

Chemical Engineering (GATE & PSUs)

Postal Correspondence

GATE & Public Sectors

Chemical Reaction Engineering

GATE 2015 Top Results

Chemical Engineering



1st Rank
Archhit Trichal



2nd Rank
Keval Pareta

GATE 2015 Result

Name	ARCHHIT TRICHAL	 <i>Archhit Trichal</i>	
Registration Number	CH8804151135		
Gender	Male		
Examination Paper	Chemical Engineering (CH)		
Marks out of 100 [†]	65.67	All India Rank in this paper	1
Qualifying Marks ^{‡‡}	27.52 (General)	24.77 (OBC (NCL))	18.34 (SC/ST/PwD)
		GATE Score	947

Highest Result in GATE 2015

Rank 1, 2, 7, 8.....

Total 39 Ranks under AIR 100

GATE 2014 Topper Chemical Engineering



1st Rank
Sandeep Kumar

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GATE 2015 Cut-off Marks

BRANCH	GENERAL	SC/ST/PD	OBC(Non-Creamy)	Total Appeared
Chemical Engineering	27.52	18.34	24.77	15874

GATE Syllabus: Chemical Engineering

Chemical Reaction Engineering: Theories of reaction rates; kinetics of homogeneous reactions, interpretation of kinetic data, single and multiple reactions in ideal reactors, non-ideal reactors; residence time distribution, single parameter model; non-isothermal reactors; kinetics of heterogeneous catalytic reactions; diffusion effects in catalysis.

CONTENT

1. INTRODUCTION AND BASIC CONCEPT	03-9
2. KINETICS OF REACTION	10-17
3. DESIGN EQUATION FOR IDEAL REACTORS	18-31
4. INTERPRETATION OF BATCH REACTOR DATA	32-44
5. DESIGN FOR SINGLE REACTION	45-66
6. DESIGN FOR MULTIPLE REACTIONS	67-82
7. HETEROGENEOUS REACTION	83-87
8. TEMPERATURE AND PRESSURE EFFECTS	88-97
9. BASIC ASPECTS OF NON IDEAL FLOW.....	98-108
10. QUESTION BASED ON GATE PAPER	109-120
11. MODEL TEST PAPER-I WITH SOLUTION	121-133
12. PRACTICE SET-1, 2, 3.....	134-171
13. Interview Practice Bank	172-182

CHAPTER-1

INTRODUCTION AND BASIC CONCEPT

1. Every industrial chemical process is designed to produce economically a designed product from a variety of starting material through a succession of treatment steps.

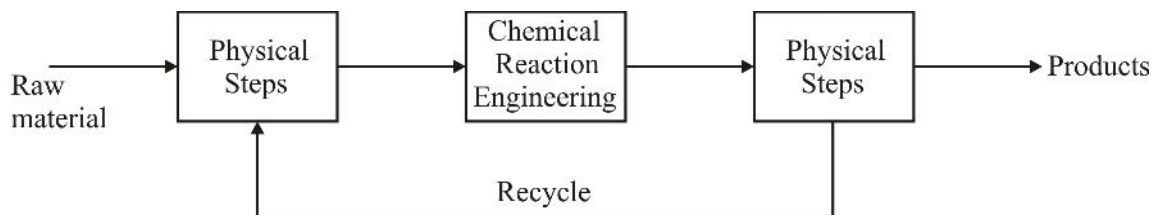


Figure: Show typical chemical process:

2. Raw material undergoes a number of physical steps to put them in the form in which they can be reacted chemically. Then material passes through the reactor. The products of reaction must then undergo further treatment.

3. In chemical reaction engineering subject we are concerned with chemical treatment step of a process. CRE combines the study of chemical kinetics (reaction rates and reaction mechanisms) with the reactors in which the reaction occurs.

A chemical reaction takes place by decomposition, combination or change in configuration of molecules.

4. We define rate of reaction in terms of component. If the rate of change in number of moles of this component due to reaction is $\frac{dN_i}{dt}$ then

$$r_i = \frac{1}{V} \frac{dN_i}{dt} = \frac{\text{Moles of } i \text{ formed}}{(\text{Volume of fluid})(\text{Time})}$$

i.e., the number of moles of component i formed per unit time per unit volume ($\text{mol}/\text{dm}^3\text{s}$). If species i is a reactant, the numerical value of r_i is a negative number (e.g. $r_i = -3\text{mol}/\text{dm}^3\text{s}$ or $-r_i = 3\text{mol}/\text{dm}^3\text{s}$)

If species i is a product, then r_i will be a positive number.

$$r_i = \frac{1}{V} \frac{dN_i}{dt}$$

For constant volume system

$$r_i = \frac{d}{dt} \left(\frac{N_i}{V} \right) = \frac{d}{dt} (C_i) = \frac{dC_i}{dt}$$

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C_i is the concentration of species i in reaction mixture.

Q.1. For a homogeneous reaction system, where C_i is the concentration of i at time t , N_i is the no. of moles of i at time t , V is the reaction volume at time t and t is the reaction time

The rate of reaction for species i is defined as

(a.) $\frac{dC_i}{dt}$ (b.) $-\left(\frac{dC_i}{dt}\right)$ (c.) $\frac{1}{V} \frac{dN_i}{dt}$ (d.) $-\left(\frac{1}{V} \frac{dN_i}{dt}\right)$

Ans. (c)

5. (i) Chemical reaction may be classified depending upon no. of phases involved as homogeneous and heterogeneous reaction. Homogeneous reaction is one which takes place in only one phase. A heterogeneous reaction is one which involves presence of more than one phases.

(ii) Reaction may be classified according to catalytic and non catalytic reaction.

(iii) Reaction may be classified on the basis of molecularity of reaction.

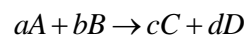
(iv) The reaction may be classified based upon the heating effect as exothermic and endothermic reaction.

(v) Reaction may be classified as reversible and irreversible reaction.

(vi) Reaction may be classified based upon the order of reaction.

6. Relative rates of reaction:

For the reaction:



The relation between the rate of participants A, B, C, D in chemical reaction with their stoichiometric coefficient is

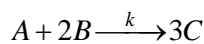
$$\frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_C}{c} = \frac{r_D}{d}$$

Also, if we compare $\frac{-r_A}{a} = \frac{r_C}{c}$

$$-r_A = \frac{a}{c} r_C$$

Rate of disappearance of A = $\frac{a}{c}$ (Rate of formation of C)

Q.2. For an elementary reaction



(a.) Rate of appearance of C is equal to rate of disappearance of A

(b.) Rate of disappearance of A is equal to rate of disappearance of B.

(c.) Rate of appearance of C is equal to rate of disappearance of B.

(d.) Rate of appearance of C is 3 times rate of disappearance of A.

Solution: $\frac{-r_A}{1} = \frac{-r_B}{2} = \frac{r_C}{3}$ [Relative Rates of reaction]

$-r_A$ = rate of disappearance of A

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$-r_B$ = rate of disappearance of B

r_C = Rate of appearance of C

$$\therefore r_C = 3(-r_A)$$

Option (D) is correct

7. Many variable may affect the rate of a chemical reaction. In homogeneous system the temperature, pressure and composition affect the rate of reaction.

In heterogeneous system factors that affect the rate of reaction are rate of mass transfer *i.e.*, heat transfer nature of catalyst if present.

Heterogeneous reactions involve more than one phase.

\therefore Rate of reaction is expressed in measure other than volume such as reaction surface area or catalyst weight.

r_i' \Rightarrow Number of moles of i formed per unit time per unit mass of catalyst (mol/s.g catalyst)

8. Rate law

An algebraic equation that relates the reaction rate and concentration



$$-r_A = k_A(T) [f_n(C_A, C_B)]$$

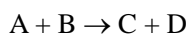
or

$$-r_A = k_A C_A^\alpha C_B^\beta$$

$k_A \rightarrow$ Rate constant/ specific reaction rate

Order of reaction (n) = $\alpha + \beta$

For the reaction where all the stoichiometric coefficients are 1 e.g.



$$k_A = k_B = k_C = k_D = k$$

Imp. Rate Laws Are determined by experimental observation.

Q.3. Rate expression of reaction

$$-r_A = 0.02C_A^2 \text{ mol / cm}^3 \text{ min}$$

If concentration is to be expressed in mol/l and time in hours, the value of rate constant would be

(a.) $0.12 \text{ hr}^{-1} (\text{mol/L})^{-1}$

(b.) $0.012 \text{ hr}^{-1} (\text{mol/L})^{-1}$

(c.) $12 \text{ hr}^{-1} (\text{mol/L})^{-1}$

(d.) $1.2 \text{ hr}^{-1} (\text{mol/L})^{-1}$

Solution: $1\text{L} = 10\text{cm}^3$

$1\text{hr} = 60\text{min}$

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$$-r_A = 0.02C_A^2 \frac{\text{mol}}{\left(\frac{1}{10}\right)^2 \left(\frac{1}{60}\right) \text{hr}}$$

$$-r_A = 0.02C_A^2 \times 600 \frac{\text{mol}}{\text{L hr}}$$

$$-r_A = 12C_A^2 \text{mol L}^{-1} \text{hr}^{-1}$$

Clearly $k = 12$

$$\text{unity of } k = \frac{r_A}{C_A^2} = \frac{\text{molL}^{-1}\text{hr}^{-1}}{\text{mol}^2\text{L}^{-2}}$$

$$\text{unit of } k = \text{mol}^{-1}\text{L hr}^{-1}$$

$$k = 12\text{hr}^{-1}(\text{mol/L})^{-1}$$

Option C is correct

Q.4. The rate of reaction for a gas phase reaction is expressed as

$$\frac{-dp_A}{dt} = 2.56P_A^2 \text{atm/hr}$$

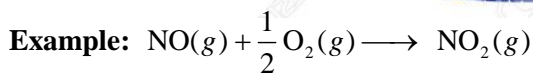
The Units of rate constant are

(a.) $\text{hr}^{-1}(\text{atm})^{-1}$ (b.) $\text{hr}^{-1}(\text{atm})^3$ (c.) hr^{-1}atm (d.) $\text{hr}^{-1}(\text{mol/L})^{-1}$

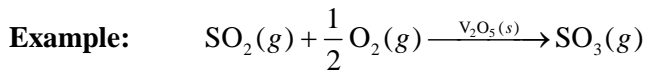
Solution: $k = \frac{-dp_A/dt}{P_A^2} = \frac{\text{atm/hr}}{\text{atm}^2} = \text{atm}^{-1}\text{hr}^{-1}$

TYPES OF REACTIONS

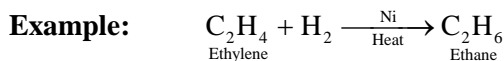
9. (i) A homogeneous reaction is one which takes place in only one phase; *i.e.*, all the reacting material and products and catalyst (if any) will be present in a similar phases.



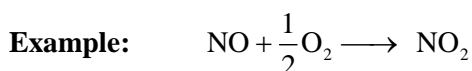
A heterogeneous reaction is one which involves the presence of more than one phase.



(ii) Catalytic reaction are those reaction which involves use of catalyst to enhance the rate of reaction.



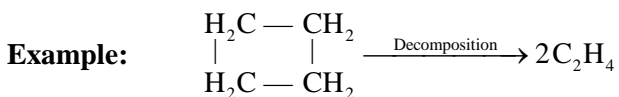
Non catalytic reactions are those reaction which does not involve use of catalyst.



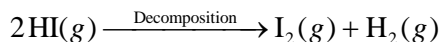
(iii) The reaction may be classified based upon the molecularity of a reaction *i.e.*, based upon the number of molecules that takes part in the reaction as unimolecular, bimolecular and trimolecular reaction.

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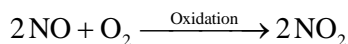
(a) Unimolecular Reaction:



(b) Bimolecular Reaction:

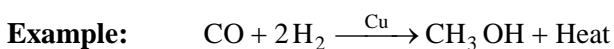


(c) Trimolecular Reaction:

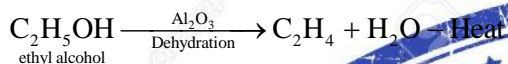


(iv) The reaction may be classified as exothermic and endothermic reaction.

Exothermic reaction is one in which heat is evolved.



Endothermic reaction is one in which heat is absorbed



(v) The reaction may be classified as reversible and irreversible reaction. Reversible reaction are those in which forward and reverse reaction takes place simultaneously.

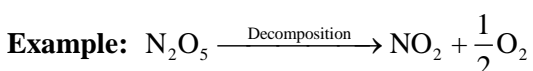


Irreversible reaction are those which can proceed only in one direction.



(vi) The reaction may be classified as first order, second order and third order reaction.

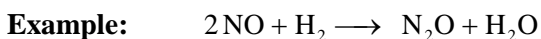
First order reaction:



Second order reaction: (Saponification of ester)



Third order reaction:



Single and Multiple Reaction:

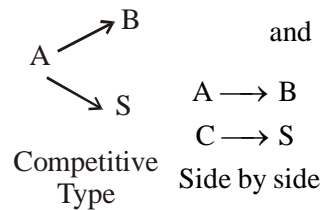
(i) When a single stoichiometric equation and single rate equation are chosen to represent the progress of the reaction, we have a single reaction. When more than one stoichiometric equation is chosen to observed changes then more than one kinetic expression is needed to follow the changes in the concentration of all the reaction component and we have multiple reaction.

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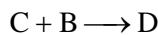
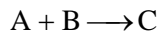
(ii) Multiple reaction may be classified as

Series Reaction: $A \longrightarrow B \longrightarrow S$

Parallel Reaction:



Complicated Reaction:



Here reaction proceeds in parallel with respect to B but in series with respect to A, C and D.

Elementary and Non Elementary Reaction:

Consider a single reaction with stoichiometric equation $A + B \longrightarrow C$

According to rate law,

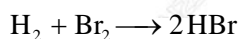
Rate of disappearance of A is given by

$$-r_A = K C_A C_B$$

Such reaction in which the rate equation corresponds to a stoichiometric equation are called elementary reaction.

When there is no direct corresponding rate and stoichiometry, then the reaction is called non-elementary reaction.

The best example of a non-elementary reaction is that between hydrogen and bromine.



Which has rate expression

$$r_{HBr} = \frac{K_1[H_2][Br_2]^{\frac{1}{2}}}{K_2 + [Br_2]}$$

10. Molecularity and Order of Reaction

The molecularity of an elementary reaction is the number of molecules involved in the reaction and this has been found to have the values of one, two or occasionally three.

Molecularity refers only to an elementary reaction.

Consider a reaction



then rate expression

$$-r_A = K C_A^a C_B^b C_C^c C_D^d \Rightarrow a + b + c + d = n$$

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where a, b, \dots, d are not necessarily related to the stoichiometric coefficient.

We call the power to which the concentration are raised the order of reaction. Hence the reaction is

a th order with respect to A

b th order with respect to B

n th order overall

Since the order refers to the empirically found rate expression, it may not to be an integer and can have a fractional value.

But, the molecularity of a reaction must be an integer because it refers to mechanism of reaction and applies only to elementary reaction.

11. Rate constant (K)

The rate constant of a chemical reaction is a measure of the rate of reaction when all the reactants are at unit concentration.

So,

for any reaction say $A \rightarrow B$

$$-r_A = K C_A$$

If we assume that the concentration are equal to unity then

$$-r_A = K$$

Where K is rate constant. The rate constant K depends on the temperature. It increases with temperature. K is also called specific rate constant.

The units of K depends upon the units of time and concentration.

Suppose : $-r_A = K C_A^n$

Then we know units of $(-r_A) = \text{mol/l} \cdot \text{sec}$

and $C_A = \left(\frac{\text{mol}}{\text{lit.}} \right)$

$$K = \frac{\frac{\text{mol}}{\text{lit.}} \cdot \text{sec.}}{\left(\frac{\text{mol}}{\text{lit.}} \right)^n} = (\text{sec})^{-1} \left(\frac{\text{mol}}{\text{lit.}} \right)^{1-n}$$

$$K = (\text{time})^{-1} (\text{concentration})^{1-n}$$

Where n is the order of reaction.

Q.5. For a gas reaction at T(K), the rate is given by

$$\frac{-dp_A}{dt} = k' p_A^2 \text{ atm/hr}$$

If the rate equation is expressed as

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$$-r_A = \frac{-1}{V} \frac{dN_A}{dt} = kC_A^2 (\text{mol} / L - \text{hr})$$

The rate constant k is given by

- (a.) $k = k'RT$ (b.) $k = k'$ (c.) $k = k' (RT)^2$ (d.) $k = k'/RT$

Solution:

$$\frac{-dp_A}{dt} = k' p_A^2$$

$$c_A = \frac{p_A}{RT}$$

$$\frac{-d}{dt}(c_A RT) = k' c_A^2 (RT)^2$$

$$-RT \frac{dc_A}{dt} = k' c_A^2 (RT)^2$$

$$-\frac{dc_A}{dt} = k' c_A^2 (RT)$$

$$-r_A = k' c_A^2 (RT)$$

$$k c_A^2 = k' c_A^2 (RT)$$

$$k = k' (RT)$$

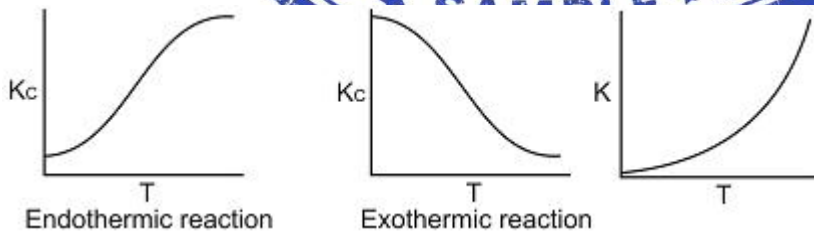
Option (A) is correct

12. For reversible reactions: $A \xrightleftharpoons[k_{-A}]{k_A} B + C$

$$\text{Equilibrium constant } (K_c) = \frac{k_A}{k_{-A}}$$

k_A → Rate constant of forward reaction

k_{-A} → Rate constant of backward reaction



During the course of a chemical reaction, the rate of a reaction decreases as the reaction proceeds

Q.6. The irreversible reaction is the special case of reversible reaction if

Concentration of reactant at equilibrium condition is _____

Solution: Zero

Conceptual Numerical Answer Practice Set

.....:SAMPLE PART:.....

CHAPTER-2

KINETICS OF REACTION

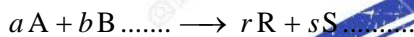
1. In homogeneous system, the possible factors that affect the rate of reaction are temperature, composition and pressure.

Hence for homogeneous system we can write rate of reaction as a function of concentration and temperature.

$$-r_A = f[\text{Temperature dependent term, Concentration dependent term}] \frac{\text{mol}}{\text{l.s}}$$

2. According to rate law rate of reaction is directly proportional to the reactant concentration. Rate law is also called rate equation, kinetic expression.

3. Consider a irreversible reaction



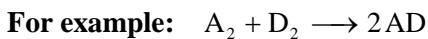
According to rate law we can write

$$-r_A = K f(C_A, C_B) = K C_A^a C_B^b \dots$$

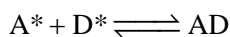
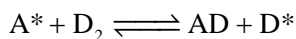
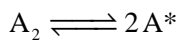
Where K is rate constant *a* and *b* are the power of concentration of reactant A, B, ... on which rate of reaction depends.

4. Kinetics Model for Non-Elementary Reactions:

To explain the kinetics of non elementary reaction we assume that a sequence of elementary reaction is actually occurring but we can not observe the intermediate formed because they are only present in very minute quantity. Hence we observe only initial reactant and final products that appears to be a single reaction.



If the kinetic of reaction shows that reaction is non-elementary then we can postulate a series of elementary steps.



where * sign shows unobserved intermediate.

Types of Intermediate:

(i) Free radicals:

Free atoms that contain one or more unpaired electrons are called free radicals.

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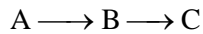
Example: $\text{CH}_3^\bullet, \text{C}_2\text{H}_5^\bullet, \text{I}^\bullet, \text{H}^\bullet, \text{CCl}_3^\bullet$

They are highly reactive and unstable.

(ii) Ions and Polar Substance: Electrically charged atoms, molecules or fragments of molecules are called ions.

Example: $\text{N}_3^-, \text{N}_a^+, \text{OH}^-, \text{I}^-$

(iii) Molecules: Consider a consecutive reaction



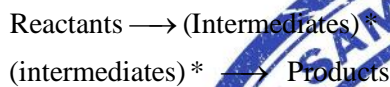
If the intermediate B is highly reactive its mean life time will be very small and its concentration in the reacting mixture can become too small to measure.

In this condition B may not be observed and can be considered to be a reactive intermediate.

(iv) Transition Complex: Unstable forms of molecule or unstable association of molecules which can either decompose to give product or by further collision return to molecules in the normal state. Such unstable forms are called transition complex.

Reaction scheme involving these four kinds of intermediate can be of two types.

(a) Non chain reaction:



(b) Chain Reaction:



Testing Kinetics Models:

Now we will see that how to test correspondence between experiment and a proposed mechanism.

In matching the predicted rate expression with the experimentally found, we rely on the following rule:

(i) If any component: Takes part in more than one reaction then its net rate of change is equal to sum of the rates of change of components i in each of the elementary reaction in which it is participated.

$$r_{i, \text{net}} = \sum r_i$$

= All elementary reaction participated.

(ii) As the intermediates are highly reactive they have very short life time and they are present in very small quantities, hence their net rate of formation is taken as zero.

$$\therefore r_A^* = 0$$

This is called the steady state approximation.

5. Temperature Dependent Term of a Rate Equation

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For many reactions and particularly elementary reactions, the rate expression can be written as a product of a temperature dependent term and a concentration dependent term or

$$r_i = f_1(\text{temperature}) f_2(\text{concentration})$$

$$r_i = K f_2(\text{concentration})$$

For such reactions the temperature dependent term, the reaction rate constant has been found in practically all cases.

(a) Temperature dependency from Arrhenius law:

From Arrhenius law rate constant K is given by:

$$K = K_o e^{-\frac{E}{RT}}$$

Where K_o is called the frequency or pre-exponential factor.

E is called activation energy of the reaction.

R = gas constant

T = absolute temperature, K

At the same concentration, but at two different temperature, Arrhenius law indicate that

$$\ln \frac{r_2}{r_1} = \ln \frac{K_2}{K_1} = \frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \left(\frac{t_1}{t_2} \right) = \frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Unit of K_o = unit of K

K_o is not a function of temperature

K_o (also known as frequency factor) does not affect the temperature sensitivity of reaction

$$\text{Also } \ln \left(\frac{K(T_2)}{K(T_1)} \right) = \frac{\Delta H_{R_x}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Here $K(T_2)$ and $K(T_1)$ are equilibrium constant at T_1 & T_2 respectively & ΔH_{R_x} is the heat of reaction

$$\text{Also } \frac{d}{dT} (\ln K) = -\frac{E}{RT^2} \Rightarrow$$

If temperature is low change in K w.r.t T is high and vice versa.

Q.1. From Arrhenius law, a plot of $\ln k$ versus $1/T$ gives a straight line with a slope of $(-E/R)$. The units of E/R are

- (a.) K/cal (b.) cal/K (c.) cal (d.) K

Solution: $\frac{E}{R} = \frac{\text{cal mol}^{-1}}{\text{cal mol}^{-1} \text{K}^{-1}} = K$

Option (d) is correct

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- Q.2.** From the chemical reaction $A \xrightarrow{k} B$ an increase in temperature from 295K to 305K causes the rate of reaction to double. The energy of activation for this reaction must be
- (a.) 12389Kcal/mol (b.) 12.38Kcal/mol
 (c.) 1.2Kcal/mol (d.) 1238Kcal/mol

Solution:

$$\ln \frac{r_2}{r_1} = \frac{E}{R} \left(\frac{1}{T} - \frac{1}{T_2} \right)$$

$$R = 1.987 \text{ cal mol}^{-1} \text{ K}^{-1}$$

$$r_2 = 2r_1$$

$$\ln \left(\frac{2r_1}{r_1} \right) = \frac{E}{1.987} \left(\frac{1}{295} - \frac{1}{305} \right)$$

On solving $E = 12389.47 \text{ cal/mol}$

Or $E = 12.38 \text{ Kcal/mol}$

Option (b) is correct

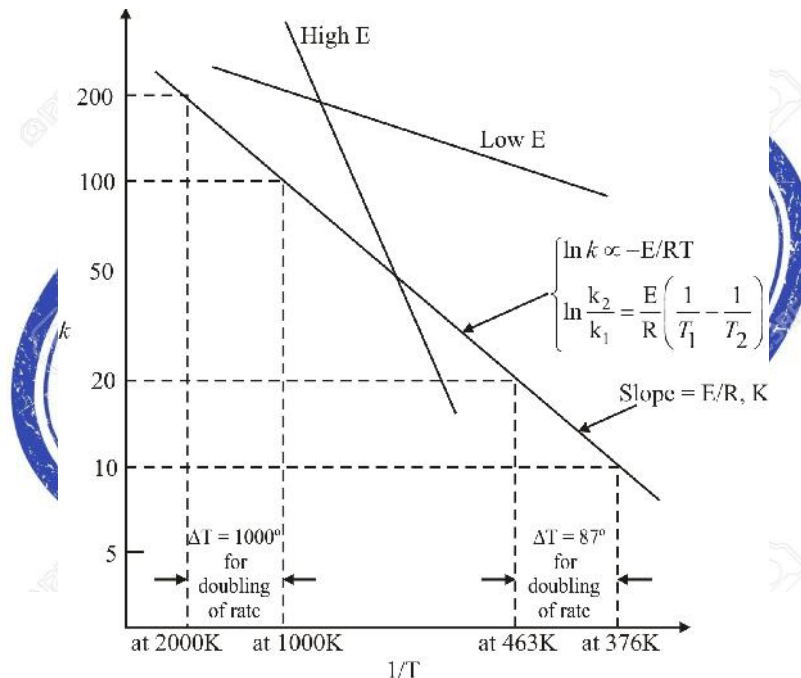


Figure: Sketch showing temperature dependency of the reaction rate.

Activation Energy and Temperature Dependency:

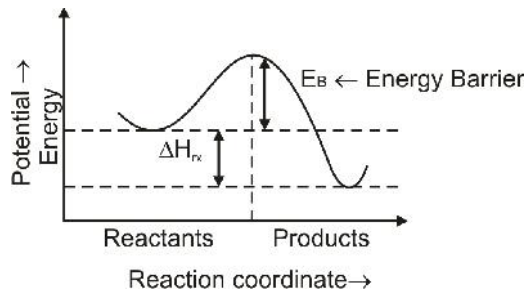
The temperature dependency of reaction is determined by the activation energy and temperature level of the reaction as shown in figure. Conclusion from figure are as follows:

- (i) From the Arrhenius law, the value of the frequency factor K_0 does not affect the temperature sensitivity.
- (ii) Any given reaction is much more temperature sensitive at a low temperature than at a high temperature.
- (iii) Reactions with high activation energy are very temperature sensitive, reaction with low activation energy are relatively temperature insensitive.
- (iv) From Arrhenius law a plot of $\ln K$ vs $\frac{1}{T}$ given a straight line with large slope for large E and small slope for small E .

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Activation Energy:

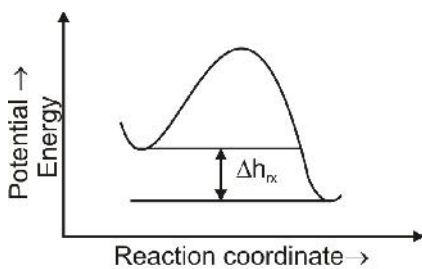
The excess energy of the reactants required to dissociate into products.



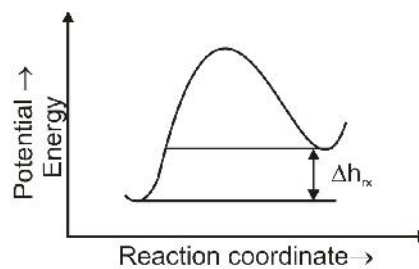
⇒ In Exothermic reaction, reactants have more energy than products

$$\Delta H_{\text{Reaction}} = \text{Energy of product} - \text{Energy of Reactant}$$

$$\Delta H_{\text{Reaction}} = -ve \text{ (for exothermic reactions)}$$



Exothermic reaction



Endothermic reaction

(b) Temperature Dependency from the Collision Theory:

Collision theory is based upon the concept that before molecule react, there must be collision between the reactant molecules and only those collision in which the colliding molecules have a certain minimum amount of energy are effective. Further this concept leads to the rate expression based upon the frequency of molecular collisions and the fraction collisions that are effective.

From collision theory rate constant K is given by

$$\boxed{K \propto T^{\frac{1}{2}} e^{-\frac{E}{RT}}} \quad \ln\left(\frac{k_2}{k_1}\right) = \frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + \frac{1}{2}\ln\left(\frac{T_2}{T_1}\right)$$

(c) Temperature Dependency from Transition State Theory:

The fundamental postulate of the theory is that (i) The reacting molecules must form unstable intermediate called activated complex before being converted (*i.e.*, there is formation of activated complex) to product. (ii) There exists an equilibrium between the activated complex and reactants at all the time.

According to transition state theory rate constant is given by:

$$\boxed{K \propto T e^{-\frac{E}{RT}}} \quad \text{or} \quad \ln\left(\frac{k_2}{k_1}\right) = \frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + \ln\left(\frac{T_2}{T_1}\right)$$

This equation describe the temperature dependency from Transition State Theory.

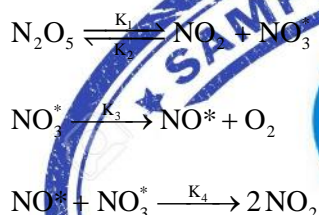
6. Difference between Collision Theory and Transition State Theory:

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Collision Theory	Transition State Theory
1. Collision theory does not agree more closely with experiments.	1. Transition state theory agrees more closely with experiments.
2. Collision theory is based on Kinetic theory of gases.	2. Transition state theory is based on statistical mechanics.
3. Collision theory view that decomposition of activated complex is very rapid.	3. Transition state theory view that formation of activated complex is very rapid.
4. Collision theory view that formation of activated complex is slow and rate controlling .	4. Transition state theory view that decomposition of activated complex is slow and rate controlling.
5. $K \propto T^{\frac{1}{2}} e^{-\frac{E}{RT}}$	5. $K \propto T e^{-\frac{E}{RT}}$

SOLVED EXAMPLE

1. The decomposition of N_2O_5 is postulated to occur by the following mechanism.



using steady state approximation derive an expression for rate of decomposition of N_2O_5 .

Solution: We know that

Rate of decomposition is given by

$$\frac{-d[N_2O_5]}{dt} = k_1[N_2O_5] - k_2[NO_2][NO_3^*] \quad \dots(a)$$

By steady state hypothesis.

$$\frac{d[NO^*]}{dt} = k_3[NO_3^*] - k_4[NO^*][NO_3^*] = 0 \quad \dots(i)$$

$$\frac{d[NO_3^*]}{dt} = k_1[N_2O_5] - k_2[NO_2][NO_3^*] - k_3[NO_3^*] - k_4[NO^*][NO_3^*] \quad \dots(ii)$$

From equation (i)

$$[NO^*] = \frac{k_3[NO_3^*]}{k_4[NO_3^*]} = \frac{k_3}{k_4} \quad \dots(iii)$$

Put equation (iii) in equation (ii)

$$k_1[N_2O_5] = k_2[NO_2][NO_3^*] + k_3[NO_3^*] + k_3[NO_3^*]$$

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$$\Rightarrow [\text{NO}_3^*] = \frac{K_1[\text{N}_2\text{O}_5]}{K_2[\text{NO}_2] + 2K_3} \quad \dots(iv)$$

Put equation (iv) in equation (a)

We get,

$$\begin{aligned} \frac{-d[\text{N}_2\text{O}_5]}{dt} &= K_1[\text{N}_2\text{O}_5] - K_2[\text{NO}_2] \left(\frac{K_1[\text{N}_2\text{O}_5]}{K_2[\text{NO}_2] + 2K_3} \right) \\ &= K_1[\text{N}_2\text{O}_5] \left(1 - \frac{K_2[\text{NO}_2]}{K_2[\text{NO}_2] + 2K_3} \right) \end{aligned}$$

2. At 500 K the rate of a bimolecular reaction is ten times the rate at 400 K. Find the activation energy for this reaction.

(a) From Arrhenius law

(b) From Collision theory

Solution: (a) We have from Arrhenius law

$$\ln(r) = -\frac{E}{RT} + \ln K_o$$

$$\ln \frac{r_2}{r_1} = -\frac{E}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \left(\frac{r_2}{r_1} \right) = \frac{E}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

We have,

$$r_2 = 10 r_1$$

$$T_1 = 400 \text{ K}$$

$$T_2 = 500 \text{ K}$$

$$R = 1.987 \text{ cal/mol K}$$

$$\ln \left(\frac{10 r_1}{r_1} \right) = \frac{E}{1.987} \left[\frac{1}{400} - \frac{1}{500} \right]$$

$$E = 9150 \text{ cal/mol K}$$

(b) From Collision theory we know that

$$K \propto T^{\frac{1}{2}} e^{-\frac{E}{RT}}$$

$$r = K_o' T^{\frac{1}{2}} e^{-\frac{E}{RT}}$$

$$\ln r = -\frac{E}{R} \left(\frac{1}{T} \right) + \ln T^{\frac{1}{2}} + \ln K_o'$$

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$$\ln r_1 = -\frac{E}{R} \left(\frac{1}{T_1} \right) + \ln T_1^{\frac{1}{2}} + \ln K'_o$$

$$\ln r_2 = -\frac{E}{R} \left(\frac{1}{T_2} \right) + \ln T_2^{\frac{1}{2}} + \ln K'_o$$

$$\ln \left(\frac{r_2}{r_1} \right) = \frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) + \ln \left(\frac{T_2^{\frac{1}{2}}}{T_1^{\frac{1}{2}}} \right)$$

$$T_1 = 400 \text{ K,}$$

$$T_2 = 500 \text{ K}$$

$$r_2 = 10 r_1$$

$$\ln \left(\frac{10 r_1}{r_1} \right) = \frac{E}{1.987} \left[\frac{1}{400} - \frac{1}{500} \right] + \ln \left[\frac{(500)^{\frac{1}{2}}}{(400)^{\frac{1}{2}}} \right]$$

$$E = 8707 \text{ cal/mol} \quad \text{Ans.}$$

3. On doubling the concentration reactant rate of reaction triples. Find the reaction order.

Solution: Let $-r_A = K C_A^n$

Suppose at concentration C_{A_1} rate of reaction is $-r_{A_1} = K C_{A_1}^n$

At concentration C_{A_2} rate of reaction is $-r_{A_2} = K C_{A_2}^n$

If $C_{A_2} = 2C_{A_1}$ we have

$$-r_{A_2} = 3(-r_{A_1})$$

$$\frac{-r_{A_2}}{-r_{A_1}} = \frac{K C_{A_2}^n}{K C_{A_1}^n}$$

$$\frac{-r_{A_2}}{-r_{A_1}} = \frac{C_{A_2}^n}{C_{A_1}^n}$$

$$\frac{3(-r_{A_1})}{-r_{A_1}} = \frac{(2C_{A_1})^n}{(C_{A_1})^n}$$

$$3 = 2^n$$

$$\Rightarrow \ln 3 = n \ln 2$$

$$n = 1.58 \approx 1.6$$

4. A certain reaction has a rate given by $-r_A = 0.005 C_A^2 \text{ mol/cm}^3 \text{ min}$

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If the concentration is expressed in mole/lit and time in hours. What would be the value and units of rate constants.

Solution: $-r_A = 0.005 C_A^2, \text{ mol/cm}^3 \text{ min}$

$$-r_A = 0.005 \left(\frac{\text{cm}^3}{\text{mol} \cdot \text{min}} \right) C_A^2 \left(\frac{\text{mol}}{\text{cm}^3} \right)^2, \frac{\text{mol}}{\text{cm}^3 \text{ min}}$$

$$K = 0.005 \frac{\text{cm}^3}{\text{mol} \cdot \text{min}}$$

We know that 1 liter = 1000 cm³

$$1 \text{ cm}^3 = \left(\frac{1}{1000} \right) \text{ l}$$

$$60 \text{ min} = 1 \text{ h}$$

$$1 \text{ min} = \frac{1}{60} \text{ h}$$

$$K = \frac{(0.005 \text{ cm}^3) \times \left(\frac{1}{1000} \right) \frac{\text{lit}}{\text{cm}^3}}{\text{mol} \cdot \text{min} \left(\frac{1}{60} \right) \left(\frac{\text{h}}{\text{min}} \right)}$$

$$K = 3 \times 10^{-4} \left(\frac{\text{lit}}{\text{mol} \cdot \text{h}} \right)$$

Value of K = 3×10^{-4}

Units of K = $\left(\frac{\text{lit}}{\text{mol} \cdot \text{h}} \right)$

5. The pyrolysis of ethane proceeds with an activation energy of about 75000 cal. How much faster is the decomposition at 650°C than at 500°C ?



$$E = 75000 \text{ cal/mol}$$

Let K_1 be the rate constant at T_1 and K_2 be the rate constant at T_2

$$T_1 = 500^\circ\text{C} = 773 \text{ K}$$

$$T_2 = 650^\circ\text{C} = 923 \text{ K}$$

$$\ln \left(\frac{K_2}{K_1} \right) = \frac{E}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$R = 1.987 \text{ cal/mol K}$$

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$$\ln\left(\frac{K_2}{K_1}\right) = \frac{75000}{1.987} \left[\frac{1}{773} - \frac{1}{923} \right]$$

$$\ln\left(\frac{K_2}{K_1}\right) = 7.951$$

$$\frac{K_2}{K_1} = 2838$$

$$K_2 = 2838 K_1$$

At 650°C, the decomposition is faster by a factor 2838 than at 500°C.

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