Marks 5

- The major pollutants NO(g), CO(g), NO_2(g) and CO_2(g), which are emitted by cars, can react according to the following equation.

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

The following rate data were collected at 225 °C.

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), $[NO_2]_0$ 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 $[NO_2]_0$ is doubled. The rate increases by a factor of four: the rate is second order with respect to [NO_2]. Overall,

$$\textbf{rate } \alpha\ [NO_2]^2 = k[NO_2]^2$$

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

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

Calculate the rate of appearance of CO_2 when [NO_2] = [CO] = 0.500 M.

When [NO_2] = 0.500 M, rate = $\frac{d[NO_2]}{dt} = (2.08 \times 10^{-4}) \times (0.500)^2 = 5.20 \times 10^{-5}\ M\ s^{-1}$

From the chemical equation, one mole of CO_2 is produced for every mole of NO_2 that is removed. Thus, rate of appearance of CO_2 = rate of loss of NO_2.

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

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

A possible mechanism is:

$$NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g) \qquad \textbf{(slow)}$$

$$NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g) \text{............} \textbf{(fast)}$$

The first step is slow and is rate determining. For this step, rate α [NO_2]^2, as observed. The second step is fast and does not affect the overall rate of the reaction and so the rate is independent of [CO(g)].