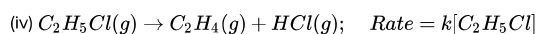
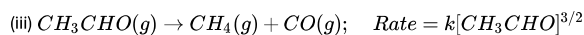
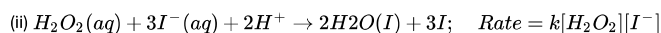
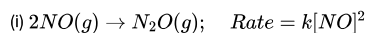
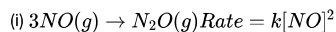


## #457523

**Topic:** Rate law expression and order of reaction

From the rate expression for the following reactions, determine their order of reaction and the dimensions of the rate constants.

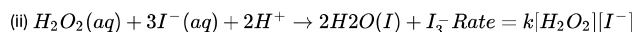
**Solution**

Order w.r.t NO is 2 and overall order is 2.

Dimensions of the rate constant

$$\frac{molL^{-1}}{s} = k(molL^{-1})^2$$

$$k = mol^{-1}L^1s^{-1}$$

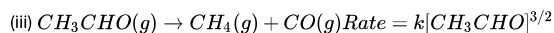


Order w.r.t  $H_2O_2$  is 1, order w.r.t  $I^-$  is 1 and overall order is 2.

Dimensions of the rate constant

$$\frac{molL^{-1}}{s} = k(molL^{-1})^2$$

$$k = mol^{-1}L^1s^{-1}$$

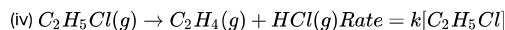


Order w.r.t  $CH_3CHO$  is 3/2 and overall order is 3/2.

Dimensions of the rate constant

$$\frac{molL^{-1}}{s} = k(molL^{-1})^{3/2}$$

$$k = mol^{-1/2}L^{1/2}s^{-1}$$



Order w.r.t  $C_2H_5Cl$  is 1, and overall order is 1.

Dimensions of the rate constant

$$\frac{molL^{-1}}{s} = k(molL^{-1})^1$$

$$k = s^{-1}$$

## #457526

**Topic:** Rate law expression and order of reaction

For the reaction:

$2A + B \rightarrow A_2B$  the rate  $= k[A][B]^2$  with  $k = 2.0 \times 10^{-6} mol^{-2}L^2s^{-1}$ . Calculate the initial rate of the reaction when  $[A] = 0.1 molL^{-1}$ ,  $[B] = 0.2 molL^{-1}$ . Calculate the rate of reaction after  $[A]$  is reduced to  $0.06 molL^{-1}$ .

**Solution**

The reaction is  $2A + B \rightarrow A_2B$

The rate law expression is as follows:

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

The rate constant  $k = 2.0 \times 10^{-6} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$ .

When  $[A] = 0.1 \text{ mol L}^{-1}$ ,  $[B] = 0.2 \text{ mol L}^{-1}$ , the initial rate of the reaction is,

$$\text{rate} = 2.0 \times 10^{-6} \times (0.1) \times (0.2)^2 = 8.0 \times 10^{-9} \text{ L mol}^{-1} \text{ s}^{-1}$$

After  $[A]$  is reduced to  $0.06 \text{ mol L}^{-1}$ , the rate of reaction is as follows:

$$\text{Rate} = 2.0 \times 10^{-6} \times 0.06 \times (0.18)^2 = 3.89 \times 10^{-9} \text{ L mol}^{-1} \text{ s}^{-1}$$

Note: A reacted  $= 0.1 - 0.06 = 0.04$

B reacted  $= 0.02$

$$[B] = 0.2 - 0.02 = 0.18 \text{ mol L}^{-1}$$

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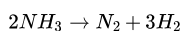
#### #457528

**Topic:** Integrated rate law equations

The decomposition of  $NH_3$  on platinum surface is zero order reaction. What are the rates of production of  $N_2$  and  $H_2$ , if  $k = 2.5 \times 10^{-4} \text{ mol}^{-1} \text{ L s}^{-1}$ ?

---

#### Solution



$$\text{Rate of reaction} = -\frac{1}{2} \frac{d}{dt}[NH_3] = \frac{d}{dt}[N_2] = \frac{1}{3} \frac{d}{dt}[H_2]$$

For a zero order reaction,

$$\text{Rate} = k = 2.5 \times 10^{-4} \text{ M/s}$$

$$\text{Rate of production of } N_2 = \frac{d}{dt}[N_2] = 2.5 \times 10^{-4} \text{ M/s}$$

$$\text{Rate of production of } H_2 = \frac{d}{dt}[H_2] = 3 \times 2.5 \times 10^{-4} \text{ M/s} = 2.5 \times 10^{-4} \text{ M/s}$$

---

#### #457532

**Topic:** Rate law expression and order of reaction

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

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

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  $k$   $p_{CH_3OCH_3}$**  If the pressure is measured in bar and time in minutes, then what are the units of rate and rate constants?

---

#### Solution

$$\text{Rate} = \frac{\text{bar}}{\text{min}} = \text{bar min}^{-1}$$

$$\text{Rate} = k(p_{CH_3OCH_3})^{3/2}$$

$$\text{bar min}^{-1} = k(\text{bar})^{3/2}$$

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

---

#### #457534

**Topic:** General introduction

Mention the factors that affect the rate of a chemical reaction

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#### Solution

Following factors affect the rate of a chemical reaction:

- 1) Reactant concentration
- 2) Reaction temperature
- 3) Nature of reactants and products
- 4) Presence of a catalyst
- 5) Surface area
- 6) Radiation exposure

---

#### #457535

**Topic:** Rate law expression and order of reaction

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 ?

#### Solution

A reaction is second order with respect to a reactant.

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

(i) If the concentration of the reactant is doubled, the rate of reaction becomes 4 times .

(ii) If the concentration of the reactant is reduced to half, the rate of reaction becomes one fourth.

#### #457536

**Topic:** Temperature, catalyst and activation energy of reactions

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

#### Solution

With increase in temperature, the rate of the reaction and the rate constant increases. As a generalization, the rate of the reaction (and the rate constant) becomes almost double for every ten degree rise in temperature. This is also called temperature coefficient. It is the ratio of rate constants of the reaction at two temperatures differing by ten degree. Thus,

$$\text{temperature coefficient} = \frac{\text{Rate constant at } (T+10) ^\circ C}{\text{Rate constant at } T ^\circ C}$$

#### #457541

**Topic:** Common examples of reactions of first order

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

t/s	0	30	60	90
$[Ester]/molL^{-1}$	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.

#### Solution

(i) The average rate of reaction between the time interval 30 to 60 is  $\frac{0.17 - 0.31}{60 - 30} = 4.67 \times 10^{-3}/s$

$$(ii) k = \frac{2.303}{t} \log \frac{[Ester]_0}{[Ester]}$$

When t = 30 s

$$k = \frac{2.303}{30} \times \log \frac{0.55}{0.31} = 1.91 \times 10^{-2}/s$$

When t = 60 s

$$k = \frac{2.303}{60} \times \log \frac{0.55}{0.17} = 1.96 \times 10^{-2}/s$$

When t = 90 s

$$k = \frac{2.303}{90} \times \log \frac{0.55}{0.085} = 2.07 \times 10^{-2}/s$$

Average rate constant  $k = 1.98 \times 10^{-2}/s$

#### #457542

**Topic:** Rate law expression and order of reaction

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?

#### Solution

It is given that a reaction is first order in A and second order in B.

i) The differential rate equation is as follows:

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

(ii) On increasing the concentration of B three times, rate becomes 9 times.

$$(d[B])^2 = 3^2 = 9$$

(iii) When the concentrations of both A and B are doubled, rate becomes 8 times.

$$d[A](d[B])^2 = 2 \times 2^2 = 8$$

#457547

**Topic:** Rate law expression and order of reaction

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:

$A/\text{molL}^{-1}$	0.20	0.20	0.40
$B/\text{molL}^{-1}$	0.30	0.10	0.05
$r_0/\text{molL}^{-1}\text{s}^{-1}$	$5.07 \times 10^{-5}$	$5.07 \times 10^{-5}$	$1.43 \times 10^{-4}$

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

**Solution**

$$\text{Rate} = k[A]^p[B]^q$$

$$\text{Rate}_1 = (0.20)^p(0.30)^q = 5.07 \times 10^{-5} \dots (i)$$

$$\text{Rate}_2 = (0.20)^p(0.10)^q = 5.07 \times 10^{-5} \dots (ii)$$

Divide equation (i) by equation (ii)

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{(0.30)^q}{(0.10)^q} = 1$$

$$3^q = 1 \text{ or } q = 0$$

Hence, the reaction is zero order in B.

$$\text{Rate}_3 = (0.40)^p(0.05)^q = 1.43 \times 10^{-4} \dots (iii)$$

Divide equation (iii) by (ii)

$$\frac{\text{Rate}_3}{\text{Rate}_2} = \frac{(0.40)^p}{(0.20)^p} = \frac{1.43 \times 10^{-4}}{5.07 \times 10^{-5}}$$

$$2^p = 2.8$$

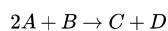
$$p = 1.5$$

The reaction order with respect to A is 1.5.

#457552

**Topic:** Rate law expression and order of reaction

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



Experiment	$[A]/\text{molL}^{-1}$	$[B]/\text{molL}^{-1}$	Initial rate of formation of $D/\text{molL}^{-1}\text{min}^{-1}$
I	0.1	0.1	$6.0 \times 10^{-3}$
II	0.3	0.2	$7.2 \times 10^{-2}$
III	0.3	0.4	$2.88 \times 10^{-1}$
IV	0.4	0.1	$2.40 \times 10^{-2}$

Determine the rate law and the rate constant for the reaction

**Solution**

The rate law expression is,  $rate = k[A]_0^p[B]_0^q$ .

From experiments *I* and *IV*, we get

$$rate_1 = k(0.1)^p(0.1)^q = 6.0 \times 10^{-3} \dots (i)$$

$$rate_4 = k(0.4)^p(0.1)^q = 2.40 \times 10^{-2} \dots (ii)$$

Divide equation (ii) by equation (i)

$$\frac{(0.4)^p}{(0.1)^p} = \frac{2.40 \times 10^{-2}}{6.0 \times 10^{-3}} = 4$$

$$4^p = 4$$

$$p = 1$$

From experiments *II* and *III*, we get

$$rate_2 = k(0.3)^p(0.2)^q = 7.2 \times 10^{-2} \dots (iii)$$

$$rate_3 = k(0.3)^p(0.4)^q = 2.88 \times 10^{-1} \dots (iv)$$

Divide equation (iv) by equation (iii)

$$\frac{(0.4)^p}{(0.2)^p} = \frac{2.88 \times 10^{-1}}{7.2 \times 10^{-1}} = 4$$

$$2^q = 4$$

$$q = 2$$

The rate law expression is,  $rate = k[A][B]^2$ .

Substitute values in equation (i)

$$6.0 \times 10^{-3} = k(0.1)(0.1)^2$$

$$k = 6.0 \text{ L}^2\text{mol}^{-2}\text{min}^{-1}$$

---

#### #457556

**Topic:** Rate law expression and order of reaction

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	$[A]/\text{molL}^{-1}$	$[B]/\text{molL}^{-1}$	Initial rate/ $\text{molL}^{-1}\text{min}^{-1}$
I	0.1	0.1	$2.0 \times 10^{-2}$
II	-	0.2	$4.0 \times 10^{-2}$
III	0.4	0.4	-
IV	-	0.2	$2.0 \times 10^{-2}$

#### Solution

The rate law expression is:

$$Rate = k[A][B]^0$$

$$2.0 \times 10^{-2} = k[0.1]$$

$$k = 0.2$$

Second line

$$4.0 \times 10^{-2} = 0.2[A]$$

$$[A] = 0.2$$

Third line

$$Rate = 0.2 \times 0.4 = 8.0 \times 10^{-2}$$

Fourth line

$$2.0 \times 10^{-2} = 0.2[A]$$

$$[A] = 0.1$$

---

#### #457560

**Topic:** Integrated rate law equations

Calculate the half-life of a first order reaction from their rate constants given below:

(i)  $200 \text{ s}^{-1}$  (ii)  $2 \text{ min}^{-1}$  (iii)  $4 \text{ years}^{-1}$

#### Solution

The relationship between the half life period and the rate constant is,  $t_{1/2} = \frac{0.693}{k}$ .

$$(i) t_{1/2} = \frac{0.693}{\frac{200}{0.693}} = 3.465 \times 10^{-3} s$$

$$(ii) t_{1/2} = \frac{0.693}{2} = 0.3465 mins$$

$$(iii) t_{1/2} = \frac{0.693}{4} = 0.1732 years$$

#### #457562

**Topic:** Integrated rate law equations

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.

#### Solution

$$\text{Decay constant } k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730 \text{ year}} = 1.209 \times 10^{-4} / \text{years}$$

The rate of counts is proportional to the number of C-14 atoms in the sample.

$$N_0 = 100, N = 80$$

$$\text{The age of the sample } t = \frac{2.303}{k} \log \frac{N_0}{N}$$

$$t = \frac{2.303}{1.209 \times 10^{-4}} \times \log \frac{100}{80} = 1846 \text{ years}$$

#### #457571

**Topic:** Integrated rate law equations

The experimental data for decomposition of  $N_2O_5$  [ $2N_2O_5 \rightarrow 4NO_2 + O_2$ ] in gas phase at  $318K$  are given below:

t/s	0	400	800	1200	1600	2000	2400	2800	3200
$10^2 \times [N_2O_5] / \text{molL}^{-1}$	1.63	1.36	1.14	0.93	0.78	0.64	0.53	0.43	0.35

(i) Plot  $[N_2O_5]$  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)

#### Solution

(ii) Initial concentration of  $N_2O_5 = 1.63 \times 10^{-2} M$

Half of initial concentration  $= 1.63 \times 10^{-2} \times 0.5 = 0.815 \times 10^{-2} M$ .

Time for half of initial concentration (i.e half life period) from plot is 1440 s

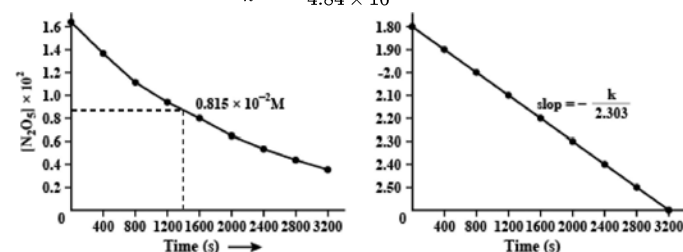
(iv)  $\log [N_2O_5]$  vs time is a straight line plot. This indicates first order reaction. The rate law expression is

$$\text{Rate} = k[N_2O_5]$$

$$(v) \text{ Slope} = \frac{-k}{2.303} = -2.10 \times 10^{-4}$$

$$k = 4.84 \times 10^{-4} / s$$

$$(vi) \text{ Half life period } t_{1/2} = \frac{0.693}{k} = \frac{0.693}{4.84 \times 10^{-4}} = 1432 s$$



#### #457572

**Topic:** Integrated rate law equations

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  $1/16$ th value?

#### Solution

Given that the rate constant for a first order reaction is  $60\text{ s}^{-1}$ .

Let  $a\text{ M}$  be the initial concentration.

Final concentration will be  $\frac{a}{16}\text{ M}$ .

Rate constant,  $k = 60\text{ /s}$

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

$$t = \frac{2.303}{60} \log \frac{a}{\frac{a}{16}}$$

$$t = 4.6 \times 10^{-2} \text{seconds}$$

---

#### #457575

**Topic:** Integrated rate law equations

During nuclear explosion, one of the products is  $^{90}\text{Sr}$  with half-life of 28.1 years. If  $1\mu\text{g}$  of  $^{90}\text{Sr}$  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 has not lost metabolically.

#### Solution

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

$$k = \frac{0.693}{28.1} = 0.0247\text{ /year}$$

(i) After 10 years, let  $x\mu$  be the concentration of  $^{90}\text{Sr}$ .

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

$$0.0247 = \frac{2.303}{10\text{ years}} \log \frac{1}{x}$$

$$x = 0.782\mu\text{g}$$

(ii) After 60 years, let  $y\mu$  be the concentration of  $^{90}\text{Sr}$ .

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

$$0.0247 = \frac{2.303}{60\text{ years}} \log \frac{1}{y}$$

$$x = 0.228\mu\text{g}$$

---

#### #457576

**Topic:** Integrated rate law equations

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

#### Solution

For a first order reaction, we have

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

Let  $a$  M be the initial concentration.

When reaction is 99% complete,

$$[A] = a - \frac{99a}{100} = 0.01a$$

$$t_{99} = \frac{2.303}{k} \log \frac{a}{0.01a}$$

$$t_{99} = \frac{2.303}{k} \times 2 \dots \dots (1)$$

When reaction is 90% complete,

$$[A] = a - \frac{90a}{100} = 0.1a$$

$$t_{90} = \frac{2.303}{k} \log \frac{a}{0.1a}$$

$$t_{90} = \frac{2.303}{k} \times 1 \dots \dots (2)$$

Divide equation (1) by (2), we get

$$\frac{t_{99}}{t_{90}} = 2 \implies t_{99} = 2t_{90}$$

---

#### #457578

**Topic:** Integrated rate law equations

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

#### Solution

Let  $a$  M be the initial concentration. After 40 minutes, the concentration is  $a - \frac{30a}{100} = 0.70a$

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

$$k = \frac{2.303}{40} \log \frac{a}{0.70a}$$

$$k = 8.92 \times 10^{-3} / \text{min}$$

$$\text{The half life period, } t_{1/2} = \frac{0.693}{k} = \frac{0.693}{8.92 \times 10^{-3} / \text{min}} = 77.7 \text{ min.}$$

---

#### #457580

**Topic:** Integrated rate law equations

For the decomposition of azoisopropane to hexane and nitrogen at  $543\text{K}$ , the following data are obtained.

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

Calculate the rate constant.

#### Solution



Let  $p_i$  be the initial pressure of azoisopropane and at time  $t$ ,  $x$  atm of azoisopropane decomposes.



At time,  $t = 0$

$$P_{\text{azoisopropane}} = p_i \quad P_{N_2} = 0 \quad P_{C_6H_{14}} = 0$$

At time,  $t$

$$P_{\text{azoisopropane}} = P_i - x \quad P_{N_2} = x \quad P_{C_6H_{14}} = x$$

(The pressure is in atm.)

$$x = P_t - P_i$$

$$P(\text{azoisopropane}) = 2P_i - P_t$$

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

$$k = \frac{2.303}{t} \log \frac{P_i}{2P_i - P_t}$$

When time is 360 s,

$$k = \frac{2.303}{360} \log \frac{35.0}{2 \times 35.0 - 54}$$

$$k = 2.17 \times 10^{-3} / s$$

When time is 720 s,

$$k = \frac{2.303}{720} \log \frac{35.0}{2 \times 35.0 - 63.0}$$

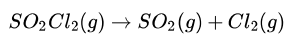
$$k = 2.24 \times 10^{-3} / s$$

$$\text{Average value of } k = 2.20 \times 10^{-3} / s$$

#### #457582

**Topic:** Integrated rate law equations

The following data were obtained during the first order thermal decomposition of  $SO_2Cl_2$  at a constant volume.



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.

#### Solution

For a first order reaction, we have

$$k = \frac{2.303}{t} \log \frac{P_i}{2P_i - P_t}$$

$$k = \frac{2.303}{100} \log \frac{0.5}{2 \times 0.5 - 0.6}$$

$$k = 2.23 \times 10^{-23} / s$$

$$\text{Rate} = kP_{SO_2Cl_2}$$

Total pressure is 0.65 atm.

$$P_{SO_2Cl_2} = 2p_i - p_t = 2 \times 0.5 - 0.65 = 0.35 \text{ atm}$$

$$\text{Hence, rate} = 2.23 \times 10^{-3} \times 0.35$$

$$\text{Rate} = 7.805 \times 10^{-4} \text{ atm/s}$$

#### #457585

**Topic:** Temperature, catalyst and activation energy of reactions

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

$T/^\circ C$	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  $30^\circ$  and  $50^\circ C$ .

#### Solution

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

$$y = mx + c$$

From the graph,

$$m = -191.4$$

$$c = -4.922$$

$$\text{Hence, } \ln k = -4.922 + \frac{-191.4}{T}$$

At 30 °C or 303 K,

$$\ln k = -4.922 + \frac{-191.4}{303}$$

$$\ln k = -5.515$$

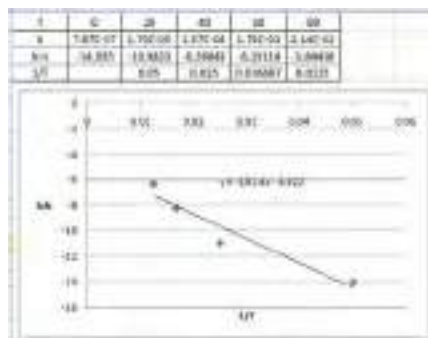
$$k = 0.003873 /s$$

At 50 °C or 323 K,

$$\ln k = -4.922 + \frac{-191.4}{323}$$

$$\ln k = -5.55$$

$$k = 0.004028 /s$$



#### #457586

**Topic:** Temperature, catalyst and activation energy of reactions

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.

#### Solution

The expression for the preexponential factor can be obtained from Arrhenius equation.

$$\log k = \log A - \frac{E_a}{2.303RT}$$

$$\log A = \log k + \frac{E_a}{2.303RT}$$

$$\log A = \log 2.418 \times 10^{-5} + \frac{179.9 \times 10^3}{2.303 \times 8.314 \times 546}$$

$$\log A = 12.592$$

The pre-exponential factor,  $A = 3.90 \times 10^{12} /s$

#### #457589

**Topic:** Integrated rate law equations

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

#### Solution

The integrated rate expression for the first order reaction is as follows:

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

$$\Rightarrow 2.0 \times 10^{-2} = \frac{2.303}{t} \log \frac{1.0}{[A]}$$

$$\Rightarrow \log \frac{1.0}{[A]} = 0.868$$

$$\Rightarrow [A] = 0.135 M$$

Hence, the concentration of A remaining after 100 seconds is 0.135 M.

#### #457590

**Topic:** Common examples of reactions of first order

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?

**Solution**

$$k = \frac{0.693}{t_{1/2} \times \frac{0.693}{3.0}} = 0.231/hr$$

Let initial concentration of sucrose be 1 M.

After 8 hours, the concentration will be  $1 - x$ .  $x$  represents the amount of sucrose decomposed.

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

$$\Rightarrow 0.231 = \frac{2.303}{8} \log \frac{1}{1-x}$$

$$\Rightarrow \log \frac{1}{1-x} = 0.8024$$

$$\Rightarrow \frac{1}{1-x} = 6.345 \Rightarrow x = 0.842$$

After 8 hours, the concentration of sucrose left is  $1 - 0.842 = 0.158$  M.

**#457592**

**Topic:** Temperature, catalyst and activation energy of reactions

The decomposition of hydrocarbon follows the equation,  $k = (4.5 \times 10^{11} s^{-1}) e^{-28000K/T}$ .

Calculate  $E_a$ .

**Solution**

The expression for  $k$  is as follows:

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

Comparing it with Arrhenius equation, we get

$$k = A e^{-E_a/RT}$$

$$-\frac{E_a}{R} = 28000K$$

$$\text{The activation energy} = E_a = 28000 \times 8.314 = 232792 J/mol = 232.792 kJ/mol$$

**#457594**

**Topic:** Temperature, catalyst and activation energy of reactions

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

$$\log k = 14.341.25 \times 10^4 K/T$$

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

**Solution**

The expression for the rate constant is as follows:

$$\log k = 14.34 - 1.25 \times 10^4 K / T \quad (i)$$

Compaign it with Arrhenius equation, we get

$$\log k = \log A - \frac{E_a}{2.303RT}$$

Therefore,

$$\frac{E_a}{2.303R} = 1.25 \times 10^4$$

$$E_a = 1.25 \times 10^4 \times 2.303 \times 8.314$$

$$\text{The activation energy} = E_a = 239339 \text{ J/mol} = 239.339 \text{ kJ/mol}$$

$$\text{Half life period, } t_{1/2} = 256 \text{ min} = 256 \times 60 \text{ s}$$

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

$$k = \frac{0.693}{256 \times 60 \text{ s}}$$

$$k = 4.51 \times 10^{-5} / \text{s}$$

Substitute in equation (i), we get

$$\log 4.51 \times 10^{-5} = 14.341.25 \times 10^4 K / T$$

$$-4.35 = 14.341.25 \times 10^4 K / T$$

$$T = 669 \text{ K}$$

Hence, the temperature at which half life period is 256 minutes is 669 K.

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#### #457596

**Topic:** Temperature, catalyst and activation energy of reactions

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

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#### Solution

It is given that the decomposition of A into product has value of  $k = 4.5 \times 10^3 \text{ s}^{-1}$  at  $10^\circ \text{C}$ .

$$\log \frac{k'}{k} = \frac{E_a}{2.303R} \left[ \frac{T' - T}{TT'} \right]$$

$$\log \frac{1.5 \times 10^4}{4.5 \times 10^3} = \frac{60 \times 10^3}{2.303 \times 8.314} \left[ \frac{T' - 283}{283T'} \right]$$

$$0.5228 = 3132.62 \left[ \frac{T' - 283}{283T'} \right]$$

$$T' - 283 = 0.0472T'$$

$$T' = 297.02 \text{ K}$$

$$T' = 297.02 \text{ K} - 273 = 24.02^\circ \text{C}$$

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#### #457598

**Topic:** Temperature, catalyst and activation energy of reactions

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

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#### Solution

For 10% completion of the reaction, we have

$$k(298) = \frac{2.303}{t} \log \frac{100}{90}$$

For 25% completion of the reaction, we have

$$k(308) = \frac{2.303}{t} \log \frac{100}{75}$$

$$\frac{k(308)}{k(298)} = \frac{\frac{2.303}{t} \log \frac{100}{75}}{\frac{2.303}{t} \log \frac{100}{90}} = 2.73$$

$$\text{But, } \log \frac{k(308)}{k(298)} = \frac{E_a}{2.303R \left[ \frac{T' - T}{TT'} \right]}$$

$$\log 2.73 = \frac{E_a}{2.303 \times 8.314} \times \frac{308 - 298}{308 \times 298}$$

$$E_a = 76623 \text{ J/mol} = 76.623 \text{ kJ/mol}$$

$$\text{But, } \log k = \log A - \frac{E_a}{2.303RT}$$

$$\log k(318K) = \log 4 \times 10^{10} - \frac{76623}{2.303 \times 8.314 \times 318} = -1.9823$$

$$k(318) = 1.042 \times 10^{-2} / s$$

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#### #457599

**Topic:** Temperature, catalyst and activation energy of reactions

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

#### Solution

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The Arrhenius equation at two different temperatures is as follows:

$$\log \frac{k'}{k} = \frac{E_a}{2.303R} \left[ \frac{1}{T} - \frac{1}{T'} \right]$$

$$\frac{k'}{k} = 4$$

$$\log 4 = \frac{E_a}{2.303 \times 8.314} \left[ \frac{1}{293} - \frac{1}{313} \right]$$

$$\text{The energy of activation, } E_a = 52863.3 \text{ J/mol} = 52.86 \text{ kJ/mol}$$