Marks
7

- Nitrogen monoxide, a noxious pollutant, reacts with oxygen to produce nitrogen dioxide, another toxic gas:

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

The following rate data were collected at 225 ^oC.

Experiment	$[NO]_0$ (M)	$[O_2]_0$ (M)	Initial rate, $-d[O_2]/dt$, (M s^{-1})
1	1.3×10^{-2}	1.1×10^{-2}	1.6×10^{-3}
2	1.3×10^{-2}	2.2×10^{-2}	3.2×10^{-3}
3	2.6×10^{-2}	1.1×10^{-2}	6.4×10^{-3}

Determine the rate law for the reaction.

Between experiments 1 and 2, [NO] is held constant and $[O_2]$ doubles. This leads to a doubling of the rate: the reaction is 1st order with respect to O_2.

Between experiments 1 and 3, $[O_2]$ is held constant and [NO] doubles. This leads to the rate increasing by a factor of 4: the rate is 2nd order with respect to NO.

The rate law is therefore:

$$-d[O_2]/dt = k[NO]^2[O_2]$$

Calculate the value of the rate constant at 225 ^oC.

In experiment 1, [NO] = 1.3×10^{-2} M, $[O_2]$ = 1.1×10^{-2} M and rate = 1.6×10^{-3} M s^{-1}. Substituting these values into the rate law gives:

$$(1.6 \times 10^{-3} \text{ M s}^{-1}) = k \times (1.3 \times 10^{-2} \text{ M})^2 \times (1.1 \times 10^{-2} \text{ M})$$

Hence:

$$k = 860 \text{ M}^{-2} \text{ s}^{-1}$$

Answer: **860 M^{-2} s^{-1}**

Calculate the rate of appearance of NO_2 when $[NO] = [O_2] = 6.5 \times 10^{-3}$ M.

Substituting the values into the rate law gives:

$$-d[O_2]/dt = k[NO]^2[O_2]$$

$$= (860 \text{ M}^{-2} \text{ s}^{-1}) \times (6.5 \times 10^{-3} \text{ M})^2 \times (6.5 \times 10^{-3} \text{ M}) = 2.35 \times 10^{-4} \text{ M s}^{-1}$$

From the chemical equation, the rate of appearance of NO_2 is *twice* the rate of loss of O_2:

$$d[NO_2]/dt = 2 \times -d[O_2]/dt = (2 \times 2.35 \times 10^{-4} \text{ M s}^{-1}) = 4.7 \times 10^{-4} \text{ M s}^{-1}$$

Answer: **4.7×10^{-4} M s^{-1}**

ANSWER CONTINUES ON THE NEXT PAGE

Suggest a possible mechanism for the reaction based on the form of the rate law. Explain your answer.

A possible mechanism is:

Step 1: $NO + NO \rightleftharpoons N_2O_2$ **fast equilibrium**

Step 2: $N_2O_2 + O_2 \rightarrow 2NO_2$ **slow (*i.e.* rate determining)**

If the first step is at equilibrium with equilibrium constant K_1:

$$K_1 = \frac{[N_2O_2]}{[NO]^2} \Rightarrow [N_2O_2] = K_1[NO]^2$$

The rate of step 2 is therefore

$$\text{rate} = k_2[N_2O_2][O_2]$$

$$= k_2K_1[NO]^2[O_2]$$

This is consistent with the experiment rate law with $k = k_1K$.