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# CHEMISTRY 

## REVISION NOTES

## EQUILIBRIA -1

## Equilibria

Reversible reactions tend to reach a state of dynamic equilibrium.

## Features of dynamic Equilibrium:

- Forward and reverse reactions proceed at equal rates.
- Concentrations of reactants and products remain constant.
- Dynamic equilibrium is established in a closed system.


## Position of equilibrium:

The term 'position of equilibrium' is used to describe the composition of the equilibrium mixture. If the position of equilibrium favors the reactants (also referred to as "towards the left"), then the equilibrium mixture will mainly contain reactants.

## Le - Chatelier's Principle:

If the conditions of a dynamic equilibrium are altered, the equilibrium shifts to offset the change.

## Effect of Temperature on Equilibrium

If the temperature is increased, the equilibrium will shift to oppose the change and move towards the endothermic direction in an attempt to absorb heat and reduce the temperature and reversely,

If the temperature decreases, the system will shift towards the exothermic direction to release heat and increase the temperature.

## What effect would increasing temperature have on the production of Carbon dioxide?

$$
\mathrm{CO}_{2}(\mathrm{~g})+3 \mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{CO}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \quad \Delta \mathrm{H}=-42 \mathrm{kj} / \mathrm{mol}
$$

If the temperature is increased, the equilibrium will shift towards the endothermic, backward direction to decrease temperature. This will result in the position of equilibrium shifting towards the left, leading to a lower yield of carbon dioxide.

## Effect of Pressure on Equilibrium

With an increase in pressure, the equilibrium shifts to the side of the reaction with fewer moles of gas. This shift reduces the pressure as fewer gas molecules occupy the system. Therefore, the reaction will favor the side with fewer gas moles to maintain equilibrium.

```
What effect would increasing temperature have on the production of Carbon dioxide?
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$$
\mathrm{CO}(\mathrm{~g})+2 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{OH}_{(\mathrm{g})}
$$

If pressure is increased, the equilibrium will shift to oppose this and move towards the side with fewer moles of gas to try to reduce the pressure. The position of equilibrium will shift towards the right because there are 3 moles of gas on the left but only 1 mole of gas on the right, giving a higher yield of methanol.

If the number of moles of gas is the same on both sides of the equation, then changing pressure will have no effect on the position of the equilibrium.

$$
\mathrm{CO}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) \rightleftharpoons \mathrm{CO}_{2}(\mathrm{~g})+\mathrm{H}_{2}(\mathrm{~g})
$$

## - Industrial conditions

Applying more pressure during a chemical reaction can result in a greater amount of product and a quicker rate of reaction. However, in an industrial setting, generating high pressures can be costly due to the high electrical energy required to pump gases and maintain the high pressure. Additionally, equipment designed to contain high pressures is expensive.

## Effect of Concentration on Equilibrium

An increase in reactant concentration will shift equilibrium towards products, while decreasing concentration will shift towards reactants.


## Effect of Catalysts on Equilibrium

A catalyst does not affect the position of equilibrium. However, it can accelerate the rate at which the equilibrium is reached. This happens because it speeds up both the forward and backward reactions by the same amount.

## Industrial process involving Le - Chateliers principle

Haber Process
$\mathrm{N}_{2}+3 \mathrm{H}_{2} \rightleftharpoons 2 \mathrm{NH}_{3} \mathrm{H}=$-ve exo
$\mathrm{T}=450^{\circ} \mathrm{C}, \mathrm{P}=200-1000 \mathrm{~atm}$, catalyst = iron

Using lower temperatures results in a higher yield but a slower reaction rate, so a compromise temperature should be used.

High pressure yields good results, but excessive pressure increases energy
costs for pumps.

## Contact Process

```
Stage 1 S (s)+ O
Stage 2 SO2 (g) + +/2 O
T=450}\mp@subsup{}{}{\circ}\textrm{C
P= 1 or 2 atm,
Catalyst = V }\mp@subsup{\textrm{V}}{2}{}\mp@subsup{\textrm{O}}{5}{
Lower temperature may result in a better yield, the reaction rate will be slower.
Therefore, it is recommended to use a moderate temperature as a compromise
between yield and reaction rate
High pressure only gives slightly better yield and high rate: too high a pressure
would lead to too high energy costs for pumps to produce the pressure
```


## EXAM QUESTIONS

$$
2 \mathrm{SO}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{SO}_{3}(\mathrm{~g})
$$

State and explain the effect, if any, of a decrease in overall pressure on the equilibrium yield of $\mathrm{SO}_{3}$

Effect $\qquad$
Explanation $\qquad$
$\qquad$

Hydrogen can be prepared on an industrial scale using the reversible reaction between methane and steam.

$$
\mathrm{CH}_{4}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) \rightleftharpoons \mathrm{CO}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \quad \Delta H=+206 \mathrm{~kJ} \mathrm{~mol}^{-1}
$$

The reaction is done at a temperature of $800^{\circ} \mathrm{C}$ and a low pressure of 300 kPa in the presence of a nickel catalyst.

Explain, in terms of equilibrium yield and cost, why these conditions are used.

Methanol can be manufactured in a reversible reaction as shown by the equation.

$$
\mathrm{CO}(\mathrm{~g})+2 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{OH}(\mathrm{~g})
$$

(a) State and explain the effect of using a catalyst on the yield of methanol in this equilibrium.

## Equilibrium Constant (Kc)

The equilibrium constant $(\mathrm{Kc})$ is a numerical value that expresses the ratio of product concentrations to reactant concentrations at a state of dynamic equilibrium for a chemical reaction.

## General Form:

- For a generic reaction: $\mathrm{aA}+\mathrm{bB} \rightleftharpoons \mathrm{cC}+\mathrm{dD}$
- The equilibrium constant expression (Kc) is written as follows:

$$
K c=[C]^{c}[D]^{d} /[A]^{a}[B]^{b}
$$

## Key Points:

- Kc Expression:

The expression is always written in terms of the concentrations of products over reactants, with each concentration raised to the power of its coefficient in the balanced chemical equation.

- Units of Kc:

The units of Kc depend on the specific reaction and are determined by the powers to which the concentrations are raised. Kc has no units if concentrations are in moles per liter ( $\mathrm{mol} / \mathrm{L}$ ).

- Magnitude of Kc:

If $K c \gg 1$, it indicates that the reaction strongly favors the formation of products at equilibrium.

If $\mathrm{Kc} \ll 1$, the reaction strongly favors the reactants at equilibrium.
If $K c \approx 1$, it suggests a relatively even mixture of products and reactants equilibrium.

## Example

Suppose you have a reaction vessel where 0.050 moles of $\mathrm{N}_{2} \mathrm{O}_{4}$ and 0.010 moles of $\mathrm{NO}_{2}$ are initially placed in a $0.5 \mathrm{dm}^{3}$ container. At equilibrium, you measure that there are 0.020 moles of $\mathrm{N}_{2} \mathrm{O}_{4}$ and 0.040 moles of $\mathrm{NO}_{2}$.

$$
\mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NO}_{2}(\mathrm{~g})
$$

## Given:

- Initial moles of $\mathrm{N}_{2} \mathrm{O}_{4}=0.050$ moles
- Initial moles of $\mathrm{NO}_{2}=0.010$ moles
- Equilibrium moles of $\mathrm{N}_{2} \mathrm{O}_{4}=0.020$ moles
- Equilibrium moles of $\mathrm{NO}_{2}=0.040$ moles
- Volume of the container $(\mathrm{V})=0.5 \mathrm{dm}^{3}$ ( 0.5 liters)

First, calculate the initial concentrations of $\mathrm{N}_{2} \mathrm{O}_{4}$ and $\mathrm{NO}_{2}$

- $\left[\mathrm{N}_{2} \mathrm{O}_{4}\right]$ (initial $)=(0.050$ moles $) /(0.5$ liters $)=0.10 \mathrm{M}$
- $\left[\mathrm{NO}_{2}\right]($ initial $)=(0.010$ moles $) /(0.5$ liters $)=0.02 \mathrm{M}$


## Now, calculate the equilibrium concentrations:

- $\left[\mathrm{N}_{2} \mathrm{O}_{4}\right]$ (equilibrium $)=(0.020$ moles $) /(0.5$ liters $)=0.04 \mathrm{M}$
- $\left[\mathrm{NO}_{2}\right]($ equilibrium $)=(0.040$ moles $) /(0.5$ liters $)=0.08 \mathrm{M}$

|  | Initial Moles <br> (moles) | Change in Moles <br> (moles) | Equilibrium Moles <br> (moles) | Concentration (M) at <br> Equilibrium |
| :--- | :--- | :--- | :--- | :--- |
| N2O4 | 0.050 | -0.030 | 0.020 | 0.040 M |
| NO 2 | 0.010 | +0.030 | 0.040 | 0.080 M |

Using the equilibrium concentrations, you can set up the expression for Kc

```
\(\mathrm{Kc}=\left(\left[\mathrm{NO}_{2}\right]^{2}\right) /\left[\mathrm{N}_{2} \mathrm{O}_{4}\right]\)
\(\mathrm{Kc}=\left(0.08^{2}\right) / 0.04\)
\(\mathrm{Kc}=0.0064 / 0.04\)
\(\mathrm{Kc}=0.16 \mathrm{M}^{-1}\)
```


## Effect of Temperature

- For Endothermic Reactions ( $\mathbf{\Delta H}>\mathbf{0}$ ): An increase in temperature will shift the equilibrium position in the direction of the endothermic reaction, favoring the products. As a result, the value of Kc will increase.
- For Exothermic Reactions $(\Delta \mathrm{H}<0)$ : An increase in temperature will shift the equilibrium position in the direction of the exothermic reaction, favoring the reactants. This leads to a decrease in the value of Kc .


## Effect of Pressure on the position of equilibrium and Kc

The value of Kc remains constant with temperature, even if the position of equilibrium changes due to alterations in pressure.

## Effect of catalyst

Catalysts have no effect on the value of Kc or the position of equilibrium as they speed up both forward and backward rates by the same amount.

## Exam Questions

A different mixture of ethanoic acid, ethane-1,2-diol and water was prepared and left to reach equilibrium at a different temperature from the experiment in part (b)

The amounts present in the new equilibrium mixture are shown in Table 2.
Table 2

| Amount in the mixture/mol |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\mathrm{CH}_{3} \mathrm{COOH}$ | $\mathrm{HOCH}_{2} \mathrm{CH}_{2} \mathrm{OH}$ | $\mathrm{C}_{6} \mathrm{H}_{10} \mathrm{O}_{4}$ | $\mathrm{H}_{2} \mathrm{O}$ |  |
| At new <br> equilibrium | To be <br> calculated | 0.264 | 0.802 | 1.15 |  |

The value of $K_{\mathrm{c}}$ was 6.45 at this different temperature.
Use this value and the data in Table 2 to calculate the amount, in mol, of ethanoic acid present in the new equilibrium mixture.

Give your answer to the appropriate number of significant figures.

A new equilibrium mixture of the substances from part (a) is prepared at a different temperature.
$\mathrm{C}_{7} \mathrm{H}_{12} \mathrm{O}_{4}(\mathrm{I})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightleftharpoons 2 \mathrm{CH}_{3} \mathrm{COOH}(\mathrm{I})+\mathrm{HO}\left(\mathrm{CH}_{2}\right)_{3} \mathrm{OH}(\mathrm{I})$
Table 2 shows the amount of each substance in this new equilibrium mixture.

## Table 2

| Amount in the mixture / mol |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | Diester | Water | Acid | Diol |  |
| At equilibrium | 0.971 | To be <br> calculated | 0.452 | 0.273 |  |

The value of the equilibrium constant, $K_{\mathrm{c}}$ is 0.161 at this temperature.
Calculate the amount of water, in mol, in this new equilibrium mixture. Show your working.


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