

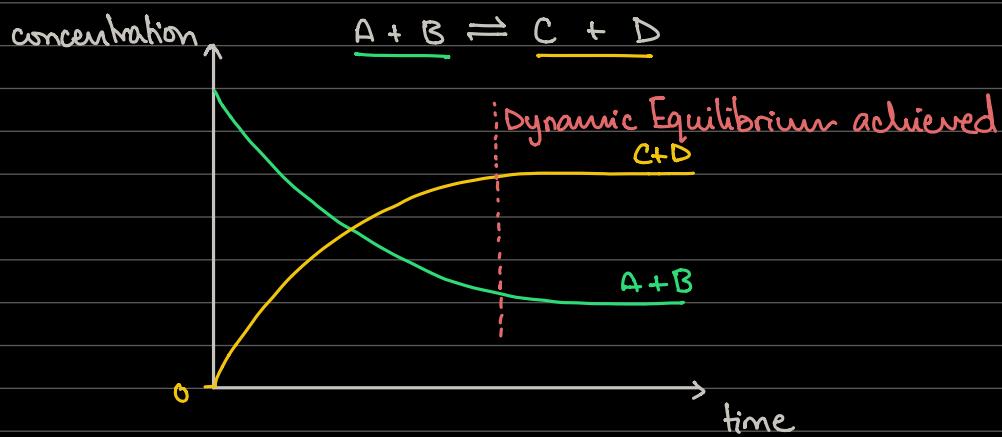
# EQUILIBRIA

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

$\rightleftharpoons$  or  $\rightleftharpoons$  signifies a reversible reaction

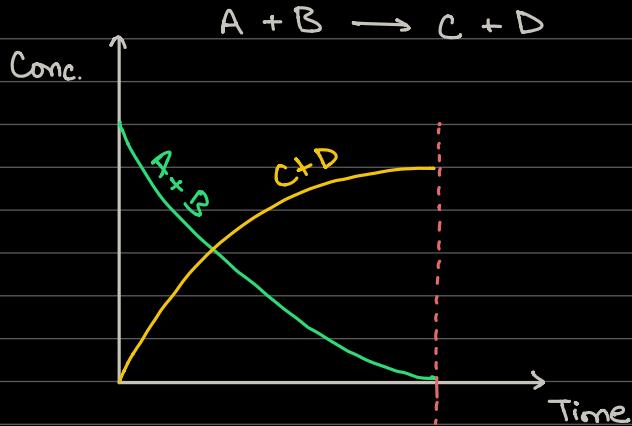


- Initially, the concentration of A and B will decrease while the concentration of C and D increases
- At the start, the rate of backward reaction is 0
- After some time, rate of forward rxn will be equal to the rate of backward rxn and at this point, dynamic equilibrium is achieved



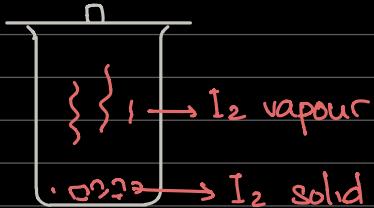
- At dynamic equilibrium, the rate of the forward rxn is equal to the rate of the reverse rxn, and the concentrations of the reactants and products are constant

## NON-REVERSIBLE REACTION



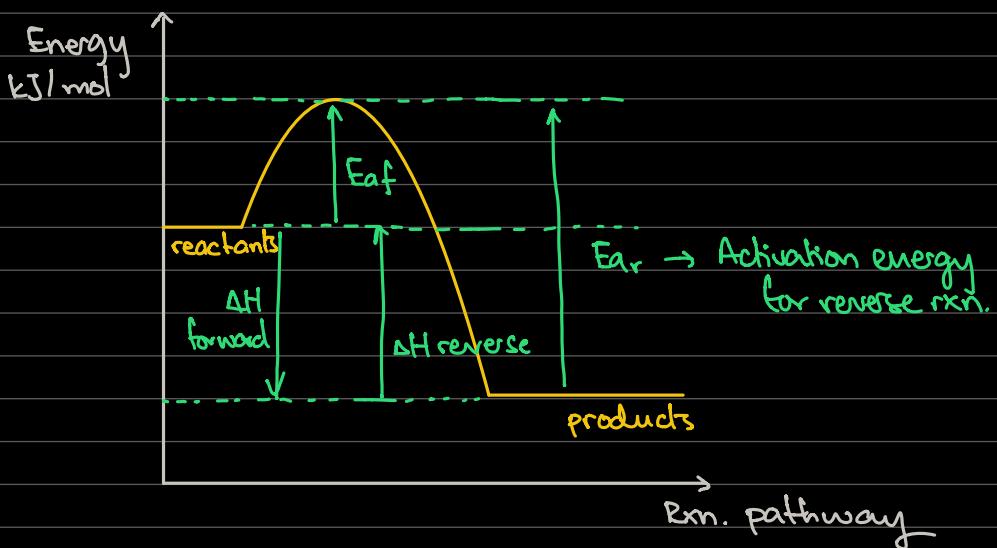
CLOSED SYSTEMS → required for dynamic equilibrium

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 ( $\text{Dec} [\text{H}^+]$ ) ...

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

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

$\text{OH}^-$  ions will neutralize the  $\text{H}^+$  ions, so it has the same effect of decreasing the concentration of the  $\text{H}^+$  ions.

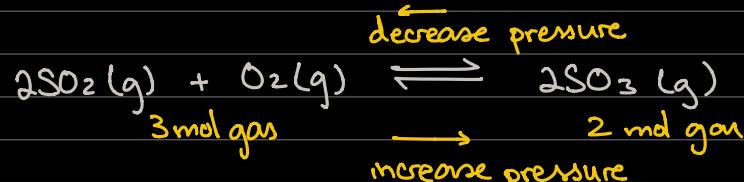
The equilibrium opposes that by making more  $H^+$  ions, hence eq. shifts to the left and the color of the solution lightens (becomes yellower)

## 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

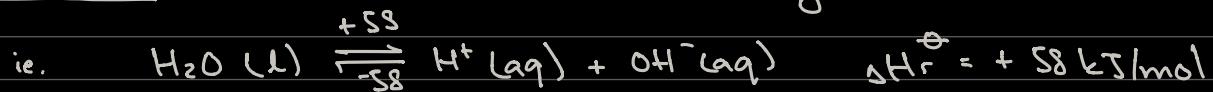
Exothermic: release heat to the surrounding



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 (NH<sub>3</sub> 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 ( $\text{NH}_3$  yield increases)

Endothermic: Absorb heat from surrounding



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

Decreasing temp: the system tries to increase it by shifting the equilibrium to the left (which is exothermic)  
 ↳ More  $\text{H}_2\text{O}$  is formed and  $[\text{H}^+]$  and  $[\text{OH}^-]$  decreases

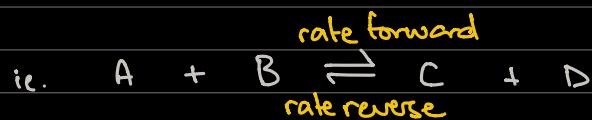
#### 4. Catalysts

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<sub>r</sub> = rate<sub>f</sub>

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

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

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

Taking stoichiometry (i.e. the moles) :

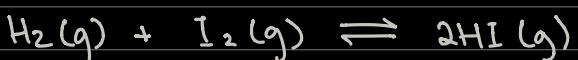


$$K_c = \frac{[C]^y [D]^z}{[A]^w [B]^x}$$

$K_c$  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  $K_c$

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

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

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

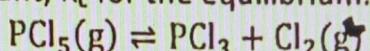
c) Explain why  $K_c$  has no units

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 dm<sup>3</sup> flask at 250 °C was found to contain 1.00 mol of PCl<sub>5</sub>(g), 2.00 mol of PCl<sub>3</sub>(g) and 0.3 mol of Cl<sub>2</sub>(g).

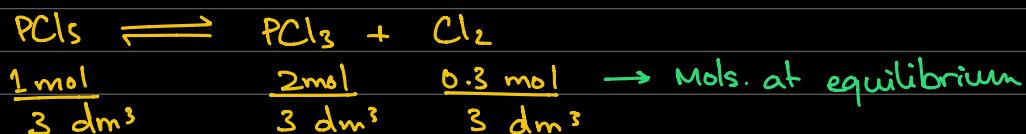
Calculate the equilibrium constant, K<sub>c</sub> for the equilibrium. Give the units of K<sub>c</sub>.



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

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

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



Convert to 1 dm<sup>3</sup>

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

Then write K<sub>c</sub> expression:

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

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

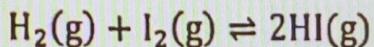
Since the ans. has vol. in it, we could NOT  
cancel it earlier

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

→ The K<sub>c</sub> 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<sub>c</sub> for the reaction.

given mol. are  
eq. mol.



Give the units of K<sub>c</sub>.

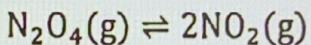


$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

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

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

**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.  $0.5 \text{ dm}^3$  of the solution was found to contain  $0.0014 \text{ mol}$  of  $NO_2$ .  $2.0 \text{ dm}^3$  of the same solution was found to contain  $1.04 \text{ mol}$  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?

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

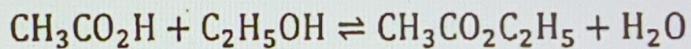
↳ Large reactant conc. relative to product results in low  $K_c$  value

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 dm<sup>3</sup>.

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)

	$\text{CH}_3\text{COOH}$	$+$	$\text{CH}_3\text{CH}_2\text{OH}$	$\rightleftharpoons$	$\text{CH}_3\text{COOC}_2\text{CH}_3$	$+$	$\text{H}_2\text{O}$
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  $K_c$ .

	$\text{CH}_3\text{COOH}$	$\text{CH}_3\text{CH}_2\text{OH}$	$\rightleftharpoons$	$\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3$	$+$	$\text{H}_2\text{O}$
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  $\text{NO}_2$  were put in a  $1 \text{ dm}^3$  flask, and heated, the equilibrium mixture contained  $\text{NO}$  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

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

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

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

1<sup>st</sup> 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

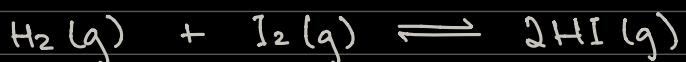
- Partial pressure of gas A in a mixture of gases A and B is equal to its mole fraction  $\times$  the total pressure

- 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  $\text{SO}_2$ , 0.12 mol of  $\text{O}_2$  and 5.0 mols of  $\text{SO}_3$ .

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