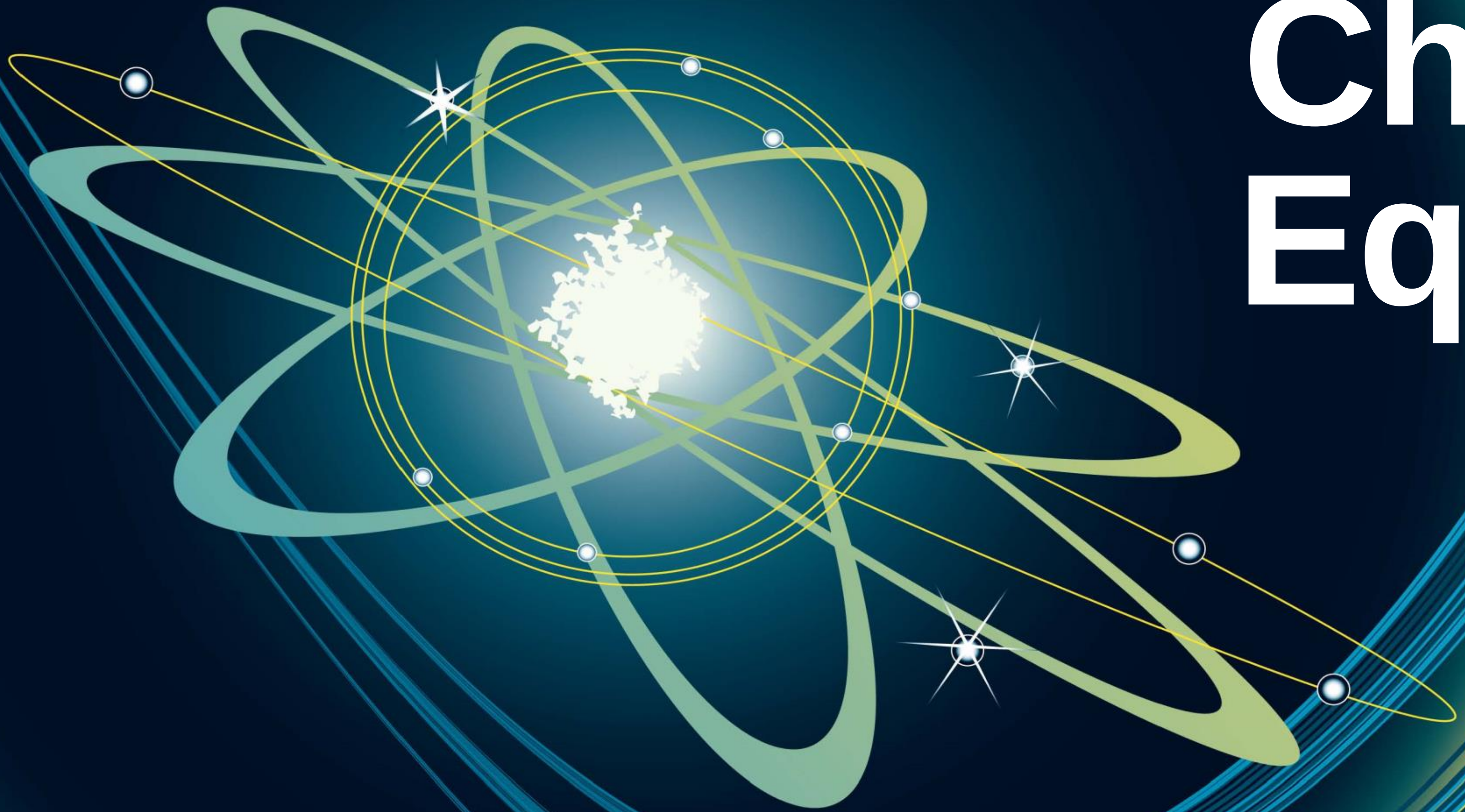
Chapter 9

Chemical Equilibria



CHAPTER ANALYSIS

This is not Equilibrium?

FOCUS

- Relatively straight forward chapter
- 4 **key** concepts

EXAM

- Always tested
- The foundations for all equilibrium constant chapters

WEIGHTAGE

- Usually incorporated into other chapters

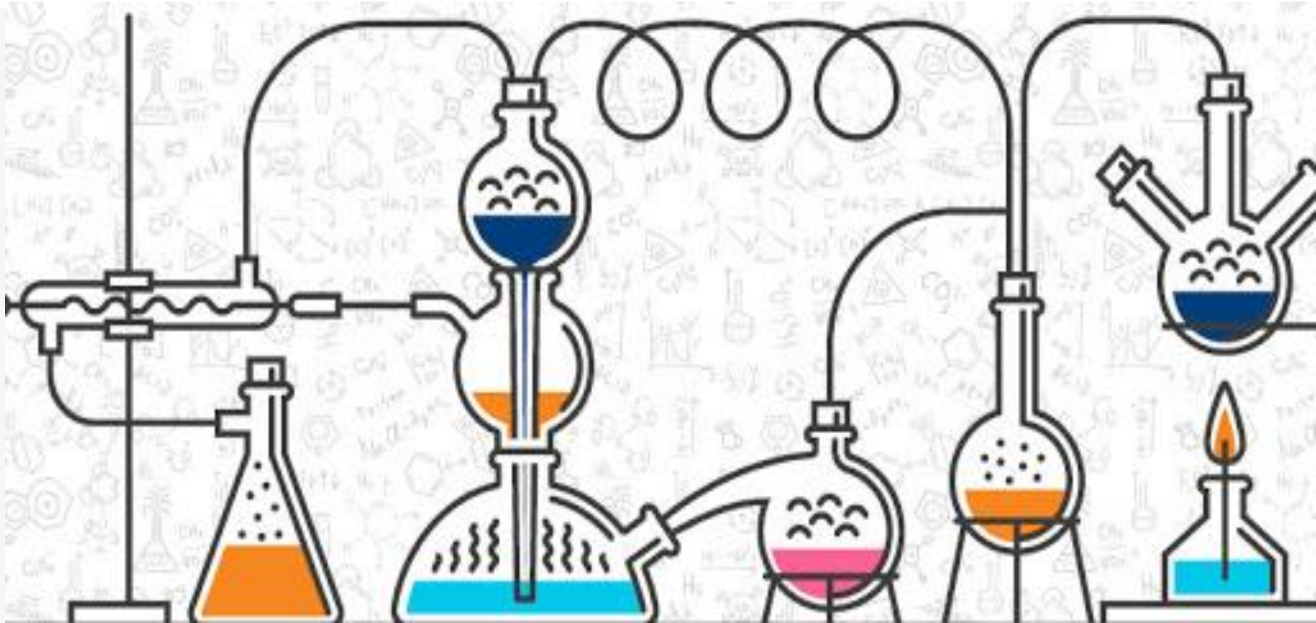
KEY CONCEPT

Dynamic Equilibrium & Equilibrium Constants

Calculations involving Equilibrium Constant (I.C.E Table)

Le Chatelier’s Principle (LCP)

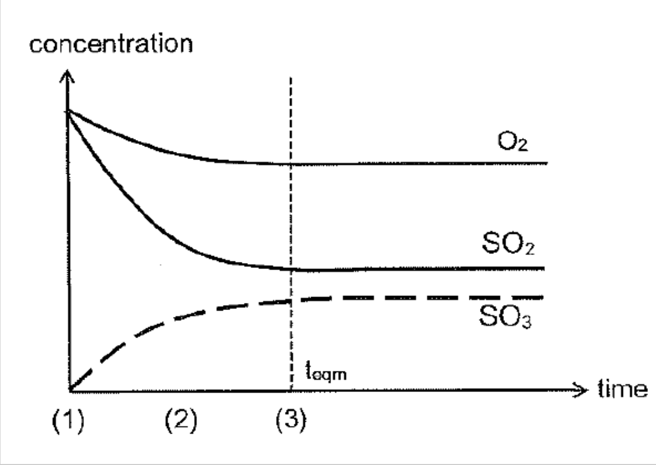
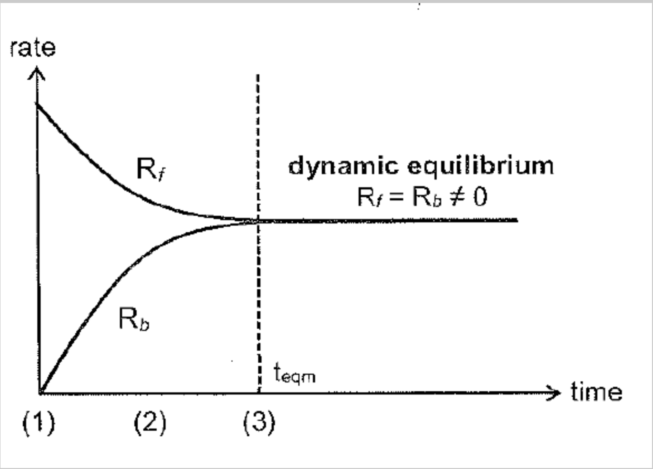
Applications of LCP – Haber Process



Dynamic Equilibrium & Equilibrium Constants

DYNAMIC EQUILIBRIUM

- It occurs when the **forward and backward reactions** are occurring at the **same rate**.
- Only in a closed system
- Concentrations of reactants and products are constant under a given conditions of temperature, pressure and initial amount of substance.
- Rate ≠ 0

Concentration against Time	**Rate against Time**
	
(1) : At the start when time = 0	(1) : At the start there is only $[SO_2]$ and $[O_2]$ hence only the forward reaction occurs. $Rate_f = k_f[SO_2][O_2]$ *Note: There is no $[SO_3]$ hence $Rate_b = 0$* *$Rate_b = k_b[SO_3]$*
(2) : As reaction proceed, $[SO_2]$ and $[O_2]$ starts to decrease as reaction takes place. $[SO_3]$ increases as products are formed. *Note: As $[SO_3]$ is formed, backward reaction is also occurring at this point.*	(2) : As reaction proceed, $[SO_2]$ and $[O_2]$ starts to decrease hence R_f decreases. $[SO_3]$ increases as products are formed and thus R_b increases *Note: Rate $\propto$ [reactants/products]*
(3) : At t_{eqm}, dynamic equilibrium is reached and $[SO_2]$, $[O_2]$ and $[SO_3]$ remain constant.	(3) : At t_{eqm}, dynamic equilibrium is reached, $R_f = R_b \neq 0$

Dynamic Equilibrium & Equilibrium Constants

$$aA + bB \rightleftharpoons cC + dD$$

EQUILIBRIUM CONSTANTS, K_c

$$K_c = \frac{[C]^c_{eqm}[D]^d_{eqm}}{[A]^a_{eqm}[B]^b_{eqm}}$$

- Units = $(\text{mol dm}^{-3})^{c+d-a-b}$
- Concentration of Water/Solvent, Excess Liquids, Solids and Immiscible Liquids are excluded from the equilibrium expression
- *Note: K_c* ***is only*** *affected by* ***temperature changes***

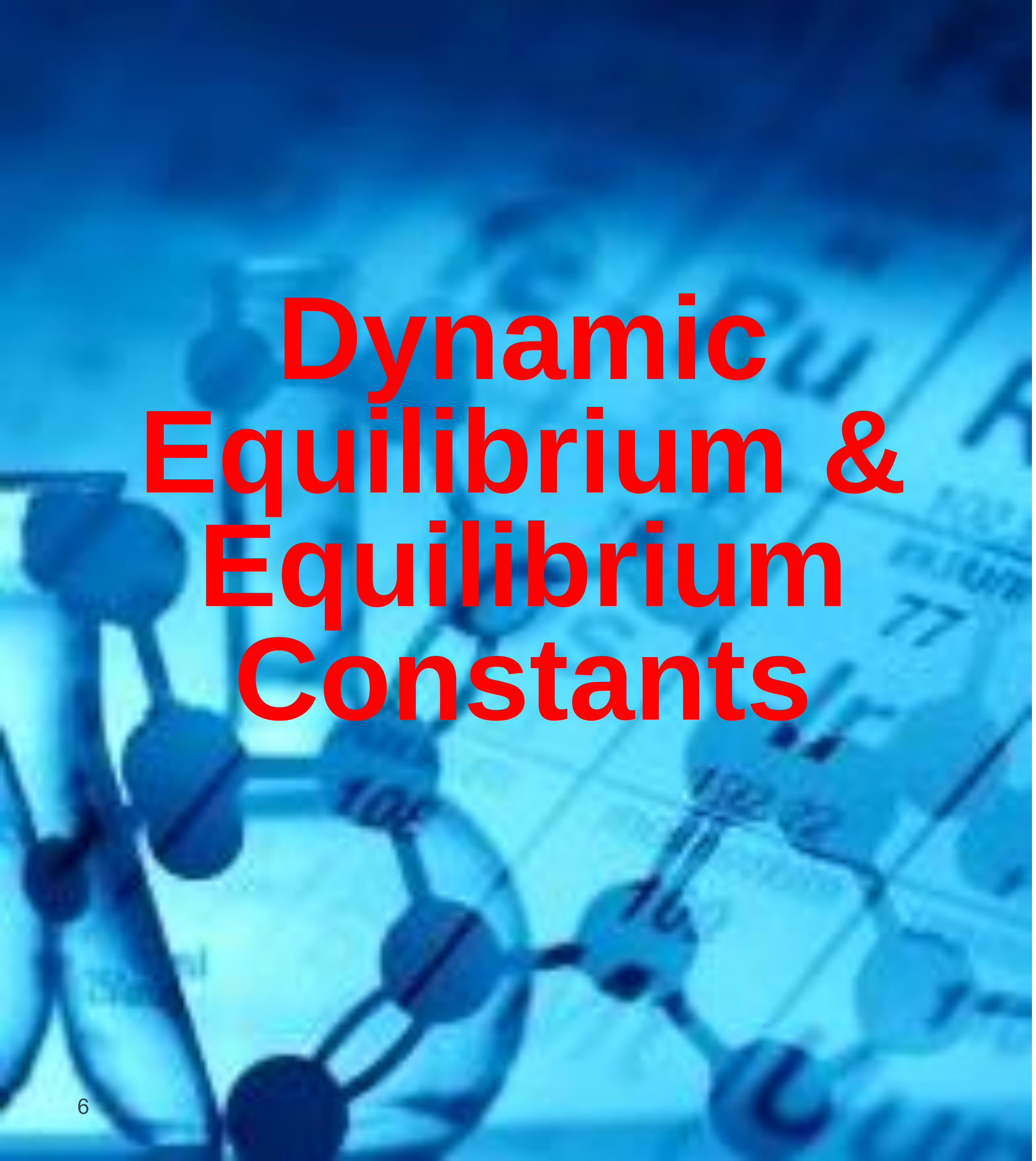
EQUILIBRIUM CONSTANTS, K_p

$$K_p = \frac{{P_C}^c_{eqm}{P_D}^d_{eqm}}{{P_A}^a_{eqm}{P_B}^b_{eqm}}$$

- Units = $(\text{Pa or atm})^{c+d-a-b}$
- It only takes into account the partial pressure of **gases**
- *Note: K_p* ***is only*** *affected by* ***temperature changes***

Note: $P_A = \frac{n_A}{n_{total}} \times P_{total}$

Dynamic Equilibrium & Equilibrium Constants



Linking K_c with rate constant (Chapter 8: Reaction Kinetics)

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

$R_f = k_f[N_2O_4]$ **;** $R_b = k_b[NO_2]^2$

At equilibrium, $R_f = R_b = k_f[N_2O_4] = k_b[NO_2]^2$

Using K_c

$$K_c = \frac{[NO_2]^2}{N_2O_4} = \frac{k_f}{k_b}$$

Linking K_c with ΔG (Chapter 7: Chemical Energetics)

- $\Delta G = -RT\ln(K_c)$
- K_c indicates the extent of reaction at equilibrium
- If K_c is large, [products] >> [reactants], and the forward reaction is almost complete, hence indicating the forward reaction is more favoured and is more spontaneous ($\Delta G<0$)

Calculations involving Equilibrium Constant (I.C.E Table)

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

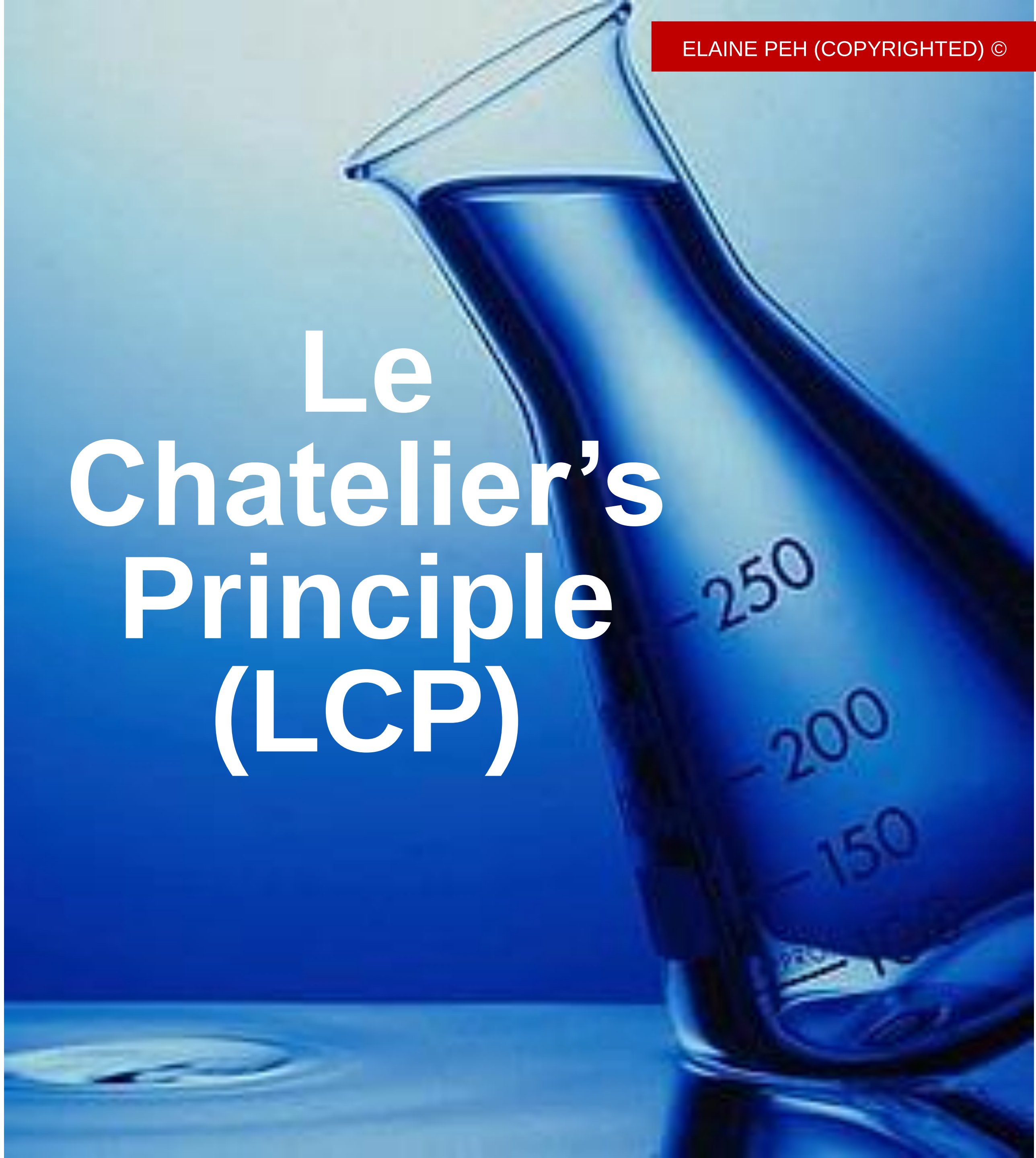
		2A	B	2C	D
I	Initial no. of mols				
C	Change (loss/gain)				
E	Eqm no. of mols				

Step 1: Write out the equation to get the mol ratio and draw out the I.C.E Table

Step 2: Fill in the information you have form the question in the I.C.E Table

Step 3: Based on the mol ratio, calculate the change for the other reactants

Step 4: Fill up the remaining information in the I.C.E Table



Le Chatelier's Principle (LCP)

POSITION OF EQUILIBRIUM (POE)

POE refers to the **relative proportion** of **products to reactants** in an **equilibrium** mixture.

LE CHATELIER'S PRINCIPLE (LCP)

LCP states that when a **system is in equilibrium** is subjected to a **change in conditions that disturb the equilibrium**, the POE **shifts in a way to reduce that change** to re-establish the equilibrium.

How to answer questions using LCP

1) *What is the immediate effect due to the disturbance*
2) *What is the counteract response to the disturbance*
3) *Direction of the shift of POE in response to the disturbance and explanation (4) Effect of the shift of POE*

Note: Addition of a catalyst will not have an impact on the POE and K_c *as it speed up both the forward and backward reaction by the same extent.*

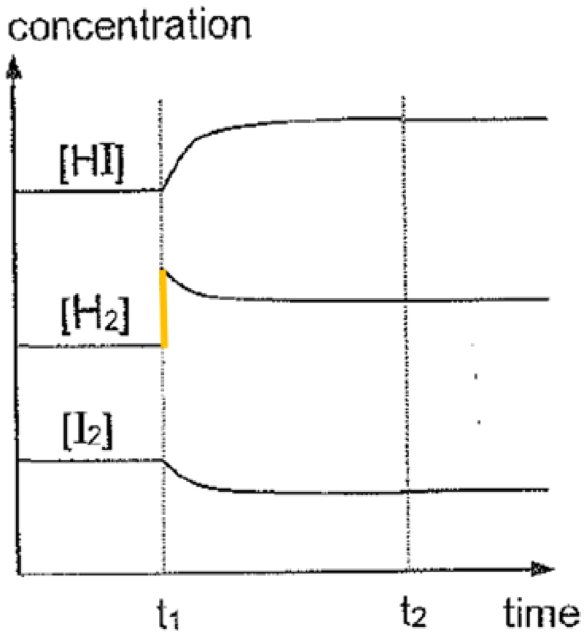
Factors Affecting LCP

FACTOR 1: Change in concentration or partial pressure of the reactants/products

- The concentration/partial pressure of the reactants/products can be changed by a direct addition/removal of the reactants/products at constant volume.
- An **increase** in concentration/partial pressure of the molecule favours the reaction that **uses up** the molecule
- A **decrease** in concentration/partial pressure of the molecule favours the reaction that **produce** the molecule

H_2 (g) + I_2 (g) ⇌ 2HI (g)

colourless purple colourless



When H_2 (g) is added at **constant volume** at t_1:

(1) Immediate Effect: $[H_2]/P_{H_2}$ increase

(2) Counteract Response: System will want to reduce $[H_2]/P_{H_2}$

(3) Direction of the shift of POE: POE shift to the right to remove H_2

(4) Effect of the shift: Therefore $[HI]/P_{HI}$ increase and the colour intensity of the mixture decrease (from t_1 to t_2). A new equilibrium is achieved at t_2, but K_c remains unchanged.

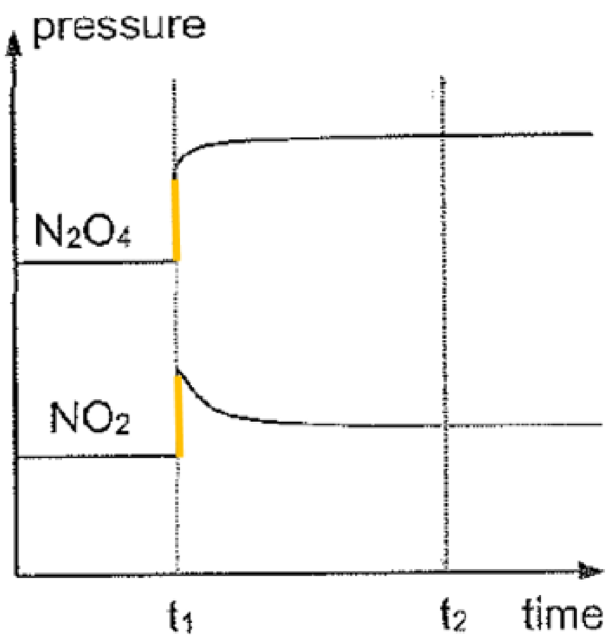
Factors Affecting LCP

FACTOR 2: Change in total pressure (only for a gaseous system)

- The total pressure of the system can be changed by (1) changing the volume of the container or (2) by adding an inert gas into the container of fixed volume.
- An **increase** in total pressure of the system favours the reaction that **decreases** the number of **gaseous molecule**
- A **decrease** in total pressure of the system favours the reaction that **increases** the number of **gaseous molecule**

Note: This only applies to gaseous system with different number of total moles of reactants and products.

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



When the **volume of the system decreases** at t_1:

(1) Immediate Effect: Total pressure, P_{NO2} and P_{N2O4} increase

(2) Counteract Response: System will want to reduce the pressure

(3) Direction of the shift of POE: POE shift to the right to decrease the total pressure as the forward reaction involves a decrease in the total number of gas molecules (from 2 mol to 1 mol)

(4) Effect of the shift: Therefore $[N_2O_4]/P_{N2O4}$ increases (from t_1 to t_2). A new equilibrium is achieved at t_2, but K_p remains unchanged.

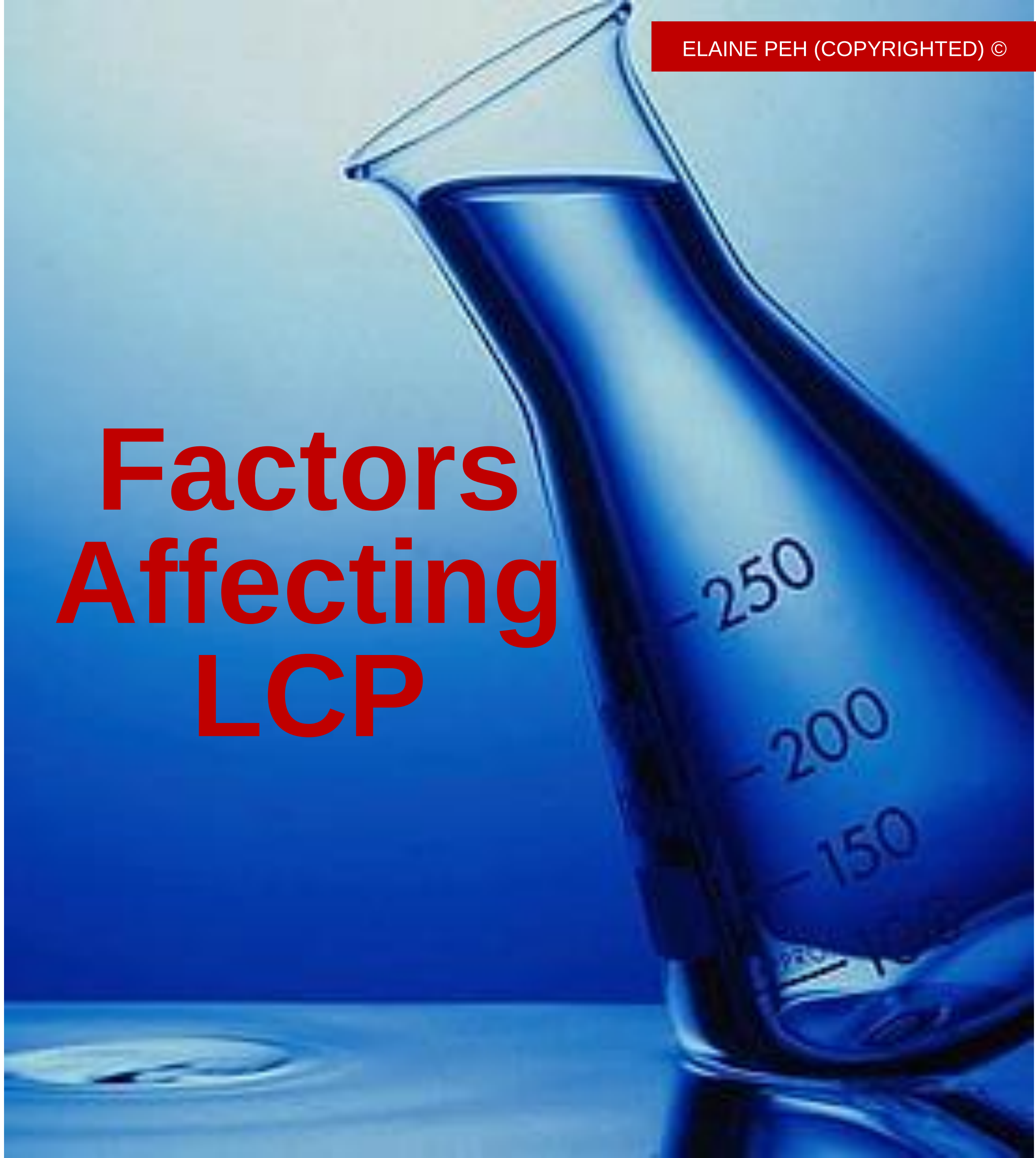
FACTOR 2: Change in total pressure (only for a gaseous system)

- When an **inert gas is added at constant volume**:

(1) Immediate Effect: Total pressure of the system increase. However P_{NO2} and P_{N2O4} remained the same due to a corresponding decrease in mole fraction of the gas.
(2-4) Counteract Response: The system is not disturbed and the POE remains unchanged.

- When an **inert gas is added at constant pressure**:

(1) Immediate Effect: P_{NO2} and P_{N2O4} decrease
(2) System will want to increase the pressure
(3) Direction of the shift of POE: POE shift to the left to increase the total pressure as the forward reaction involves an increase in the total number of gas molecules (from 1 mol to 2 mol)
(4) Effect of the shift: Therefore P_{NO2} increase and a new equilibrium is achieved.



Factors Affecting LCP

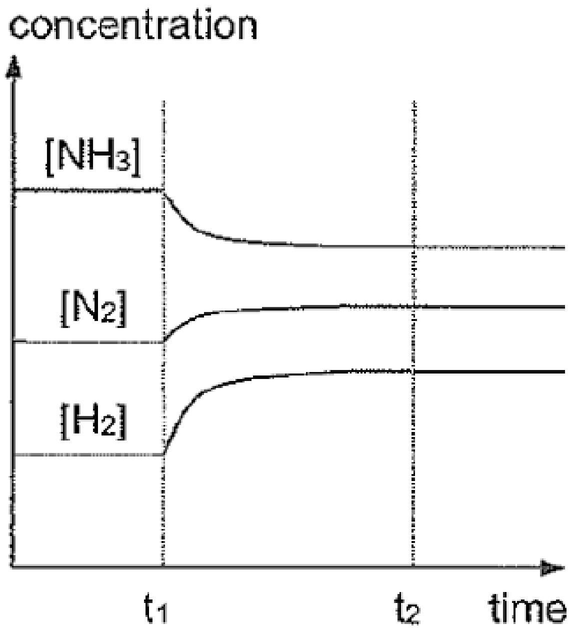
Factors Affecting LCP

FACTOR 3: Change in Temperature

- An **increase** in temperature favours the **endothermic reaction** to **absorb** the heat added.
- A **decrease** in temperature favours the **exothermic reaction** to **produce** heat that was loss.
- *Note: Unlike the previous two factors, a change in temperature will result in a change in K_c. Favouring the forward reaction increase K_c while favouring the backward reaction decrease the K_c*

*Note: Unlike the previous two factors, a change in temperature does not result in an **immediate change** in the concentration or pressure of the reactants/products. The concentration only changes after some time as the system reacts to the change in temperature.*

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



When **heat is added** at t_1::

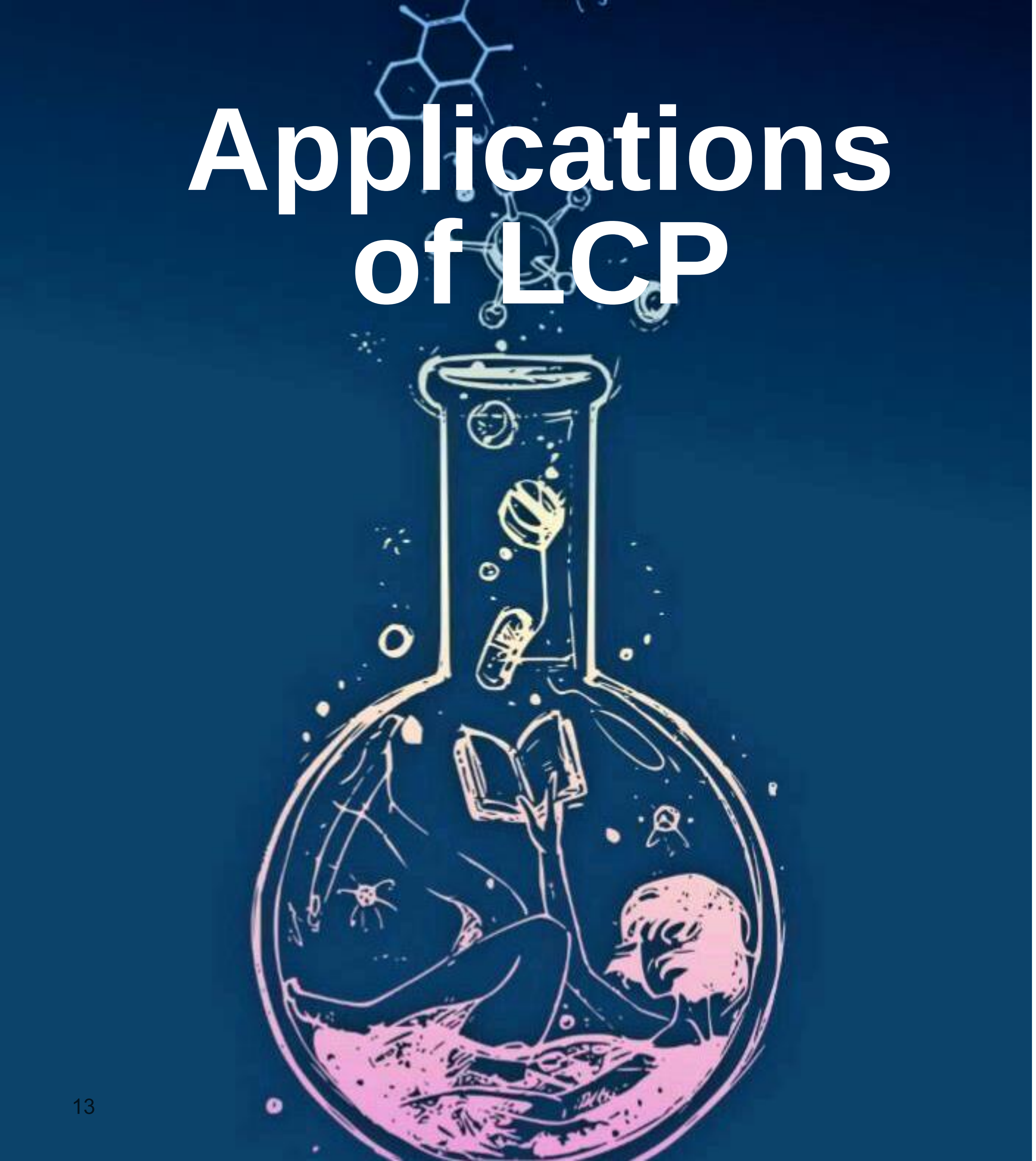
(1) Immediate Effect: Temperature increases

(2) Counteract Response: System will want to absorb the heat added

(3) Direction of the shift of POE: POE shift to the left to absorb the heat added as the backward reaction is endothermic

(4) Effect of the shift: Therefore $[N_2]$ and $[H_2]$ increase while $[NH_3]$ decreases (from t_1 to t_2). A new equilibrium is achieved at t_2, and K_c decreases.

Applications of LCP



APPLICATIONS OF LCP

To design an efficient procedure, 3 most important factors to consider are:

1. Rate of reaction: faster the better
2. Yield of product: higher the percentage yield the better
3. Economic Cost: minimise the production cost

COMMONLY TEST EXAMPLE: HABER PROCESS

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

According to LCP, **high pressure** favours a high yield of NH_3 as the **POE shifts to the right** to reduce the total number of gaseous molecules – However a **very high pressure** used will incur **high maintenance and operating cost**

According to LCP, **low temperature** favours a high yield of NH_3 as the **POE shifts to the right** to produce heat – However a **low temperature** will result in a **slower rate of reaction**

Therefore by taking into consideration all 3 factors and LCP, the optimum conditions used for Haber Process are **200 atm**, **450^{o}C** and **iron catalyst**.

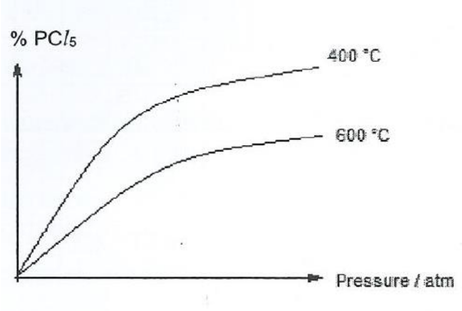
- 200 atm: enable a high yield (high K_c)
- 450^{o}C and iron catalyst: enable reaction to occur at a faster speed (high k)

Practice Questions

Question: When 4 mol of nitrogen dioxide were put into a 2 dm^3 container and heated, the equilibrium mixture contained 0.8 mol of oxygen. Determine the value of K_c for this reaction and state its unit.
Answer: 0.178 mol dm^{-3}

Question: At 1000K and 1 total pressure of 1 atm, N_2O_4 is 50% dissociated into NO_2. Calculate K_p at this temperature and state its unit.
Ans: 1.33 atm

Question: PCl_5 is formed through the reaction between PCl_3 and Cl_2. The figure below shows how the percentage of PCl_5 (g) in the vessel varies with pressure at 400^{o}C and 600^{o}C respectively:By using LCP, explain if the reaction is exothermic or endothermic.



Answer: Reaction is exothermic.

Practice Questions

Question: One molecule of haemoglobin can bind up to four molecules of oxygen to form one molecule of oxyhaemoglobin.

i. Experiment have shown that when $[O_2] = 7.6 \times 10^{-6}$ mol dm^{-3}. The concentration of haemoglobin and oxyhaemoglobin are equal. Use this information to calculate a value of K_c.
ii. Using your value calculated, calculate the $[O_2]$ necessary for 99% of the haemoglobin to be converted to oxyhaemoglobin.
iii. Myoglobin has a higher affinity for oxygen as compared to haemoglobin, it binds to oxygen to form oxymyoglobin. However unlike haemoglobin, it only binds to one oxygen molecule for each myoglobin molecule. Given that the K_c for this reaction is, calculate the percentage of oxymyoglobin when $[O_2] = 7.6 \times 10^{-6}$ mol dm^{-3}.

Ans:

i. 3×10^{20} *mol*$^{-4}$ *dm*^{12}
ii. 2.4×10^{-5} *mo*^{4} *dm*$^{-3}$
iii. *88.4%*

Question: State and explain how the composition of the equilibrium mixture will change when O_2 is added to the equilibrium mixture in a container of fixed volume and the effect on K_c?

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

Answer: Equilibrium mixture will have more SO_3 *and less* SO_2. K_c *will not change.*

Question: State and explain how the composition of the equilibrium mixture will change when the volume of the container decreases, and the effect on K_p?

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

Answer: Equilibrium mixture will have more SO_3 *and lesser* SO_2 *and* O_2. K_p *will not change.*

Practice Questions

Question: State and explain how the composition of the equilibrium mixture will change when the volume of the container decreases, and the effect on K_p?
N_2 (g) + O_2 (g) $\rightleftharpoons$ 2NO (g)
Answer: Both the equilibrium mixture and K_p will not change.

Question: State and explain how the composition of the equilibrium mixture will change when the temperature decreases, and the effect on K_c?
$2SO_2$ (g) + O_2 $\rightleftharpoons$ $2SO_3$ (g), $\Delta H = -198.4$ kJ mol^{-1}
Answer: Equilibrium mixture will have more SO_3 and lesser SO_2 and O_2. K_c will increase.

Question: If 2 mol of SO_2 and 2 mol of O_2 were mixed and allowed to reach equilibrium, what must be the total pressure be to obtain 20% conversion of SO_2?
The value of $K_p = 0.13$ atm^{-1} at 2481K.
Ans: 1.02 atm

Question: When 1g of GDL ($M_r = 178$) was dissolved in 50 cm^3 of water and the solution allowed to reach equilibrium, the concertation of the product formed (gluconic acid) was found to be 0.067 mol dm^{-3}. Assuming $[H_2O] = 55.5$ mol dm^{-3} throughout the experiment, calculate the K_c.
Ans: 0.0266 mol^{-1} dm^3

Test yourself!

(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 concentration, pressure or temperature, on a system at equilibrium

(c) deduce whether changes in concentration, pressure or temperature 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, *Kc*, and partial pressures, *Kp* [treatment of the relationship between *Kp* and *Kc* is **not** required]

Test yourself!

(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) show understanding that the position of equilibrium is dependent on the standard Gibbs free energy change of reaction, ΔG [Quantitative treatment is **not** required]

(h) describe and explain the conditions used in the Haber process, as an example of the importance of an understanding of chemical equilibrium in the chemical industry

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