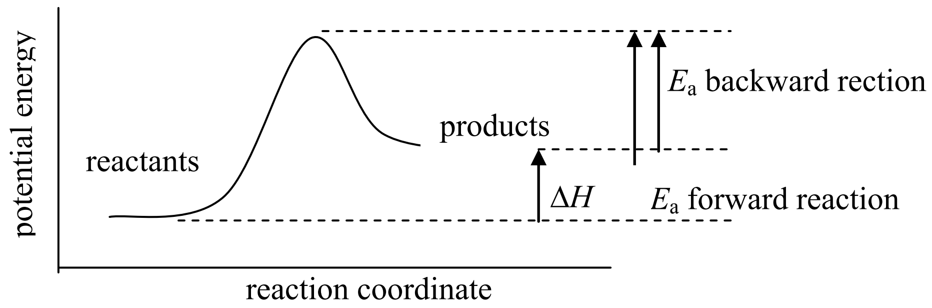
Marks

- Draw the potential energy diagram for an endothermic reaction. Indicate on the diagram the activation energy for both the forward and reverse reaction, and the enthalpy of reaction.

3



As the reaction is endothermic, the energy of the products is higher than that of the reactants.

- Consider the reaction: $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

4

The experimentally determined rate equation is: Rate = $k[NO_2(g)]^2$

Show the rate expression is consistent with the following mechanism:

Step 1	$2NO_2(g) \rightleftharpoons N_2O_4(g)$	fast
Step 2	$N_2O_4(g) \rightarrow NO(g) + NO_3(g)$	slow
Step 3	$NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$	fast

Step 2 is rate determining step and this will determine the rate of the reaction. The subsequent step can be ignored in working out the rate.

Step 2 involves the decomposition of N_2O_4 and depends only on its concentration:

rate = $k_2[N_2O_4(g)]$

As this involves the concentration of a reaction intermediate, it is not experimentally testable. The rate law should only involve the concentration of reactants, as their concentrations can be controlled.

As step 2 is slow, step 1 will be able to reach rapid equilibrium.

The forward reaction involves two NO_2 molecules reacting so has a rate:

rate of forward reaction = $k_1[NO_2(g)]^2$

ANSWER CONTINUES ON THE NEXT PAGE

The backward reaction involves the decomposition of N_2O_4 and so depends only on its concentration:

rate of backward reaction = $k_{-1}[N_2O_4(g)]$

If step 1 is at equilibrium then the rate of the forward and backward reactions will be equal:

$$k_1[NO_2(g)]^2 = k_{-1}[N_2O_4(g)] \quad \text{or} \quad [N_2O_4(g)] = \frac{k_1}{k_{-1}}[NO_2(g)]^2 = K_{eq}[NO_2(g)]^2$$

Using this expression for $[N_2O_4(g)]$ gives:

$$\text{rate} = k_2[N_2O_4(g)] = \frac{k_1 k_2}{k_{-1}}[NO_2(g)]^2 \quad \text{or rate} = k_2 K_{eq}[NO_2(g)]^2$$

This is consistent with the experiment rate law with $k = \frac{k_1 k_2}{k_{-1}} = k_2 K_{eq}$.