KINETICS AHL (HL only)

Please ensure that you have also completed the Core (SL & HL) questions

1. The following reaction occurs at high temperature:

$$NO(g) + CO(g) + O_2(g) \rightarrow NO_2(g) + CO_2(g)$$

(a) Given the data for four experiments below, deduce the order of reaction for each reactant, and write the rate expression. **Explain your reasoning.**

Experiment	[NO(g)] / mol dm^{-3}	[CO(g)] / mol dm^{-3}	[O_2(g)] / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	1.00×10^{-3}	1.00×10^{-3}	1.00×10^{-1}	4.40×10^{-4}
2	2.00×10^{-3}	1.00×10^{-3}	1.00×10^{-1}	1.76×10^{-3}
3	2.00×10^{-3}	2.00×10^{-3}	1.00×10^{-1}	1.76×10^{-3}
4	4.00×10^{-3}	1.00×10^{-3}	2.00×10^{-1}	7.04×10^{-3}

[4]

2nd order with respect to [NO] as double [NO] then the rate quadruples (x4) seen in Expt 1 to Expt 2.

zero order with respect to [CO] as double [CO] has no effect on the rate, seen in Expt 2 to Expt 3

zero order with respect to [O_2] as double [O_2] has no effect on the rate, seen in Expt 2 to Expt 4 in which rate is x4 due to doubling of [NO] – no effect of [O_2]

Rate = k[NO]^2

allow ecf from incorrect orders

(b) Calculate a value for the rate constant, stating its units.

[2]

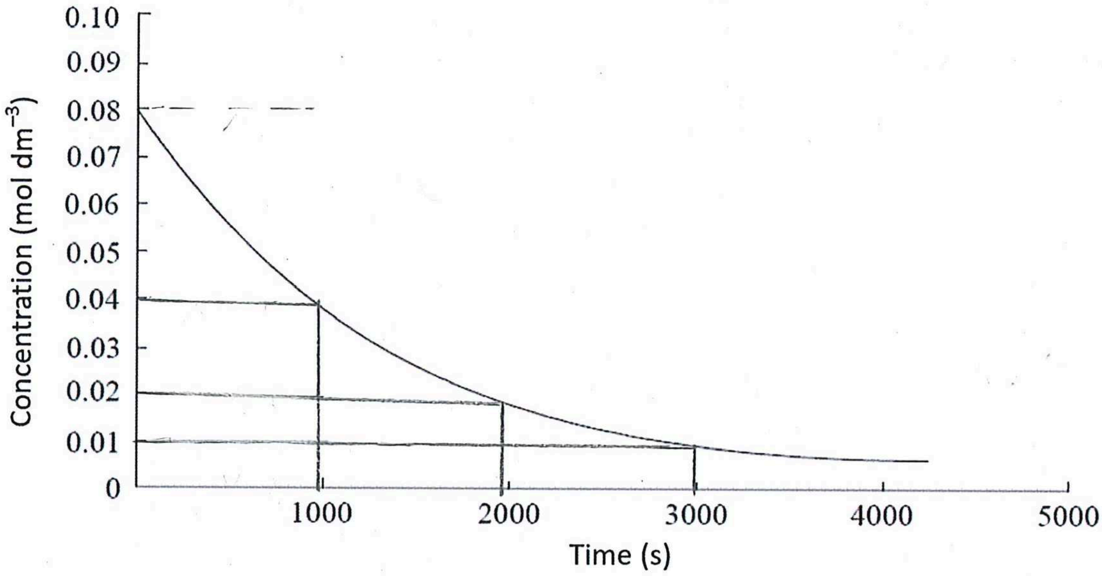
$4.40\times10^{-4} = k(1.00\times10^{-3})^2$

$k = \dfrac{4.40\times10^{-4}}{(1.00\times10^{-3})^2} = 440$ mol^{-1} dm^3 s^{-1}

$\dfrac{\cancel{mol\ dm^{-3}}\ s^{-1}}{(mol\ dm^{-3})^{\cancel{2}}}$

2. The decomposition of a sample of hydrogen peroxide, after addition of a catalyst, was followed over time:

$$H_2O_2(aq) \rightarrow \tfrac{1}{2}O_2(g) + H_2O(l)$$



(a) Using the graph (show your working) determine the half-life of the hydrogen peroxide.

[2]

1000 seconds ✓ (± 100) working on graph ✓ (see above)

(b) Deduce the order of reaction with respect to H_2O_2. Explain your reasoning.

[1]

1st order as the half-life is constant ✓

(c) Given that $t_{½} = \frac{ln2}{k}$, calculate a value for the rate constant for this reaction (units not required).

[1]

$1000 = \frac{\ln 2}{k}$ $k = \frac{0.693}{1000} = 6.93 \times 10^{-4}$ ✓

or value from (a)

(d) State how the rate constant will change with increasing temperature.

[1]

The rate constant will increase ✓ (exponentially)

(e) The decomposition reaction of hydrogen peroxide was conducted at different temperatures. Using section 1 of the data booklet, describe how the data from these experiments could be used to draw a graph to determine the activation energy.

[3]

Plot a graph of $\ln k$ against $\frac{1}{T}$ ✓

(or something proportional to $\ln k$ against $\frac{1}{T}$)

Then $\ln k = \frac{-E_a}{R} \cdot \frac{1}{T} + \ln A$ is $y = mx + c$ ✓

and so gradient (m) will be $-E_a/R$ ✓

$E_a = -m \times 8.31$ / $E_a = -m \times R$ ✓

any 3

(f) Activation energy can also be found using two data points. Using section 1 and section 2 of the data booklet, calculate the activation energy for this reaction (in kJ mol^{-1}) if the rate constant was found to be 8.20×10^{-4} s^{-1} at 298K and 9.50×10^{-4} s^{-1} at 308K. Give your answer to three significant figures.

[4]

$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ so $\ln\left(\frac{8.20}{9.50}\right) = \frac{E_a}{8.31}\left(\frac{1}{308} - \frac{1}{298}\right)$ ✓

$E_a = 8.31 \times \left(\ln\left(\frac{8.20}{9.50}\right) \Big/ \left(\frac{1}{308} - \frac{1}{298}\right)\right)$

$E_a = 8.31 \times \ln 0.8631\ldots / -1.0895 \times 10^{-4}$ ✓

$= 8.31 \times 1350.689\ldots$

$E_a = 11224$ J ✓ $E_a = 11.2$ (kJ mol^{-1}) ✓

allow ecf 3 sig figs

3. The following is a proposed mechanism for the reaction of NO(g) with H_2(g).

Step 1: $2NO(g) \rightarrow N_2O_2(g)$

Step 2: $N_2O_2(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$

(a) Identify the intermediate in the reaction.

[1]

$N_2O_2(g)$ ✓ state symbol not required

(b) Write an equation for the overall reaction between NO(g) and H_2(g)

[1]

$2NO_{(g)} + H_{2(g)} \rightarrow N_2O_{(g)} + H_2O_{(g)}$

state symbols not required

(c) Deduce a rate expression if **step 1** were the rate determining step. Explain your reasoning.

[2]

Rate = $k[NO]^2$

because there are two moles of NO in the RDS (rate determining step).

(d) Deduce a rate expression if **step 2** were the rate determining step. Explain your reasoning.

[3]

Rate = $k[NO]^2[H_2]$

because there in one mole of H_2 in RDS

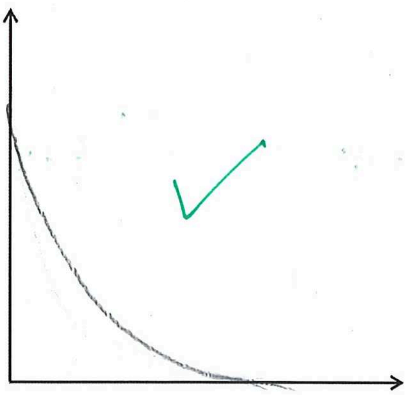
and one mole of N_2O_2, but this is an intermediate

and comes from two moles of NO.

(e) Assuming that the reaction is second order with respect to NO, sketch the two graphs below.

[2]

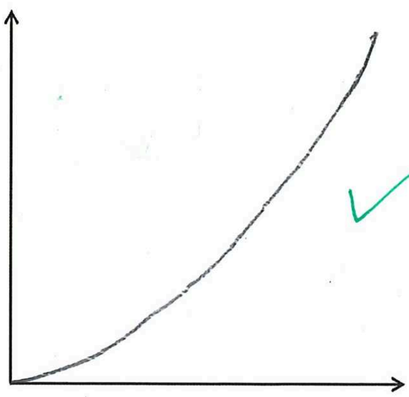
[NO]



Time

(any concave up decreasing)

Rate



[NO]

(any concave up increasing)

Total Marks 27 (41 minutes)