

**3.091 – Introduction to Solid State Chemistry****Lecture Notes No. 8****THEORY OF REACTION RATES**

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Sources for Further Reading:

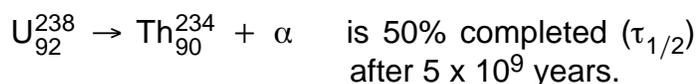
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2. Moore, W.J., Physical Chemistry, Prentice-Hall, 1962.
3. Moeller, T., Inorganic Chemistry, John Wiley, 1982.
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**1. INTRODUCTION**

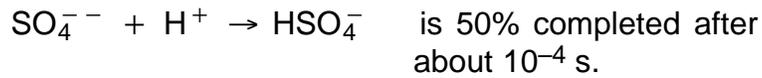
We can readily understand that chemical reactions normally are preceded by collisions of atoms, ions, or molecules. However, the rate of such collisions in solids, liquids and gases is so great that all reactions would be very rapid were it only necessary for collisions to occur. "Chemical" reactions will not proceed more rapidly than molecular collisions allow, but many reactions proceed much more slowly. It is thus apparent that not every molecular collision leads to reaction. We have also seen from earlier examples that the driving force for physical as well as chemical reactions is the (free) energy change - which must be negative for reactions to occur spontaneously. However, while providing a "go/no-go" answer, this criterion alone cannot give us any information concerning the rate at which reactions occur, nor can it tell us which factors influence the reaction velocity.

Rates at which reactions occur vary considerably. For example, the nuclear reaction:



$$\tau_{1/2} = 5 \times 10^9 \text{ years}$$

On the other hand, the chemical reaction:



$$\tau_{1/2} = 3 \times 10^{-4} \text{ seconds}$$

*Reaction kinetics (rate theory)* deals to a large extent with the factors which influence the reaction velocity. Take corrosion (rusting of iron), for example. We all know that it requires air and water to provoke rusting and we also know, much to our sorrow, that rusting proceeds much more rapidly near the ocean where salt is present. We also know that the rate of rusting depends strongly on the composition of iron (pure Fe and steel corrode much less rapidly than cast iron, for example). It is primarily kinetic studies which lead to the elucidation of chemical reactions and, in the case of corrosion, to the development of more corrosion resistant materials.

The principal experimental approach to the study of the reaction process involves the measurement of the rate at which a reaction proceeds and the determination of the dependence of this reaction rate on the concentrations of the reacting species and on the temperature. These factors are grouped together in the term *reaction kinetics* and the results for a given reaction are formulated in a *rate equation* which is of the general form:

$$\text{Rate} = k(T) \times \text{function of concentration of reactants}$$

The quantity  $k(T)$  is called the *rate constant* and is a function only of the temperature if the term involving the reactant concentrations correctly expresses the rate dependence on concentration. Thus the experimental information on the reaction process is summarized in the rate equation by the nature of the concentration function and by the value and temperature dependence of the rate constant.

## 2. EXPERIMENTAL METHODS IN REACTION RATE STUDIES

Since we know that chemical reactions are temperature dependent, kinetic investigations will require rigorous temperature control (thermostats). Furthermore, we have to be able to observe and investigate concentration changes of reactions and products. For this purpose it frequently is customary to interrupt a reaction (for example, by quenching - the abrupt lowering of temperature) and to make a chemical analysis. In other instances, particularly for very fast reactions, a direct measurement of concentration changes is physically impossible. In such cases it is necessary to quantitatively follow reactions indirectly, through the accompanying changes in specific physical properties such as:

- (1) electrical conductivity
- (2) optical absorption
- (3) refractive index
- (4) volume
- (5) dielectric constant

as well as by other means. In the last twenty years, for example, the use of isotopes (as "tracer" elements) has become a valuable tool for the study of reaction kinetics (in slow reactions).

## 3. CONCENTRATION DEPENDENCE OF REACTION RATES

Normally experimental data of kinetic investigations are records of concentrations of reactants and/or products as a function of time for constant temperatures (taken at various temperatures).

Theoretical expressions for reaction rates (involving concentration changes) are differential equations of the general form:

$$\frac{dc}{dt} = f(c_1^m, c_2^n, c_3^o \dots)$$

where (c) are concentration terms which have exponents that depend on details of the reaction.

If we want to compare the theory with the experiment, it is therefore necessary to either integrate the theoretical laws or to differentiate experimental concentration vs time data.

The rate laws are of importance since they provide analytical expressions for the course of individual reactions and enable us to calculate expected yields and optimum conditions for “economic” processes.

In most instances the differential rate equation is integrated before it is applied to the experimental data. Only infrequently are slopes of concentration vs time curves taken to determine  $dc/dt$  directly (fig. 1).

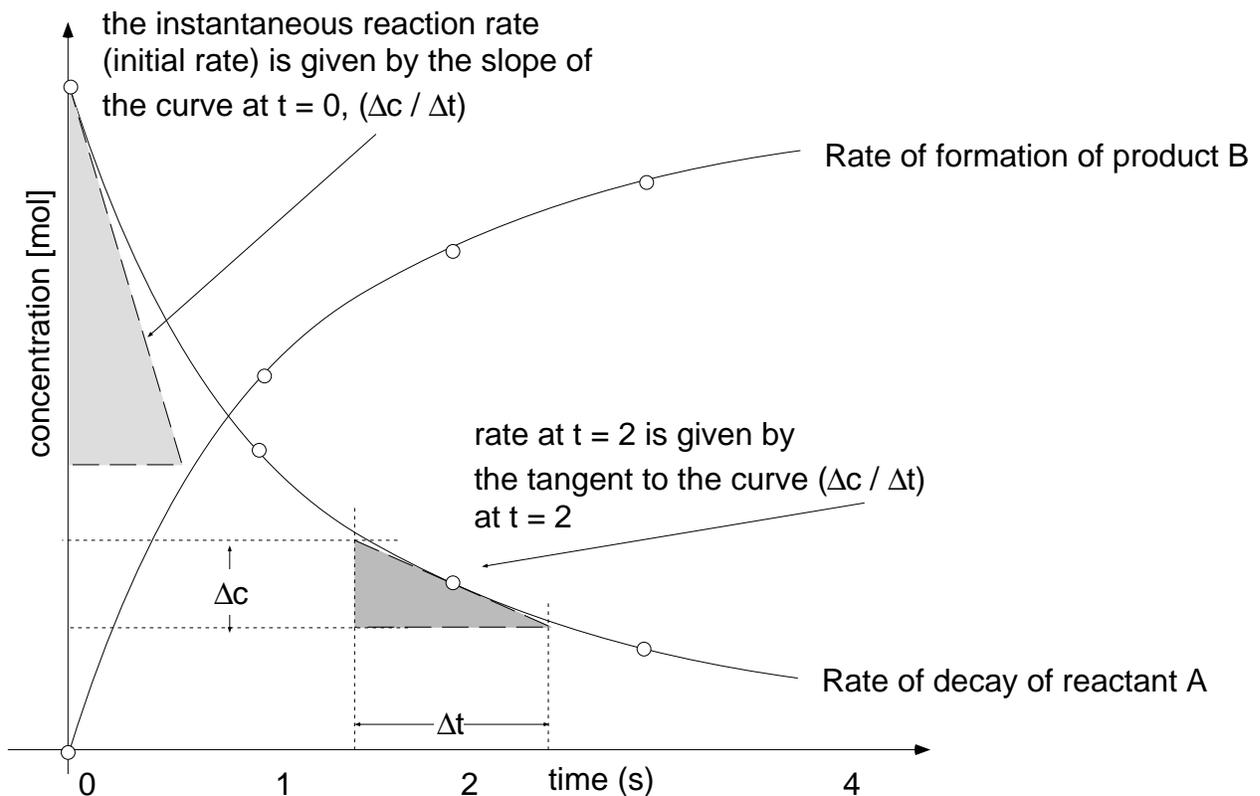


Figure 1 Variation with time of the concentration of a reactant (A) and of a product (B)

Let us look at a simple reaction, the decay of  $\text{H}_2\text{O}_2$  to water and oxygen:

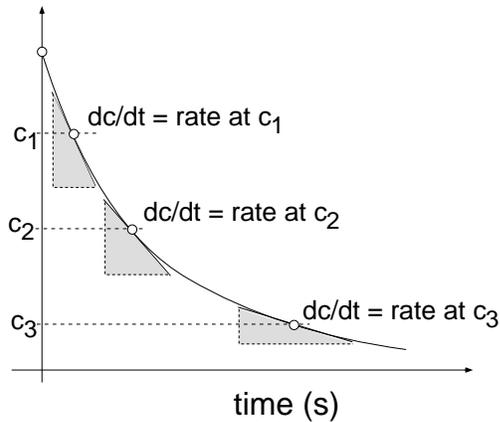
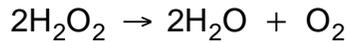


Figure 2 Decay curve ( $dc/dt$  vs.  $c$ ) for  $\text{H}_2\text{O}_2$

Experimentally we obtain a curve (such as fig. 2) by plotting the concentration of remaining  $\text{H}_2\text{O}_2$  in moles/liter, normally written  $[\text{H}_2\text{O}_2]$ , as a function of time. The rate is then given by the time differential:

$$\text{Rate} \left( \frac{\text{moles}}{\text{liter} \cdot \text{s}} \right) = \frac{-d[\text{H}_2\text{O}_2]}{dt}$$

If we now determined and plotted the variation of the reaction rate,  $[-d[\text{H}_2\text{O}_2]/(d \text{ time})]$ , with concentration,  $[\text{H}_2\text{O}_2]$ , we would find a straight line (fig. 3). Thus:

$$-\frac{d[\text{H}_2\text{O}_2]}{dt} = k[\text{H}_2\text{O}_2] \quad \text{or generally,} \quad -\frac{dc}{dt} = kc$$

Upon integration:

$$\int \frac{dc}{c} = -k \int dt$$

we have:

$$\ln c = -kt + \text{const.}$$

Taking  $c = c_0$  for  $t=0$ , we get ( $\text{const} = \ln c_0$ ) and:

$$\ln c = -kt + \ln c_0$$

or:

$$c = c_0 e^{-kt} \quad \text{and} \quad k = \frac{1}{t} \times \ln \frac{c_0}{c}$$

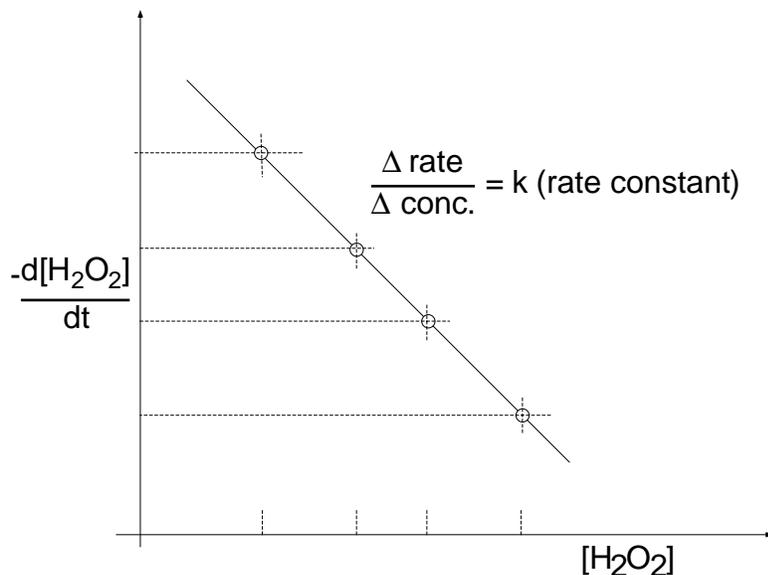


Figure 3 Concentration dependence of the rate of reaction

Alternately:

$$k = \frac{2.3}{t} \times \log \frac{c_0}{c} \quad \text{and} \quad k = \frac{2.3}{t_2 - t_1} \times \log \frac{c_1}{c_2}$$

From the above we see that for decay of  $\text{H}_2\text{O}_2$  a plot of  $(\ln c)$  vs.  $t$  results in a straight line (fig. 4). This behavior is characteristic of *first order reactions* in which the concentration exponent ( $n$ ) is “one”:

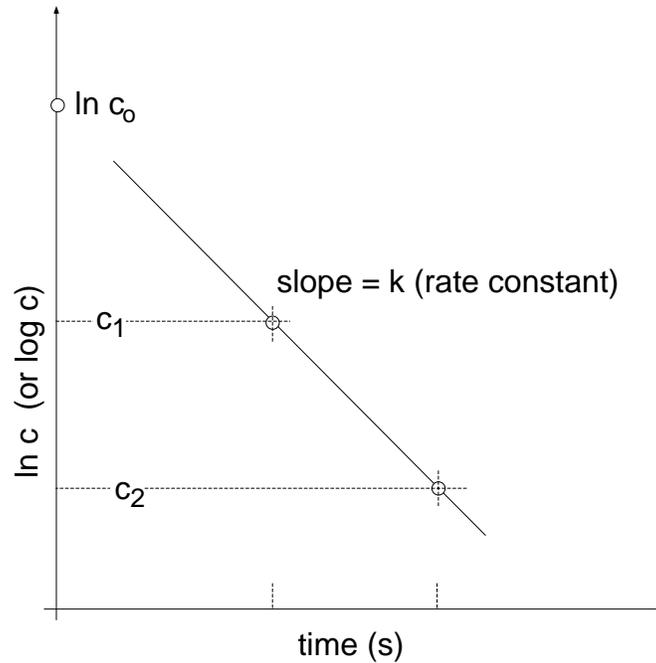
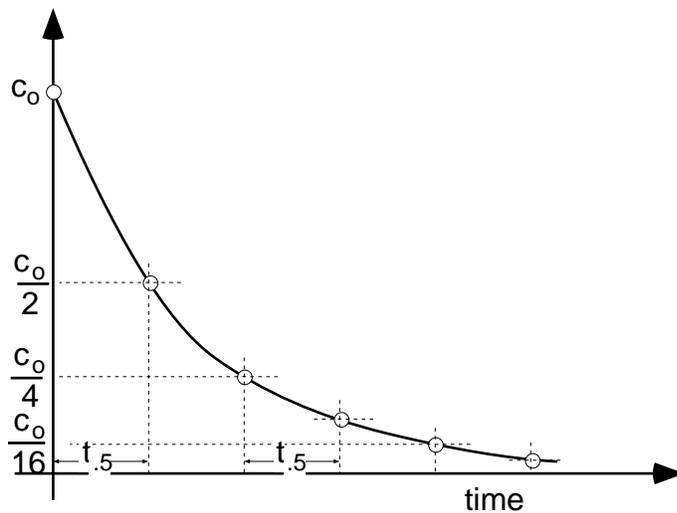
$$-\frac{dc}{dt} = kc$$

#### First Order Reactions: Radioactive Decay

From the relationship:

$$k = \frac{2.3}{t_2 - t_1} \times \log \frac{c_1}{c_2}$$

which relates the rate constant ( $k$ ) to the concentration change ( $\Delta c$ ) for the time interval ( $\Delta t$ ), we can show that (for first order reactions) the time required to complete a reaction to 1/2 or 1/4 or any fraction of the initial concentration is independent of the initial concentration of reactant present (fig. 5).

Figure 4 Plot of  $\ln c$  vs. timeFigure 5 Concentration independent half life ( $t_{1/2}$ ) of First order reactions.

When discussing radioactive decay it is customary to call the “rate constant” ( $k$ ) the “decay constant”. It is furthermore customary to consider the time it takes to decrease the number of originally present species (normally called reactants) to 0.5 (by

50%). We then talk about the *half-life*. Accordingly, the above equation can be reformulated as:

$$k = \frac{2.3}{t_{1/2}} \times \log \frac{C_1}{\frac{C_1}{2}} = \frac{2.3}{t_{1/2}} \times \log 2$$

or:

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

This means that from the half-life ( $t_{1/2}$ ) we may obtain the decay constant (rate constant in general). Vice versa, knowing the rate constant, we can calculate the time it takes to complete 50% of the reaction (or decay).

#### 4. REACTION ORDER

Reactions of first order, such as the decay of  $\text{H}_2\text{O}_2$  or radioactive decay, do not require molecular or atomic collisions - in principle they reflect inherent instability. A multitude of chemical reactions do involve collisions, however. For example, take the decay of HI:



The rate law for this reaction reflects the requirement of a collision in the concentration exponent:

$$-\frac{d[\text{HI}]}{dt} = k[\text{HI}] \times [\text{HI}] = k[\text{HI}]^2$$

The reaction is referred to as a *second order reaction* which can readily be identified since upon integration the rate law yields:

$$\frac{1}{[\text{HI}]} = kt + \text{const}$$

or, more generally:

$$\frac{1}{c} = kt + \text{const}$$

A plot of  $1/c$  vs  $t$  will yield a straight line.

It is interesting to note that a determination of the reaction order from experimental data supplies insight to the details of how molecules and atoms react with each other. Even though rate data involve measurements of gross numbers of molecules, their interpretation (through the reaction order) permits us to formulate the probable step (or steps) which individual molecules undergo.

## 5. TEMPERATURE DEPENDENCE OF REACTION RATES

Although a chemical reaction may be “thermodynamically” favored (which means the free energy of the system will be lowered as a result of the reaction), reaction may nevertheless not take place. Thus, H<sub>2</sub> and O<sub>2</sub> gases can exist in intimate contact over a considerable temperature range before reaction takes place. Nevertheless, a lighted match or a platinum powder catalyst can nucleate an immediate explosive reaction. Another example with which we are familiar is glass: some glasses remain “supercooled liquids” for thousands of years at room temperature unless reheated to some definite temperature for at least some minimum period of time. Many different factors may influence the rate of a reaction - for example:

- (1) Existing interatomic (or intermolecular) bonds must be broken.
- (2) Atoms must be moved to and away from the reaction site.
- (3) A new boundary is required wherever a new “phase” is to be nucleated.

All three steps cited require work or a supply of energy. Furthermore, all three steps are temperature dependent. At the beginning of this chapter we have stated:

$$\text{Rate} = k(T) \times \text{function of concentration of reactants}$$

In other words: the reaction rate is proportional to the concentration of reactants. The proportionality constant  $k$  is a function of temperature  $k(T)$ . The temperature dependence of  $k$  (which represents the temperature dependence of the rate of a given reaction) can be studied by performing experiments (with constant concentrations) at

different temperatures. From such experiments it can be seen that the value of the rate constant ( $k$ ) is much greater at higher temperatures - the reactions proceed faster.

In 1899 Arrhenius showed that the rate constant of reactions increased in an exponential manner with  $T$ . By an empirical procedure he found that a plot of  $\log k$  versus  $1/T$  gives a linear relation.

Remember: In all kinetic and thermodynamic calculations it is mandatory to use the "absolute temperature scale" in Kelvin (K) which is given by:

$$K = ^\circ\text{C} + 273.16$$

Thus  $0\text{K} = -273.16\text{ C}$ , which corresponds to the thermodynamic absolute zero temperature. Linear plots of  $\log k$  vs  $1/T$  imply the relation:

$$\ln k \propto \frac{1}{T}$$

$$k \propto e^{\text{const}/T}$$

In view of later deductions this empirical relation can be conveniently written as:

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

where  $A$  is a proportionality constant sometimes called the reaction constant,  $R$  is the gas constant and equals  $8.31\text{ J/mole K}$ ,  $E$  is the activation energy in Joules/mole and  $e$  is the base of the natural (Naperian) system of logarithms. Since  $\ln x = 2.3 \log_{10}x$ , we can rewrite the above equation:

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

or

$$\log k = \log A - \frac{E}{2.3 \times 8.3 \times T}$$

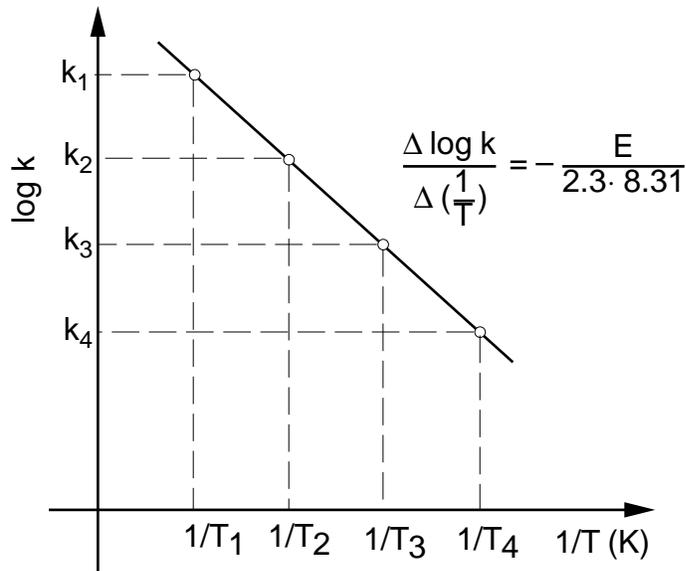


Figure 6 Arrhenius plot permitting the determination of activation energies

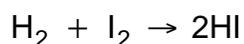
If the above equation is obeyed, a plot of  $\log k$  versus  $1/T$  (fig. 6) will be a straight line from which the characteristic activation energy can be determined since the slope is  $-E/19.15$ . The reaction constant ( $\log A$ ) may in turn be evaluated by extrapolating the rate line to the point at which  $1/T$  equals zero.

It is important to realize that many reactions involve a succession of steps, in which case the rate is controlled by the slowest step. The corresponding values of  $E$  and  $A$  must be determined by experimental methods.

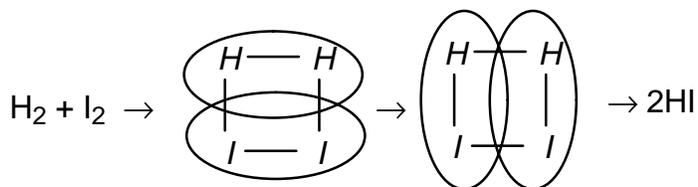
## 6. THE ARRHENIUS THEORY

Arrhenius developed a primarily qualitative theory for molecular reactions which led to empirical expressions for the rate constant. Later theories (which are beyond the scope of 3.091) elaborate and make these original ideas more quantitative.

The very simple (reversible) vapor-phase reaction of hydrogen and iodine to give hydrogen iodide can be used to illustrate the ideas of Arrhenius. The reaction



apparently proceeds by a one-step (one collision) four-center process such that the path of the reaction can be depicted as follows:



For more complicated systems, even when a mechanism has been postulated, it is not so easy to see how the electrons and atoms move around as the reaction proceeds. However, even Arrhenius recognized that any reaction process can proceed first by means of the formation of some “high-energy species” (which we now call the “activated-complex”) and secondly by the breakdown of this complex into products.

If the activated-complex is assumed to have an energy,  $E_a$ , greater than the reactants, then, in analogy to earlier considerations, the number of activated-complex molecules compared with the number of reactant molecules can be written in terms of the *Boltzmann distribution* as:

$$\frac{[\text{activated - complex molecules}]}{[\text{reactant}]} = e^{-E_a/RT}$$

The rate of reaction thus becomes proportional to the concentration of activated-complex molecules:

$$\text{Rate} \propto (\text{activated-complex molecules})$$

or

$$\text{Rate} = A \times e^{-E_a/RT} \times \text{reactants}$$

Making

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

we find

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

Moreover, the theory says that the empirical constant,  $E_a$ , is to be interpreted as the energy of the activated-complex compared with that of the reactant molecules.

The idea of an activated-complex can be presented on a plot (fig. 7) of the energy of

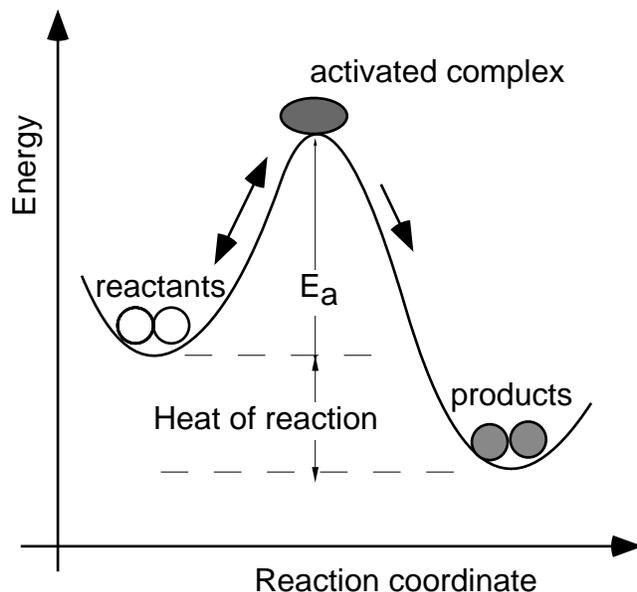


Figure 7 Schematic of a reaction via activated complex formation

the system as ordinate versus the *reaction coordinate* as abscissa. The reaction coordinate is not any single internuclear distance, but rather depends on all the internuclear distances that change as the reactant molecules are converted into product molecules. In general it is impossible, and for the present purpose unnecessary, to give a quantitative description of the reaction coordinate. It consists of the transformation from reactants to products.

The Arrhenius theory leads to a considerable improvement in our understanding of the reaction process. It is, however, still a very qualitative theory in that it does not show how the pre-exponential factor  $A$  depends on the molecular properties of the reaction system, nor does it attempt to predict the value of  $E_a$ .

## 7. THE ACTIVATION ENERGY

The basic distribution of molecular (or atomic) energies at two different temperatures is given in fig. 8. It can be shown that  $e^{-E_a/RT}$  is the fraction of molecules or atoms having

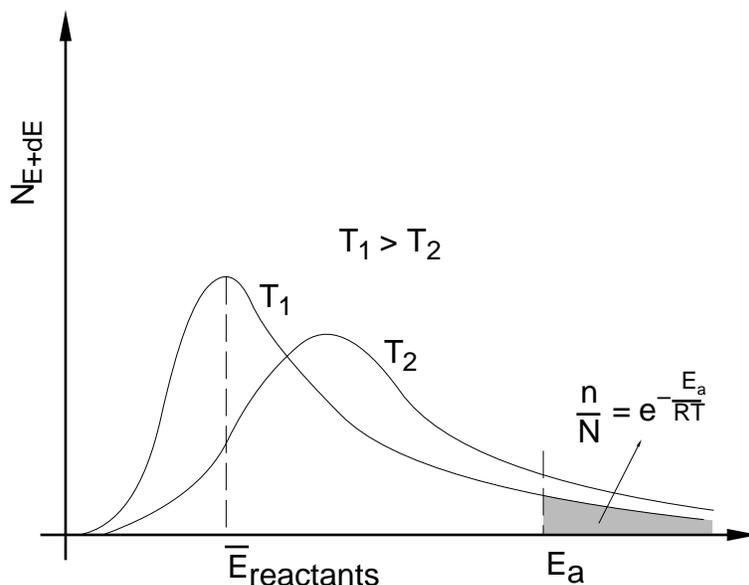


Figure 8 Maxwell Boltzmann energy distribution

an energy of  $E_a$  or greater. The Arrhenius equation holds only if the interacting species have between them at least the certain critical energy  $E_a$ . Since the fraction having this energy or greater is  $e^{-E_a/RT}$ , the reaction rate is proportional to this quantity.

As the value of  $E_a$  increases, the energy requirement increases and it becomes more difficult for the molecules to acquire this energy. In contrast,  $e^{-E_a/RT}$  increases rapidly with increasing temperature ( $T$ ).

The change of a reaction rate with increasing temperature is usually much greater than expected from the corresponding increase in the average velocity of molecules and atoms. The average velocity of molecules and atoms is proportional to the square root of the absolute temperature. Thus, if the temperature is raised  $10^\circ$  from  $298^\circ$  to  $308^\circ$ , the average velocity increase,  $(308/298)^{1/2}$ , is but 2% whereas the rate of reaction increases by about 100%. From this we must conclude that the reaction rate is controlled not only by the number of collisions, but also by the activation energy.

We now realize that in order for a reaction to proceed we have to supply activation energy. We also know that for given conditions of concentration and  $T$  the rate of any reaction is inversely proportional to the energy of activation.

Since, particularly in industry, time is a major factor which can make a process economically feasible or unfeasible, considerable efforts have been put into accelerating reactions by means of *catalysts*. In catalytic reactions the “catalyst”, which effectively lowers the required activation energy (fig. 9), is characterized by the following criteria:

- (1) unchanged chemically at the end of a reaction;
- (2) required in small amounts only;
- (3) catalytic action is frequently proportional to its surface area;
- (4) catalysis can be selective: if different reactions are possible, catalysis can enhance the rate of either one without affecting the alternate reaction.

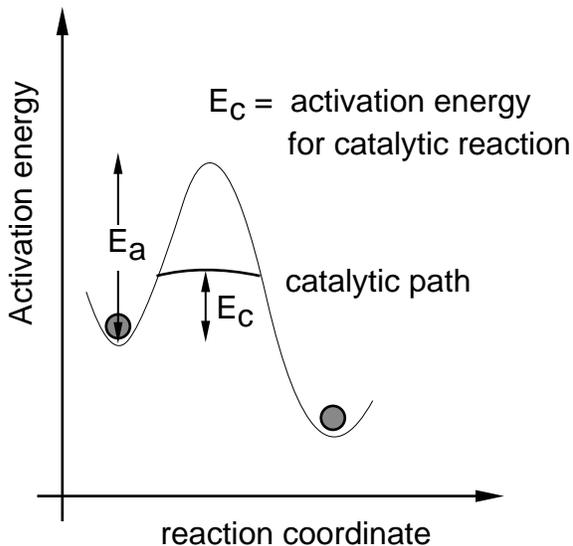
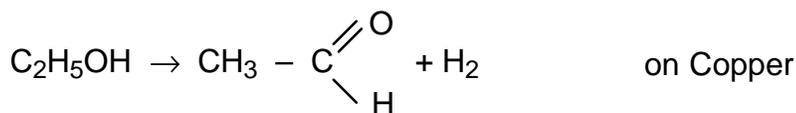
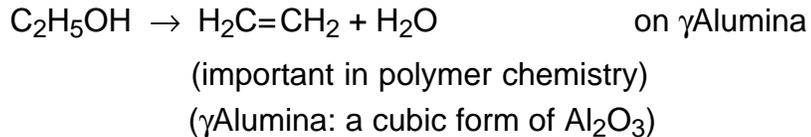


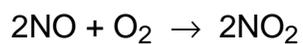
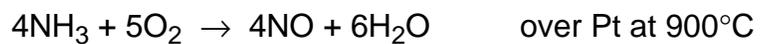
Figure 9 Effect of catalysis on activation energy in chemical reaction.

For example:

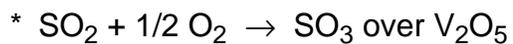


While the exact action of catalysis is still quite unclear, we do have some concrete information. The most frequently encountered case, heterogeneous catalysis (the presence of certain solids which increase gas reactions) is attributed to activation by adsorption. From infrared studies we know that upon adsorption of compounds the bonds within the compound are weakened and reactions can subsequently occur with decreased activation energy.

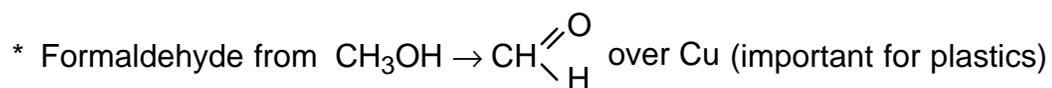
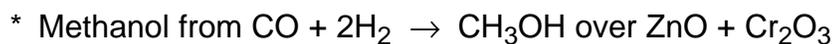
Catalysis has certainly had considerable impact on our daily life. Until 1940 gasoline was exclusively made from crude oil. Also, possibly more important, nitrates and ammonia came primarily from Chile (Chile saltpeter). In the Fischer-Tropsch process, coal and steam are converted into gasoline hydrocarbons with the aid of Ni-Co catalysts. The Haber-Bosch process,  $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$  (ammonia) + 99 kJ, is likely the most important catalytic reaction practiced: From the "Le Chatelier" principle (if in a reaction the number of molecules present decreases, the reaction can be accelerated by applying increased pressures) we know that high pressures will favor this synthesis, but we also know that high temperature will favor the reverse reaction, i.e., decay of ammonia; at high temperatures complex molecular structures tend to decay to more elemental, basic species. Catalysis (Fe,  $\text{Al}_2\text{O}_3 + \text{K}_2\text{O}$  in solid form) makes it possible at 400°C and at about 600 atm to convert about 60% of the gas mixture  $\text{N}_2 + 3\text{H}_2$  to  $\text{NH}_3$ . Nitrates (important as fertilizers and explosives) are predominantly produced by catalytic oxidation.



Other examples are:



\* Synthetic rubber from butadiene and styrene



\* In nature we have a large number of catalysts in the form of enzymes.

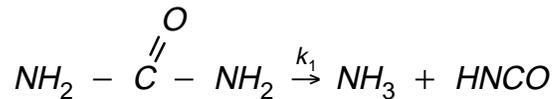
## EXERCISE FOR THE IDLE MIND

1. What is the activation energy of a process which is observed to increase by a factor of three (3) when the temperature is increased from room temperature (20°C) to 40°C?
2. A first order chemical reaction is found to have an activation energy ( $E_A$ ) of 250 kJ/mole and a pre-exponential (A) of  $1.7 \times 10^{14} \text{ s}^{-1}$ .
  - (a) Determine the rate constant at  $T = 750^\circ\text{C}$ .
  - (b) What fraction of the reaction will be completed at 600°C in a period of 10 minutes?
  - (c) At what temperature will the reaction be three times as fast as at 750°C?
3. A compound decomposes by a first order reaction. If the concentration of the compound is 0.025 M after 65 s for an initial concentration of 0.035 M, what will the concentration be after 98 s?
4. The decomposition of a given solid proceeds as follows with time:
 

<u>time (min)</u>	<u>[conc] (M)</u>
0.0	0.1000
5.0	0.0804
10.0	0.0648
15.0	0.0519

  - (a) Determine the reaction order.
  - (b) Determine the rate constant, k.
5. The “diffusion constant” (D) in diffusion processes corresponds to a rate constant (k). At what temperature (in °C) will a diffusion constant (D) be  $5 \times 10^{-11} \text{ (cm}^2\text{/s)}$ ? (Given are  $E_A = 315 \text{ kJ/mole}$  and  $D_0$ , the pre-exponential, equals  $1.70 \text{ cm}^2\text{s}^{-1}$ .)
6. Whiskey, suspected to be of the “moonshine” variety, is analyzed for its age by determining its amount of naturally occurring tritium (T) which is a radioactive hydrogen isotope ( $\text{H}^3$ ) with a half-life of 12.5 years. In this “shine” the activity is found to be 6% of that encountered in fresh bourbon. What is the age of the whiskey in question?
7. If 28% of a sample of radioactive Ag decays in 1.52 hours, what is the half-life of this Ag isotope (in hours)?
8. A sample of plutonium-238 weighing  $3.5 \times 10^{-6} \text{ g}$  decays at a rate of  $2.3 \times 10^6 \text{ atoms/second}$ . Determine the decay constant of plutonium-238 (in  $\text{s}^{-1}$ ).

9. A sample of Cu containing  $\text{Cu}^{64}$  registers 88 disintegrations/second on a counter system. After 9.5 hours the same sample yields 53 counts/sec. What is the half-life of  $\text{Cu}^{64}$  (in hours)?
10. A French publication gives the following experimental data for the catalytical decomposition of urea:



T°C:	131.5	139.5	147.5	160.5
$k_1$ ( $\text{min}^{-1}$ ):	$2.44 \times 10^{-3}$	$5.00 \times 10^{-3}$	$10.57 \times 10^{-3}$	$31.5 \times 10^{-3}$

What is the activation energy ( $E_A$ ) for this reaction?

11. What order rate law fits the following experimental data?



$[\text{N}_2\text{O}_5]$ ( $10^{-3}$ mole/liter):	5.00	4.20	3.53	2.56	2.48
t (min):	0	4	8	12	16

After how many minutes will this reaction be 70% complete?

12. Radiocarbon  $\text{C}^{11}$  is made by neutron activation in a reactor; its half-life is 20 min.
- How much of a sample (in %) remains three (3) hours after it has been formed?
  - You receive the sample of  $\text{C}^{11}$  two (2) hours after it was formed; what fraction (in %) of the amount of  $\text{C}^{11}$  which you received will remain three (3) hours after you have received it?
13. The kinetics of a first order reaction in which acid is produced is studied by periodically withdrawing a sample and titrating with standard alkali. The volumes (standard alkali) required at the various times are:
- |              |   |       |      |          |
|--------------|---|-------|------|----------|
| Time (min):  | 0 | 27    | 60   | $\infty$ |
| Volume (ml): | 0 | 18.10 | 26.0 | 29.7     |
- Prove that this reaction is first order.
  - Calculate the half-life ( $t_{1/2}$ ).

14. A chemical reaction which has an activation energy of 167.0 kJ/mole is to proceed at  $T = 450\text{K}$  with a very constant rate; the rate is allowed to vary at most by  $\pm 1\%$ . How constant must the temperature be to achieve this required rate stability? (For  $T \gg \Delta T$ ,  $T_1 \times T_2 = T^2$ .)
15. In rate studies it is convenient for data analysis to use graphic presentations of the variables (for example,  $c$  and  $t$  or  $k$  and  $T$ ). In each of the following expressions,  $x$  and  $y$  are variables and other terms are constants. What function of  $x$  and what function of  $y$  would you plot in each case to achieve a straight line presentation?
- (1)  $ax = by + c$
  - (2)  $x = Ae^{-y/RT}$
  - (3)  $xy = ax + by$
16. While carbon dating is a customary approach to the determination of the age of carbon-containing objects, "tritium dating" is convenient in dating hydrogen-containing materials ranging in age from 5 to about 100 years. (Tritium,  ${}_1\text{H}^3$ , a hydrogen isotope, is formed in nature by cosmic radiation. It is a  $\beta$  emitter with a half-life of  $t_{1/2} = 12.5$  years.)  
The age of water, and thus the age of whiskey, may be determined by measuring its radioactive tritium ( ${}_1\text{H}^3$ ) content. If a suspected counterfeit whiskey exhibits a tritium count which is 0.14 times the tritium count of fresh water, what is the age of the whiskey?
17. Determine the diffusivity ( $D$ ) of Li in silicon at  $1200^\circ\text{C}$ , knowing that  $D_{1100^\circ\text{C}} = 10^{-5} \text{ cm}^2/\text{s}$  and  $D_{695^\circ\text{C}} = 10^{-6} \text{ cm}^2/\text{s}$ .
18. A silicon wafer is placed into a diffusion reactor operating at  $1600\text{K}$ . Using  $\text{InCl}_3$  (in an inert gas stream) a constant In concentration is established on the surface of the wafer. How long must the wafer be subjected to diffusion (at the indicated temperature) if, at a depth of  $10^{-3} \text{ cm}$  below the surface of the silicon, an indium concentration is to be established which is one-half of the concentration at the wafer surface? ( $D_{1600} = 8 \times 10^{-12} \text{ cm}^2/\text{sec}$ )

19. For a chemical reaction, the concentrations of reactant as a function of time are given below for 25°C and for 50°C.

<u>at 25°C</u>		<u>at 50°C</u>	
<u>time (h)</u>	<u>conc. (mole·ltr<sup>-1</sup>)</u>	<u>time (min)</u>	<u>conc. (mole·ltr<sup>-1</sup>)</u>
.00	0.1039	0	0.1056
3.15	0.0896	9	0.0961
10.00	0.0639	18	0.0856
13.50	0.0529	54	0.0536
26.00	0.0270	105	0.0270
37.30	0.0142	180	0.0089

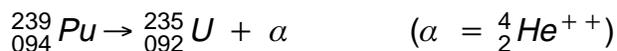
- (a) Indicate schematically (in two different graphic presentations) how you could prove, given concentration data at certain times, that a reaction is of first order.
- (b) Determine, from graphic presentations, the rate constants (k) for the given reaction at 25°C and 50°C.
- (c) Determine the half-life ( $t_{1/2}$ ) for the reaction at 50°C.
- (d) Determine the half-life ( $t_{1/2}$ ) for the reaction at 70°C.
- (e) What is the time required for the reaction at 25°C to be completed to the extent of 42%?
20. The half-life of radium ( ${}_{88}^{226}\text{Ra}$ ) is 1590 years. What fraction of any given amount of Ra will decay in 15 years?
21. Automobile tires, when stored, “age” through oxidation and other reactions of the rubber. Assuming an activation energy ( $E_A$ ) of 50 kJ/mole, by what factor could the shelf-life of tires be increased by lowering the storage temperature from 25°C to 10°C?
22. A chemical reaction yielded the following concentration change with time:

<u>t (sec)</u>	<u>C (moles/ltr)</u>
0	2.33
184	2.08
319	1.91
526	1.67
867	1.36
1198	1.11
1877	0.72
2315	0.55
3144	0.34

- (a) What is the order of the reaction?
- (b) Determine the rate constant (k) of the reaction.

23. If a first order reaction has an activation energy of 104 kJ/mole and a pre-exponential A of  $5 \times 10^{13} \text{ s}^{-1}$ , at what temperature will the reaction have a half-life of:
- one (1) minute?
  - one month of 30 days?
24. What activation energy ( $E_A$ ) is required to cause a reaction rate to increase by a factor of 3 for a  $10^\circ\text{C}$  temperature rise at:
- 300K?
  - 1000K?
25. The first order rate constant (k) for the reaction  $\text{SO}_2\text{Cl}_2 \rightarrow \text{SO}_2 + \text{Cl}_2$  is  $2.2 \times 10^{-5} \text{ s}^{-1}$  at  $320^\circ\text{C}$ . What percentage of  $\text{SO}_2\text{Cl}_2$  is decomposed on heating for 2 hours at  $320^\circ\text{C}$ ?
26. At 700K, what is the half-life ( $t_{1/2}$ ) of  $\text{SiH}_4$ ? The equation for the first order rate constant is  $k = 2 \times 10^{13} e^{-(216.1 \times 10^{-3})/RT}$ .
27. A substance (X) decomposes into A and B in parallel paths with rate constants given by:
- $$k_A = 10^{15} e^{-(125,000/RT)}$$
- $$k_B = 10^{13} e^{-(83,600/RT)}$$
- At what temperature will the two products be formed at the same rate?
28. A chemical first order reaction is found to be half-completed after 100 s at  $300^\circ\text{C}$  and after 20 s at  $500^\circ\text{C}$ . What is the activation energy ( $E_A$ ) for the reaction (in J/mole)?
29. For a chemical reaction the following concentration/time data are available:
- | <u>t (sec)</u> | <u>C (moles/ltr)</u> |
|----------------|----------------------|
| 0              | 2.33                 |
| 867            | 1.36                 |
| 1877           | 0.72                 |
| 3144           | 0.34                 |
- Determine the reaction order.
  - Determine the rate constant for the reaction.
  - Determine the concentration after 4500 s.

30. Calculate the half-life ( $t_{1/2}$ ) in years of plutonium (Pu) isotope of mass number 239 from the information that one microgram (Pu) emits 140,000  $\alpha$  particles per minute through the decay reaction:



31. Studying the rate of a chemical gas reaction, the following data were obtained.

<u>conc. (m-moles/ltr)</u>	<u>time (min)</u>
6.50	0
4.61	1.5
3.25	3.0
2.50	4.2
1.45	6.5
0.85	8.8

- (a) Prove that this reaction follows a first order rate equation (is a first order reaction).  
 (b) Determine the rate constant for the reaction.  
 (c) Determine the half-life for the reaction.  
 (d) What would the concentration be at time  $t = 11$  min?
32. A first order reaction has an activation energy ( $E_A$ ) of 120 kJ/mole and a pre-exponential factor ( $A$ ) of  $6 \times 10^{12} \text{ s}^{-1}$ . At what temperature will the reaction have a half-life ( $t_{1/2}$ ) of 30 days?

33. For a chemical reaction the following  $k$  values were obtained at the indicated temperatures:

T°C:	0	25	35	45
$k \text{ (s}^{-1}\text{):}$	$1.06 \times 10^{-5}$	$3.19 \times 10^{-4}$	$9.86 \times 10^{-4}$	$2.92 \times 10^{-3}$

What is the pre-exponential factor ( $A$ ) of the Arrhenius equation?

34. It is frequently stated that, for chemical reactions proceeding at room temperature, the rate increases by a factor of two (2) upon temperature rise of  $10^\circ\text{C}$ . Assuming this statement to be reasonable, what would be the activation energy ( $E_A$ ) of such chemical reactions?
35. The decomposition of  $\text{N}_2\text{O}_5$  to  $\text{NO}_2$  and  $\text{O}_2$  is of first order and has a rate constant ( $k$ ) of  $4.80 \times 10^{-4}/\text{sec}$  at  $45^\circ\text{C}$ .
- (a) If the initial concentration is  $1.65 \times 10^{-2}$  mole/L, what is the concentration after 825 seconds?  
 (b) How long would it take for the concentration of  $\text{N}_2\text{O}_5$  to decrease from the initial value given in (a) to  $1.0 \times 10^{-2}$  mole/L?

36. In a chemical reaction the concentration of a rate determining component is measured (in moles) at one minute intervals from zero to 5 minutes. The data are:  $1.0 \times 10^{-2}$ ,  $0.683 \times 10^{-2}$ ,  $0.518 \times 10^{-2}$ ,  $0.418 \times 10^{-2}$ ,  $0.350 \times 10^{-2}$  and  $0.301 \times 10^{-2}$ .
- Determine the order (n) of this reaction.
  - Determine the rate constant (k).
  - Determine the half-life of this reaction.
37. Determine the activation energy ( $E_A$ ) for a reaction which triples upon a temperature increase from  $20^\circ\text{C}$  to  $40^\circ\text{C}$ .
38. A chemical reaction has a rate constant (k) of  $9.3 \times 10^{-6}$  per second at 350K and of  $6.9 \times 10^{-4}$  per second at 400K.
- Determine the activation energy ( $E_A$ ) for this reaction.
  - Determine the rate constant for 450K.