

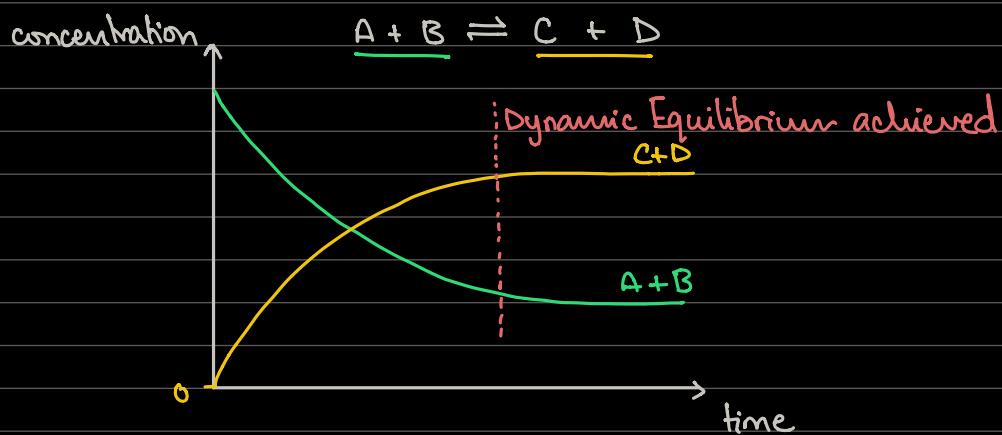
EQUILIBRIA

- A reversible reaction can proceed in both the forwards and reverse direction

\rightleftharpoons or \rightleftharpoons signifies a reversible reaction

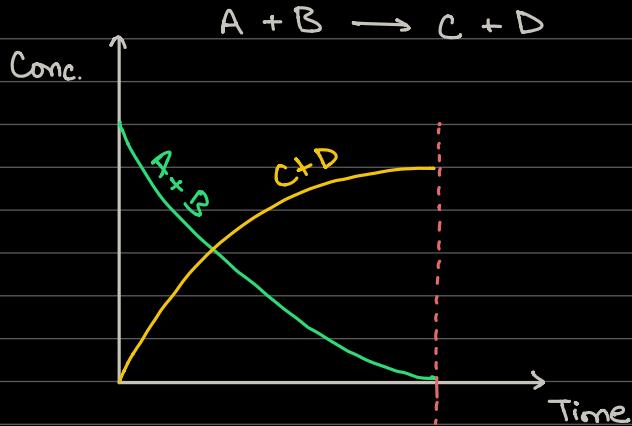


- Initially, the concentration of A and B will decrease while the concentration of C and D increases
- At the start, the rate of backward reaction is 0
- After some time, rate of forward rxn will be equal to the rate of backward rxn and at this point, dynamic equilibrium is achieved



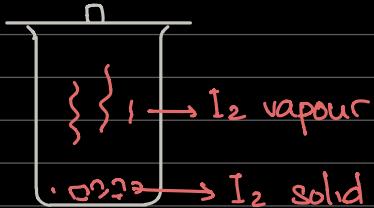
- At dynamic equilibrium, the rate of the forward rxn is equal to the rate of the reverse rxn, and the concentrations of the reactants and products are constant

NON-REVERSIBLE REACTION



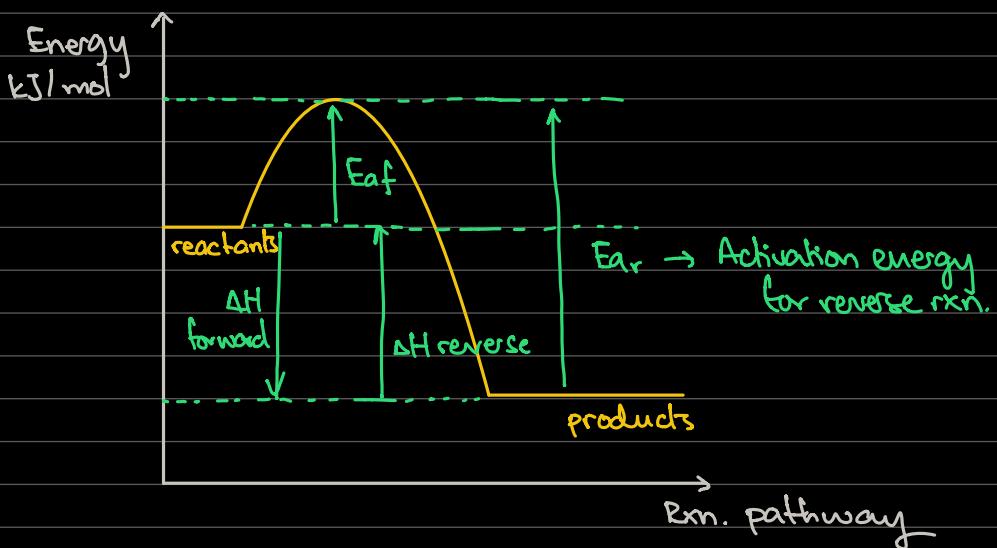
CLOSED SYSTEMS → required for dynamic equilibrium

i) Physically Closed



ii) Chemically Closed

- Nothing is added or removed from the reaction at equilibrium
- Also, the temperature and pressure must be the same (no changes)
- Whether a reaction is reversible or not depends on the activation energy of the reverse reaction
 - ↳ It also depends on the stability of the reactants and products



FACTORS AFFECTING EQUILIBRIA

Le Chatelier's Principle

States that for a given rxn, if a change is made to a system in equilibrium, the system reacts in such a way so as to oppose the change, and a new equilibrium is established

1. Concentration



If we increase the concentration of chromate ($\text{Inc} [\text{CrO}_4^{2-}]$) ...

the color darkens (becomes more orange) as the equilibrium shifts to the RHS

If we decrease hydrogen ions by dilution (Dec [H⁺]) ...

the equilibrium shifts to the left, and the colour of the solution lightens (becomes more yellow)

If we add OH^- ions ($\text{inc } [\text{OH}^-]$) ...

OH^- ions will neutralize the H^+ ions, so it has the same effect of decreasing the concentration of the H^+ ions.

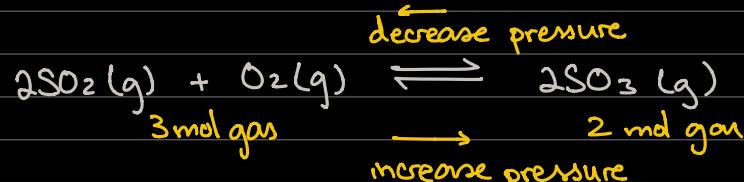
The equilibrium opposes that by making more H^+ ions, hence eq. shifts to the left and the color of the solution lightens (becomes yellower)

2. Pressure

↳ only affects gaseous reactants and products

Increasing the pressure causes the equilibrium to shift towards the side that has fewer moles of gas

Decreasing the pressure causes the equilibrium to shift towards the side that has more moles of gas



Note: Ignore solids and liquids in a reversible rxn
when changes in pressure are being made

Note : change in pressure when mols of gasses are the same on both sides does not cause a shift in the equilibrium

3. Temperature

The effect of temperature on the equilibrium position depends on whether the reaction is endothermic or exothermic

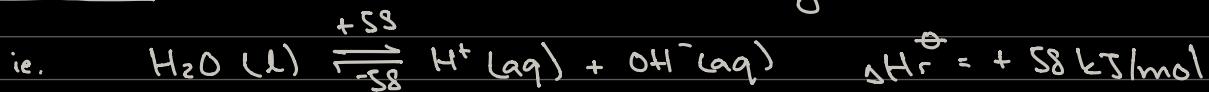
Exothermic: release heat to the surrounding



When we increase temp: The system will try to 'absorb' the extra heat energy by shifting the equilibrium to the LHS, as the backward reaction is endothermic (NH₃ yield will decrease)

When we decrease temp: The system will try to increase the temp by shifting the equilibrium towards the RHS, as the forward reaction is exothermic (NH_3 yield increases)

Endothermic: Absorb heat from surrounding



Increasing temp: System absorbs heat and forward reaction is favored since its endothermic. H^+ and OH^- yield increases

Decreasing temp: the system tries to increase it by shifting the equilibrium to the left (which is exothermic)
 ↳ More H_2O is formed and $[\text{H}^+]$ and $[\text{OH}^-]$ decreases

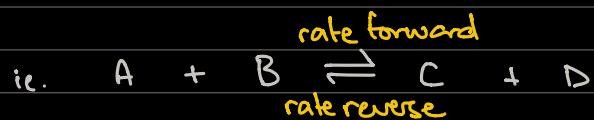
4. Catalysts

Increase the rate of both the forwards and backwards by the same amount, therefore the position of the equilibrium is unaffected

Note: Catalysts do not affect equilibrium

EQUILIBRIUM CONSTANTS: K_c and K_p

K_c : The eq. constant when concentration(s) are taken into account



The rate of a reaction can only be found by experiment and not by looking at the balanced eq.

Note: [] means 'concentration'

Suppose rate forward is \propto to conc. of A and \propto to conc. of B

$$\text{Rate forward} \propto [A][B]$$

① $\text{Rate}_f = K_1 [A][B]$

Suppose the reverse rate of rxn is \propto to the conc. of C and \propto to the conc. of D

$$\text{Rate reverse} \propto [C][D]$$

② $\text{Rate}_r = K_2 [C][D]$

At equilibrium, rate_r = rate_f

$$k_1[A][B] = k_2[C][D]$$

$$\left[\frac{k_1}{k_2} \right] = \frac{[C][D]}{[A][B]}$$

$$K_c = \frac{[C][D]}{[A][B]}$$

Taking stoichiometry (i.e. the moles) :



$$K_c = \frac{[C]^y[D]^z}{[A]^w[B]^x}$$

K_c Equilibrium Expression or
Equilibrium Law

the moles, or the coefficients become the power to which
the concentration term is raised

UNITS OF K_c



$$K_c = \frac{[HI]^2}{[H_2][I_2]} \quad \frac{(mol/dm^3)^2}{(mol/dm^3)}$$



$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} \quad \frac{(mol/dm^3)^2}{(mol/dm^3)^3}$$



$$K_c = \frac{[B]^2[C]}{[A]} \quad \frac{(mol/dm^3)^3}{(mol/dm^3)}$$

Example:

- Q. A mixture of 6g of ethanoic acid and 6g of ethanol was added to 4.2g of ethyl ethanoate ($CH_3CO_2CH_2CH_3$) and the mixture was allowed to come to equilibrium. It was found that 0.04 mol of ethanoic acid was present at equilibrium.

a) Calculate the no. of moles of each compound, both initially and at equilibrium



i (initial)	0.1	0.13	0.05	0
c (change)	-0.06	-0.06	+ 0.06	0.06
e (equilibrium)	0.04	0.07	0.11	0.06

+ instead of - cuz we switched to product side

① Calculating mol. (Initial)

$$n(\text{CH}_3\text{COOH}) = \frac{6 \text{ g}}{60 \text{ Mr}} = 0.1 \text{ mol}$$

$$n(\text{CH}_3\text{CH}_2\text{OH}) = \frac{6 \text{ g}}{46} = 0.13 \text{ mol}$$

$$n(\text{ester}) = \frac{4.4}{88} \approx 0.05$$

b) Write the K_c expression and calculate K_c

$$③ \quad K_c = \frac{[\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{CH}_3\text{CH}_2\text{OH}]}$$

$$K_c = \frac{(0.11/\nu)(0.06/\nu)}{(0.04/\nu)(0.07/\nu)} \rightarrow \text{bc. volume is the same for all of them}$$

$$K_c = 2.36 \text{ and no units}$$

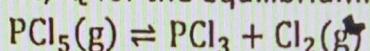
c) Explain why K_c has no units

Ans. K_c has no units in this case because same number of moles on both sides of the reaction, hence the units cancel out, resulting in a dimensionless quantity.

PRACTICE QUESTIONS

Q1. The equilibrium mixture present in a 3 dm³ flask at 250 °C was found to contain 1.00 mol of PCl₅(g), 2.00 mol of PCl₃(g) and 0.3 mol of Cl₂(g).

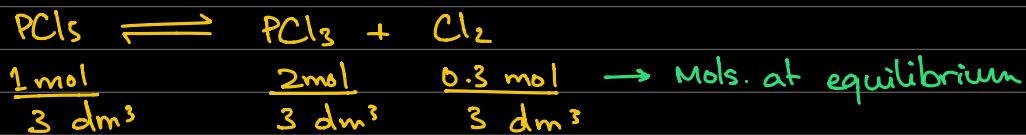
Calculate the equilibrium constant, K_c for the equilibrium. Give the units of K_c.



$$\text{PCl}_5 \rightarrow 1 \text{ mol}$$

$$\text{PCl}_3 \rightarrow 2 \text{ mol}$$

$$\text{Cl}_2(\text{g}) \rightarrow 0.3 \text{ mol}$$



Convert to 1 dm³

$$0.333 \frac{\text{mol}}{\text{dm}^3} \quad 0.667 \frac{\text{mol}}{\text{dm}^3} \quad 0.1 \frac{\text{mol}}{\text{dm}^3}$$

Then write K_c expression:

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

$$= \frac{(0.667)(0.1)}{(0.333)}$$

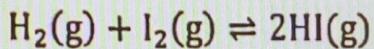
Since the ans. has vol. in it, we could NOT cancel it earlier

$$K_c = \frac{0.2 \frac{\text{mol}}{\text{dm}^3}}{\text{Ans.} \rightarrow \text{value} \quad \text{Ans.} \rightarrow \text{units}}$$

→ The K_c value for this rxn.

Q2. A sealed flask contained 2 moles of iodine, 19 moles of hydrogen iodide and 4 moles of hydrogen at equilibrium. Calculate the equilibrium constant, K_c for the reaction.

given mol. are
eq. mol.



Give the units of K_c.

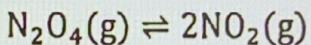


$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

$$= \frac{(19\text{M})^2}{(4\text{M})(2\text{M})} \quad \text{volume cancels out}$$

$$K_c = 45.1 \quad \underline{\text{no units}} \rightarrow \underline{\text{Ans}}$$

Q3. A quantity of dinitrogen tetroxide, N_2O_4 was dissolved in trichloromethane. The N_2O_4 dissociates according to the equation.



A solution of N_2O_4 and NO_2 at equilibrium in $CHCl_3$ at $10^\circ C$ was analyzed. 0.5 dm^3 of the solution was found to contain 0.0014 mol of NO_2 . 2.0 dm^3 of the same solution was found to contain 1.04 mol of N_2O_4 .

(a) Calculate K_c for the equilibrium above and give its units.

(b) What is K_c for $2NO_2 \rightleftharpoons N_2O_4$?

a)



$$0.52 \text{ mol/dm}^3 \quad 0.0028 \text{ mol/dm}^3$$

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

$$= \frac{(0.0028)^2}{0.52} \quad \text{Note: Very small } K_c \text{ value.}$$

$$K_c = 1.5 \times 10^{-5} \text{ mol/dm}^3 \rightarrow \underline{\text{Ans}}$$

b) Find K_c for the reverse equation

$$\begin{aligned} K_c \text{ for reverse rxn} &= \frac{1}{1.5 \times 10^{-5}} \quad \text{Note: very large } K_c \text{ value} \\ &= 66326.5 \frac{\text{dm}^3}{\text{mol}} \rightarrow \underline{\text{Ans}} \end{aligned}$$

What does K_c really tell us?

$$K_c = \frac{[\text{Product}]}{[\text{reactants}]} \longrightarrow \begin{array}{l} \text{Large product conc. relative to reactant results in} \\ \text{high } K_c \text{ value} \end{array}$$

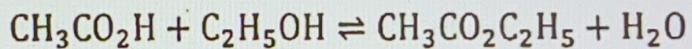
↳ Large reactant conc. relative to product results in low K_c value

If K_c is very large, then the conc of the products is higher, which means that equilibrium lies in the forward direction.

If K_c is very small, there is likely to be a higher proportion of reactants, i.e. equilibrium must lie in the reverse direction

Q4. Alcohols and esters are important organic compounds which are widely used as solvents.

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



This reaction is an example of a dynamic equilibrium.

- Explain what is meant by the term dynamic equilibrium.
- Write the expression for the equilibrium constant for this reaction, K_c .
- For this equilibrium, the value of K_c is 4.0 at 298 K.

A mixture containing 0.5 mol of ethanoic acid, 0.5 mol ethanol, 0.1 mol ethyl ethanoate and 0.1 mol water was set up and allowed to come to equilibrium at 298 K. The final volume of solution was V dm³.

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

a) At dynamic equilibrium for a given reaction, the rate of forward reaction is equal to the rate of the reverse reaction.

OR

At dynamic equilibrium, the concentrations of the reactants and the products are constant.

b)

	CH_3COOH	$+$	$\text{CH}_3\text{CH}_2\text{OH}$	\rightleftharpoons	$\text{CH}_3\text{COOC}_2\text{CH}_3$	$+$	H_2O
initial	0.5		0.5		0.1		0.1
change	- x		- x		+ x		+ x
equilibrium	$0.5 - x$		$0.5 - x$		$0.1 + x$		$0.1 + x$

0.2 0.2 0.4 0.4

$$K_c = \frac{[\text{CH}_3\text{COOCH}_2\text{CH}_3][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{CH}_3\text{CH}_2\text{OH}]}$$

$$K_c = \frac{(0.1+\alpha)(0.1+\alpha)}{(0.5-\alpha)(0.5-\alpha)} \rightarrow \text{Ans (b)}$$

$$\sqrt{4} = \sqrt{\frac{(0.1+\alpha)^2}{(0.5-\alpha)^2}}$$

$$2 = \frac{0.1 + \alpha}{0.5 - \alpha}$$

$$1 - 2\alpha = 0.1 + \alpha$$

$$0.9 = 3\alpha$$

$$0.3 = \alpha$$

Final values:



Q5. 2.0 mol of ethanoic acid and 2.0 mol of ethanol are mixed and allowed to come to equilibrium with ethyl ethanoate and water produced. At equilibrium, the amount of ethanoic acid present is 0.67 mol. Calculate K_c .

	CH_3COOH	$\text{CH}_3\text{CH}_2\text{OH}$	\rightleftharpoons	$\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3$	$+$	H_2O
initial	2	2		0	0	
change	-1.33	-1.33		+1.33	+1.33	
equilibrium	0.67	0.67		1.33	1.33	

$$K_c = \frac{[\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{CH}_3\text{CH}_2\text{OH}]}$$

$$K_c = \frac{(1.33)(1.33)}{(0.67)(0.67)}$$

$$K_c = 3.94 \text{ no units}$$

Extra Question: where the mole ratio is not 1:1

Q. When 4 mols of NO_2 were put in a 1 dm^3 flask, and heated, the equilibrium mixture contained NO and 0.8 mols of oxygen. Calculate K_c for this reaction.

	$2\text{NO}_2 \rightleftharpoons 2\text{NO} + \text{O}_2$
initial	4 0 0
change	-2(0.8) +2(0.8) +0.8
equilibrium	2.4 1.6 0.8

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

$$K_c = \frac{(1.6)^2 (0.8)}{(2.4)^2}$$

$$K_c = 0.35 \text{ mol/dm}^3$$

1st March, 2021

K_p : equilibrium constant for gases, taking partial pressure into consideration

Partial Pressure: In a mixture of gases, each gas exerts its own pressure which is independent of other gases

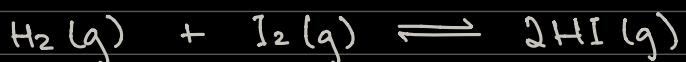
- Partial pressure of gas A in a mixture of gases A and B is equal to its mole fraction \times the total pressure

- The symbol 'p' represents partial pressure

$$\begin{aligned} \text{partial pressure of A} &= \text{mole fraction} \times \text{Total Pressure} \\ &= \frac{\text{mol A}}{\text{mol A} + \text{mol B}} \times \text{Total Pressure} \end{aligned}$$

$$\begin{aligned} \text{partial pressure of B} &= \frac{\text{mol B}}{\text{mol A} + \text{mol B}} \times \text{Total Pressure} \end{aligned}$$

Example 1:



$$K_p = \frac{(\rho_{\text{HI}})^2}{(\rho_{\text{H}_2})(\rho_{\text{I}_2})}$$

Note: don't use [], because they're used for concentration.
 → Use () to represent partial pressure instead.



initial 0.5 0.5 0

change -0.39 -0.39 + 2(0.39)

equilibrium 0.11 0.11 0.78

→ put the equilibrium
moles or partial pressures
into the K_p expression

$$\text{Total Pressure} = 5 \times 10^4 \text{ Pa}$$

Find the partial pressure of each gas and calculate K_p

$$p_{\text{H}_2} = \frac{0.11}{1.0} \times 5 \times 10^4 = 5.5 \times 10^3 \text{ Pa}$$

$$p_{\text{I}_2} = \frac{0.11}{1.0} \times 5 \times 10^4 = 5.5 \times 10^3 \text{ Pa}$$

$$p_{\text{HI}} = \frac{0.78}{1.0} \times 5 \times 10^4 = 3.9 \times 10^4 \text{ Pa}$$

$$K_p = \frac{(3.9 \times 10^4)^2}{(5.5 \times 10^3)(5.5 \times 10^3)} = 50.3 \text{ no units} \rightarrow \underline{\underline{A_m}}$$

Example 2:

Q. The equilibrium mixture in a flask was found to consist of 0.5 mol of SO_2 , 0.12 mol of O_2 and 5.0 mols of SO_3 .

All three substances were gaseous. The pressure in the flask was $8.0 \times 10^5 \text{ Pa}$

a) Calculate the partial pressure of each gas

$$p_{\text{SO}_2} = \frac{0.5}{5.62} \times 8 \times 10^5 = 7.1 \times 10^4 \text{ Pa}$$

$$p_{\text{O}_2} = \frac{0.12}{5.62} \times 8 \times 10^5 = 1.7 \times 10^4 \text{ Pa}$$

$$p_{\text{SO}_3} = \frac{5}{5.62} \times 8 \times 10^5 = 7.12 \times 10^5 \text{ Pa}$$

b) Write K_p expression



$$K_p = \frac{(\rho_{\text{SO}_3})^2}{(\rho_{\text{SO}_2})^2 (\rho_{\text{O}_2})}$$

$$= \frac{(7.12 \times 10^4)^2}{(7.1 \times 10^4)^2 (1.7 \times 10^4)}$$

c) Give value of K_p and its units.

$$K_p = 5.88 \times 10^{-3} \text{ Pa}^{-1}$$

Significance of K_p and K_c

$$K_c = \frac{\text{[product]}}{\text{[reactant]}} \quad K_p = \frac{(\rho_{\text{Product}})}{(\rho_{\text{Reactant}})}$$

or K_p

- When K_c is very small \rightarrow there is likely to be a higher proportion of reactants in the equilibrium mixture. Equilibrium lies more towards the LHS of the rxn.
- When K_c or K_p is really large \rightarrow there is likely to be a higher proportion of products in the equilibrium mixture, as equilibrium lies in the forward reaction.

FACTORS AFFECTING K_c AND K_p

ONLY temperature affects the magnitude of K_c and K_p - as it depends on whether the reaction is exothermic or endothermic



If temp is increased : equilibrium shifts to the LHS, more A and B will be produced, so K_c / K_p will decrease

If temp is decreased : equilibrium shifts to the RHS, more C and D will be produced, so K_c / K_p will increase



Opposite of what happens in an exothermic reaction

Changes in pressure + concentration do not affect K_c and K_p , as they are ratios, and they remain constant

Catalysts also don't affect the equilibrium position. Catalysts increase the rate of the forward and reverse rxns.

Note: with K_c , ignore solids