• The major pollutants NO(g), CO(g), NO<sub>2</sub>(g) and CO<sub>2</sub>(g), which are emitted by cars, can react according to the following equation.

Marks 5

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

The following rate data were collected at 225 °C.

Experiment	$[NO_2]_0(M)$	[CO] <sub>0</sub> (M)	Initial rate (d[NO <sub>2</sub> ]/dt, M s <sup>-1</sup> )
1	0.263	0.826	$1.44 \times 10^{-5}$
2	0.263	0.413	$1.44 \times 10^{-5}$
3	0.526	0.413	$5.76 \times 10^{-5}$

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,

rate 
$$\alpha [NO_2]^2 = k[NO_2]^2$$

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

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

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

When [NO<sub>2</sub>] = 0.500 M, rate = 
$$\frac{d[NO_2]}{dt}$$
 =  $(2.08 \times 10^{-4}) \times (0.500)^2$  = 5.20 × 10<sup>-5</sup> M s<sup>-1</sup>

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

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

A possible mechanism is:

$$NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g)$$
 (slow)

$$NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$$
....(fast)

The first step is slow and is rate determining. For this step, rate  $\alpha$  [NO<sub>2</sub>]<sup>2</sup>, 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)].