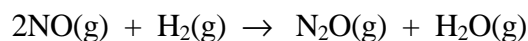


- Nitric oxide, a noxious pollutant, and hydrogen react to give nitrous oxide and water according to the following equation.



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), [H₂]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 [H₂]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 H₂.

Thus, overall, rate = $k[\text{NO}]^2[\text{H}_2]$

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

Using experiment (1), the rate – $2.6 \times 10^{-5} \text{ M s}^{-1}$ when [NO]₀ = $6.4 \times 10^{-3} \text{ M}$ and [H₂]₀ = $2.2 \times 10^{-3} \text{ M}$. 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: $290 \text{ M}^{-2} \text{ s}^{-1}$

Calculate the rate of appearance of N₂O when [NO] = [H₂] = $6.6 \times 10^{-3} \text{ M}$.

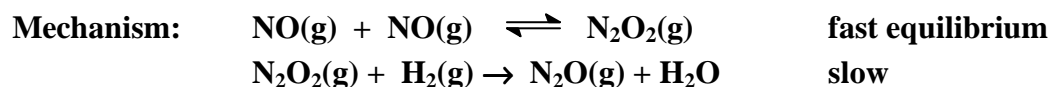
From the chemical equation, *one* N₂O is made by the reaction of *two* NO. The rate of appearance of N₂O is one half of the rate of disappearance of NO:

$$\begin{aligned} \text{rate} &= 0.5 \times k[\text{NO}]^2[\text{H}_2] = 0.5 \times (290 \text{ M}^{-2} \text{ s}^{-1}) \times (6.6 \times 10^{-3} \text{ M})^2 \times (6.6 \times 10^{-3} \text{ M}) \\ &= 4.2 \times 10^{-5} \text{ M s}^{-1} \end{aligned}$$

Answer: $4.2 \times 10^{-5} \text{ M s}^{-1}$

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 followed by the rate determining step:



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:

$$\text{rate of reaction} = \text{rate of step 2} = k_2[\text{N}_2\text{O}_2\text{(g)}][\text{H}_2\text{(g)}]$$

However, the rate law as written contains $[\text{N}_2\text{O}_2\text{(g)}]$. 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,

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

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

$$\text{rate} = k_2[\text{N}_2\text{O}_2\text{(g)}][\text{H}_2\text{(g)}] = k_2 K_{\text{eq}}[\text{NO(g)}]^2 [\text{H}_2\text{(g)}] = k[\text{NO(g)}][\text{H}_2\text{(g)}]$$

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