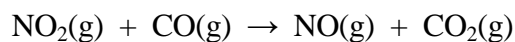


- The major pollutants NO(g), CO(g), NO₂(g) and CO₂(g) are emitted by cars and can react according to the following equation.



The following rate data were collected at 225 °C.

Marks
7

Experiment	[NO ₂] ₀ (M)	[CO] ₀ (M)	Initial rate (d[NO ₂]/dt, M s ⁻¹)
1	0.263	0.826	1.44 × 10 ⁻⁵
2	0.263	0.413	1.44 × 10 ⁻⁵
3	0.526	0.413	5.76 × 10 ⁻⁵

Determine the rate law for the reaction.

Between experiments (1) and (2), [NO₂]₀ is constant and [CO]₀ is halved. The rate does not change. The rate is independent of [CO]: zero order with respect to [CO].

Between experiments (2) and (3), [CO]₀ is kept constant and [NO₂]₀ is doubled. The rate increases by a factor of four: the rate is second order with respect to [NO₂].

Overall,

$$\text{rate} \propto [\text{NO}_2]^2 = k[\text{NO}_2]^2$$

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

In experiment (1), rate = 1.44 × 10⁻⁵ M s⁻¹ when [NO₂] = 0.263 M. Using the rate law:

$$1.44 \times 10^{-5} = k \times (0.263)^2 \quad \text{so } k = 2.08 \times 10^{-4}$$

The units of k can be deduced from the rate law:

$$\text{rate} = k[\text{NO}_2]^2$$

$$\text{M s}^{-1} = (\text{units of } k) \times (\text{M})^2 \quad \text{so } k \text{ must have units of "M}^{-1} \text{s}^{-1}\text{"}$$

Answer: $2.08 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$

ANSWER CONTINUES ON THE NEXT PAGE

Calculate the rate of appearance of CO₂ when [NO₂] = [CO] = 0.500 M.

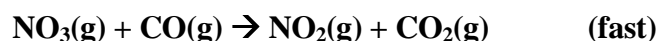
$$\text{When } [\text{NO}_2] = 0.500 \text{ M, rate} = \frac{d[\text{NO}_2]}{dt} = (2.08 \times 10^{-4}) \times (0.500)^2 = 5.20 \times 10^{-5} \text{ M s}^{-1}$$

From the chemical equation, one mole of CO₂ is produced for every mole of NO₂ that is removed. Thus, rate of appearance of CO₂ = rate of loss of NO₂.

Answer: $5.20 \times 10^{-5} \text{ M s}^{-1}$

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

A possible mechanism is:



The first step is slow and is rate determining. For this step, rate $\propto [\text{NO}_2]^2$, as observed. The second step is fast and does not contribute to the overall rate of the reaction and so the rate is independent of [CO(g)].