ANDERSON SERANGOON JUNIOR COLLEGE H2 CHEMISTRY <u>CHEMICAL EQUILIBRIA</u>

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Syllabus objectives

CONTENT

- Reversible reactions and dynamic equilibrium
- Equilibrium constants
- Factors affecting chemical equilibria
- Le Chatelier's Principle
- The Haber process

LEARNING OUTCOMES

- (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, K_c , and partial pressures, K_p [treatment of the relationship between K_p and K_c is **not** required]
- (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.

References

- 1. Chemistry for Advanced Level; Peter Cann and Peter Hughes
- 2. Chemistry The Central Science; Brown, Le May, Bursten 8th edition
- 3. A-Level Chemistry; E.N. Ramsden; 4th Edition

1 Introduction

The definition of equilibrium in the dictionary is 'balance or harmony of opposing forces'. The concept of chemical equilibrium is also about balance – between the forward and backward directions of reversible reactions.

1.1 Irreversible vs Reversible Reactions

Irreversible Reaction	Reversible Reaction		
Chemical reactions that <u>take place in one</u> <u>direction</u> (forward), indicated by the single arrow line (\longrightarrow).	Chemical reactions that <u>take place in both</u> <u>directions</u> (forward and backward), indicated by the double arrow line (====).		
$A + B \longrightarrow C + D$	forward reaction A + B ==== C + D backward reaction		
	Concentration		
C + D (products	C + D (products)		
A + B (reactants used up) Time t (for complete reaction)	A + B (reactants) Time $t (to reach equilibrium)$		
What happens in the Concentration vs Time graph above for an Irreversible reaction?	What happens in the Concentration vs Time graph above for a Reversible reaction?		
• At the beginning, only reactants A and B are present, forward reaction takes place to produce C and D .	• At the beginning, only reactants A and B are present, forward reaction takes place to produce C and D .		
• Thus [A] and [B] decrease while [C] and [D] increase.	• Thus [A] and [B] decrease while [C] and [D] increase.		
• Eventually at time <i>t</i> , when one (or both) of the reactants is used up, the <u>reaction is</u> complete	• The moment C and D are produced, the reverse reaction occurs to produce A and B .		
 Here, [A] and [B] equals to zero and [C] and [D] are constant. 	• Eventually at time <i>t</i> , [A] , [B] , [C] and [D] no longer changes and a <u>mixture of <i>both</i> the</u> <u>reactants and products is obtained</u> . Equilibrium is reached.		



1.2 Dynamic Equilibrium

A state of dynamic equilibrium is one where rate of forward reaction equals to rate of backward reaction for a reversible reaction such that there is no net change in the concentration of the reactants and products in a closed system.



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Characteristics of Dynamic Equilibrium

- Although the rate of forward reaction is equal to the rate of reverse reaction, the [reactants] and [products] are not equal to each other most of the time.
- [reactants] and [products] are constant (remain unchanged). However, the equilibrium mixture is still reacting (both forward and reverse reactions are ongoing).
- The same equilibrium position is reached regardless of whether the reversible reaction was started by mixing chemicals on the left or right side of the equation.
- Equilibrium can only be achieved in a <u>closed</u> system in which there is no loss or gain of matter to and from surroundings. An open system may allow matter to escape or enter. Thus equilibrium cannot be reached.

1.3 Closed and Open Systems

Consider the following example: $H_2O(g) + C(s) \implies CO(g) + H_2(g)$

- In an open system,
- The black carbon is placed in an open jar and heated with steam.
- The black carbon will gradually disappear after some time as all of it reacted to form gaseous products which escape from the system.



Open System

- In a closed system,
- The black carbon is placed in a jar with lid and heated with steam.
- Some black carbon will remain after some time.
- Without any disturbance such as temperature or pressure, the system will remain like this indefinitely as reverse reaction is taking place too.
- A state of dynamic equilibrium will be achieved.



Exercise 1:

Substance **A** decomposes into substances **B** and **C**, according to the following equation:

$$2\mathbf{A}(g) \rightleftharpoons 2\mathbf{B}(g) + \mathbf{C}(g)$$

In an experiment, a known quantity of **A** was allowed to decompose. The results of the experiment are shown in the *concentration–time* graph below:



- (a) How long did the reaction take to reach equilibrium? Give a reason for your answer.
 - What was the *initial* concentration of substance **A**?
 - At *equilibrium*, what were the concentrations of (i) **A** (ii) **B** (iii) **C**.

2. Equilibrium Constants, K

- Equilibrium constant is derived from the equation of the reversible reaction of interest. The equilibrium constant allows the reversible reaction to be studied *quantitatively* by expressing the relationship between products and reactants at equilibrium with respect to a specific unit. Equilibrium constants can be expressed in concentrations (*K*_c) or pressures of gases (*K*_p).
- For a general reaction in equilibrium, **reactants** \implies **products** Equilibrium constant expression may be simplified as $K = \frac{[products] \text{ at equilibrium}}{[reactants] \text{ at equilibrium}}$ [For complete guide on how to write K_c or K_p , please refer to Section 2.1 and 2.2]
- Units of *K* is dependent on how the expression is written.
- Equilibrium constant, *K*, is a constant at a given temperature. It is <u>unaffected</u> by changes in concentration, pressure and catalyst.
 You must remember that only <u>CHANGE IN TEMPERATURE</u> affects the value of *K*!!!

Writing Equilibrium Constant Expressions

2.1 Equilibrium constant (K_c) in concentrations

- K_c is the ratio of the concentrations of the products to the concentrations of the reactants, raised to the powers of their stoichiometric coefficients in a balanced chemical equation.
- For a general reversible reaction,

aA + bB == cC + dD

The expression of K_c is



c: in terms of 'concentration'

Indices: Stoichiometric coefficient in equation

Numerator: Concentration

Square bracket, []: concentration in mol dm⁻³

• Units of $K_c = (\text{mol dm}^{-3})^{c+d-a-b}$

To deduce unit of K_c , unit of $K_c = \frac{(mol \, dm^{-3})^c (mol \, dm^{-3})^d}{(mol \, dm^{-3})^a (mol \, dm^{-3})^b} = (mol \, dm^{-3})^{c+d-a-b}$

2.2 Equilibrium constant (*K*_p) in partial pressures

- For reactions involving <u>gases</u>, it is usually more convenient to express the amount of gas present in terms of its **partial pressure** rather than its molar concentration. This is possible because pressure is directly proportional to concentration (*p* = c RT at constant T).
- For a general reversible reaction,



• Units of $K_p = (Pa \text{ or } atm)^{c+d-a-b}$

Other units of the partial pressures include bar or Nm⁻² depending on the data given.

Exercise 2:

(a) Write the expression of equilibrium constant in terms of concentration. State the units for K_c .

Reversible reaction	<i>K_c</i> expression	Units
1. $2SO_2(g) + O_2(g) \Longrightarrow 2SO_3(g)$	$\mathcal{K}_{c} = \frac{[\mathbf{SO}_{3}]^{2}}{[\mathbf{SO}_{2}]^{2}[\mathbf{O}_{2}]}$	mol ^{−1} dm ³
2. $2SO_3(g) = 2SO_2(g) + O_2(g)$		

(b) Write the expression of equilibrium constant in terms of pressures. State the units for K_{ρ} .

Reversible reaction	$K_{ ho}$ expression	Units
 N₂(g) + 3H₂(g) = 2NH₃(g) Units of partial pressure is given in atm. 	$K_{p} = \frac{P_{NH3}^{2}}{P_{N2}^{2} P_{H2}^{3}}$	atm ⁻²
2. $CH_4(g) + H_2O(g) \implies CO(g) + 3H_2(g)$ Units of partial pressure is given in Pa .		

2.3 Equilibrium constant (K_c) in Heterogeneous Systems

Heterogeneous equilibria describes a reversible reaction in which the substances involved are present in <u>more than one phase</u>.

Examples:

- (a) $H_2O(g) + C(s) \implies H_2(g) + CO(g)$
- (b) $CaCO_3(s) \iff CaO(s) + CO_2(g)$
- (c) $[AI(H_2O)_4(OH)_2]^+$ (aq) + OH⁻(aq) = $[AI(H_2O)_3(OH)_3]$ (s) + H₂O(I)

To write the equilibrium constants (K_c or K_p) for *heterogeneous* systems, the following terms which are **<u>CONSTANT</u>** are **<u>EXCLUDED</u>** in the K expressions:

X Pure solids (s)
X Pure liquids (*l*)
X Solvents (usually water)

Reasons:

- Concentrations of pure solids and liquids are equivalent to their densities which are <u>constants</u>.
- Vapour pressures of solids and pure liquids are small and are constants.
- Solvents (usually water) are present in large amount such that their concentrations will not vary much and remains relatively <u>constant</u> throughout the reaction.

Consider the *heterogeneous* equilibrium:

$$CaCO_3(s) \implies CaO(s) + CO_2(g)$$

$$\mathcal{K} = \frac{[CaO(s)][CO_2(g)]}{[CaCO_3(s)]}$$

Hence, since CaCO₃ and CaO are solids, equilibrium expression can be rewritten as:

$$\frac{\mathcal{K}[CaCO_3(s)]}{[CaO(s)]} = \mathcal{K}_c = [CO_2(g)] \text{ and } \mathcal{K}_p = \mathcal{P}_{CO2}$$

Exercise 3: Write the expression for K_c and/or K_p for the following reactions.

1.	Ni(s) + 4CO(g) = Ni(CO) ₄ (g)	$\mathcal{K}_{c} = rac{[Ni(CO)_{4}]}{[CO]^{4}} ext{ and } \mathcal{K}_{p} = rac{\mathcal{P}_{Ni(CO)_{4}}}{\mathcal{P}_{CO}^{4}}$
2.	$BaCO_3$ (s) \longrightarrow $Ba^{2+}(aq) + CO_3^{2-}(aq)$	
3.	$HF(aq) + H_2O(I) \longrightarrow H_3O^+(aq) + F^-(aq)$	

3 Calculations Involving K

Equilibrium constants enable us to calculate the composition of a reaction mixture that has reached equilibrium, and is therefore useful if we are preparing a 'target compound' via a reversible reaction.

Procedure	Procedure for solving equilibrium problems						
Step 1:	Identify the balanced chemical equation for the reaction which is given.						
Step 2:	Construct the 'ICE' table. (Only when equilibrium information is not sufficient)						
	 <u>Initial amount/concentration/partial pressure</u> <u>Change in amount/concentration/partial pressure</u> <u>Equilibrium amount/concentration/ partial pressure</u> (If equilibrium amount is calculated in moles, always remember to convert to concentration in mol dm⁻³ or partial pressures.) 						
Step 3:	Check if the reaction is in homogeneous or heterogeneous equilibrium. Write down the equilibrium constant (<i>K</i>) expression .						
Step 4:	Substitute the calculated EQUILIBRIUM concentrations/partial pressures into the equilibrium constant expression and solve. There are 2 scenarios: i. Given composition of substances at equilibrium, solve <i>K</i> . ii. Given <i>K</i> value, solve equilibrium composition of substances						

Calculations involving Kc

3.1 <u>Calculating K_c Given Equilibrium Composition</u>

Exercise 4:

A sealed flask contained 4 mol of hydrogen, 2 mol of iodine and 19 mol of hydrogen iodide gas at equilibrium. Calculate the equilibrium constant, K_c for the reaction stating it units.

HINT: Let volume of flask be V dm³.								
	H ₂ (g)	+	l ₂ (g)	\rightarrow	2HI (g)			
Eqm. moles / mol	4		2		19			
Eqm. conc ./ mol dm⁻³								

NOTE: K_c has no units and although the volume, *V*, cancels out, working still has to be shown that **concentration** (and NOT no. of moles) is used for calculation of K_c .

Exercise 5:

2.0 mol of ethanoic acid and 2.0 mol of ethanol are allowed to mix at a constant temperature. When equilibrium is reached, 1.33 mol of water is found to be present and the total volume of solution is 0.5 dm³. Calculate the equilibrium constant, K_c , for the reaction.

Initial moles/mol	CH₃COOH(I) 2.0	+	C₂H₅OH(I) 2.0		CH₃COOC₂H₅(I) 0	+	H₂O(I) 0
Change in moles /mol							
Eqm moles/mol							
Eqm conc . / mol dm ⁻³	$\frac{0.67}{0.5}$		$\frac{0.67}{0.5}$		$\frac{1.33}{0.5}$		1.33 0.5

 $K_{c} = \frac{[CH_{3}COOC_{2}H_{5}][H_{2}O]}{[CH_{3}COOH][C_{2}H_{5}OH]} =$

3.2 Calculating Equilibrium Composition Given Kc

Exercise 6:

When pure H_2O and pure D_2O are mixed, exchange of H and D atoms takes place and the following equilibrium is established.

 $D_2O(I) + H_2O(I) \implies 2HDO(I)$ $K_c = 3.56 \text{ at } 298 \text{ K}$

If a mixture containing 1.50 mol of D_2O and 1.50 mol of H_2O is made up, how many moles of HDO will be present at equilibrium at 298 K?

Solution to Exercise 6: Let x be the amount of D₂O or H₂O reacted.

	D ₂ O(I)	+	H ₂ O(I)	 2HDO(I)
Initial moles / mol	1.50		1.50	0
Change in moles / mol				
Eqm moles / mol				

Eqm conc. / mol dm⁻³

$$K_{c} = \frac{[\text{HDO}]^{2}}{[\text{D}_{2}\text{O}][\text{H}_{2}\text{O}]}$$

$$3.56 = \frac{(\frac{2x}{\text{V}})^{2}}{(\frac{1.50 - x}{\text{V}})(\frac{1.50 - x}{\text{V}})}$$

$$3.56 = \frac{(2x)^{2}}{(1.50 - x)(1.50 - x)}$$

$$\sqrt{3.56} = \frac{2x}{1.50 - x}$$

Taking square root of both sides,

 \Rightarrow x = 0.73 (reject the negative value)

Therefore, n(HDO) = 2x = 2(0.73) = 1.46 mol

Think: Why is the negative value rejected?

Exercise 7:

For the reaction A + B \implies 2C, an equilibrium mixture was made by adding 50 cm³ of 2 mol dm⁻³ solution of A to 50 cm³ of 2 mol dm⁻³ solution of B. What will be the concentration of A, B and C at equilibrium? (Given $K_c = 4$)

Solution to Exercise 7: Let *x* be the number of moles of A or B reacted.

 A
 +
 B
 =
 2C

 Initial moles / mol
 $\frac{50}{1000} \times 2 = 0.1$ $\frac{50}{1000} \times 2 = 0.1$ 0

 Change in moles / mol
 Eqm moles / mol
 Eqm conc. / mol dm⁻³
 Hence, $[A] = \frac{0.1 - 0.05}{0.1} = 0.500 \text{ mol dm}^{-3}$

 (Total volume =
)
 $K_c = \frac{[C]^2}{[A][B]}$ Hence, $[A] = \frac{0.1 - 0.05}{0.1} = 0.500 \text{ mol dm}^{-3}$
 $[A] = [B] = 0.500 \text{ mol dm}^{-3}$ $[C] = \frac{2 \times 0.05}{0.1} = 1.00 \text{ mol dm}^{-3}$

Note: You may also start the ICE Table above in terms of concentrations instead of amount in mole.

4 Calculations Involving K_p

4.1 Calculating K_p given Initial Partial Pressures

For **gaseous equilibria**, the concentrations of the reactants and products are usually more convenient when expressed in terms of their **partial pressures**. In order to use pressures rather than concentrations, the effect of pressure of each gas must be considered separately.

In these cases, the *initial partial pressures of the reactants or products and the total pressure at equilibrium* are usually given, and the K_p is required to be calculated.

Exercise 8:

 $SO_2(g)$ and $O_2(g)$, at partial pressures of 1.00 atm and 0.50 atm respectively, are allowed to reach equilibrium at 675 K. When equilibrium is established, the total pressure in the container is found to be 1.01 atm. Calculate the K_p for the reaction at 675 K.

 $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$

Note:

At *constant temperature*, the partial pressure of a gas is dependent on *moles* <u>and</u> the *volume* of the reaction vessel.

Recall: pV = nRT

In this context, since there is a change in the total pressure (from 1.50 to 1.01 atm) when there is a change in number of moles of gas from reactants to products (from 3 moles to 2 moles), we assume that <u>moles \propto partial pressure</u> at *constant volume* (*container of known volume*) and we can use partial pressures in the 'ICE' table.

Let x be the partial pressure of O_2 reacted.									
	2SO ₂ (g)	+	O ₂ (g)		2SO₃(g)				
Initial <i>Partial pressure</i> / atm	1.00		0.50		0				
Change in <u>Partial Pressure</u> /atm									
Eqm <i><u>Partial pressure</u> /</i> atm						p _{total} at eqm = 1.01 atm			

At equilibrium, $p_{SO2} + p_{O2} + p_{SO3} = 1.01$ atm

(1.0 –	$2x$) + (0.50 - x) + (2x) = 1.01 \Rightarrow x = 0.49 atm
Hence,	p _{SO2} = 1.00 – 2(0.49) = 0.02 atm
	p _{O2} = 0.50 – 0.49 = 0.01 atm
	p _{SO3} = 2(0.49) = 0.98 atm
Therefore	$K_{\rho} = \frac{(p_{SO3})^2}{(p_{SO2})^2(p_{O2})} = \frac{(0.98)^2}{(0.02)^2(0.01)} = 2.40 \times 10^5 \text{ atm}^{-1}$

4.2 <u>Calculating K_p given mole fractions and total Pressure at</u> Equilibrium

Sometimes, the *initial partial pressures of the reactants are not given*. In these cases, *moles or mole fractions and the total pressure at equilibrium* are usually given so that *Dalton's Law* below can be used to determine a value for the equilibrium partial pressures of the reactants and products, and hence the value for K_{p} .



Exercise 9:

Carbon dioxide reacts with hydrogen according to the following equation.

 $CO_2(g) + H_2(g) \implies CO(g) + H_2O(g)$

At temperature T and a total pressure of 10 atm, it is found that initial amounts of 1 mole each of CO₂ and H₂ gas produce 0.01 mole each of CO and H₂O at equilibrium. What is the approximate value of K_p at temperature T?

	CO ₂ (g)	+ H ₂ (g)	CO(g)	+ H₂O(g)
Initial moles / mol	1	1	0	0
C hange in moles / mol	-0.01	-0.01	+0.01	+0.01
Eqm moles / mol	0.99	0.99	0.01	0.01
E qm partial pressure / atm	(0.99 / 2) x 10 = 4.95	(0.99 / 2) x 10 = 4.95	(0.01 / 2) x 10 = 0.05	(0.01 / 2) x 10 = 0.05

$$K_{\rm p} = \frac{{\sf P}_{{\sf H}_2{\sf O}}{\sf P}_{{\sf CO}_2}}{{\sf P}_{{\sf CO}_2}{\sf P}_{{\sf H}_2}} = \frac{(0.05)^2}{(4.95)^2} = 1.02 \times 10^{-4}$$
 (no unit)

Exercise 10:

A nitrogen–hydrogen mixture, initially in the mole ratio of 1:3 reached equilibrium with ammonia when 50% of the nitrogen has reacted. The total pressure is 2 atm.

 $N_2(g) + 3H_2(g) \implies 2NH_3(g)$

Calculate the value of K_p giving its units.

Let the initial amount of nitrogen be x mol.

	N ₂ (g)	+	3H₂(g)	<u> </u>
Initial moles / mol	х		3x	0
Change in moles / mol	-0.5x		-1.5x	+1.0x
Eqm moles / mol	0.5x		1.5x	1.0x
Eqm partial pressure / atm				

Exercise 11 (Similar to Exercise 10. Students to self-read):

Steam dissociates into its elements at very high temperatures. At a high temperature and a total pressure of 1 atm, 20% of the steam is dissociated into hydrogen and oxygen.

Calculate the pressure that each of the three gases exerts at equilibrium, and hence the value for K_p , giving its units.

Let initial amount of H₂O be x mol.		Step 1: Since we do not know the initial amount of reactant, we let it be x mol before filling in the ICE Table to find equilibrium amounts.			
	2H ₂ O (g)		2H ₂ (g)	+	O ₂ (g)
Initial moles / mol	х	[0		0
C hange in moles / mol	-0.20x	Step 2: Determine ti eqm amts in terms of x.	he +0.20x		$+\frac{1}{2}(0.20x)$ =+0.10x
Eqm moles / mol	x – 0.20x = 0.80x		0.20x		0.10x
E qm partial pressure / atm	$\frac{0.80x}{0.80x + 0.20x + 0.10} = 0.727$	<u> </u>	$\frac{0.20x}{0.80x + 0.20x + 0.10x} = 0.182$	x 1	$\frac{0.10x}{0.80x + 0.20x + 0.10x} x1$ = 0.0909
Therefore, $K_{p} = \frac{1}{2}$	$\frac{p_{H_2}}{\left(p_{H_2O}\right)^2} \left(p_{O_2}\right) = \frac{(0.182)}{(0.182)}$	$\frac{32)^{2}(0.0909)}{(0.727)^{2}} = 5.70 \times 10^{-3} atm$ Step 3: Using the end amounts in terms of the mole fractions of and find partial press 3 gases.		3: Using the equilibrium ints in terms of x, obtain hole fractions of all gases ind partial pressure of the ses.	
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REVIEW Characteristics of Kc and Kp

For a general reversible reaction,
 aA (g) + bB (g) = cC (g) + dD (g)

The expression of K_c is



- The expression of K_p is $K_p = \frac{\mathbf{P_c}^{c} \mathbf{P_D}^{d}}{\mathbf{P_A}^{a} \mathbf{P_D}^{b}}$
- Units of $K_c = (\text{mol dm}^{-3})^{c+d-a-b}$
- Units of $K_p = (Pa \text{ or atm})^{c+d-a-b}$
- i) For heterogeneous systems, concentrations that are constant are not included in the expression.

 K_c and K_p have <u>no fixed units</u> (units dependent on the reaction equation).

ii) Factors affecting values of K_c and K_p

 K_c and K_p are constants at <u>constant</u> temperature.

 K_c and K_p are only affected by temperature and are **not** affected by

- a) changes in <u>concentration</u>
- b) changes in <u>pressure</u>
- c) presence of <u>catalyst</u>

iii) Values of K_c and K_p are determined <u>experimentally</u>.

 K_c and K_p **do not** give any information on the

- a) numerical values of rates of forward and reverse reactions (we only know that both rates of forward and reverse reactions are the same).
- b) time required for the equilibrium to be established.
- iv) The magnitude of K_c and K_p is an indication of how far the reaction has gone to completion and the position of the equilibrium.
 - (iv) position of equilibrium
 - (iii) experimentally
 - (ii) constant; parts a, b and c are concentration/pressure/catalyst
 - stinu bəxit on (i)
 - Answers for blanks

5. <u>Position of Equilibrium</u>

The **proportion of products to the reactants** in the equilibrium mixture is described as the position of the equilibrium.

aA + bB → cC + dD	aA + bB → cC + dD	
If the conversion of reactants (A and B) into	If the equilibrium mixture is composed	
products (C and D) is very small, there is	largely of the products (C and D),	
greater proportion of reactants compared to	\Rightarrow equilibrium position <u>lies to the right</u> .	
the products.	$\Rightarrow K_c >>> 1$ (i.e. very large)	
\Rightarrow equilibrium position <u>lies to the left</u> .		
$\Rightarrow K_c <<< 1$ (i.e. very small)		

6. Factors Affecting the Position of Equilibrium

Once an equilibrium is established, the *position of equilibrium (or composition of the equilibrium mixture) can be changed* by varying the following conditions:

- (a) Concentrations of species involved
- (b) Pressure (for reactions involving gases)
- (c) Temperature

Le Chatelier's Principle

• Le Chatelier's Principle summarises the effect on the position of equilibrium (or composition of an equilibrium mixture) when the conditions (a) to (c) stated above are changed.

Le Chatelier's Principle states that <u>if a change occurs</u> in one of the conditions (concentration, temperature, or pressure) under which a reversible reaction is in dynamic equilibrium, the <u>position of equilibrium shifts</u> so as to <u>minimise that change</u> (and to re–establish equilibrium).

6.1 Changing the Concentration

Consider the following system in equilibrium at constant temperature:



A + B == C + D

Change Effect on position of equilibrium		Effect on equilibrium mixture	Effect on <i>K</i> c
lf extra A is added, [A] increases	Equilibrium position will shift to the <u>right</u> in order to <u>remove</u> some of the excess A .	[B] decreases [C] and [D] increase	Unchanged
If some A is removed, [A] decreases	Equilibrium position will shift to the <u>left</u> in order to <u>produce</u> more A.	[B] increases, [C] and [D] decrease	Unchanged

Summary of the effect of changing the concentrations of the reactants.

A concentration–time graph illustrating the effect of <u>increasing the concentration of reactant **A** in the equilibrium:</u>



NOTE

- The system <u>cannot completely</u> cancel the change in the external factor but it shifts in the direction that will <u>minimise</u> the change.
- At constant temperature, <u>K_c remains UNCHANGED but the COMPOSITION of the</u> reactants and products CHANGES when additional **A** is added to the equilibrium mixture.

Exercise 12: Application of Le Chatelier's Principle

 $Co(H_2O)_6^{2^+}(aq) + 4Cl^-(aq) \implies CoCl_4^{2^-}(aq) + 6H_2O(l)$ pink colour blue colour

Use Le Chatelier's Principle to predict and explain the effect of:

(i) increasing [Cl⁻(aq)];

- The equilibrium position shifts to the _____to remove some of the $Cl^{-}(aq)$ added.
- Thus the [Co(H₂O)₆²⁺(aq)] _____ and the [CoCl₄²⁻(aq_____, resulting in ______solution formed.

(ii) decreasing $[Co(H_2O)_6^{2+}(aq)];$

- The equilibrium position shifts to the <u>left</u> to <u>increase</u> $[Co(H_2O)_6^{2+}(aq)]$.
- Thus the $[CoCl_4^2(aq)]$ decreases, resulting in a <u>pink</u> solution formed.

Effect of Adding Water into Aqueous Equilibrium Systems

(iii) adding water into the aqueous solution (Refer to 'Hint')

- Adding water _____
- The equilibrium position shifts to the <u>left</u> to <u>produce more ions</u> since the left side produces <u>more aqueous ions</u> compared to the right (<u>5 moles of aq ions</u> versus <u>1 mole of aq ions</u>).
- Thus the concentration of $[CoCl_4]^{2-}(aq)$ decreases, resulting in a <u>pink</u> solution formed.

HINT:

To study the **effect of adding water** into aqueous equilibrium systems, we can consider these questions:

How will the concentration of $Co(H_2O)_6^{2^+}$, Cl^- , $CoCl_4^{2^-}$ and water change respectively? Concentrations of $Co(H_2O)_6^{2^+}$, Cl^- and $CoCl_4^{2^-}$ decrease and concentration of water remains unchanged.

What is the specific change after adding water that causes shift in the position of equilibrium?

Adding water results in <u>a decrease in the concentrations of all aqueous ions.</u> This leads to a shift in position of equilibrium to the <u>left to produce more aqueous ions</u> as there are more aqueous reactants than aqueous products in the reaction equation. Or

<u>Concentrations of reactants decreases more than products</u> as there are more aqueous species on the left side of the equation. <u>Position of equilibrium will shift left to increase the concentration of aqueous reactants in the system</u>.

6.2 Changing the Pressure (ONLY affect GASEOUS reactions)

- The pressure of the equilibrium can be increased by
 - 1) Adding more gaseous reactants or gaseous products (refer to "changing the concentration")
 - 2) Decreasing volume of the container
 - 3) Introduction of an inert gas
- When applying Le Chatelier's Principle to predict the effect of a pressure change on the equilibrium position, the factor to consider here is the <u>number of moles of gaseous</u> <u>reactants and products</u> in the <u>chemical equation</u>.

Consider the following reversible reaction at <u>constant temperature</u>.

$$\begin{array}{c} PCl_{5}(g) \\ \hline 1 \ mol \ of \ gas \end{array} \begin{array}{c} PCl_{3}(g) + Cl_{2}(g) \\ \hline 2 \ mol \ of \ gas \end{array}$$

Change	Effect on position of equilibrium	Effect on equilibrium mixture	Effect on <i>K</i> _p
	Equilibrium position will shift to the	P_{PCl_3} and P_{Cl_2}	
If pressure increases,	<u>left</u> to <u>decrease</u> pressure by producing <u>fewer gaseous</u> <u>molecules</u> .	decreases P _{PC/s} increases	Unchanged
	Equilibrium position will shift to the	P_{PCl_3} and P_{Cl_2}	
If pressure	<u>right</u> to <u>increase</u> pressure by	increases	Unchanged
decreases,	producing <u>more gaseous</u> <u>molecules</u> .	$P_{PC_{l_5}}$ decreases	

Exercise 13:

Consider the decomposition of hydrogen iodide:



State how the composition of the equilibrium mixture would change if there is an increase in pressure.

An increase in pressure will have _____ on the position of the equilibrium

since both the forward and backward reaction produce the ______.

... Composition of equilibrium mixture ______.

(**NOTE:** Though in this case, there is no shift in position, the increase in pressure (hence causes an increase in concentration) will <u>speed up</u> both the forward and reverse reactions, allowing equilibrium to be reached <u>more quickly</u>. Refer to 'Reaction Kinetics'.)

Exercise 14:

Consider the dimerisation of NO₂ at equilibrium:

 $\begin{array}{c} 2NO_2 \left(g \right) \implies N_2O_4 \left(g \right) \\ \text{brown} \qquad \text{colourless} \end{array}$

Use Le Chatelier's Principle to predict and explain the following effects. State the observations.

(i) increasing pressure;

Equilibrium position will **shift to the**_____to ____pressure by producing ______(2 gaseous NO₂ on the left while one gaseous N₂O₄ on the right.). The colour of the gas turned from brown _____.

(ii) decreasing pressure;

Equilibrium position will **shift to the <u>left</u>** to <u>increase</u> pressure by producing <u>more gaseous</u> <u>molecules</u>. The brown colour of the gas turned <u>darker</u>.

Effect of adding Inert Gas on Gaseous Equilibrium Systems

(iii) Adding neon (inert gas) at <u>constant volume</u> (Refer to Hint (1))

An addition of Ne at constant volume ______the partial pressures of NO $_2$ and N $_2O_4$.

Hence, there will be ______ on the position of the equilibrium.

Hint (1):

Study the below diagrams, predict how these pressures changes after adding inert gas at constant volume.

Total pressure of the system, P_{T} :

partial pressure of N₂O₄, $P_{N_2O_4}$

partial pressure of NO₂, P_{NO_2}



(iv) Adding neon (inert gas) at constant pressure (Refer to Hint (2))

An addition of Ne at constant pressure <u>decreases the partial pressures of NO₂ and N₂O₄</u>. Hence, equilibrium position will shift to the <u>left</u> to <u>increase</u> pressure by producing <u>more</u> <u>gaseous molecules</u>. The colour intensity of the reaction mixture lightens initially but turns <u>darker brown</u> when equilibrium is reestablished.

Hint (2):

Adding a gas at constant pressure can be achieved by increasing the volume of the vessel. Study the below diagrams, predict how these pressures changes after adding inert gas at constant pressure.

Total pressure of the system, P_{τ} : constant (6 gas particles in 1 unit volume)

partial pressure of N₂O₄, $P_{N_2O_4}$: *decrease*

partial pressure of NO₂, P_{NO_2} : *decrease*



Exercise 15:

Consider the following equilibrium system:

 $N_2(g) + 3H_2(g) = 2NH_3(g)$

Change at constant	Position of equilibrium shifts	p _{NH3} at equilibrium
temperature		
Total pressure increased		
Total pressure decreased		
Addition of argon gas at		
constant total volume		
Addition of argon gas at		
constant total pressure		

6.3 Changing the Temperature

When applying Le Chatelier's Principle to predict the effect of a temperature change on the equilibrium position, the factor to consider here is whether the forward reaction is exothermic $(\Delta H < 0)$ or endothermic $(\Delta H > 0)$.

Consider the following reversible reaction:

 $N_2(g) + 3H_2(g) \implies 2NH_3(g) \qquad \Delta H = -92 \text{ kJmol}^{-1}$

Exothermic

An *increase* in temperature favours the *endothermic* reaction;

A decrease in temperature favours the exothermic reaction.

Change	Effect on position of equilibrium	Effect on equilibrium mixture	*Effect on <i>K</i> c
If temperature increases,	Reverse endothermic reaction is favoured. Equilibrium position will shift to the <u>left</u> to <u>reduce</u> temperature by <u>absorbing the extra heat</u> .	[N ₂] and [H ₂] increase, [NH ₃] decreases	$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$ decreases
If temperature decreases,	Forward exothermic reaction is favored. Equilibrium position will shift to the <u>right</u> to <u>increase</u> temperature by <u>producing more</u> <u>heat</u> .	[N ₂] and [H ₂] decrease, [NH ₃] increases.	$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$ increases

NOTE: Increase in temperature not only affect the position of equilibrium and value of K, but also speed up both the forward and reverse reactions, allowing equilibrium to be reached more quickly. Refer to 'Reaction Kinetics'.

Exercise 16:

Predict the direction in which the position of equilibrium will shift, and the change to the K_c value for the systems below:

(a)
$$4NH_3(g) + 5O_2(g) \implies 4NO(g) + 6H_2O(g)$$
 $\Delta H < 0$
Temperature increases, position of equilibrium shifts to the ______K_c _____
(b) $H_2(g) + I_2(g) \implies 2HI(g)$ $\Delta H > 0$
Temperature increases, position of equilibrium shifts to the ______K_c _____
(c) $2AgC/O_3(s) + Cl_2(g) \implies 2AgCl(s) + 2ClO_2(g) + O_2(g)$ $\Delta H = 0$
Temperature decreases, position of equilibrium ______K_c

6.4 <u>Presence of catalyst</u>

The addition of a catalyst only help the reaction to reach the same position of equilibrium at a faster rate. There is no change in the equilibrium constant, K.

Look at the table below. Do you notice the difference in effects of adding a catalyst from changing temperature of a reaction?

Change	Rate constants of forward and reverse reactions, <i>k</i>	Equilibrium constant, <i>K</i>	Position of Equilibrium
Addition of CATALYST	increase to the <u>same</u> extent (because activation energies are lowered by the same magnitude)	Unchanged but equilibrium is established faster	Unchanged
Increase in TEMPERATURE	increase to <u>different</u> extent	CHANGED	CHANGED

*Refer to Extra Reading regarding relationship between kinetics and equilibrium on page 29 and 30.

7. <u>Application of Principles of Reaction Rates and Equilibria to</u> <u>Industrial Processes</u>

The principles of reaction rates and chemical equilibria play an important part in the design and conditions of industrial processes. Other than economical reasons, the major factors determining these designs and conditions are to be able to convert reactants to products:

- (i) as quickly; and (i.e. kinetics obtain maximum rate of reaction and product formation)
- (ii) as completely as possible (equilibrium maximise proportion of product)

Le Chatelier's Principle can be used to predict the choice of conditions such as:

- (a) temperature
- (b) pressure
- (c) catalyst

for **maximum yield** of product at equilibrium.

The Haber Process

The Haber process is an industrial process for manufacturing ammonia, NH₃, from hydrogen and nitrogen gas. The reaction is reversible and exothermic.



Choice of Temperature

- Since the forward reaction is exothermic, then applying Le Chatelier's Principle, the production of NH₃ is favoured by a <u>low temperature</u>. (At low temperature, POE shifts to the right to produce more heat and NH₃.)
- However, if the temperature is too low, the <u>rate</u> of reaction will be <u>too slow</u> making the process uneconomical.
- Hence a moderate temperature of <u>450 °C</u> is used to obtain a reasonable yield of NH₃ in a <u>short time</u>.

Choice of Pressure

- Since there are lesser moles of gaseous products than reactants, then applying Le Chatelier's Principle, the production of NH₃ is favoured by a very <u>high pressure</u>. (At high pressure, POE shifts to the right to produce fewer gas particles.)
- However, very high pressure demands higher <u>costs of plant construction and</u> <u>maintenance</u> since more expensive and thicker vessels (hydrogen can diffuse through many metals at high temperature and pressure) have to be employed in order to withstand high pressures.
- Hence a pressure of moderately high pressure of **<u>250 atm</u>** is used.

Choice of Catalyst

- To further speed up the rate of production, *finely divided iron catalyst* is employed.
- The role of the iron catalyst is mainly to *increase the rate at which equilibrium is achieved*. The *YIELD of NH*₃ *is NOT affected* by the presence of the catalyst.

Invention of Ammonia: Good or bad?

- Used <u>widely as refrigerant</u> and in the <u>manufacture of nitric acid</u> which is used to make *explosives, dye stuffs, nylon, pharmaceuticals etc.*
- Lastly it can be used as a precursor for production of nitrates for fertilizers.
- However, fertilisers may lead to eutrophication where fertilisers washed off from land into lakes and rivers. Increased nitrates promote algae growth over the water surface. This prevents sunlight from reaching the water plants. Plants die and decompose, depleting the oxygen in water to the extent that no aquatic life is possible again.
- Lastly, Haber's work also boosted the nitrate supply for the manufacture of explosives in Germany in the early 1900s, which indirectly prolonged World War I.

8. <u>Relationship between K and spontaneity of reaction</u>

• A graph depicting the Gibbs free energy, *G* of a reaction mixture at various compositions is shown below.

In any spontaneous reactions at constant temperature and pressure, the Gibbs free energy, G decreases as the reaction proceeds and the composition of reactants and products changes. The G of the reaction mixture decreases until it reaches a minimum value at point X. When this minimum is reached, a state of equilibrium exists, $\Delta G = 0$.



At point A, value of ΔG can be found by calculating the gradient of the tangent at point A. The ratio of products to reactants, called reaction quotient, **Q**, tells us the composition of the reaction mixture (**Q** = $\frac{[products]}{[reactants]}$).

Note: Q has the same expression as *K*, but represents the quantity of reactants and products at **any composition**. *K* on the other hand only represents the quantity of reactants and products **at equilibrium**, where $\Delta G = 0$.

- This explains why when a system at equilibrium is disturbed by the addition or removal of reactants or products and hence $\frac{[products]}{[reactants]}$ changes from K to Q, the position of
 - equilibrium will shift to restore equilibrium (Le Chatelier's Principle).
 - An equation to relate ΔG and ΔG^{θ} (standard Gibbs free energy) is as follows:

 $\Delta G = \Delta G^{\theta} + RT \ln Q$

At equilibrium, $\Delta G = 0$ and Q = K, therefore

$$\Delta \boldsymbol{G}^{\boldsymbol{\theta}} = - \operatorname{RT} \ln \boldsymbol{K}$$

where R is molar gas constant: 8.31 J K⁻¹ mol⁻¹ T is temperature: K ΔG^{θ} : J mol⁻¹

Note:

- ΔG^{θ} are mostly given in kJ mol⁻¹. In order to be consistent with the unit of R, you are reminded to convert the units to J mol⁻¹.
- *K* is known as the *standard* equilibrium constant or *thermodynamic* constant and is dimensionless (i.e. no units) since K is taken as ratio of [products] to [reactants].

Relationship between ΔG^{θ} and K

From the equation, we can see

 ΔG^{θ} is negative : K > 1 ΔG^{θ} is zero : K = 1 ΔG^{θ} is positive : K < 1

[Note: Positive value of In K implies K > 1.]

Relationship between ΔG^{θ} and position of equilibrium

The sign of ΔG^{θ} tells us whether reactants or products are dominant at equilibrium.

Thus, for a reaction: reactants \Longrightarrow products ΔG^{θ}



FYI: Given $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ and $\Delta G^{\circ} = -RT \ln K$, these two equations can be combined to give the following:

$$\ln \mathbf{K} = -\frac{\Delta \mathsf{H}^{\theta}}{\mathsf{R}\mathsf{T}} + \frac{\Delta \mathsf{S}^{\theta}}{\mathsf{R}}$$

Exercise 17:

Ammonia can be formed from its elements. $\frac{1}{2} N_2(g) + \frac{3}{2} H_2(g) \longrightarrow NH_3(g) \quad \Delta G^{\circ} = -16.6 \text{ kJ mol}^{-1}$ Suggest whether the ratio of $\frac{[\text{products}]}{[\text{reactants}]}$ at equilibrium for the formation of ammonia at 298 K will be less than, equal to or greater than 1. Give a reason for your answer.

K is greater than 1 because ΔG° is negative.

*Extra Reading

9 Relationship between Equilibrium and Kinetics

To understand why K_c or K_p values only change with temperature, the two equations involving rate constants, k, have to be considered.

(a) Arrhenius equation

$$k = Ae^{-E_a/RT}$$

where *A* is Arrhenius constant E_a is the activation energy of the reaction *R* is the gas constant and *T* is the temperature

NOTE:

- Rate constant, *k* is only affected by *E*_a and T.
- Most reversible reactions have different *E*_a for the forward and reverse reactions.

(b) Relationship between equilibrium constant, K_c (or K_p) and rate constant, k.

Consider a reversible reaction: $A + B \implies C + D$

Recall concept of *dynamic* equilibrium:

rate of forward reaction = rate of reverse reaction

In 'Reaction Kinetics', you learnt that rate equation can be written as:

rate of forward reaction = k_f [A][B] rate of reverse reaction = k_b [C][D]

Combining both concepts you will get \Rightarrow k_f [A][B] = k_b [C][D]

Rearranging,

$$\frac{d}{d} \left[[D] \right] = \frac{k_f}{k_b} \Longrightarrow \qquad K_c = \frac{k_f}{k_b}$$

Conclusion:

- Since rate constants for both forward and backward reactions changes to the same extent on addition of catalyst, K_c is not affected.
- Changes in temperature leads to a change in the k_f and k_b to different extent. Hence, K_c will change.

* Extra Reading

Mathematical explanations for students who are interested.

So why K_c decreases when temperature increases? (For exothermic forward reaction)



For an exothermic forward reaction, magnitude of $E_{a \text{ (forward)}}$ is <u>smaller</u> than $E'_{a \text{ (backward)}}$. Thus, the term ($E'_{a \text{ (backward)}} - E_{a \text{ (forward)}}$) is a <u>positive</u> value.

(Note: If forward reaction is endothermic, the term will be a negative value).

When <u>temperature increases</u>, it results in the term $e^{\frac{E_{a(backward)}^{-E_{a(forward)}}}{RT}}$ to be <u>smaller</u>. Hence K_c <u>decreases</u> when temperature increases.

Reason 2:

$$\ln K = -\frac{\Delta H^{\theta}}{RT} + \frac{\Delta S^{\theta}}{R}$$

- Since ΔH is exothermic, In $K \propto \frac{1}{T}$
- When temperature increases, K_c decreases.

Think!

How does K_c change as the temperature increase for an endothermic reaction? Are you able to explain using the mathematical relationships above?

SUMMARY OF CHEMICAL EQUILIBRIA

Consider the reversible *heterogeneous* reaction:

 $A(g) + 2B(g) \implies C(g) + D(s)$

 $\Delta H > 0$

Expression of $K_c = \frac{[C]}{[A][B]^2}$ (units of conc.)⁻²

Pure solids (s), Pure liquids (I)

Solvents (usually water)

Х

Х

$K_{p} = \frac{p_{C}}{p_{A} p_{B}^{2}}$ (units of pressure)⁻²

- CONSTANTS not in K expressions Significance of K • Large *K* implies equilibrium position lies on the right.
 - K cannot tell us how fast the reactions are.

Le Chatelier's Princ	iple can help us	predict how the above ed	quilibrium reacts to changes:
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Chang	le	Equilibrium position shifts to the	Effect on <i>K</i> c or <i>K</i> p	Effect on rate constants, <i>k</i> ∉and <i>k</i> ⊳	Remarks
1) [A]↑		right	No change	No change	
2) [C] ↑		left	No change	No change	
3) Pressure	e ↑	right	No change	No change	
4) Tempera	ture ↑	right	Increases	Both <i>k</i> _f and <i>k</i> ⊳ increase (to different extent).	<u>∱ in temp. favours</u> <u>endothermic reaction.</u> Rates of both forward and reverse reactions ↑.
5) Tempera	ture ↓	left	Decreases	Both <i>k</i> _f and <i>k</i> ₅ decrease (to different extent).	<u>√ in temp. favours</u> <u>exothermic reaction.</u> Rates of both forward and reverse reactions ↓.
6) Catalyst		No change	No change	Both <i>k</i> _f and <i>k</i> _b increase (to the same extent).	Equilibrium is established faster.

Note: the system cannot completely cancel the change in the external factor but the position of equilibrium shifts in the direction that will minimise the change.

Useful equations to help in calculating pressure of gases in the system:

$$\left(\boldsymbol{p}_{A} = \frac{n_{A}}{n_{total}} \times p_{total} \quad \underline{or} \quad \boldsymbol{p}_{A} \vee = n_{A} RT\right)$$

REVIEW

Can you answer the following questions without referring to lecture notes?

Questions/concepts	Answer	Time to seek consultation! Questions to clarify with my teachers
1. Explain, what is meant by a reversible reaction and dynamic equilibrium		
 In terms of rates of the forward and reverse reactions 		
In terms of the concentration of reactants and products		
2. Write the K _c expressions in terms of concentrations for		
• $2Fe^{3+}(aq) + 2I^{-}(aq) \implies 2Fe^{2+}(aq) + I_2(aq)$		
• CH ₃ COOH(aq) + H ₂ O(I) = CH ₃ COO⁻(aq) + H ₃ O⁺(aq)		
3. Write the K_p expressions in terms of partial pressures in Pa for this system. State its unit		
• $3O_2(g) = 2O_3(g)$		
• $Ag_2UU_3(s) - Ag_2U(s) + UU_2(g)$		
4. Given $2NO_2(g) \implies 2NO(g) + O_2(g)$		
When 4 mol of NO ₂ were put into 1 dm ³ container and		
heated, the equilibrium mixture contained 0.8 mol of O_2 .		
What is the value of K_c at the temperature of the experiment?		
5. Consider this equilibrium $4NH_3(a) + 5O_2(a) = 4NO(a) + 6H_2O(a)$		
$\Delta H = -950 \text{ kJ mol}^{-1}$		
By applying Le Chatelier's Principle, state the shift in the		
equilibrium position of the above reaction.		
 increase in pressure 		
increase in temperature		
addition of a catalyst		
6. List the factor(s) that affect equilibrium constant K.		

Questions/concepts	Answer	Time to seek consultation! Questions to clarify with my teachers
 When the system H₂(g) + I₂(g) == 2HI(g) is at 444 and 1 atm, the value of K_p is 50. What is the value of K_p at a pressure of 2 atm at the same temperature? 	⊦∘C	
(A) 25 (B) 50 (C) 100 (D) 200		
 8. Steam, at an initial pressure of 1 atm, dissociates at according to the following equation: 2H₂O(g) = 2H₂(g) + O₂(g) 	ТК	
If the total pressure at equilibrium is 1.3 atm, what is numerical value of the equilibrium constant, K_{p} , of reaction at $T K$?	the the	
 Suggest the sign and magnitude of ∆G^e given the K : K = 1 and K < 1. 	> 1,	
10. State the optimum industrial conditions in Ha Process.	aber	

3. $\mathbf{K}_{p} = \frac{\mathbf{p}_{02}^{02}}{\mathbf{p}_{02}^{02}} \mathbf{ba}^{-1}; \mathbf{K}_{p} = \mathbf{p}_{cos} \mathbf{ba}$	8. 0.675 9. negative; zero; positive 10. 450 °C, 250 atm, Fe catalyst
Answers for the Review $\lambda_{c} = \frac{[Fe^{2+}]^{2}[I_{-}]^{2}}{[Fe^{2+}]^{2}[I_{-}]^{2}}$; $K_{c} = \frac{[CH_{3}COO^{-}][H_{3}O^{+}]}{[CH_{3}COO^{+}]}$	4. 0.356 5. Right; Left; Left; No effect 6. Temperature 7. B

END