CHEMISTRY ONLINE
TUITION

Phone: +442081445350

www.chemistryonlinetuition.com

Email:asherrana@chemistryonlinetuition.com

CHEMISTRY
PHYSICAL CHEMISTRY

Level & Board	CIE (A-LEVEL)
TOPIC:	REACTION KINETICS
PAPER TYPE:	QUESTION PAPER - 1
TOTAL QUESTIONS	10
TOTAL MARKS	101

REACTION KINETICS - 1

1)

The equation for the partial decomposition of gaseous hydrogen iodide at 400 ^{0}C is shown.

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

The values for the initial rates of decrease in hydrogen iodidie concentration at various initial concentrations have been determined. These are shown in the table below.

Initial concentration /mold m^{-3}	1.67	2.34	5.01	6.68
Initial rate /mold m^{-3} s^{-1}	0.41	1.64	3.69	6.56

(a) (i) Determine the rate equation for this reaction. Give your reasoning.

(ii) Calculate the rate constant for this reaction. Give the units. **[4]**

(b) (i) At 400^{0}C the activation energy for the forward reaction is 184 KJ mol^{-1} and that for the reverse reaction is 163 KJ mol^{-1}. In the space below sketch the reaction pathway diagram for this reaction.

(ii) Determine and state the value of the enthalpy change which can be calculated from these data. **[3]**

(c) What will be the effects of increasing the temperature on the decomposition of hydrogen iodide? Give reasons to explain your answer. **[3]**

(d) In the presence of a gold catalyst, the activation energy for the reverse reaction is 85 KJ mol^{-1}. On your sketch in **(b)(i)** draw the draw the energy profile of the

catalyzed reaction. Label this clearly.

Suggest a value for the activation energy for the decomposition of 2 HI under these conditions. **[2]**

2)

(a) The reaction between nitric oxide and oxygen is an important intermediate step in the industrial production of nitric acid. It is also one of the reactions involved in atmospheric pollution fro car exhausts.

Kinetic studies have shown that the reaction is third order overall, and it has been suggested that the mechanism involves the following two steps.

$$2NO \xrightarrow{fast} N_2O_2$$

$$N_2O_2 + O_2 \xrightarrow{fast} 2NO_2$$

(i) Construct a rate equation for this reaction.

(ii) Explain the meaning of the following terms.

- rate constant
- order of reaction
- rate – determining step **[4]**

(b) The decomposition of hydrogen peroxide is a first order reaction.

$$H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2 \quad \Delta H^{\ominus} = -98 \text{ KJ mol}^{-1}$$

The uncatalysed reaction has an activation energy of 79 KJ mol-1. Both platinum and the enzyme catalase act as catalysts, and speed up the reaction.

(i) Use the data provided to construct a reaction pathway diagram for the uncatalysed reaction.

(ii) Explain what is meant by the term *activation energy*.

(iii) Describe how the activation energy is affected by the presence of a catalyst, and explain how this increases the rate.

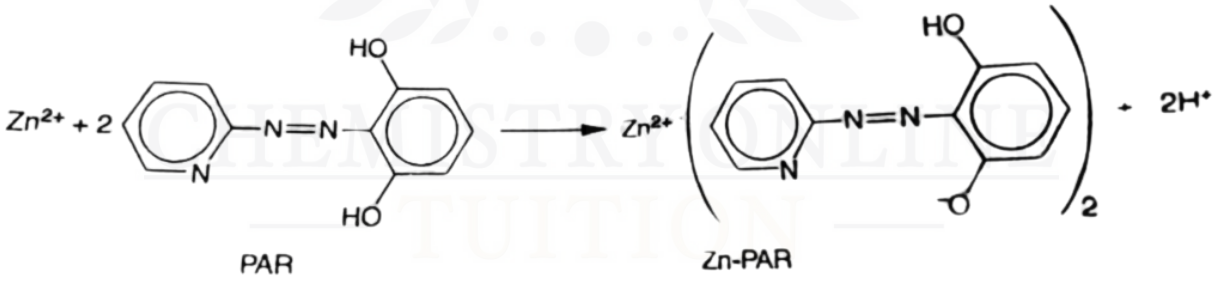
(iv) What effect will the presence of the catalyst have on the rate constant for this reaction.? Explain your answer. **[6]**

3)

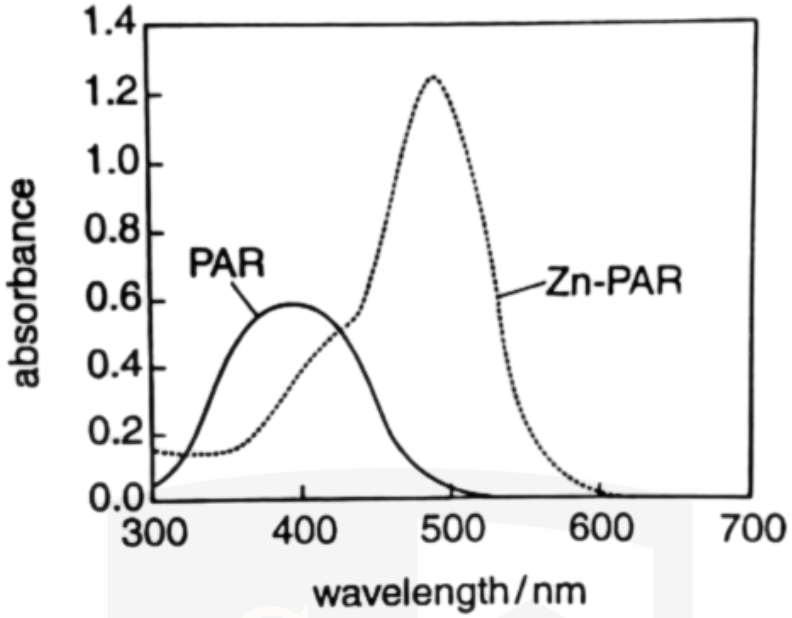
Zinc chloride is one of the most important compounds of zinc. It is used in dry cell Batteries, as a flux for soldering and tinning, as a corrosion inhibitor in cooling towers and in the manufacture of rayon.

(d) Zinc is an essential element for plant and animal life. It is often administered in the form of a chelate, which is a corrosion inhibitor in cooling towers and in the manufacture of rayon.

The rate of the reaction between zinc ions and the ligand 4 – (2 – pyridylazo) Resorcinol, PAR, has been studied.



Both PAR and its zinc complex absorb radiation in the UV – visible region. The figure below shows their absorption spectra.



(i) Devise a suitable experimental technique for studying how the rate of this reaction varies with [Zn2+(aq)].

(ii) Describe a reaction you could carry out to show that PAR is a phenol. **[7]**

4)

In the late 19th century the two ploneers of the study of reaction kinetics, Vernon Harcourt and William Esson, studied the rate of the reaction between hydrogen peroxide and iodide ions in acidic solution.

$$H_2O_2 + 2I^- + 2H^+ \rightarrow 2H_2O + I^2$$

This reaction is considered to go by the follow9ing steps.

Step 1 $H_2O_2 + I^- \rightarrow IO^- + H_2O$

Step 2 $IO^- + H^+ \rightarrow HOI$

Step 3 $HOI^- H^+ + I^- \rightarrow I_2 + H_2$

The general form of the rate equation is as follow.

$$rate = k[H_2O_2]^a[I^-]^b[H^+]^c$$

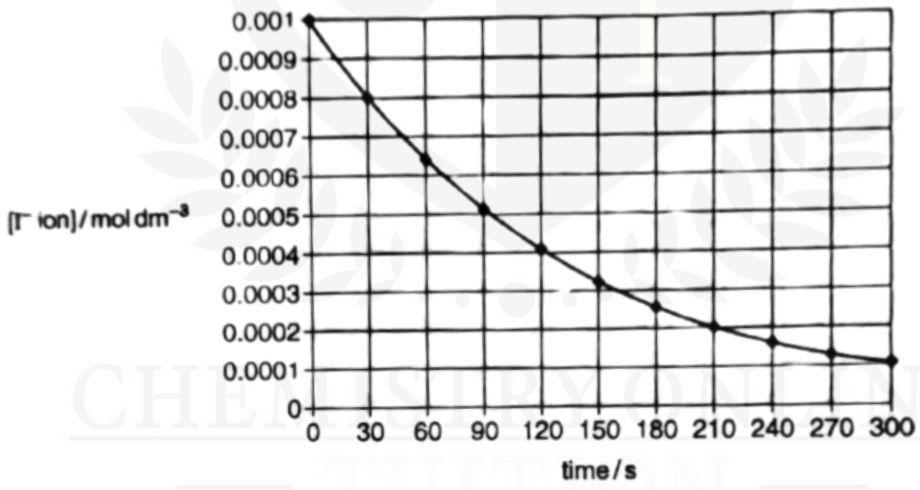
(a) Suggest how the appearance of the solution might change as the reaction takes place. **[1]**

(b) Suggest values for the orders a, b and c in the rate equation for each of the following cases.

case	numerical value		
	a	b	c
Step 1 is the slowest overall			
Step 2 is the slowest overall			
Step 3 is the slowest overall			

[3]

A study was carried out in which both $[H_2O_2]$ and $[H^+]$ were kept constant at 0.05 mol dm^{-3} , and $[I^-]$ was plotted against time. The following curve was obtained.



To gain full marks for the following answers you will need to draw relevant construction lines on the graph opposite to show your working. Draw the using a pencil and ruler.

(c) Calculate the initial rate of this reaction and state its units. **[2]**

(d) Use half – life data calculated from the graph to show that the reaction is first

order with respect to [I^-] **[2]**

(e) Use the following data to deduce the orders with respect to [H_2O_2] and [H_+], explaining your reasoning.

[H2O2] / mol dm^{-3}	[H+] / mol dm^{-3}	Relative rate
0.05	0.05	1.0
0.07	0.05	1.4
0.09	0.07	1.8

[2]

(f) from your results, deduce which of the three steps is the slowest (rate determining) step. **[1]**

5)

(a) The reaction between iodide ions and persulfate ions, $S_2O_8^{2-}$, is slow.

$$2I^- + S_2O_8^{2-} \longrightarrow I2 + 2\ SO_4^{2-} \qquad \mathbf{1}$$

The reaction can be speeded up by adding a small amount of Fe^{2+} or Fe^{3+} ions. The following tow reactions then take place.

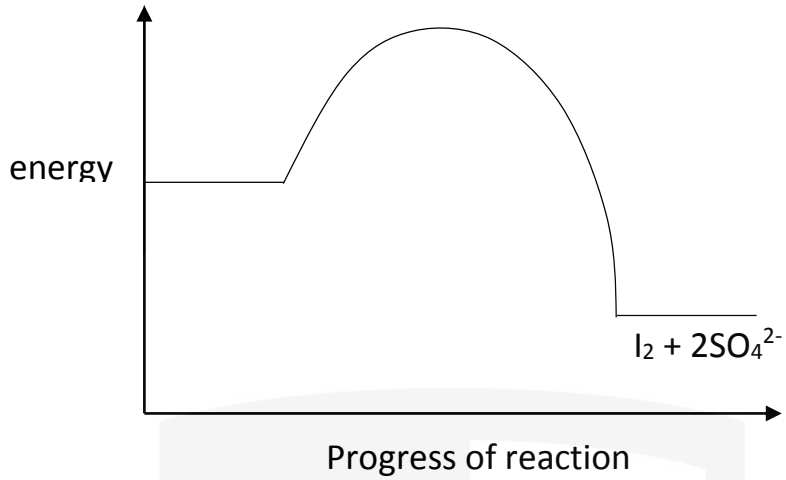
$$2I^- + Fe^{3+} \longrightarrow I_2 + 2Fe^{2+} \qquad \mathbf{2}$$

$$2Fe^{2+} + S_2O_8^{2-} \longrightarrow 2\ Fe^{3+} + 2\ SO_4^{2-} \qquad \mathbf{3}$$

(i) What type of catalysis is occurring here?

(ii) The rates of reactions 2 and 3 are both faster than that of reaction 1. By considering the species involved in these reactions suggest a reason for this.

(iii)



Use the same axes to draw the enthalpy profiles of reaction 2 followed by reaction 3.

Starting reaction 2 at the same enthalpy level as reaction 1. **[4]**

(c) The oxidation of SO_2 to SO_3 in the atmosphere is speeded up by the presence of nitrogen oxides.

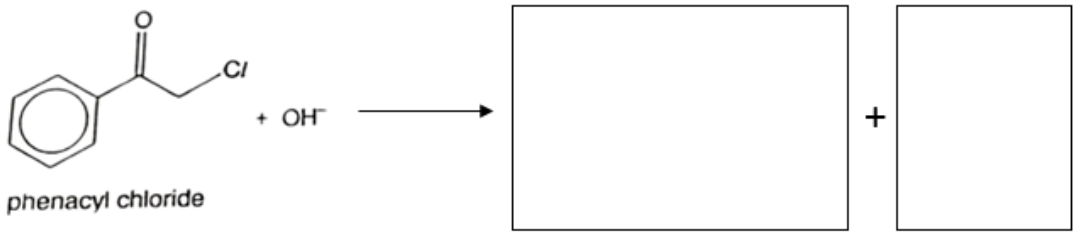
(i) Describe the environmental significance of the reaction.

(ii) Describe a major source of SO2 in the atmosphere.

(iii) By means of suitable equations, show how nitrogen oxides speed up this reaction. **[4]**

6)

Phenacyl chloride has been used as a component of some tear gases. Its lachrymatory and irritant properties are due to it reacting with water inside body tissues to produce hydrochloric acid.



phenacyl chloride

(a) (i) What is meant by the term order of reaction?

(ii) Use the above data to deduce the order with respect to each reaction.

Explain your reasoning.

(iii) Write the overall rate equation for the reaction.

(iv) Describe the mechanism for this reaction that is consistent with your overall rate equation.

You should show all intermediates and/or transition states and partial charges, and you should represent the movements of electron pairs by curly arrow. **[7]**

(c) (i) Describe an experiment that would show that CH3CoCl reacts with water at a much faster rate the phenacyl chloride. Include the reagents you would use, and the observations you would make with each chloride.

(ii) Suggest an explanation for this difference in reactivity. **[4]**

7)

Carbon monoxide, CO, occurs in the exhaust gases of internal combustion engines.

(a) (i) Suggest a dot – and – cross diagram for CO.

(ii) Suggest one reason why CO is produced in addition to CO_2 in some internal combustion engines.

(iv) Carbon monoxide can be removed from the exhaust gases by a catalytic converter.

Write an equation for a reaction that occurs in a catalytic converter that removes CO. **[3]**

(b) The standard enthalpy change of formation, $\Delta H_t^{\ominus}$, of CO is – 111 kJ mol^{-1}, and

that of CO_2 IS – 394 kJ mol^{-1}.

Calculate the standard enthalpy change of the following reaction.

$$C(s) + CO_2(g) \longrightarrow 2CO(g)$$

(d) Carbon monoxide reacts with a ruthenium (II) chloride complex according to the equation

$$[Ru(H_2O)_2Cl_4]^{2-} + CO \longrightarrow [Ru(H_2O)(CO)Cl_4]^{2-} + H_2O.$$

(i) Describe the type of reaction that is occurring here.

(ii) During the reaction, the colour of the solution changes from deep blue to green.

Explain the origin of colour in transition element complexes, and why different complexes often have different colours.

The following tale shows how the initial rate of this reaction varies with different Concentrations of reactants.

$[Ru(H_2O)_2Cl_4]^{2-}$ / mol dm^{-3}	[CO] / mol dm^{-3}	rate / mol dm^{-3} s^{-1}
1.1×10^{-2}	1.7×10^{-3}	1.6×10^{-7}
1.6×10^{-2}	3.6×10^{-3}	2.3×10^{-7}
2.2×10^{-2}	2.7×10^{-3}	3.2×10^{-7}

(iii) Use these data to determine the order of reaction with respect to each reagent, and write the rate equation for the reaction.

There are three possible mechanisms for this reaction, which are described below.

mechanism 1 $[Ru(H_2O)_2Cl_4]^{2-} + CO \xrightarrow{slow} [Ru(H_2O)(CO)Cl_4]^{2-} + H_2O$

$[Ru(H_2O)_2Cl_4]^{2-} + CO \xrightarrow{slow} [Ru(H_2O)Cl_4]^{2-} + H_2O$

mechanism 2 $[Ru(H_2O)Cl_4]^{2-} + CO \xrightarrow{slow} [Ru(H_2O)(CO)Cl_4]^{2-}$

$[Ru(H_2O)_2Cl_4]^{2-} + CO \xrightarrow{fast} [Ru(H_2O)_2(CO)Cl_4]^{2-}$

mechanism 3 $[Ru(H_2O)_2(CO)Cl_4]^{2-} \xrightarrow{fast} [Ru(H_2O)(CO)Cl_4]^{2-} + H_2O$

(iv) Deduce which of these three mechanisms is consistent with the rate equation you suggested in part (III). Explain your answer. **[10]**

7)

(a) Catalysts can be described as homogeneous or heterogeneous.

(i) What is meant by the terms *homogeneous* and *heterogeneous*?

(ii) By using iron and its compounds as examples, outline the different modes of action of homogeneous and heterogeneous catalysts.

- state what the catalyst is and whether it is acting as a homogeneous or a heterogeneous catalyst.
- Write a balanced equation for the reaction.
- Outline how the catalyst you have chosen works to decrease the activation energy. **[8]**

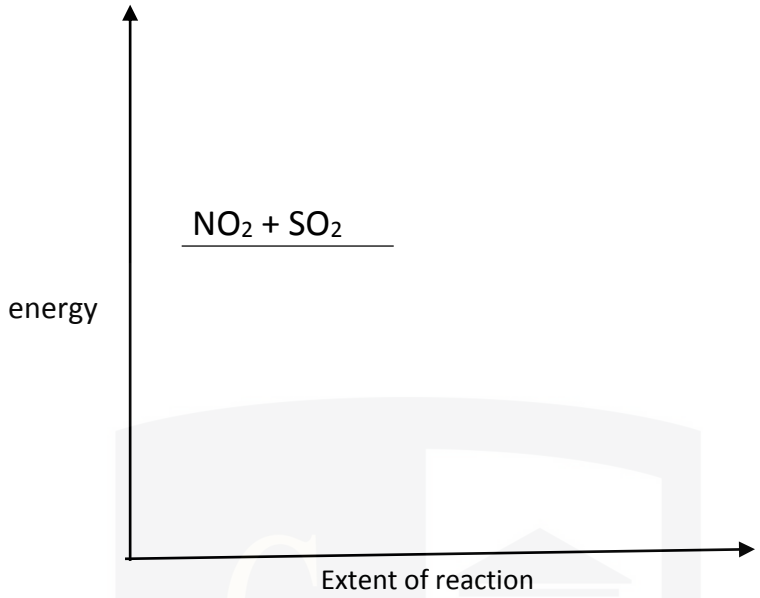
(b) The reaction between SO_2, NO_2 and O_2 occurs in two stops.

$NO_2 + SO_2 \rightarrow NO + SO3 \quad \Delta H_1^{\ominus} = -88 \text{ KJ mol}^{-1}$

$NO + \frac{1}{2} O_2 \rightarrow NO_2 \quad \Delta H_2^{\ominus} = -57 \text{ KJ mol}^{-1}$

The activation energy of the first reaction, E_a, is higher than that of the second reaction, E_{a_2}.

Use the axes below to construct a fully – labelled reaction pathway diagram for this reaction, labelling E_{a_1}, E_{a_2}, $\Delta H_1^{\ominus}$ and $\Delta H_2^{\ominus}$.



[2]

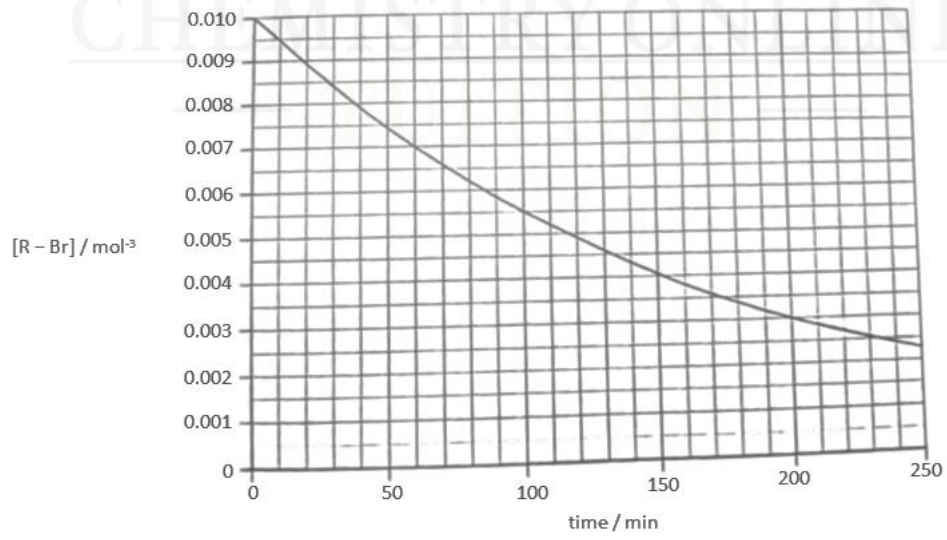
9)

A bromoalkane, R – Br, is hydrolysed y aqueous sodium hydroxide.

(a) (i) Write a balanced equation for this reaction.

(ii) What *type of reaction* is this? **[2]**

(b) The concentration of bromoalkane was determined at regular time intervals as the reaction progressed.



When the experiment was repeated using [NaOH] = 0.15 mol dm^{-3}, the following results were obtained.

time / min	[R – Br] / mol dm^{-3}
0	0.0100
40	0.0070
80	0.0049
120	0.0034
160	0.0024
200	0.0017
240	0.0012

(i) Plot these date on the axes above, and draw a line of best fit.

(ii) Use one of the graphs to confirm that the reaction is fist order with respect To R – Br.

Show all your working, and show clearly any construction lines you draw.

(iii) Use the graphs to calculate the order of reaction with respect to NaOH.

Show all your working, and show clearly any construction lines you draw on the graphs.

(iv) Write the rate equation for this reaction, and calculate the value of the rate constant. **[2]**

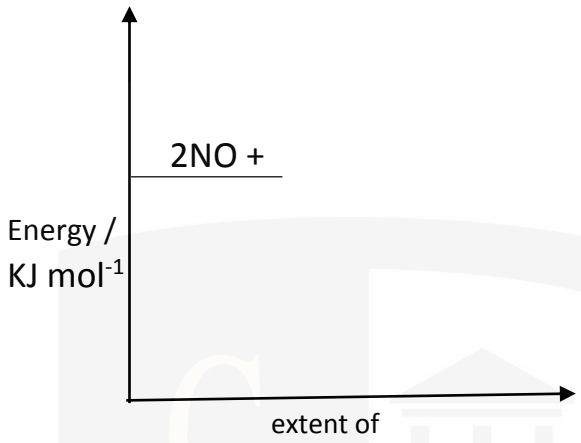
(C) Nitric oxide, NO, and bromine vapour react together according to the following equation.

$$2NO(g) + Br_2(g) \longrightarrow 2NOBr(g) \quad \Delta H = -23 \text{ KJ mol}^{-1}$$

The reaction has an activation energy of + 5.4 KJ mol^{-1}.

Use the following axes to sketch a fully – labelled reaction pathway diagram for this reaction.

Include all numerical data on your diagram.



[2]

10)

(a) The oxidation of nitrogen (II) oxide is shown in the equation.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

The initial rate of this reaction was measured, starting with different concentrations of the two reactants. The following results were obtained.

Experiment number	[NO] / mol dm^{-3}	[O_2] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.032	0.012	4.08×10^{-3}
2	0.032	0.024	8.15×10^{-3}
3	0.064	0.024	3.28×10^{-2}
4	0.096	0.036	

(i) Use the data in the table to determine the order with respect to each reactant.

Show your reasoning.

(ii) Calculate the initial rate in experiment 4. Give your answer to two significant figures.

(iii) Write the rate equation for this reaction.

(v) Use the results of experiment 1 to calculate the rate constant, K, for this reaction.. Include the unite of K. **[6]**

(b) (i) On the following exes

- draw two Boltzmann distribution curves, at two different temperatures, T_1 and T_2 ($T_2 > T_1$),
- Label the curves and the axes.

(ii) State and explain, using your diagram, the effect of increasing temperature on the rate of reaction. **[5]**

(c) the compound nitrosyl fluoride, NOF, can be formed by the following reaction,.

$$2NO(g) + F_2(g) \rightleftharpoons 2NOF(g)$$

The rate is first order with respect to NO and F_2.

The reaction mechanism has two steps.

Suggest equations for the two steps of this mechanism, starting which is the rate determining slower step. **[2]**

DR. ASHAR RANA

CHEMISTRY ONLINE
TUITION

Phone: +442081445350
www.chemistryonlinetuition.com
Email: asherrana@chemistryonlinetuition.com

- Founder & CEO of Chemistry Online Tuition Ltd.
- Tutoring students in UK and worldwide since 2008
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CONTACT INFORMATION FOR **CHEMISTRY ONLINE TUITION**

- UK Contact: 02081445350
- International Phone/WhatsApp: 00442081445350
- Website: www.chemistryonlinetuition.com
- Email: asherrana@chemistryonlinetuition.com
- Address: 210-Old Brompton Road, London SW5 OBS, UK