Methods to determine rate law expression.

Question

A reaction is first order in A and second order in B.

i) Write the differential rate equation

ii) How is the rate affected on increasing the concentration of B three times

iii) How is the rate affected when the concentration of both A and B are doubled?

Answer:

i) $r = \frac{dx}{dt} = k[A][B]^2$

ii) $\frac{r_2}{r_1} = \frac{[A_2][B_2]^2}{[A_1][B_1]^2} = \frac{[A_1][3B_1]^2}{[A_1][B_1]^2} = 9$

Thus reaction rate becomes 9 times.

iii) $\frac{r_2}{r_1} = \frac{[A_2][B_2]^2}{[A_1][B_1]^2} = \frac{[2A_1][2B_1]^2}{[A_1][B_1]^2} = 8$

Thus reaction rate becomes 8 times.

Question

In a reaction between A and B, the initial rate of reaction (r_0) was measured for different initial concentrations of A and B as given below:

$[A]$ (mol L^{-1})	0.2 (A_1)	0.2 (A_2)	0.4 (A_3)
$[B]$ (mol L^{-1})	0.3 (B_1)	0.1 (B_2)	0.05 (B_3)
r_0 (mol $L^{-1}s^{-1}$)	5.07×10^{-5} (r_1)	5.07×10^{-5} (r_2)	1.43×10^{-4} (r_3)

What is order of reaction w.r.t. A and B.

Answer:

Let rate law expression be:

$r = k[A]^x[B]^y$

$r_1 = k[A_1]^x[B_1]^y = k(0.2)^x(0.3)^y = 5.07\times10^{-5}$

$r_2 = k[A_2]^x[B_2]^y = k(0.2)^x(0.1)^y = 5.07\times10^{-5}$

$r_3 = k[A_3]^x[B_3]^y = k(0.4)^x(0.05)^y = 1.43\times10^{-4}$

$\frac{r_1}{r_2} = \frac{(0.2)^x(0.3)^y}{(0.2)^x(0.1)^y} = 3^y$

$\frac{5.07\times10^{-5}}{5.07\times10^{-5}} = 3^y,\ 1 = 3^y,\ y = 0$

$\frac{r_3}{r_2} = \frac{(0.4)^x(0.05)^y}{(0.2)^x(0.1)^y} = 2^x$

$\frac{1.43\times10^{-4}}{5.07\times10^{-5}} = 2^x,\ 2.82 = 2^x,\ x = 1.5\ (approx)$

Thus order w.r.t A is 1.5 and order w.r.t B is zero.

Question

The following results have been obtained during the kinetic studies of the reaction:

$$2A + B \rightarrow C + D$$

Experiment	[A] mol L^{-1}		[B] mol L^{-1}		r_D (mol L^{-1} min^{-1})	
I	0.1	A_1	0.1	B_1	6.0×10^{-3}	r_1
II	0.2	A_2	0.2	B_2	7.2×10^{-2}	r_2
III	0.2	A_3	0.4	B_3	2.88×10^{-1}	r_3
IV	0.4	A_4	0.1	B_4	2.4×10^{-2}	r_4

Determine the rate law and the rate constant for the reaction.

Answer:

Let rate law expression be

$r = k[A]^x[B]^y$

$r_1 = k[A_1]^x[B_1]^y = k(0.1)^x(0.1)^y = 6\times10^{-3}$

$r_2 = k[A_2]^x [B_2]^y = k(0.3)^x (0.2)^y = 7.2 \times 10^{-2}$

$r_3 = k[A_3]^x [B_3]^y = k(0.3)^x (0.4)^y = 2.88 \times 10^{-1}$

$r_4 = k[A_4]^x [B_4]^y = k(0.4)^x (0.1)^y = 2.4 \times 10^{-2}$

$$\frac{r_3}{r_2} = \frac{(0.3)^x (0.4)^y}{(0.3)^x (0.2)^y} = 2^y$$

$$\frac{2.88 \times 10^{-1}}{7.2 \times 10^{-2}} = 2^y, \quad 4 = 2^y, \quad y = 2$$

$$\frac{r_4}{r_1} = \frac{(0.4)^x (0.1)^y}{(0.1)^x (0.1)^y} = 4^x$$

$$\frac{2.4 \times 10^{-2}}{6 \times 10^{-3}} = 4^x, \quad 4 = 4^x, \quad x = 1$$

Thus rate law is: $r = k[A]^1 [B]^2$

Rate constant is given by

$$k = \frac{r}{[A]^1 [B]^2}$$

From experiment 1

$$k = \frac{6.0 \times 10^{-3}}{0.1 \times 0.1} = 6 \ L^2 mol^{-2} min^{-1}$$

From experiment 2

$$k = \frac{7.2 \times 10^{-2}}{0.3 \times 0.2} = 6 \ L^2 mol^{-2} min^{-1}$$

From experiment 3

$$k = \frac{2.88 \times 10^{-1}}{0.3 \times 0.4} = 6 \ L^2 mol^{-2} min^{-1}$$

From experiment 4

$$k = \frac{2.4 \times 10^{-2}}{0.4 \times 0.1} = 6 \ L^2 mol^{-2} min^{-1}$$

Thus rate constant, $k = 6 \ L^2 mol^{-2} min^{-1}$

Question

The reaction between A and B is first order w.r.t A

and zero order w.r.t. B. Fill in the blanks in the following table:

Experiment	[A] mol L^{-1}	[B] mol L^{-1}	Initial rate mol L^{-1} min^{-1}
I	0.1	0.1	2.0×10^{-2}
II	---	0.2	4.0×10^{-2}
III	0.4	0.4	---
IV	---	0.2	2.0×10^{-2}

Answer: As reaction is first order w.r.t A and zero order w.r.t B the rate law expression is given by:

$$r = k[A]^1[B]^0 = k[A]$$

From first experiment

$$k = \frac{r_1}{[A_1]} = \frac{2.0 \times 10^{-2}}{0.1} = 0.2 \text{ min}^{-1}$$

From experiment 2:

$$[A_2] = \frac{r_2}{k} = \frac{4.0 \times 10^{-2}}{0.2} = 0.2 \text{ mol } L^{-1}$$

From experiment 3:

$$r_3 = k[A_3] = 0.2 \times 0.4 = 0.08 \text{ mol } L^{-1} \text{ min}^{-1}$$

From experiment 4:

$$[A_4] = \frac{r_4}{k} = \frac{2.0 \times 10^{-2}}{0.2} = 0.1 \text{ mol } L^{-1}$$