Marks 2

- Briefly explain how a catalyst works.

A catalyst provides an alternative reaction pathway that has a lower activation energy. This allows the reaction to proceed at lower temperatures or under milder conditions. The catalyst is not consumed during the reaction and does not affect the final position of equilibrium.

Marks 5

- The following data were obtained for the iodide-catalysed decomposition of hydrogen peroxide, H_2O_2.

Experiment	$[I^-]$(M)	$[H_2O_2]$ (M)	Initial rate(M s^{-1})
1	0.375	0	0
2	0.375	0.235	0.000324
3	0.375	0.470	0.000657
4	0.375	0.705	0.001024
5	0.375	0.940	0.001487
6	0	0.948	0
7	0.050	0.948	0.00045
8	0.100	0.948	0.00095
9	0.150	0.948	0.00140
10	0.200	0.948	0.00193

Determine the rate law from these data.

The rate law is of the form, rate = $k[I^-]^x[H_2O_2]^y$.

Between experiments 2 and 3, $[I^-]$ is unchanged. The increase in rate is due to the increase in $[H_2O_2]$:

$$\frac{\text{rate (3)}}{\text{rate (2)}} = \frac{\cancel{k(0.375)^x}(0.470)^y}{\cancel{k(0.375)^x}(0.235)^y} = \frac{(0.470)^y}{(0.235)^y} = \frac{0.000657}{0.000324} \quad \text{so } y = 1$$

Between experiments 7 and 8, $[H_2O_2]$ is unchanged. The increase in rate is due to the increase in $[I^-]$:

$$\frac{\text{rate (8)}}{\text{rate (7)}} = \frac{k(0.100)^x\cancel{(0.948)^y}}{k(0.050)^x\cancel{(0.948)^y}} = \frac{(0.100)^y}{(0.050)^y} = \frac{0.00095}{0.00045} \quad \text{so } x = 1$$

Hence,

rate = $k[I^-][H_2O_2]$

Use the data from Experiment 10 to calculate the rate constant for this reaction.

In experiment 10, $[I^-]$ = 0.200 M, $[H_2O_2]$ = 0.948 M and rate = 0.00193 M s^{-1}. Hence:

k = rate / $[I^-][H_2O_2]$ = (0.00193 M s^{-1}) / (0.200 M × 0.948 M)

= 0.0102 M^{-1} s^{-1}

k = **0.0102 M^{-1} s^{-1}**

ANSWER CONTINUES ON THE NEXT PAGE

Iodide ion is used as a catalyst in this reaction. What is the role of a catalyst in a chemical reaction?

A catalyst provides a reaction pathway of lower activation energy and hence increases the rate of the reaction. It is unchanged at the end of the reaction and does not change the equilibrium position.

Marks
4

The mechanism for this reaction has been postulated to be that below.

$$2NO(g) \rightleftharpoons N_2O_2(g) \quad \text{fast}$$
$$N_2O_2(g) + Cl_2 \rightarrow 2NOCl(g) \quad \text{slow}$$

Work out the rate law expected for this mechanism and hence show that it is consistent with the experimental rate law and the chemical equation.

The rate determining step is the slow, second step. As this is an elementary step, its rate law can be written down from its stoichiometry:

$$\text{rate} = k_2[N_2O_2(g)][Cl_2(g)]$$

where k_2 is the rate constant for this step.

This rate law involves the reactive intermediate N_2O_2. The concentration of this cannot be controlled so this rate law cannot be experimentally tested.

The first reaction is a fast equilibrium. The rate laws for the forward and backward elementary reactions are:

$$\text{rate of forward reaction} = k_1[NO(g)]^2$$
$$\text{rate of backward reaction} = k_{-1}[N_2O_2(g)]$$

where k_1 and k_{-1} are the rate constants for the forward and backward reactions, respectively.

At equilibrium, the rate of the forward and backward reactions are equal so

$$k_1[NO(g)]^2 = k_{-1}[N_2O_2(g)]$$

$$[N_2O_2(g)] = \frac{k_1}{k_{-1}}[NO(g)]^2 \quad \text{and} \quad \frac{[N_2O_2(g)]}{[NO(g)]^2} = \frac{k_1}{k_{-1}} = K_c$$

Substituting this value into the rate law for the second step gives,

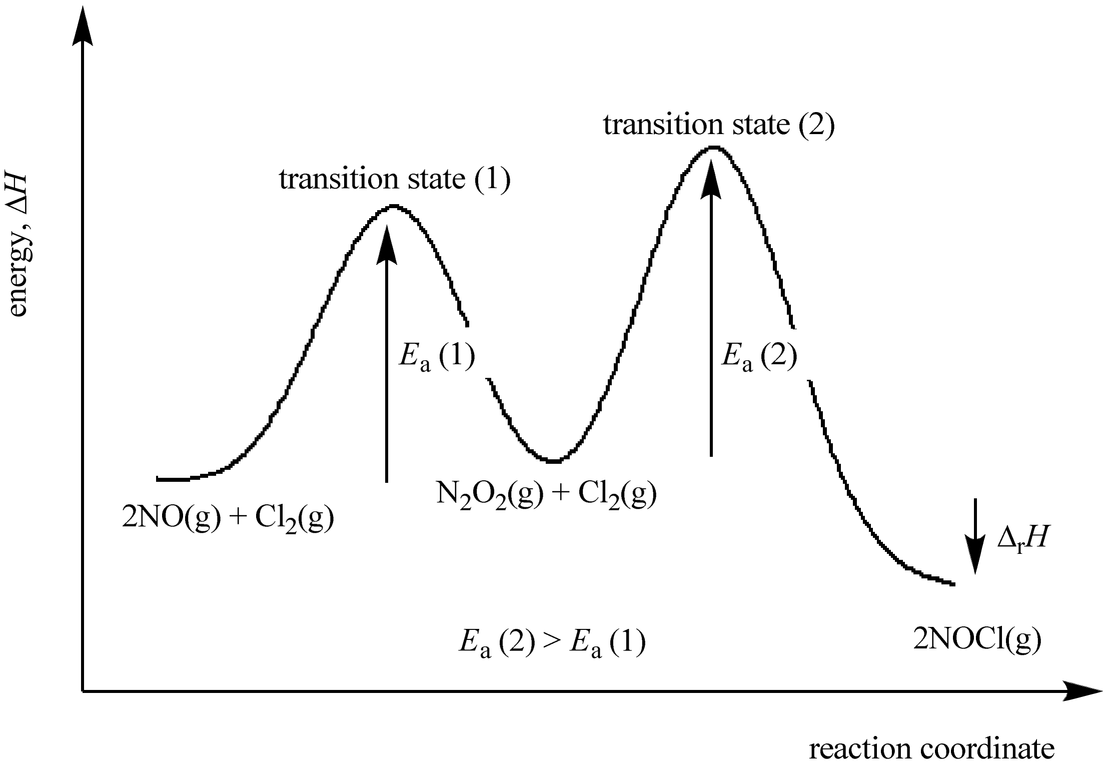
$$\text{rate} = k_2[N_2O_2(g)][Cl_2(g)]$$
$$= k_2\frac{k_1}{k_{-1}}[NO(g)]^2[Cl_2(g)] = k'[NO(g)]^2[Cl_2(g)] \quad \text{with } k' = k_2\frac{k_1}{k_{-1}} = k_2K_c$$

This rate law is second order with respect to NO and first order with respect to Cl_2, just as in the experimentally determined rate law in 2008-N-8. The proposed mechanism is thus consistent with the experiment.

ANSWER CONTINUES ON THE NEXT PAGE

The reaction is exothermic. Draw the potential energy *vs* reaction coordinate diagram for this mechanism, labelling all species that can be isolated.

The second step is the rate determining step so it has the larger activation energy. The reaction is exothermic so the products have lower enthalpy than the reactants.



- Briefly describe two factors that determine whether a collision between two molecules will lead to a chemical reaction. 1

For a collision to lead to a chemical reaction:

- **the molecules must collide with sufficient energy to overcome the activation energy for the reaction, and**
- **the molecules need to be orientated in the correct way for the reaction to occur.**