moles ions}) \\
 &= (0.2986 \text{ mol L}^{-1}) (\frac{1}{2}) \\
 &= \underline{0.1493 \text{ mol L}^{-1}} \\
 &= \underline{\underline{0.15 \text{ mol L}^{-1}}}
 \end{aligned}$$

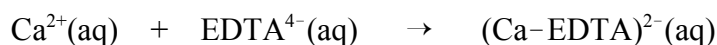
PART D QUESTION 4

Given: 50.00 mL water sample
 0.01346 mol L⁻¹ EDTA
 22.65 mL of EDTA to reach the Eriochrome Black indicator endpoint

To find: hardness of water as expressed in:

- (a) mol L⁻¹ of Ca²⁺
- (b) ppm of Ca²⁺

Assume the Ca²⁺ is the only cation that will be titrated against EDTA⁴⁻. The reaction is:



$$\begin{aligned}
 n(\text{EDTA}^{4-}) &= c(\text{EDTA}^{4-}) \times V(\text{EDTA}^{4-}) \\
 &= (0.01346 \text{ mol L}^{-1}) \times (22.65 \times 10^{-3} \text{ L}) \\
 &= \underline{3.0486 \times 10^{-4} \text{ mol}}
 \end{aligned}$$

1 mole of $\text{Ca}^{2+}(\text{aq})$ reacts with 1 mole of $\text{EDTA}^{4-}(\text{aq})$

$$\begin{aligned}n(\text{Ca}^{2+}) &= n(\text{EDTA}^{4-}) \times (1 \text{ mole Ca}^{2+} \div 1 \text{ mole EDTA}^{4-}) \\&= (3.0486 \times 10^{-4} \text{ mol}) (1) \\&= \underline{3.0486 \times 10^{-4} \text{ mol}}\end{aligned}$$

$$\begin{aligned}\text{(a) } c(\text{Ca}^{2+}) \text{ in } \underline{\text{mol L}^{-1}} &= n(\text{Ca}^{2+}) \div V(\text{Ca}^{2+} \text{ present in water sample}) \\&= (3.0486 \times 10^{-4} \text{ mol}) \div (50.00 \times 10^{-3} \text{ L}) \\&= \underline{6.09738 \times 10^{-3} \text{ mol L}^{-1}} \\&= \underline{\underline{6.097 \times 10^{-3} \text{ mol L}^{-1}}}\end{aligned}$$

$$M(\text{Ca}^{2+}) = 40.08 \text{ g mol}^{-1} = 40.08 \times 10^3 \text{ mg mol}^{-1}$$

$1 \text{ ppm} = 1 \text{ mg L}^{-1}$

$$\begin{aligned}\text{(b) } c(\text{Ca}^{2+}) \text{ in } \underline{\text{ppm}} &= (6.09738 \times 10^{-3} \text{ mol L}^{-1}) \times (40.08 \times 10^3 \text{ mg mol}^{-1}) \\&= \underline{244.38 \text{ mg L}^{-1}} \\&= \underline{\underline{244.4 \text{ ppm}}}\end{aligned}$$