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 whilst $[NO]_0$ doubles. This causes the rate to increase by a factor of $(1.0 \times 10^{-4} / 2.6 \times 10^{-5}) = 3.8 \sim 4$. The reaction is second order with respect to NO.

Between experiments (1) and (3), $[NO]_0$ is constant whilst $[H_2]_0$ doubles. This causes the rate to increase by a factor of $(5.1 \times 10^{-5} / 2.6 \times 10^{-5}) = 2.0$. The reaction is first order with respect to H_2.

Thus, overall, rate = $k[NO]^2[H_2]$

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

Using experiment (1), the rate – 2.6×10^{-5} M s^{-1} when $[NO]_0 = 6.4 \times 10^{-3}$ M and $[H_2]_0 = 2.2 \times 10^{-3}$ M. Hence, inserting these values into the rate equation gives

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

The units of *k* are obtained by ensuring that the units on the left and right-hand side of the equation balance.

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

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

From the chemical equation, *one* N_2O is made by the reaction of *two* NO. The rate of appearance of N_2O is one half of the rate of disappearance of NO:

rate = $0.5 \times k[NO]^2[H_2] = 0.5 \times (290 \text{ M}^{-2} \text{ s}^{-1}) \times (6.6 \times 10^{-3} \text{ M})^2 \times (6.6 \times 10^{-3} \text{ M})$

$= 4.2 \times 10^{-5}$ M s^{-1}

Answer: **4.2×10^{-5} M s^{-1}**

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

As collisions of three molecules is *very* unlikely, a possible reaction mechanism involves a fast equilibrium follow by the rate determining step:

Mechanism: $NO(g) + NO(g) \rightleftharpoons N_2O_2(g)$ **fast equilibrium**

$N_2O_2(g) + H_2(g) \rightarrow N_2O(g) + H_2O$ **slow**

The second step is the slowest and is rate determining. It involves the reaction of one N_2O_2 molecule with one H_2 molecule so its rate law is first order with respect to each:

$$\text{rate of reaction} = \text{rate of step 2} = k_2[N_2O_2(g)][H_2(g)]$$

However, the rate law as written contains $[N_2O_2(g)]$. The concentration of this highly reactive reaction intermediate cannot be controlled or measured. To test the rate law experimentally, it should contain only species whose concentrations can be changed. N_2O_2 molecules are generated by the first step.

If the first step is in equilibrium,

$$K_{eq} = \frac{[N_2O_2(g)]}{[NO(g)]^2} \quad \text{or } [N_2O_2(g)] = K_{eq}[NO(g)]^2$$

Putting this expression into the rate law for the rate determining step (step 2) gives:

$$\text{rate} = k_2[N_2O_2(g)][H_2(g)] = k_2\,K_{eq}[NO(g)]^2\,[H_2(g)] = k[NO(g)][H_2(g)]$$

This mechanism gives the same rate law as found experimentally. It is thus a *possible* mechanism.