Marks
5

- Nitric oxide, a noxious pollutant, and hydrogen react to give nitrous oxide and water according to the following equation.

$$2NO(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$$

The following rate data were collected at 225 °C.

Experiment	$[NO]_0$ (M)	$[H_2]_0$ (M)	Initial rate (d[NO]/dt, M s^{-1})
1	6.4×10^{-3}	2.2×10^{-3}	2.6×10^{-5}
2	1.3×10^{-2}	2.2×10^{-3}	1.0×10^{-4}
3	6.4×10^{-3}	4.4×10^{-3}	5.1×10^{-5}

Determine the rate law for the reaction.

Between experiments 1 and 2, $[H_2]_0$ is constant. Doubling $[NO]_0$ leads to the rate increasing by a factor of four. The rate is second-order with respect to NO.

Between experiments 1 and 3, $[NO]_0$ is constant. Doubling $[H_2]_0$ leads to the rate doubling. The rate is second-order with respect to H_2.

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

Calculate the value of the rate constant at 225 °C.

Using experiment 1, the rate is 2.6×10^{-5} M s^{-1} when $[NO]_0 = 6.4 \times 10^{-3}$ M and $[H_2]_0 = 2.2 \times 10^{-3}$. Hence,

$$2.6 \times 10^{-5} \text{ M s}^{-1} = k(6.4 \times 10^{-3} \text{ M})^2 \times (2.2 \times 10^{-3} \text{ M})$$
$$k = 290 \text{ M}^{-2} \text{ s}^{-1}$$

The units of *k* are found by requiring that the units in the rate law balance:

$$-d[NO]/dt = k[NO]^2[H_2]$$
$$\text{M s}^{-1} = (\text{units of k}) \times (\text{M})^2 \times (\text{M})$$
$$\text{units of k} = \text{M}^{-2} \text{ s}^{-1}$$

Answer: **290 M^{-2} s^{-1}**

THE ANSWER CONTINUES ON THE NEXT PAGE

Calculate the rate of appearance of N_2O when [NO] = $[H_2]$ = 6.6×10^{-3} M.

As $-d[NO]/dt = 290[NO]^2[H_2]$,

$$-d[NO]/dt = (290\ M^{-2}\ s^{-1}) \times (6.6 \times 10^{-3}\ M)^2 \times (6.6 \times 10^{-3}\ M) = 8.3 \times 10^{-5}\ M\ s^{-1}$$

From the chemical equation, two NO are lost for every one N_2O that is made. Hence the rate of appearance of N_2O is half this value:

$$-d[NO]/dt = ½ \times 8.3 \times 10^{-5}\ M\ s^{-1} = 4.1 \times 10^{-5}\ M\ s^{-1}$$

Answer: **4.1×10^{-5} M s^{-1}**

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

$$NO + NO \rightleftharpoons (NO)_2 \qquad \textbf{(fast)}$$
$$(NO)_2 + H_2 \rightarrow N_2O + H_2O \qquad \textbf{(slow)}$$

The second step is rate determining as it is slow. For this elementary step, the rate law can be written down using the stoichiometry of the reaction equation:

$$\text{rate} = k_2[(NO)_2][H_2]$$

If the equilibrium in the first step is rapidly obtained then,

$$K_{eq} = \frac{[(NO)_2]}{[NO]^2} \quad \text{or } [(NO)_2] = K_{eq}[NO]^2$$

Substituting this back into the rate law for the rate determining step gives,

$$\text{rate} = k_2[(NO)_2][H_2] = k_2 \times K_{eq}[NO]^2 \times [H_2] = k_{eff}[NO]^2[H_2]$$

This rate law is consistent with the one determined experimentally and so the proposed mechanism is consistent.