Class XII

Answer

(i) Given rate = $k [NO]^2$

Therefore, order of the reaction = 2

$$k = \frac{\text{Rate}}{[\text{NO}]^2}$$

$$= \frac{\text{mol } \text{L}^{-1} \text{ s}^{-1}}{(\text{mol } \text{L}^{-1})^2}$$

$$= \frac{\text{mol } \text{L}^{-1} \text{ s}^{-1}}{\text{mol}^2 \text{ L}^{-2}}$$

$$= \text{L mol}^{-1} \text{ s}^{-1}$$

(ii) Given rate = $k [H_2O_2] [I^-]$

Therefore, order of the reaction = 2

 $k = \frac{\text{Rate}}{[\text{H}_2\text{O}_2][\Gamma]}$ Dimension of $= \frac{\text{mol } L^{-1} \text{ s}^{-1}}{(\text{mol } L^{-1})(\text{mol } L^{-1})}$ $= L \text{ mol}^{-1} \text{ s}^{-1}$ (iii) Given rate = k [CH_3CHO]^{3/2} Therefore, order of reaction = $\frac{3}{2}$ $k = \frac{\text{Rate}}{[\text{CH}_3\text{CHO}]^{\frac{3}{2}}}$ Dimension of $= \frac{\text{mol } L^{-1} \text{ s}^{-1}}{(\text{mol } L^{-1})^{\frac{3}{2}}}$ $= \frac{\text{mol } L^{-1} \text{ s}^{-1}}{\text{mol}^{\frac{3}{2}} L^{-\frac{3}{2}}}$ $= L^{\frac{1}{2}} \text{ mol}^{-\frac{1}{2}} \text{ s}^{-1}$ (iv) Given rate = k [C_2H_5CI] Therefore, order of the reaction = 1

 $k = \frac{\text{Rate}}{[C_2H_5\text{Cl}]}$ $= \frac{\text{mol } L^{-1} \text{ s}^{-1}}{\text{mol } L^{-1}}$ $= \text{ s}^{-1}$

Question 4.2:

For the reaction:

 $2A\,+\,B\rightarrow A_2B$

the rate = $k[A][B]^2$ with $k = 2.0 \times 10^{-6} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$. Calculate the initial rate of the reaction when $[A] = 0.1 \text{ mol} \text{ L}^{-1}$, $[B] = 0.2 \text{ mol} \text{ L}^{-1}$. Calculate the rate of reaction after [A] is reduced to 0.06 mol L⁻¹.

Answer

The initial rate of the reaction is

Rate = $k [A][B]^2$ = (2.0 × 10⁻⁶ mol⁻² L² s⁻¹) (0.1 mol L⁻¹) (0.2 mol L⁻¹)² = 8.0 × 10⁻⁹ mol⁻² L² s⁻¹

When [A] is reduced from 0.1 mol L^{-1} to 0.06 mol⁻¹, the concentration of A reacted = (0.1 - 0.06) mol L^{-1} = 0.04 mol L^{-1}

 $= \frac{1}{2} \times 0.04 \text{ mol } L^{-1}$ Therefore, concentration of B reacted = 0.02 mol L⁻¹ Then, concentration of B available, [B] = (0.2 - 0.02) mol L⁻¹ = 0.18 mol L⁻¹ After [A] is reduced to 0.06 mol L⁻¹, the rate of the reaction is given by, Rate = k [A][B]² = (2.0 × 10⁻⁶ mol⁻² L² s⁻¹) (0.06 mol L⁻¹) (0.18 mol L⁻¹)² = 3.89 mol L⁻¹ s⁻¹

Question 4.3:

The decomposition of NH₃ on platinum surface is zero order reaction. What are the rates of production of N₂ and H₂ if $k = 2.5 \times 10^{-4} \text{ mol}^{-1} \text{ L s}^{-1}$?

Answer

The decomposition of NH₃ on platinum surface is represented by the following equation.

$$2 \operatorname{NH}_{3(g)} \xrightarrow{\operatorname{Pt}} \operatorname{N}_{2(g)} + 3 \operatorname{H}_{2(g)}$$

Therefore,

Rate =
$$-\frac{1}{2}\frac{d[\mathrm{NH}_3]}{dt} = \frac{d[\mathrm{N}_2]}{dt} = \frac{1}{3}\frac{d[\mathrm{H}_2]}{dt}$$

However, it is given that the reaction is of zero order. Therefore,

$$-\frac{1}{2}\frac{d[NH_3]}{dt} = \frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt} = k$$
$$= 2.5 \times 10^{-4} \text{ mol } L^{-1} \text{ s}^{-1}$$

Therefore, the rate of production of N_2 is

$$\frac{d[N_2]}{dt} = 2.5 \times 10^{-4} \text{ mol } \text{L}^{-1} \text{s}^{-1}$$

And, the rate of production of H_2 is

$$\frac{d[H_2]}{dt} = 3 \times 2.5 \times 10^{-4} \text{ mol } \text{L}^{-1} \text{s}^{-1}$$
$$= 7.5 \times 10^{-4} \text{ mol } \text{L}^{-1} \text{ s}^{-1}$$

Question 4.4:

The decomposition of dimethyl ether leads to the formation of CH_4 , H_2 and CO and the reaction rate is given by

Rate = $k [CH_3OCH_3]^{3/2}$

The rate of reaction is followed by increase in pressure in a closed vessel, so the rate can also be expressed in terms of the partial pressure of dimethyl ether, i.e.,

Rate =
$$k \left(p_{\text{CH}_{3}\text{OCH}_{3}} \right)^{\frac{3}{2}}$$

If the pressure is measured in bar andtime in minutes, then what are the units of rate and rate constants?

Answer

If pressure is measured in bar and time in minutes, then Unit of rate = bar min^{-1}

$$Rate = k \left(p_{CH_{3}OCH_{3}} \right)^{\frac{3}{2}}$$
$$\Rightarrow k = \frac{Rate}{\left(p_{CH_{3}OCH_{3}} \right)^{\frac{3}{2}}}$$

$$(k) = \frac{\operatorname{bar} \min^{-1}}{\operatorname{bar}^{\frac{3}{2}}}$$

Therefore, unit of rate constants

 $= bar^{-1/2} min^{-1}$

Question 4.5:

Mention the factors that affect the rate of a chemical reaction.

Answer

The factors that affect the rate of a reaction are as follows.

(i) Concentration of reactants (pressure in case of gases)

(ii) Temperature

(iii) Presence of a catalyst

Question 4.6:

A reaction is second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is

(i) doubled (ii) reduced to half?

Answer

Let the concentration of the reactant be [A] = a

Rate of reaction, $R = k [A]^2$

 $= ka^2$

(i) If the concentration of the reactant is doubled, i.e. [A] = 2a, then the rate of the reaction would be

 $R' = k (2a)^{2}$ = 4ka² = 4 R Therefore, the rate of the reaction would increase by 4 times. (ii) If the concentration of the reactant is reduced to half, i.e. $[A] = \frac{1}{2}a$, then the rate of the reaction would be

$$R'' = k \left(\frac{1}{2}a\right)^2$$
$$= \frac{1}{4}ka$$
$$= \frac{1}{4}R$$

Therefore, the rate of the reaction would be reduced to 4

Question 4.7:

What is the effect of temperature on the rate constant of a reaction? How can this temperature effect on rate constant be represented quantitatively?

 1^{th}

Answer

The rate constant is nearly doubled with a rise in temperature by 10° for a chemical reaction.

The temperature effect on the rate constant can be represented quantitatively by Arrhenius equation,

 $k = \mathrm{A} e^{-E_a/\mathrm{R}T}$

where, k is the rate constant,

A is the Arrhenius factor or the frequency factor,

R is the gas constant,

T is the temperature, and

 E_a is the energy of activation for the reaction

Question 4.8:

In a pseudo first order hydrolysis of ester in water, the following results were obtained:

t/s	0	30	60	90
[Ester]mol L ⁻¹	0.55	0.31	0.17	0.085

(i) Calculate the average rate of reaction between the time interval 30 to 60 seconds.(ii) Calculate the pseudo first order rate constant for the hydrolysis of ester.Answer

 $=\frac{d[\text{Ester}]}{dt}$

(i) Average rate of reaction between the time interval, 30 to 60 seconds,

$$= \frac{0.31 - 0.17}{60 - 30}$$

$$= \frac{0.14}{30}$$

$$= 4.67 \times 10^{-3} \text{ mol } L^{-1} \text{ s}^{-1}$$
(ii) For a pseudo first order reaction,

$$k = \frac{2.303}{t} \log \frac{[\text{R}]_0}{[\text{R}]}$$
For $t = 30 \text{ s}$, $k_1 = \frac{2.303}{30} \log \frac{0.55}{0.31}$

$$= 1.911 \times 10^{-2} \text{ s}^{-1}$$
For $t = 60 \text{ s}$, $k_2 = \frac{2.303}{60} \log \frac{0.55}{0.17}$

$$= 1.957 \times 10^{-2} \text{ s}^{-1}$$
For $t = 90 \text{ s}$, $k_3 = \frac{2.303}{90} \log \frac{0.55}{0.085}$

$$= 2.075 \times 10^{-2} \text{ s}^{-1}$$
Then, average rate constant, $k = \frac{k_1 + k_2 + k_3}{3}$

$$= \frac{(1.911 \times 10^{-2}) + (1.957 \times 10^{-2}) + (2.075 \times 10^{-2})}{3}$$

Question 4.9:

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 concentrations of both A and B are doubled? Answer

(i) The differential rate equation will be

$$-\frac{d[\mathbf{R}]}{dt} = k[\mathbf{A}][\mathbf{B}]^2$$

(ii) If the concentration of B is increased three times, then

$$-\frac{d[\mathbf{R}]}{dt} = k[\mathbf{A}][\mathbf{3B}]^2$$
$$= 9 \cdot k[\mathbf{A}][\mathbf{B}]^2$$

Therefore, the rate of reaction will increase 9 times.

(iii) When the concentrations of both A and B are doubled,

$$-\frac{d[\mathbf{R}]}{dt} = k[\mathbf{A}][\mathbf{B}]^{2}$$
$$= k[\mathbf{2A}][\mathbf{2B}]^{2}$$
$$= 8 \cdot k[\mathbf{A}][\mathbf{B}]^{2}$$

Therefore, the rate of reaction will increase 8 times.

Question 4.10:

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}	0.20	0.20	0.40
B/ mol L ⁻¹	0.30	0.10	0.05
$r_0/ \text{ mol } L^{-1} \text{ s}^{-1}$	5.07×10^{-5}	5.07×10^{-5}	1.43×10^{-4}

What is the order of the reaction with respect to A and B?

Answer

Let the order of the reaction with respect to A be x and with respect to B be y. Therefore,

$$\mathbf{r}_{0} = k \left[\mathbf{A} \right]^{x} \left[\mathbf{B} \right]^{y}$$

$$5.07 \times 10^{-5} = k [0.20]^{x} [0.30]^{y}$$
 (i)

$$5.07 \times 10^{-5} = k [0.20]^x [0.10]^y$$
 (ii)

$$1.43 \times 10^{-4} = k [0.40]^x [0.05]^y$$
 (iii)

Dividing equation (i) by (ii), we obtain

$$\frac{5.07 \times 10^{-5}}{5.07 \times 10^{-5}} = \frac{k [0.20]^x [0.30]^y}{k [0.20]^x [0.10]^y}$$
$$\Rightarrow 1 = \frac{[0.30]^y}{[0.10]^y}$$
$$\Rightarrow \left(\frac{0.30}{0.10}\right)^0 = \left(\frac{0.30}{0.10}\right)^y$$
$$\Rightarrow y = 0$$

Dividing equation (iii) by (ii), we obtain

$$\frac{1.43 \times 10^{-4}}{5.07 \times 10^{-5}} = \frac{k [0.40]^x [0.05]^y}{k [0.20]^x [0.30]^y}$$

$$\Rightarrow \frac{1.43 \times 10^{-4}}{5.07 \times 10^{-5}} = \frac{[0.40]^x}{[0.20]^x} \qquad \begin{bmatrix} \text{Since } y = 0, \\ [0.05]^y = [0.30]^y = 1 \end{bmatrix}$$

$$\Rightarrow 2.821 = 2^x$$

$$\Rightarrow \log 2.821 = x \log 2 \qquad \text{(Taking log on both sides)}$$

$$\Rightarrow x = \frac{\log 2.821}{\log 2}$$

= 1.496

= 1.5 (approximately)

Hence, the order of the reaction with respect to A is 1.5 and with respect to B is zero.

Question 4.11:

The following results have been obtained during the kinetic studies of the reaction: $2\mathsf{A}$ + B \rightarrow C + D

Experiment	A/ mol L^{-1}	$B/ mol L^{-1}$	Initial rate of formation of D/mol L^{-1} min ⁻¹
I	0.1	0.1	6.0×10^{-3}
II	0.3	0.2	7.2×10^{-2}
III	0.3	0.4	2.88×10^{-1}
IV	0.4	0.1	2.40×10^{-2}

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

Answer

Let the order of the reaction with respect to A be x and with respect to B be y.

Therefore, rate of the reaction is given by,

Rate = $k [A]^{x} [B]^{y}$

According to the question,

$$6.0 \times 10^{-3} = k [0.1]^x [0.1]^y$$
(i)

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

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

$$2.40 \times 10^{-2} = k [0.4]^x [0.1]^y$$
 (iv)

Dividing equation (iv) by (i), we obtain

$$\frac{2.40 \times 10^{-2}}{6.0 \times 10^{-3}} = \frac{k \left[0.4\right]^x \left[0.1\right]^y}{k \left[0.1\right]^x \left[0.1\right]^y}$$
$$\Rightarrow 4 = \frac{\left[0.4\right]^x}{\left[0.1\right]^x}$$
$$\Rightarrow 4 = \left(\frac{0.4}{0.1}\right)^x$$
$$\Rightarrow (4)^1 = 4^x$$
$$\Rightarrow x = 1$$

Dividing equation (iii) by (ii), we obtain

$$\frac{2.88 \times 10^{-1}}{7.2 \times 10^{-2}} = \frac{k [0.3]^x [0.4]^y}{k [0.3]^x [0.2]^y}$$
$$\Rightarrow 4 = \left(\frac{0.4}{0.2}\right)^y$$
$$\Rightarrow 4 = 2^y$$
$$\Rightarrow 2^2 = 2^y$$
$$\Rightarrow y = 2$$

Therefore, the rate law is Rate = k [A] [B]²

$$\Rightarrow k = \frac{\text{Rate}}{[A][B]^2}$$

From experiment I, we obtain

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

= 6.0 L² mol⁻² min⁻¹
From experiment II, we obtain

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

= 6.0 L^2 mol⁻² min⁻¹

From experiment III, we obtain

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

= 6.0 L^2 mol⁻² min⁻¹

From experiment IV, we obtain

$$k = \frac{2.40 \times 10^{-2} \text{ mol } \text{L}^{-1} \text{ min}^{-1}}{(0.4 \text{ mol } \text{L}^{-1})(0.1 \text{ mol } \text{L}^{-1})^2}$$

= 6.0 L² mol⁻² min⁻¹

Therefore, rate constant, $k = 6.0 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1}$

Question 4.12:

The reaction between A and B is first order with respect to A and zero order with respect to 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
Ι	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

The given reaction is of the first order with respect to A and of zero order with respect to B.

Therefore, the rate of the reaction is given by,

```
Rate = k [A]^{1} [B]^{0}

\Rightarrow Rate = k [A]

From experiment I, we obtain

2.0 \times 10^{-2} \text{ mol } L^{-1} \min^{-1} = k (0.1 \text{ mol } L^{-1})

\Rightarrow k = 0.2 \min^{-1}

From experiment II, we obtain

4.0 \times 10^{-2} \text{ mol } L^{-1} \min^{-1} = 0.2 \min^{-1} [A]

\Rightarrow [A] = 0.2 \text{ mol } L^{-1}

From experiment III, we obtain

Rate = 0.2 \min^{-1} \times 0.4 \text{ mol } L^{-1}

= 0.08 \text{ mol } L^{-1} \min^{-1}

From experiment IV, we obtain

2.0 \times 10^{-2} \text{ mol } L^{-1} \min^{-1} = 0.2 \min^{-1} [A]

\Rightarrow [A] = 0.1 \text{ mol } L^{-1}
```

Question 4.13: Calculate the half-life of a first order reaction from their rate constants given below: (i) 200 s⁻¹ (ii) 2 min⁻¹ (iii) 4 years⁻¹ Answer (i) Half life, $t_{\frac{1}{2}} = \frac{0.693}{k}$ $= \frac{0.693}{200 \text{ s}^{-1}}$ = 3.47 s (approximately)(ii) Half life, $t_{\frac{1}{2}} = \frac{0.693}{k}$ $= \frac{0.693}{2 \text{ min}^{-1}}$ = 0.35 min (approximately)(iii) Half life, $t_{\frac{1}{2}} = \frac{0.693}{k}$ $= \frac{0.693}{4 \text{ years}^{-1}}$ = 0.173 years (approximately)

Question 4.14:

The half-life for radioactive decay of 14 C is 5730 years. An archaeological artifact containing wood had only 80% of the 14 C found in a living tree. Estimate the age of the sample.

Answer

Here,

$$k = \frac{0.693}{t_{\frac{1}{2}}}$$

 $=\frac{0.693}{5730}$ years⁻¹

It is known that,

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$
$$= \frac{2.303}{\frac{0.693}{5730}} \log \frac{100}{80}$$

= 1845 years (approximately)

Hence, the age of the sample is 1845 years.

Question 4.15:

The experimental data for decomposition of N_2O_5

 $\left[2N_2O_5 \longrightarrow 4NO_2 + O_2\right]$

in gas phase at 318K are given below:

<i>t</i> (s)	0	400	800	120	160	200	240	280	320
				0	0	0	0	0	0
$10^2 \times [N_2O_5] \text{mol } \text{L}^{-1}$	1.6 3	1.3 6	1.1 4	0.93	0.78	0.64	0.53	0.43	0.35

(i) Plot [N₂O₅] against t.

(ii) Find the half-life period for the reaction.

(iii) Draw a graph between log $[N_2O_5]$ and t.

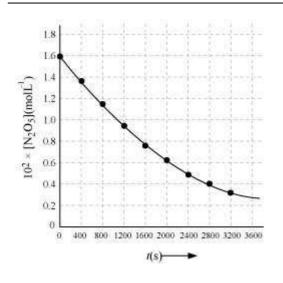
(iv) What is the rate law?

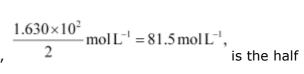
(v) Calculate the rate constant.

(vi) Calculate the half-life period from k and compare it with (ii).

Answer

i.

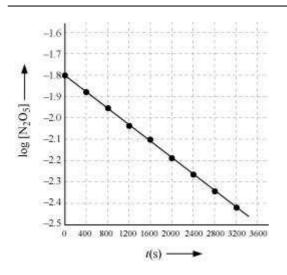




(ii) Time corresponding to the concentration, 2 life. From the graph, the half life is obtained as 1450 s.

(iii)

t(s)	$10^2 \times [N_2O_5] / mol L^{-1}$	$log[N_2O_5]$
0	1.63	- 1.79
400	1.36	- 1.87
800	1.14	- 1.94
1200	0.93	- 2.03
1600	0.78	- 2.11
2000	0.64	- 2.19
2400	0.53	- 2.28
2800	0.43	- 2.37
3200	0.35	- 2.46



(iv) The given reaction is of the first order as the plot, $\log[N_2O_5]_{v/s} t$, is a straight line. Therefore, the rate law of the reaction is

Rate = $k [N_2O_5]$

(v) From the plot, $\log[N_2O_5]_{v/s} t$, we obtain

Slope =
$$\frac{-2.46 - (-1.79)}{3200 - 0}$$

= $\frac{-0.67}{3200}$

Again, slope of the line of the plot $\log[N_2O_5]_{v/s t}$ is given by

$$-\frac{k}{2.303}$$

Therefore, we obtain,

.

$$-\frac{k}{2.303} = -\frac{0.67}{3200}$$
$$\implies k = 4.82 \times 10^{-4} \,\mathrm{s}^{-1}$$

(vi) Half-life is given by,

$$t_{1/2} = \frac{0.639}{k}$$

= $\frac{0.693}{4.82 \times 10^{-4}} s$
= $1.438 \times 10^{3} s$
= $1438 s$

This value, 1438 s, is very close to the value that was obtained from the graph.

Question 4.16:

The rate constant for a first order reaction is 60 s^{-1} . How much time will it take to reduce the initial concentration of the reactant to its $1/16^{\text{th}}$ value?

Answer

It is known that,

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$

= $\frac{2.303}{60 \text{ s}^{-1}} \log \frac{1}{1/6}$
= $\frac{2.303}{60 \text{ s}^{-1}} \log 16$
= $4.6 \times 10^{-2} \text{ s (approximately)}$

Hence, the required time is 4.6×10^{-2} s.

Question 4.17:

During nuclear explosion, one of the products is 90 Sr with half-life of 28.1 years. If 1µg of 90 Sr was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 years and 60 years if it is not lost metabolically.

Answer

$$k = \frac{0.693}{t_{\frac{1}{2}}} = \frac{0.693}{28.1} \text{ y}^{-1}$$

Here,

It is known that,

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$

$$\Rightarrow 10 = \frac{2.303}{\frac{0.693}{28.1}} \log \frac{1}{[R]}$$

$$\Rightarrow 10 = \frac{2.303}{\frac{0.693}{28.1}} (-\log[R])$$

$$\Rightarrow \log[R] = -\frac{10 \times 0.693}{2.303 \times 28.1}$$

$$\Rightarrow [R] = \operatorname{antilog} (-0.1071)$$

$$= \operatorname{antilog} (\overline{1.8929})$$

$$= 0.7814 \mu g$$

Therefore, 0.7814 μg of ^{90}Sr will remain after 10 years. Again,

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$
$$\Rightarrow 60 = \frac{2.303}{\frac{0.693}{28.1}} \log \frac{1}{[R]}$$
$$\Rightarrow \log[R] = -\frac{60 \times 0.693}{2.303 \times 28.1}$$
$$\Rightarrow [R] = \operatorname{antilog} (-0.6425)$$
$$= \operatorname{antilog} (\overline{1.3575})$$
$$= 0.2278 \mu g$$

Therefore, 0.2278 μg of ^{90}Sr will remain after 60 years.

Question 4.18:

For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.

Answer

For a first order reaction, the time required for 99% completion is

$$t_{1} = \frac{2.303}{k} \log \frac{100}{100 - 99}$$
$$= \frac{2.303}{k} \log 100$$
$$= 2 \times \frac{2.303}{k}$$

For a first order reaction, the time required for 90% completion is

$$t_2 = \frac{2.303}{k} \log \frac{100}{100 - 90}$$
$$= \frac{2.303}{k} \log 10$$
$$= \frac{2.303}{k}$$

Therefore, $t_1 = 2t_2$

Hence, the time required for 99% completion of a first order reaction is twice the time required for the completion of 90% of the reaction.

Question 4.19:

A first order reaction takes 40 min for 30% decomposition. Calculate $t_{1/2}$.

Answer

For a first order reaction,

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$
$$k = \frac{2.303}{40 \text{ min}} \log \frac{100}{100 - 30}$$
$$= \frac{2.303}{40 \text{ min}} \log \frac{10}{7}$$
$$= 8.918 \times 10^{-3} \text{ min}^{-1}$$

Therefore, $t_{1/2}$ of the decomposition reaction is

$$t_{\frac{1}{2}} = \frac{0.693}{k}$$
$$= \frac{0.693}{8.918 \times 10^{-3}} \min$$

= 77.7 min (approximately)

Question 4.20:

For the decomposition of azoisopropane to hexane and nitrogen at 543 K, the following data are obtained.

t (sec)	P(mm of Hg)
0	35.0
360	54.0
720	63.0

Calculate the rate constant.

Answer

The decomposition of azoisopropane to hexane and nitrogen at 543 K is represented by the following equation.

$$(CH_3)_2 CHN=NCH(CH_3)_{2(g)} \longrightarrow N_{2(g)} + C_6H_{14(g)}$$

At $t = 0$ P₀ 0 0
At $t = t$ P₀ - p p p
After time, t, total pressure, $P_t = (P_0 - p) + p + p$

$$\Rightarrow P_t = P_0 + p$$

$$\Rightarrow p = P_t - P_0$$

Therefore, $P_0 - p = P_0 - (P_t - P_0)$

$$= 2P_0 - P_t$$

For a first order reaction,

$$k = \frac{2.303}{t} \log \frac{P_0}{P_0 - p}$$

= $\frac{2.303}{t} \log \frac{P_0}{2P_0 - P_t}$
When $t = 360$ s, $k = \frac{2.303}{360 \text{ s}} \log \frac{35.0}{2 \times 35.0 - 54.0}$

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= $2.175 \times 10^{-3} \text{ s}^{-1}$ $k = \frac{2.303}{720 \text{ s}} \log \frac{35.0}{2 \times 35.0 - 63.0}$ = $2.235 \times 10^{-3} \text{ s}^{-1}$

Hence, the average value of rate constant is

$$k = \frac{\left(2.175 \times 10^{-3}\right) + \left(2.235 \times 10^{-3}\right)}{2} \mathrm{s}^{-1}$$

 $= 2.21 \times 10^{-3} \text{ s}^{-1}$

Note: There is a slight variation in this answer and the one given in the NCERT textbook.

Question 4.21:

The following data were obtained during the first order thermal decomposition of SO_2CI_2 at a constant volume.

 $SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$

Experiment	Time/s ^{−1}	Total pressure/atm
1	0	0.5
2	100	0.6

Calculate the rate of the reaction when total pressure is 0.65 atm.

Answer

The thermal decomposition of SO_2CI_2 at a constant volume is represented by the following equation.

 $SO_2Cl_{2(g)} \longrightarrow SO_{2(g)} + Cl_{2(g)}$ At t = 0 P_0 0 0At t = t $P_0 - p$ p pP = (P - p) + p + p

After time, *t*, total pressure, $P_t = (P_0 - p) + p + p$

 $\Rightarrow \mathbf{P}_{t} = \mathbf{P}_{0} + p$ $\Rightarrow p = \mathbf{P}_{t} - \mathbf{P}_{0}$ $Therefore, \mathbf{P}_{0} - p = \mathbf{P}_{0} - (\mathbf{P}_{t} - \mathbf{P}_{0})$ $= 2 P_0 - P_t$

For a first order reaction,

$$k = \frac{2.303}{t} \log \frac{P_0}{P_0 - p}$$

= $\frac{2.303}{t} \log \frac{P_0}{2P_0 - P_t}$
When $t = 100$ s, $k = \frac{2.303}{100} \log \frac{0.5}{2 \times 0.5 - 0.6}$
= $2.231 \times 10^{-3} \text{ s}^{-1}$
When $P_t = 0.65$ atm, $P_0 + p = 0.65$
 $\Rightarrow p = 0.65 - P_0$
= $0.65 - 0.5$
= 0.15 atm

Therefore, when the total pressure is 0.65 atm, pressure of $SOCI_2$ is

 $P_{SOCI_2} = P_0 - p$ = 0.5 - 0.15 = 0.35 atm

Therefore, the rate of equation, when total pressure is 0.65 atm, is given by,

Rate = $k(P_{SOCI_2})$ = (2.23 × 10⁻³ s⁻¹) (0.35 atm) = 7.8 × 10⁻⁴ atm s⁻¹

Question 4.22:

The rate constant for the decomposition of N_2O_5 at various temperatures is given below:

T∕°C	0	20	40	60	80
$10^5 \times k/s^{-1}$	0.0787	1.70	25.7	178	2140

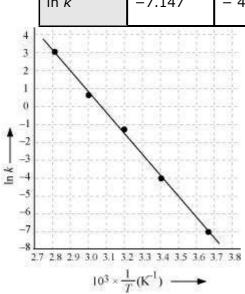
Draw a graph between ln k and 1/T and calculate the values of A and E_a .

Predict the rate constant at 30° and 50°C.

Answer

T/°C 0 20 40 60 80 T/K 273 293 313 333 353 $\frac{1}{T}/K^{-1}$ 3.0×10^{-3} 3.66×10^{-3} 3.41×10^{-3} 3.19×10^{-3} 2.83×10^{-3} $10^5 \times k / s^{-1}$ 0.0787 25.7 2140 1.70 178 ln *k* -7.147 - 4.075 -1.359 -0.577 3.063

From the given data, we obtain



Slope of the line,

$$\frac{y_2 - y_1}{x_2 - x_1} = -12.301 \text{K}$$

According to Arrhenius equation,

Slope =
$$-\frac{E_a}{R}$$

 $\Rightarrow E_a = -Slope \times R$
= $-(-12.301 \text{ K}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1})$
= $102.27 \text{ kJ mol}^{-1}$

Again,

 $\ln k = \ln A - \frac{E_a}{RT}$ $\ln A = \ln k + \frac{E_a}{RT}$ When $T = 273 \,\mathrm{K}$, $\ln k = -7.147$ Then, $\ln A = -7.147 + \frac{102.27 \times 10^3}{8.314 \times 273}$ = 37.911Therefore, $A = 2.91 \times 10^6$ When T = 30 + 273 K = 303 K, $\frac{1}{T} = 0.0033 \text{ K} = 3.3 \times 10^{-3} \text{ K}$ then, at $\frac{1}{T} = 3.3 \times 10^{-3} \,\mathrm{K}$, $\ln k = -2.8$ Therefore, $k = 6.08 \times 10^{-2} \text{ s}^{-1}$ Again, when T = 50 + 273 K = 323 K, $\frac{1}{T} = 0.0031 \text{ K} = 3.1 \times 10^{-3} \text{ K}$ $\frac{1}{T} = 3.1 \times 10^{-3} \, \text{K},$ Then, at $\ln k = -0.5$ Therefore, $k = 0.607 \, \text{s}^{-1}$

Question 4.23:

The rate constant for the decomposition of hydrocarbons is $2.418 \times 10^{-5} s^{-1}$ at 546 K. If the energy of activation is 179.9 kJ/mol, what will be the value of pre-exponential factor. Answer $k = 2.418 \times 10^{-5} s^{-1}$

T = 546 K

 $E_{\rm a}$ = 179.9 kJ mol⁻¹ = 179.9 × 10³ J mol⁻¹

According to the Arrhenius equation,

$$\begin{split} k &= Ae^{-E_a/RT} \\ \Rightarrow \ln k = \ln A - \frac{E_a}{RT} \\ \Rightarrow \log k = \log A - \frac{E_a}{2.303 \text{ RT}} \\ \Rightarrow \log A = \log k + \frac{E_a}{2.303 \text{ RT}} \\ &= \log \left(2.418 \times 10^{-5} \text{ s}^{-1}\right) + \frac{179.9 \times 10^3 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ Jk}^{-1} \text{ mol}^{-1} \times 546 \text{ K}} \\ &= (0.3835 - 5) + 17.2082 \\ &= 12.5917 \\ \text{Therefore, A = antilog (12.5917)} \\ &= 3.9 \times 10^{12} \text{ s}^{-1} \text{ (approximately)} \end{split}$$

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Question 4.24:
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Consider a certain reaction $A \rightarrow$ Products with $k = 2.0 \times 10^{-2} \text{ s}^{-1}$. Calculate the concentration of A remaining after 100 s if the initial concentration of A is 1.0 mol L⁻¹. Answer

$$k = 2.0 \times 10^{-2} \text{ s}^{-1}$$

 $T = 100 \text{ s}$
 $[\text{A}]_{\text{o}} = 1.0 \text{ moL}^{-1}$

Since the unit of k is s^{-1} , the given reaction is a first order reaction.

$$k = \frac{2.303}{t} \log \frac{\left[A\right]_0}{\left[A\right]}$$

Therefore,

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$$\Rightarrow 2.0 \times 10^{-2} \text{ s}^{-1} = \frac{2.303}{100 \text{ s}} \log \frac{1.0}{[\text{A}]}$$
$$\Rightarrow 2.0 \times 10^{-2} \text{ s}^{-1} = \frac{2.303}{100 \text{ s}} \left(-\log[\text{A}]\right)$$
$$\Rightarrow -\log[\text{A}] = \frac{2.0 \times 10^{-2} \times 100}{2.303}$$
$$\Rightarrow [\text{A}] = \operatorname{anti} \log \left(-\frac{2.0 \times 10^{-2} \times 100}{2.303}\right)$$

= 0.135 mol L^{-1} (approximately) Hence, the remaining concentration of A is 0.135 mol L^{-1} .

Question 4.25:

Sucrose decomposes in acid solution into glucose and fructose according to the first order rate law, with $t_{1/2}$ = 3.00 hours. What fraction of sample of sucrose remains after 8 hours?

Answer

For a first order reaction,

$$k = \frac{2.303}{t} \log \frac{\left[\mathrm{R}\right]_0}{\left[\mathrm{R}\right]}$$

It is given that, $t_{1/2} = 3.00$ hours

 $k = \frac{0.693}{t_{1/2}}$ Therefore,

 $= \frac{0.693}{3} h^{-1}$ $= 0.231 h^{-1}$

Then, 0.231 h⁻¹ =
$$\frac{2.303}{8 \text{ h}} \log \frac{[\text{R}]_0}{[\text{R}]}$$

$$\Rightarrow \log \frac{\left[R\right]_{0}}{\left[R\right]} = \frac{0.231 \text{ h}^{-1} \times 8 \text{ h}}{2.303}$$
$$\Rightarrow \frac{\left[R\right]_{0}}{\left[R\right]} = \text{antilog}(0.8024)$$
$$\Rightarrow \frac{\left[R\right]_{0}}{\left[R\right]} = 6.3445$$
$$\Rightarrow \frac{\left[R\right]_{0}}{\left[R\right]_{0}} = 0.1576 \text{ (approx)}$$
$$= 0.158$$

Hence, the fraction of sample of sucrose that remains after 8 hours is 0.158.

Question 4.26:

The decomposition of hydrocarbon follows the equation

$$k = (4.5 \times 10^{11} \,\mathrm{s}^{-1}) \,\mathrm{e}^{-28000 \,\mathrm{K/T}}$$

Calculate E_a .

Answer

The given equation is

 $k = (4.5 \times 10^{11} \,\mathrm{s}^{-1}) \,\mathrm{e}^{-28000 \,\mathrm{K}/T}$ (i)

Arrhenius equation is given by,

$$k = \operatorname{Ae}^{-E_{g}/RT}$$
 (ii)

From equation (i) and (ii), we obtain

$$\frac{E_a}{RT} = \frac{28000 \text{ K}}{T}$$

$$\Rightarrow E_a = \text{R} \times 28000 \text{ K}$$

= 8.314 J K⁻¹ mol⁻¹ × 28000 K
= 232792 J mol⁻¹
= 232.792 kJ mol⁻¹

Question 4.27:

The rate constant for the first order decomposition of H_2O_2 is given by the following equation:

 $\log k = 14.34 - 1.25 \times 10^4 \,\mathrm{K/T}$

Calculate E_a for this reaction and at what temperature will its half-period be 256 minutes?

Answer

Arrhenius equation is given by,

$$k = Ae^{-E_a/RT}$$

$$\Rightarrow \ln k = \ln A - \frac{E_a}{RT}$$

$$\Rightarrow \ln k = \log A - \frac{E_a}{RT}$$

$$\Rightarrow \log k = \log A - \frac{E_a}{2.303 RT}$$
(i)

The given equation is

 $\log k = 14.34 - 1.25 \times 10^4 \text{ K/T}$ (ii)

From equation (i) and (ii), we obtain

$$\frac{E_a}{2.303 \text{ RT}} = \frac{1.25 \times 10^4 \text{ K}}{T}$$

$$\Rightarrow E_a = 1.25 \times 10^4 \text{ K} \times 2.303 \times \text{R}$$

= 1.25 × 10⁴ K × 2.303 × 8.314 J K⁻¹ mol⁻¹
= 239339.3 J mol⁻¹ (approximately)
= 239.34 kJ mol⁻¹
Also, when $t_{1/2}$ = 256 minutes,

$$k = \frac{0.693}{t_{1/2}}$$

$$= \frac{0.693}{256}$$

256= 2.707 × 10⁻³ min⁻¹ = 4.51 × 10⁻⁵ s⁻¹

It is also given that, $\log k = 14.34 - 1.25 \times 10^4 \text{ K/T}$

$$\Rightarrow \log(4.51 \times 10^{-5}) = 14.34 - \frac{1.25 \times 10^4 \text{ K}}{T}$$
$$\Rightarrow \log(0.654 - 05) = 14.34 - \frac{1.25 \times 10^4 \text{ K}}{T}$$
$$\Rightarrow \frac{1.25 \times 10^4 \text{ K}}{T} = 18.686$$
$$\Rightarrow T = \frac{1.25 \times 10^4 \text{ K}}{18.686}$$
$$= 668.95 \text{ K}$$

= 669 K (approximately)

Question 4.28:

The decomposition of A into product has value of k as $4.5 \times 10^3 \text{ s}^{-1}$ at 10°C and energy of activation 60 kJ mol⁻¹. At what temperature would k be $1.5 \times 10^4 \text{ s}^{-1}$?

Answer

From Arrhenius equation, we obtain

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 \,\text{R}} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$
Also, $k_1 = 4.5 \times 10^3 \,\text{s}^{-1}$
 $T_1 = 273 + 10 = 283 \,\text{K}$
 $k_2 = 1.5 \times 10^4 \,\text{s}^{-1}$
 $E_a = 60 \,\text{kJ} \,\text{mol}^{-1} = 6.0 \times 10^4 \,\text{J} \,\text{mol}^{-1}$
Then,
 $\log \frac{1.5 \times 10^4}{4.5 \times 10^3} = \frac{6.0 \times 10^4 \,\text{J} \,\text{mol}^{-1}}{2.303 \times 8.314 \,\text{J} \,\text{K}^{-1} \,\text{mol}^{-1}} \left(\frac{T_2 - 283}{283 T_2} \right)$
 $\Rightarrow 0.5229 = 3133.627 \left(\frac{T_2 - 283}{283 T_2} \right)$

$$\Rightarrow \frac{0.5229 \times 283 T_2}{3133.627} = T_2 - 283$$

$$\Rightarrow 0.0472 T_2 = T_2 - 283$$

$$\Rightarrow 0.9528 T_2 = 283$$

$$\Rightarrow T_2 = 297.019 \text{ K (approximately)}$$

= 297 K

= 24°C

Hence, k would be $1.5 \times 10^4 \text{ s}^{-1}$ at 24°C.

Note: There is a slight variation in this answer and the one given in the NCERT textbook.

Question 4.29:

The time required for 10% completion of a first order reaction at 298 K is equal to that required for its 25% completion at 308 K. If the value of A is $4 \times 10^{10} \text{ s}^{-1}$. Calculate k at 318 K and E_a .

Answer

For a first order reaction,

$$t = \frac{2.303}{k} \log \frac{a}{a - x}$$
At 298 K, $t = \frac{2.303}{k} \log \frac{100}{90}$

$$= \frac{0.1054}{k}$$
At 308 K, $t' = \frac{2.303}{k'} \log \frac{100}{75}$

$$= \frac{2.2877}{k'}$$

According to the question,

$$t = t'$$

$$\Rightarrow \frac{0.1054}{k} = \frac{0.2877}{k'}$$

$$\Rightarrow \frac{k'}{k} = 2.7296$$

From Arrhenius equation, we obtain

$$\log \frac{k'}{k} = \frac{E_a}{2.303 \,\text{R}} \left(\frac{T' - T}{TT'} \right)$$

$$\log (2.7296) = \frac{E_a}{2.303 \times 8.314} \left(\frac{308 - 298}{298 \times 308} \right)$$

$$E_a = \frac{2.303 \times 8.314 \times 298 \times 308 \times \log (2.7296)}{308 - 298}$$

= 76640.096 J mol⁻¹
= 76.64 kJ mol⁻¹

To calculate k at 318 K,

It is given that, $A = 4 \times 10^{10} \,\mathrm{s}^{-1}$, $T = 318 \,\mathrm{K}$

Again, from Arrhenius equation, we obtain

$$\log k = \log A - \frac{E_a}{2.303 \text{ R } T}$$

= $\log (4 \times 10^{10}) - \frac{76.64 \times 10^3}{2.303 \times 8.314 \times 318}$
= $(0.6021 + 10) - 12.5876$
= -1.9855
Therefore, k = Antilog (-1.9855)
= $1.034 \times 10^{-2} \text{ s}^{-1}$

Question 4.30:

The rate of a reaction quadruples when the temperature changes from 293 K to 313 K. Calculate the energy of activation of the reaction assuming that it does not change with temperature.

Answer

From Arrhenius equation, we obtain

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 \,\text{R}} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

It is given that, $k_2 = 4k_1$
 $T_1 = 293 \,\text{K}$
 $T_2 = 313 \,\text{K}$
Therefore, $\log \frac{4k_1}{k_2} = \frac{E_a}{2.303 \times 8.314} \left(\frac{313 - 293}{293 \times 313} \right)$
 $\Rightarrow 0.6021 = \frac{20 \times E_a}{2.303 \times 8.314 \times 293 \times 313}$
 $\Rightarrow E_a = \frac{0.6021 \times 2.303 \times 8.314 \times 293 \times 313}{20}$
 $= 52863.33 \,\text{J mol}^{-1}$
 $= 52.86 \,\text{kJ mol}^{-1}$

Hence, the required energy of activation is 52.86 kJmol^{-1} .

Question 5.1:

Write any two characteristics of Chemisorption.

Answer

1. Chemisorption is highly specific in nature. It occurs only if there is a possibility of chemical bonding between the adsorbent and the adsorbate.

2. Like physisorption, chemisorption also increases with an increase in the surface area of the adsorbent.

Question 5.2:

Why does physisorption decrease with the increase of temperature? Answer

Physisorption is exothermic in nature. Therefore, in accordance with Le-Chateliere's principle, it decreases with an increase in temperature. This means that physisorption occurs more readily at a lower temperature.

Question 5.3:

Why are powdered substances more effective adsorbents than their crystalline forms? Answer

Powdered substances are more effective adsorbents than their crystalline forms because when a substance is powdered, its surface area increases and physisorption is directly proportional to the surface area of the adsorbent.

Question 5.4:

Why is it necessary to remove CO when ammonia is obtained by Haber's process? Answer

It is important to remove CO in the synthesis of ammonia as CO adversely affects the activity of the iron catalyst, used in Haber's process.

Question 5.5:

Why is the ester hydrolysis slow in the beginning and becomes faster after sometime? Answer

Ester hydrolysis can be represented as:

Ester + Water \longrightarrow Acid + Alcohol

The acid produced in the reaction acts as a catalyst and makes the reaction faster. Substances that act as catalysts in the same reaction in which they are obtained as products are known as autocatalysts.

Question 5.6:

What is the role of desorption in the process of catalysis?

Answer

The role of desorption in the process of catalysis is to make the surface of the solid catalyst free for the fresh adsorption of the reactants on the surface.

Question 5.7:

What modification can you suggest in the Hardy-Schulze law?

Answer

Hardy-Schulze law states that 'the greater the valence of the flocculating ion added, the greater is its power to cause precipitation.'

This law takes into consideration only the charge carried by an ion, not its size. The smaller the size of an ion, the more will be its polarising power. Thus, Hardy-Schulze law can be modified in terms of the polarising power of the flocculating ion. Thus, the modified Hardy-Schulze law can be stated as 'the greater the polarising power of the flocculating ion added, the greater is its power to cause precipitation.'

Question 5.8:

Why is it essential to wash the precipitate with water before estimating it quantitatively? Answer

When a substance gets precipitated, some ions that combine to form the precipitate get adsorbed on the surface of the precipitate. Therefore, it becomes important to wash the precipitate before estimating it quantitatively in order to remove these adsorbed ions or other such impurities.

Question 5.1:

Distinguish between the meaning of the terms adsorption and absorption.

Give one example of each.

Answer

Adsorption is a surface phenomenon of accumulation of molecules of a substance at the surface rather than in the bulk of a solid or liquid. The substance that gets adsorbed is called the 'adsorbate' and the substance on whose surface the adsorption takes place is called the 'adsorbent'. Here, the concentration of the adsorbate on the surface of the adsorbent increases. In adsorption, the substance gets concentrated at the surface only. It does not penetrate through the surface to the bulk of the solid or liquid. For example, when we dip a chalk stick into an ink solution, only its surface becomes coloured. If we break the chalk stick, it will be found to be white from inside.

On the other hand, the process of *absorption* is a bulk phenomenon. In absorption, the substance gets uniformly distributed throughout the bulk of the solid or liquid.

Question 5.2:

What is the difference between physisorption and chemisorption? Answer

Ph	ysisorption	Chemisorption		
1.	In this type of adsorption, the adsorbate is attached to the surface of the adsorbent with weak van der Waal's forces of attraction.			
2.	No new compound is formed in the process.	New compounds are formed at the surface of the adsorbent.		
3.	It is generally found to be reversible in nature.	It is usually irreversible in nature.		

4.	Enthalpy of adsorption is low as weak van der Waal's forces of attraction are involved. The values lie in the range of 20-40 kJ mol ⁻¹ .	Enthalpy of adsorption is high as chemical bonds are formed. The values lie in the range of 40-400 kJ mol ⁻¹ .
5.	It is favoured by low temperature conditions.	It is favoured by high temperature conditions.
6.	It is an example of multi-layer adsorption	It is an example of mono-layer adsorption.

Question 5.3:

Give reason why a finely divided substance is more effective as an adsorbent.

Answer

Adsorption is a surface phenomenon. Therefore, adsorption is directly proportional to the surface area. A finely divided substance has a large surface area. Both physisorption and chemisorption increase with an increase in the surface area. Hence, a finely divided substance behaves as a good adsorbent.

Question 5.4:

What are the factors which influence the adsorption of a gas on a solid?

Answer

There are various factors that affect the rate of adsorption of a gas on a solid surface.

(1) Nature of the gas:

Easily liquefiable gases such as NH_3 , HCl etc. are adsorbed to a great extent in comparison to gases such as H_2 , O_2 etc. This is because Van der Waal's forces are stronger in easily liquefiable gases.

(2) Surface area of the solid

The greater the surface area of the adsorbent, the greater is the adsorption of a gas on the solid surface.

(3) Effect of pressure

Adsorption is a reversible process and is accompanied by a decrease in pressure. Therefore, adsorption increases with an increase in pressure.