

Chemical Kinetics

Introduction

The purpose of **stability testing** is to provide evidence on how the **quality** of a **drug substance** or **drug product** varies with **time** under the influence of a variety of **environmental factors**, such as **temperature**, **humidity**, and **light**, and to establish a retest period for the drug substance or a **shelf life** for the drug product and recommended **storage conditions**,

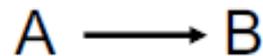
Rates, Order, and Molecularity of Reactions

The rate, velocity, or speed of a reaction is given by the expression dc/dt , where dc is **the increase or decrease of concentration of product or reactant over an infinitesimal time interval dt** . According to the law of mass action, **the rate of a chemical reaction** is proportional to the product of the molar concentration of the reactants each raised to a power usually equal to the number of molecules, a and b , of the substances A and B , respectively, undergoing reaction. In the reaction



Chemical Kinetics

Reaction rate is the change in the concentration of a reactant or a product with time (M/s).



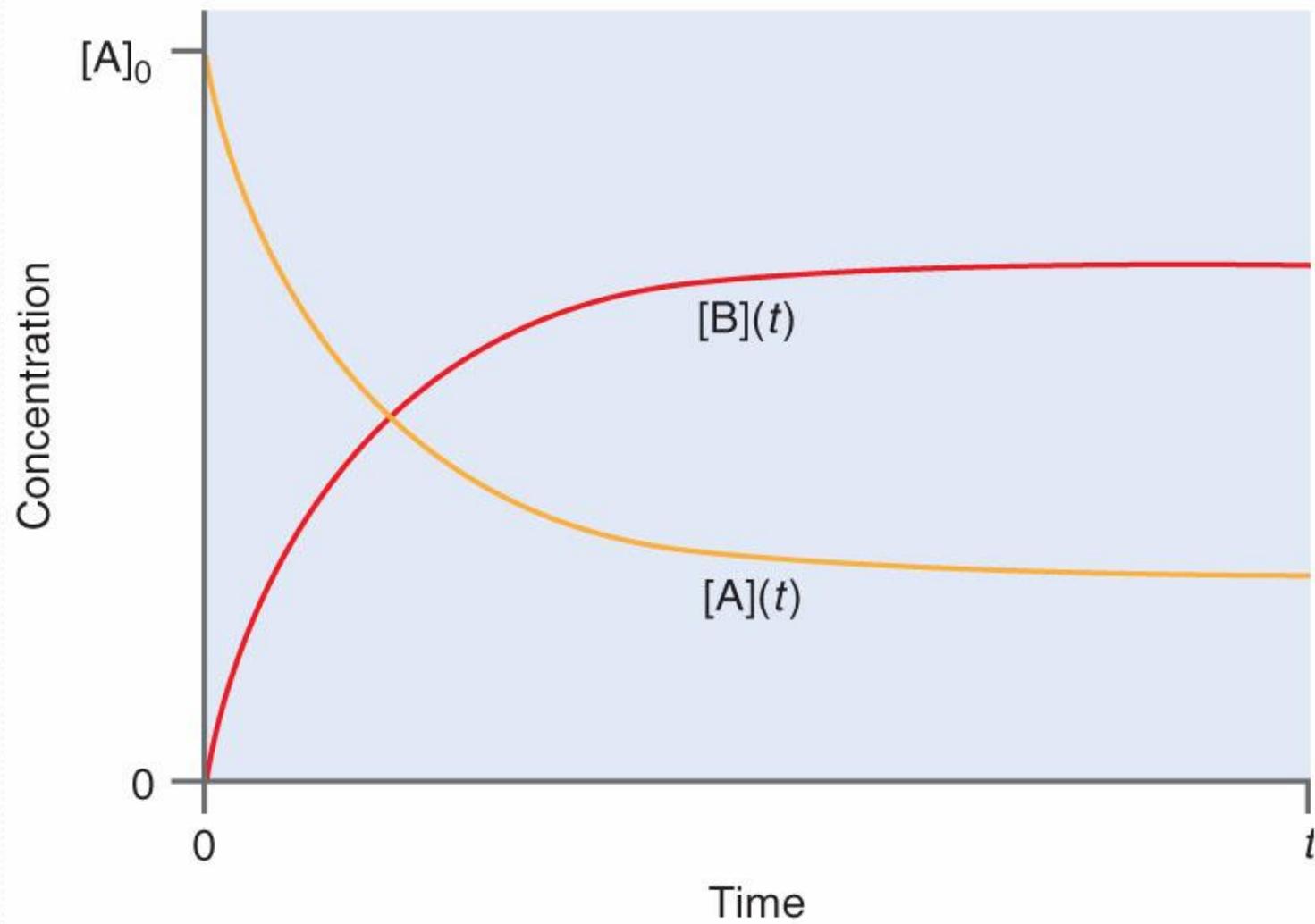
$$\text{rate} = - \frac{\Delta[A]}{\Delta t}$$

$\Delta[A]$ = change in concentration of A over time period Δt

$$\text{rate} = \frac{\Delta[B]}{\Delta t}$$

$\Delta[B]$ = change in concentration of B over time period Δt

Because [A] decreases with time, $\Delta[A]$ is negative.



the rate of the reaction is

$$\begin{aligned}\text{Rate} &= \frac{1}{a} \frac{d[A]}{dt} \\ &= \frac{1}{b} \frac{d[B]}{dt} = \dots k[A]^a[B]^b \dots\end{aligned}\quad (14-2)$$

where k is the *rate constant*. The overall *order* of a reaction is the sum of the exponents [$a + b$, e.g., in equation (14-2)] of the concentration terms, A and B . The order with respect to one of the reactants, A or B , is the exponent a or b of that particular concentration term. In the reaction of ethyl acetate with sodium hydroxide in aqueous solution, for example,



the rate expression is

$$\begin{aligned}\text{Rate} &= \frac{d[\text{CH}_3\text{COOC}_2\text{H}_5]}{dt} \\ &= -\frac{d[\text{NaOH}]}{dt} = k[\text{CH}_3\text{COOC}_2\text{H}_5]^1 [\text{NaOH}]^1\end{aligned}\quad (14-3)$$

The reaction is first order ($a = 1$) with respect to ethyl acetate and first order ($b = 1$) with respect to sodium hydroxide solution; overall the reaction is second order ($a + b = 2$).

Suppose that in this reaction, **sodium hydroxide** as well as **water was in great excess** and **ethyl acetate** was in a relatively **low concentration**. As the reaction proceeded, ethyl acetate would change appreciably from its **original concentration**, whereas the **concentrations of NaOH** and water would **remain essentially unchanged** because they are present in great excess. In this case, the contribution of sodium hydroxide to the rate expression is considered constant and the reaction rate can be written as

$$\frac{d[\text{CH}_3\text{COOC}_2\text{H}_5]}{dt} = k'[\text{CH}_3\text{COOC}_2\text{H}_5] \quad (14-4)$$

where $k' = k[\text{NaOH}]$. The reaction is then said to be a *pseudo-first-order* reaction because it depends only on the first power ($a = 1$) of the concentration of ethyl acetate. In general, when one of the reactants is present in such great excess that its concentration may be considered constant or nearly so, the reaction is said to be of *pseudo-order*.

Example 14-1

Reaction Order

In the reaction of acetic anhydride with ethyl alcohol to form ethyl acetate and water,



the rate of reaction is

$$\begin{aligned} \text{Rate} &= - \frac{d[(\text{CH}_3\text{CO})_2\text{O}]}{dt} \\ &= k[(\text{CH}_3\text{CO})_2\text{O}] [\text{C}_2\text{H}_5\text{OH}]^2 \end{aligned} \quad (14-5)$$

Q\What is the order of the reaction with respect to acetic anhydride? With respect to ethyl alcohol? What is the overall order of the reaction?

If the alcohol, which serves here as the solvent for acetic anhydride, is in large excess such that a small amount of ethyl alcohol is used up in the reaction, write the rate equation for the process and state the order.

Answer: The reaction appears to be first order with respect to acetic anhydride, second order with respect to ethyl alcohol, and overall third order. However, because alcohol is the solvent, its concentration remains essentially constant, and the rate expression can be written as

$$-\frac{d[(\text{CH}_3\text{CO})_2\text{O}]}{dt} = k'[(\text{CH}_3\text{CO})_2\text{O}] \quad (14-6)$$

Kinetically the reaction is therefore a pseudo-first-order reaction,

Molecularity is the number of molecules, atoms, or ions reacting in an elementary process. In the reaction



the process is *unimolecular* because the *single molecule*, Br₂, decomposes to form two bromine atoms. The single-step reaction called *simple reaction*. *Chemical reactions* that proceed through *more than one step* are known as *complex reactions*. The overall order determined *kinetically* may *not be identical* with the *molecularity* because the reaction consists of several steps, each with its own molecularity. For the overall reaction



the order has been found experimentally to be 2. The reaction is not **termolecular**, in which two molecules of NO would collide simultaneously with one molecule of O₂. Instead, the mechanism is postulated to consist of two elementary steps, each being **bimolecular**



Rate Constants, Half-Life, Shelf Life, and Apparent or Pseudo-Order

- Specific Rate Constant

The constant, k , appearing in the rate law associated with a single-step (elementary) reaction is called the *specific rate constant* for that reaction. Any change in the conditions of the reaction, for example, in temperature or solvent, will lead to a rate law having a **different value for the specific rate constant**. Variations in the specific rate constant are of great physical significance because a change in this constant necessarily represents a change at the **molecular level as a result of a variation in the reaction conditions**. For Zero-order reaction.

$$k = -\frac{dA}{dt} = \frac{\text{moles/liter}}{\text{second}}$$
$$= \frac{\text{moles}}{\text{liter second}} = \text{moles liter}^{-1} \text{second}^{-1}$$

For first order reaction.

$$k = -\frac{dA}{dt} \frac{1}{A} = \frac{\text{moles/liter}}{\text{second-moles/liter}}$$
$$= \frac{1}{\text{second}} = \text{second}^{-1}$$

and for a second-order reaction,

$$k = \frac{dA}{dt} \frac{1}{A^2} = \frac{\text{moles/liter}}{\text{second (moles/liter)}^2}$$
$$= \frac{\text{liter}}{\text{moles-second}} = \text{liter second}^{-1} \text{ mole}^{-1}$$

where A is the molar concentration of the reactant.

Reaction	Order	Differential form	Integrated form
$A \rightarrow P$	zeroth	$\frac{d[A]}{dt} = -k$	$[A] = [A]_0 - kt$
$A \rightarrow P$	first	$\frac{d[A]}{dt} = -k [A]$	$\ln[A] = \ln[A]_0 - kt$
$A + A \rightarrow P$	second	$\frac{1}{2} \frac{d[A]}{dt} = -k [A]^2$	$\frac{1}{[A]} = \frac{1}{[A]_0} + 2kt$
$A + B \rightarrow P$	second	$\frac{d[A]}{dt} = -k [A][B]$	$kt = \frac{1}{[B]_0 - [A]_0} \ln \frac{[B]_0 [A]}{[A]_0 [B]}$

Zero-Order Reactions

Garrett and Carper found that the loss in color of a multisulfa product (as measured by the decrease of spectrophotometric absorbance at a wavelength of 500 nm) followed a zero-order rate. The rate expression for the change of absorbance, A , with time is therefore

$$-\frac{dA}{dt} = k_0 \quad (14-7)$$

where the minus sign signifies that the absorbance is decreasing (i.e., the color is fading). The velocity of fading is seen to be constant and independent of the concentration of the colorant used. The rate equation can be integrated between the initial absorbance, A_0 , corresponding to the original color of the preparation at $t = 0$, and A_t , the absorbance after t hours:

$$\int_{A_0}^{A_t} dA = -k_0 \int_0^t dt$$

$$A_t - A_0 = -k_0 t$$

$$A_t = A_0 - k_0 t \quad (14-8)$$

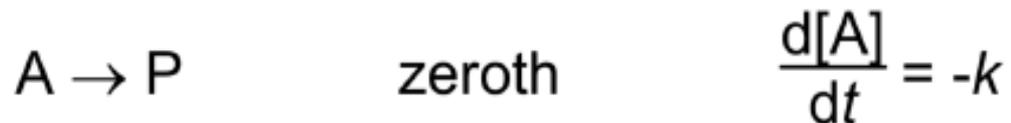
The initial concentration corresponding to A_0 is ordinarily written as a and the concentration remaining at time t as c .

When this linear equation is plotted with c on the vertical axis against t on the horizontal axis, the slope of the line is equal to $-k_0$. Garrett and Carper³ obtained a value for k of **0.00082** absorbance decreases per hour at 60°C, indicating that the color was fading at this constant rate independent of concentration.

Because the *half-life* is the time required for one-half of the material to disappear, in the present case $A_0 = 0.470$ and $A_0 = 0.235$:

$$t_{1/2} = \frac{\frac{1}{2}A_0}{k_0} = \frac{0.235}{8.2 \times 10^{-4}} = 2.9 \times 10^2 \text{ hr}$$

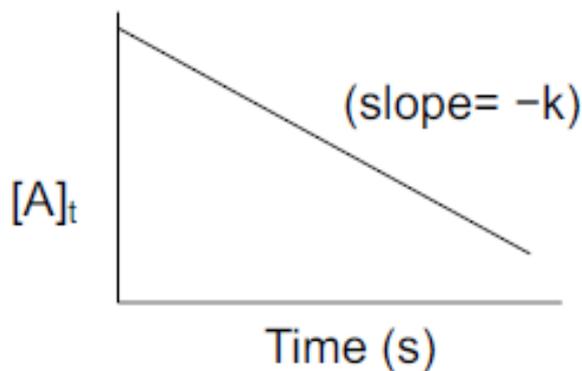
Zero-Order Processes



reaction rate = $-\frac{\Delta[A]_t}{\Delta t} = k$ (**constant**)

So... $[A]_t = -kt + [A]_0$

- This equation has the general form for a straight line, $y=mx+b$, so a plot of $[A]_t$ vs. t is a straight line with slope $(-k)$ and intercept $[A]_0$.



Half-Life and Shelf Life

The *half-life* is the time required for one-half of the material to disappear; it is the time at which A has decreased to $\frac{1}{2} A$. The shelf life is the time required for 10% of the material to disappear; it is the time at which A has decreased to 90% of its original concentration (i.e., $0.9 A$).

half-life:

$$t_{1/2} = \frac{A_0 - 1/2A_0}{k_0}$$

∴

$$t_{1/2} = \frac{1/2A_0}{k_0}$$

Shelf-life:

$$t_{10\%} = \frac{A_0 - 0.9A_0}{k_0}$$

where

k_0 = specific rate constant for
zero-order kinetic

A_0 = Initial concentration

Suspensions. Apparent Zero-Order Kinetics

Suspensions are another case of zero-order kinetics, in which the concentration in solution depends on the drug's solubility. As the drug decomposes in solution, more drug is released from the suspended particles so that the concentration remains constant.

This concentration is, of course, the drug's equilibrium solubility in a particular solvent at a particular temperature. The important point is that the amount of drug in solution remains constant despite its decomposition with time. The reservoir of solid drug in suspension is responsible for this constancy.

The equation for an ordinary solution, with no reservoir of drug to replace that depleted, is the first-order expression,

$$\frac{-d[A]}{dt} = k[A]$$

where $[A]$ is the concentration of drug remaining undecomposed at time t , and k is known as a first-order rate constant. When the concentration $[A]$ is rendered constant, as in the case of a suspension, we can write

$$k[A] = k_0 \quad (14-9)$$

so that the first-order rate law (14-11) becomes

$$-\frac{d[A]}{dt} = k_0 \quad (14-10)$$

Equation (14-10) obviously is a zero-order equation. It is referred to as an *apparent zero-order equation*, being zero order only because of the suspended drug reservoir, which ensures constant concentration. Once all the suspended particles have been converted into drug in solution, the system changes to a first-order reaction.

Example (14-2) : Shelf Life of an Aspirin Suspension

A prescription for a liquid aspirin preparation is called for. It is to contain 325 mg/5 mL or 6.5 g/100 mL. The solubility of aspirin at 25°C is 0.33 g/100 mL; therefore, the preparation will definitely be a suspension. The other ingredients in the prescription cause the product to have a pH of 6.0. The first-order rate constant for aspirin degradation in this solution is $4.5 \times 10^{-6} \text{ sec}^{-1}$. Calculate the zero-order rate constant. Determine the shelf life, t_{90} , for the liquid prescription, assuming that the product is satisfactory until the time at which it has decomposed to 90% of its original concentration (i.e., 10% decomposition) at 25°C. *Answer:* $k_0 = k \times [\text{Aspirin in solution}]$, from equation (14-9).

$$k_0 = (4.5 \times 10^{-6} \text{ sec}^{-1}) \times (0.33 \text{ g/100 mL})$$

$$k_0 = 1.5 \times 10^{-6} \text{ g/100 mL sec}^{-1}$$

$$t_{90} = \frac{0.10[A]_0}{k_0} = \frac{(0.10)(6.5 \text{ g/100 mL})}{(1.5 \times 10^{-6} \text{ g/100 mL sec}^{-1})}$$
$$= 4.3 \times 10^5 \text{ sec} = 5.0 \text{ days}$$

First-Order Reactions

In 1918, Harned⁵ showed that the decomposition rate of hydrogen peroxide catalyzed by 0.02 M KI was proportional to the concentration of hydrogen peroxide remaining in the reaction mixture at any time. The data for the reaction



are given in Table 14-1. Although two molecules of hydrogen peroxide appear in the stoichiometric equation as just written, the reaction was found to be first order. The rate equation is written as

$$-\frac{dc}{dt} = kc \quad (14-11)$$

where c is the concentration of hydrogen peroxide remaining undecomposed at time t and k is the first-order velocity constant. Integrating equation (14-11) between concentration c_0 at time $t = 0$ and concentration c at some later time, t , we have

$$\int_{c_0}^c \frac{dc}{c} = -k \int_0^t dt$$
$$\ln c - \ln c_0 = -k(t - 0)$$
$$\ln c = \ln c_0 - kt \quad (14-12)$$

Converting to common logarithms yields

$$\log c = \log c_0 - kt/2.303 \quad (14-13)$$

$$k = \frac{2.303}{t} \log \frac{c_0}{c} \quad (14-14)$$

Table 14-1 Decomposition of Hydrogen Peroxide at 25°C in Aqueous Solution Containing 0.02 m KI*

Table 14-1 Decomposition of Hydrogen Peroxide at 25°C in Aqueous Solution Containing 0.02 m KI*		
Time	C	<i>K</i> (min⁻¹)
0	57.90	—
5	50.40	0.0278
10	43.90	0.0277
25	29.10	0.0275
45	16.70	0.0276
65	9.60	0.0276
∞	0	—

In exponential form, equation (14-12) becomes

$$c = c_0 e^{-kt} \quad (14-15)$$

and equation (14-13) becomes

$$c = c_0 10^{-kt/2.303} \quad (14-16)$$

Equations (14-15) and (14-16) express the fact that, in a first-order reaction, the concentration decreases exponentially with time. As shown in Figure 14-1, the concentration begins at C_0 and decreases as the reaction becomes progressively slower. The concentration asymptotically approaches a final value C_∞ as time proceeds toward infinity. Equation (14-14) is often written as

$$k = \frac{2.303}{t} \log \frac{a}{a-x} \quad (14-17)$$

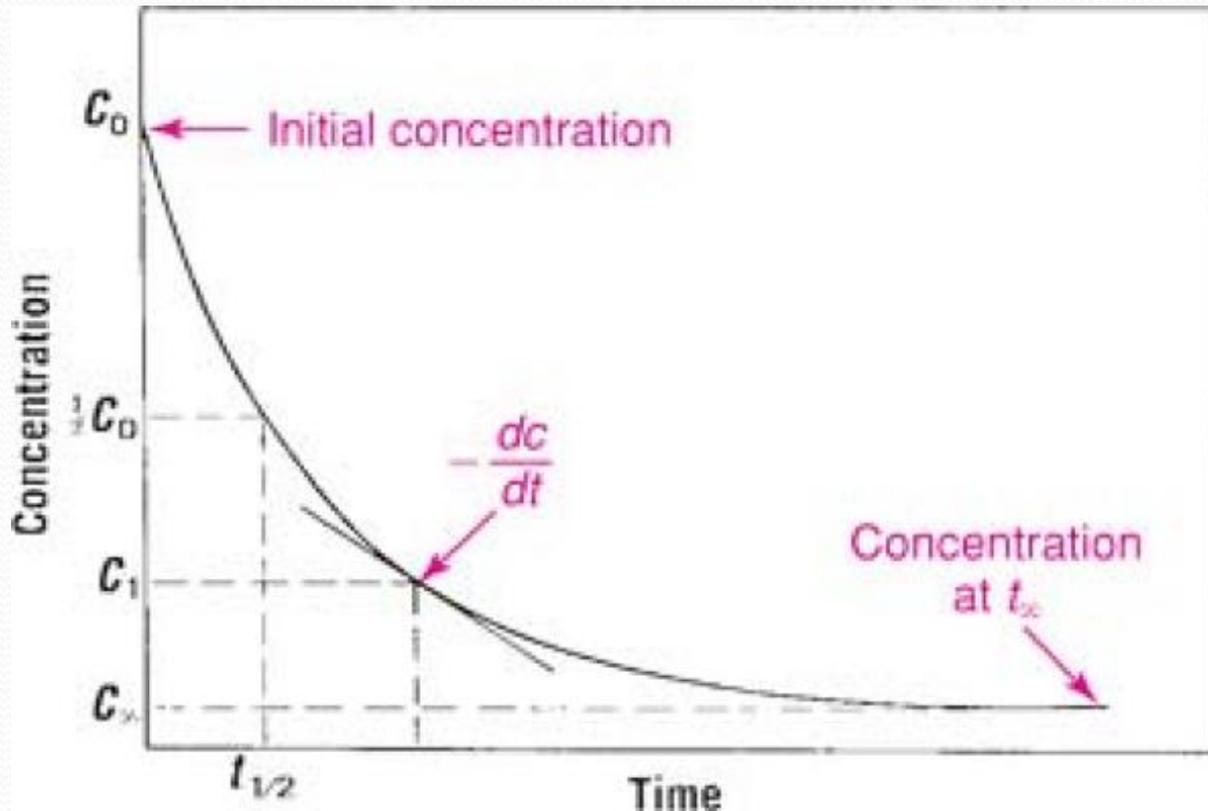
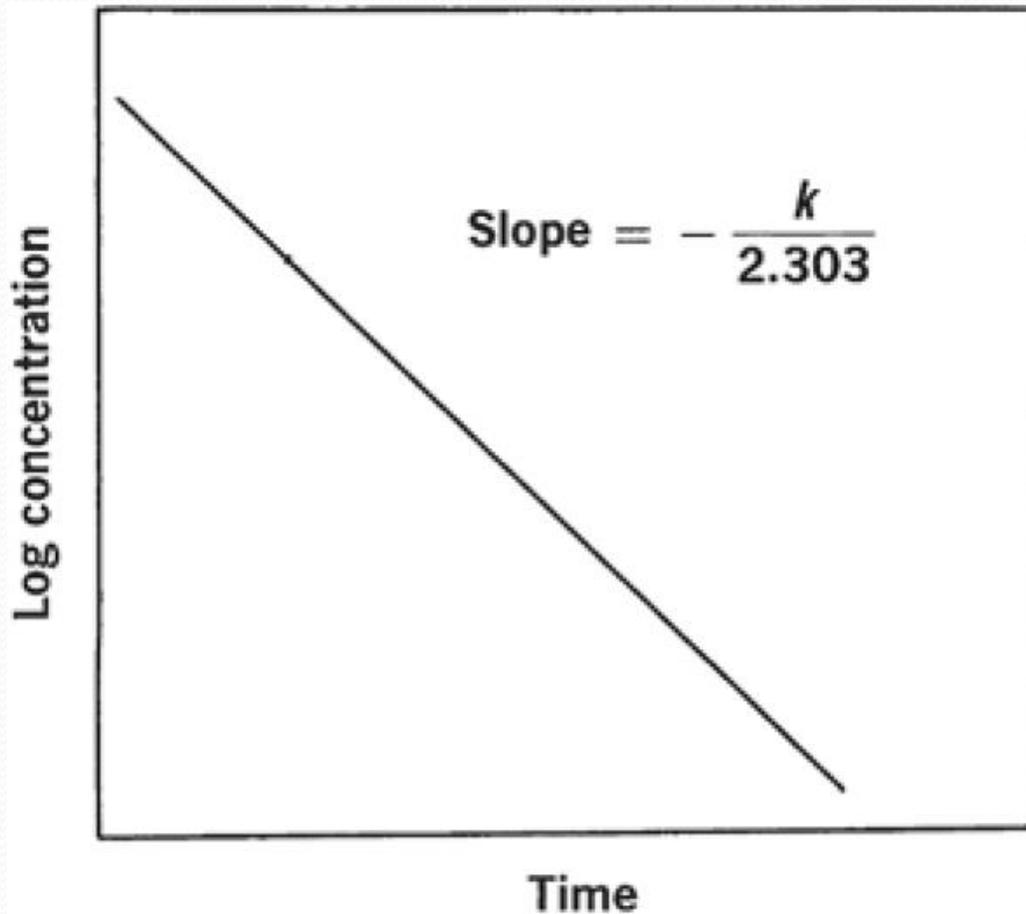


Fig. 14-1. Fall in concentration of a decomposing drug with time. In addition to C_0 and C_∞ , $\frac{1}{2}C_0$ and the corresponding time, $t_{1/2}$, are shown

The rate of decrease of concentration with time, $-dC/dt$, at an arbitrary concentration, C_1 , is also shown.



where the symbol a is customarily used to replace c_0 , x is the decrease of concentration in time t , and $a - x = c$. The specific reaction rates listed in Table 14-1 were calculated by using equation (14-17). Probably the best way to obtain an average k for the reaction is to plot the **logarithm of the concentration against the time**, as shown in Figure 14-2. The linear expression in equation (14-13) shows that the *slope of the line is $-k/2.303$* , from which the rate constant is obtained. If a *straight line* is obtained, it indicates that the reaction is *first order*. Once the rate constant is known, the concentration of reactant remaining at a definite time can be computed as demonstrated in the following examples

Rules of logarithms

$$\log(1) = 0$$

$$\log(10) = 1$$

$$\log(100) = 2$$

$$\text{Log}(10^x) = x$$

$$\ln(1) = 0$$

$$\ln(e) = 1$$

$$\ln(e^x) = x$$

$$\log A^x = x \log A$$

$$\ln A^x = x \ln A$$

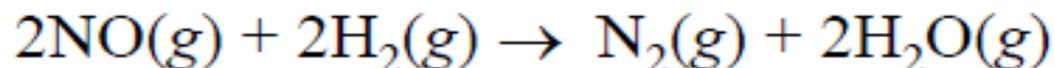
$$\log\left(\frac{A^x}{B^x}\right) = \log\left(\frac{A}{B}\right)^x = x \log\left(\frac{A}{B}\right)$$

$$\log(AB) = \log A + \log B$$

$$\log\left(\frac{A}{B}\right) = \log A - \log B$$

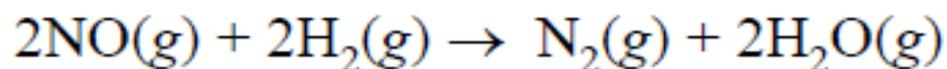
Determining Reaction Order: *The Method of Initial Rates*

The reaction of nitric oxide with hydrogen at 1280°C is:



From the following data, determine the rate law and rate constant.

Run	$[\text{NO}]_0$ (M)	$[\text{H}_2]_0$ (M)	Initial Rate (M/min)
1	0.0100	0.0100	0.00600
2	0.0200	0.0300	0.144
3	0.0100	0.0200	0.0120



The rate law for the reaction is given by:

$$\text{Rate}(\text{M}/\text{min}) = k [\text{NO}]^x [\text{H}_2]^y$$

Taking the ratio of the rates of runs 3 and 1 one finds:

$$\frac{\text{Rate}(3)}{\text{Rate}(1)} = \frac{k [\text{NO}]_{(3)}^x [\text{H}_2]_{(3)}^y}{k [\text{NO}]_{(1)}^x [\text{H}_2]_{(1)}^y}$$

$$\frac{0.0120\text{M}/\text{min}}{0.00600\text{M}/\text{min}} = 2 = \frac{\cancel{k} [0.0100]^x [0.0200]^y}{\cancel{k} [0.0100]^x [0.0100]^y} = \frac{[0.0200]^y}{[0.0100]^y}$$

$$\frac{[0.0200]^y}{[0.0100]^y} = \left[\frac{0.0200}{0.0100} \right]^y$$

$$\log \left(\left[\frac{0.0200}{0.0100} \right]^y = 2 \right)$$

$$\log \left(\frac{0.0200}{0.0100} \right)^y = \log 2$$

$$y \log(2) = \log 2$$

$$y = 1$$

Now that “y” is known, we may solve for x in a similar manner:

$$\frac{\text{Rate}(1)}{\text{Rate}(2)} = \frac{k [\text{NO}]_{(1)}^x [\text{H}_2]_{(1)}^y}{k [\text{NO}]_{(2)}^x [\text{H}_2]_{(2)}^y}$$

$$\frac{0.00600}{0.144} = \frac{k [0.0100]^x [0.0100]}{k [0.0200]^x [0.0300]}$$

$$\frac{1}{24} = \left(\frac{1}{2} \right)^x \times \left(\frac{1}{3} \right)$$

$$\left(\frac{1}{2} \right)^x = \frac{1}{8}$$

$$x \log \left(\frac{1}{2} \right) = \log \left(\frac{1}{8} \right)$$

$$x = 3$$

The Rate Law is:

$$\text{Rate(M/min)} = k [\text{NO}]^3[\text{H}_2]$$

To find the rate constant, choose one set of data and solve:

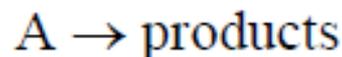
$$0.0120 \frac{\text{M}}{\text{min}} = k (0.0100\text{M})^3 (0.0200\text{M})$$

$$k = \frac{0.0120 \frac{\text{M}}{\text{min}}}{(0.0100\text{M})^3 (0.0200\text{M})} = \frac{0.0120 \frac{\text{M}}{\text{min}}}{(0.0100)^3 (0.0200) \text{M}^4}$$

$$k = 6.00 \times 10^5 \frac{\text{M}^{-3}}{\text{min}}$$

Integrated Rate Laws: time dependence of concentration

For a first order process, the rate law can be written:



$$\text{Rate}(\text{Ms}^{-1}) = -\frac{\Delta[A]}{\Delta t} = k[A]$$

This is the “*average rate*”

If one considers the infinitesimal changes in concentration and time the rate law equation becomes:

$$\text{Rate}(\text{Ms}^{-1}) = -\frac{d[A]}{dt} = k[A]$$

This is the “*instantaneous rate*”

Integrating in terms of $d[A]$ and dt :

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -k \int_0^t dt$$

where $[A] = [A]_0$ at time $t = 0$
and $[A] = [A]$ at time $t = t$

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -k \int_0^t dt \quad \longrightarrow \quad \ln \left(\frac{[A]}{[A]_0} \right) = -kt$$

Taking the exponent to each side of the equation:

$$\frac{[A]}{[A]_0} = e^{-kt} \quad \text{or} \quad [A] = [A]_0 e^{-kt}$$

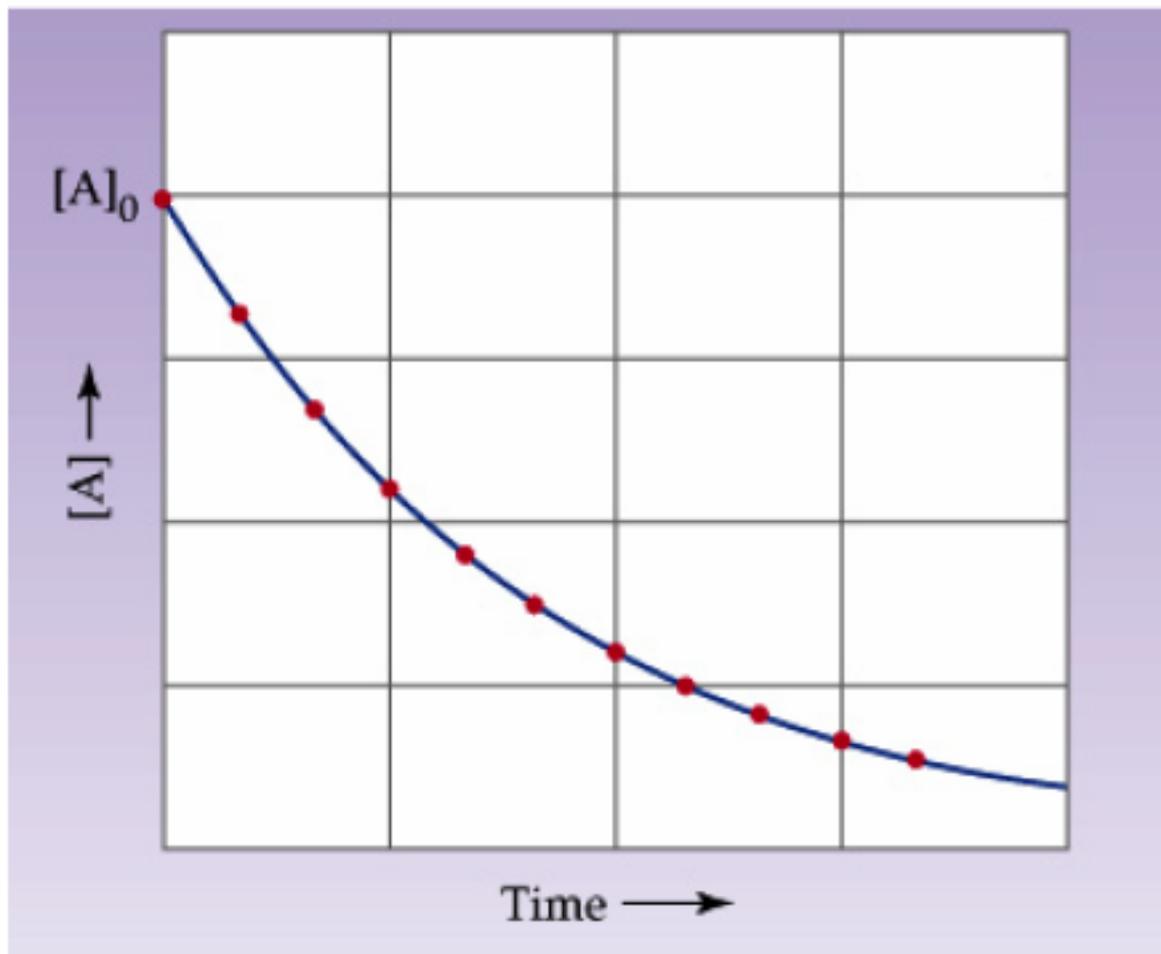
Conclusion: The concentration of a reactant governed by first order kinetics falls off from an initial concentration exponentially with time.

Recognizing a first order process:



Whenever the conc. of a reactant falls off exponentially, the kinetics follow first order.

$$[A] = [A]_0 e^{-kt}$$

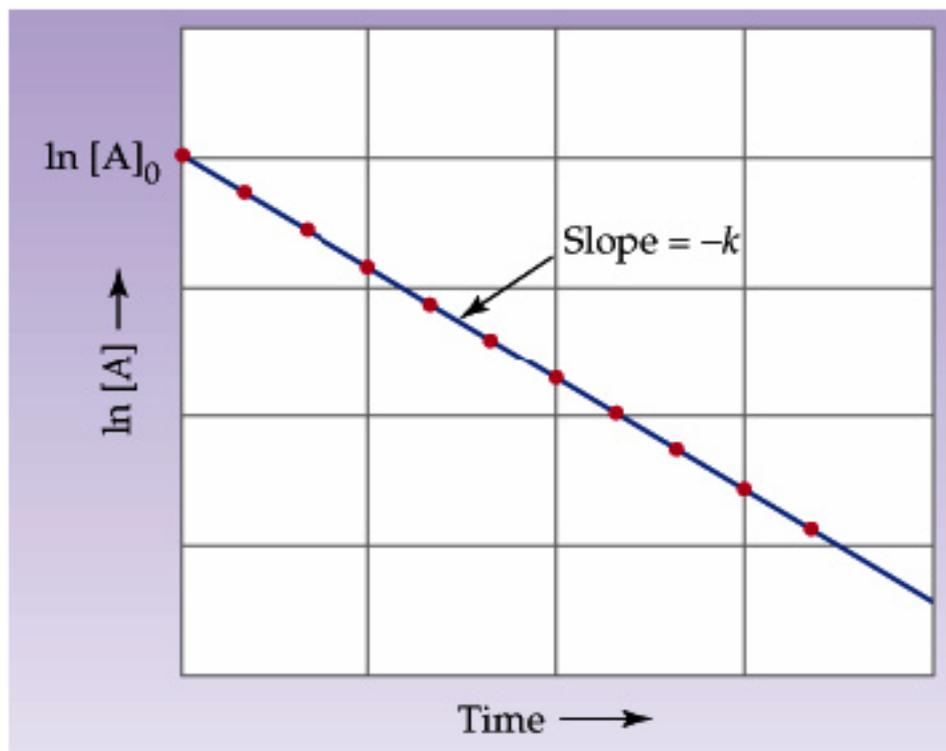


Determining the Rate constant for a first order process

Taking the log of the integrated rate law for a first order process we find:

$$\ln([A] = [A]_0 e^{-kt}) \longrightarrow \ln[A] = \ln[A]_0 - k \times t$$

A plot of $\ln[A]$ versus time (t) is a straight line with slope $-k$ and intercept $\ln[A]_0$.



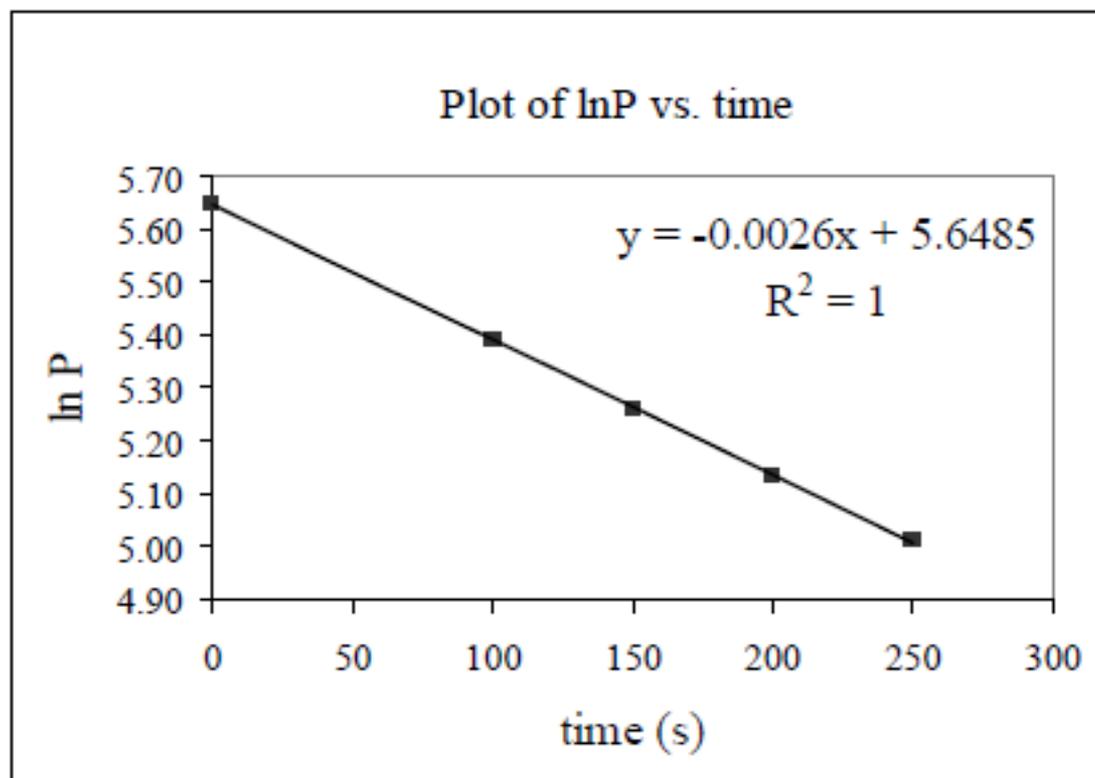
Example: The rate of decomposition of azomethane ($C_2H_6N_2$) was studied by monitoring the partial pressure of the reactant as a function of time.

Determine if the data below support a first order reaction.

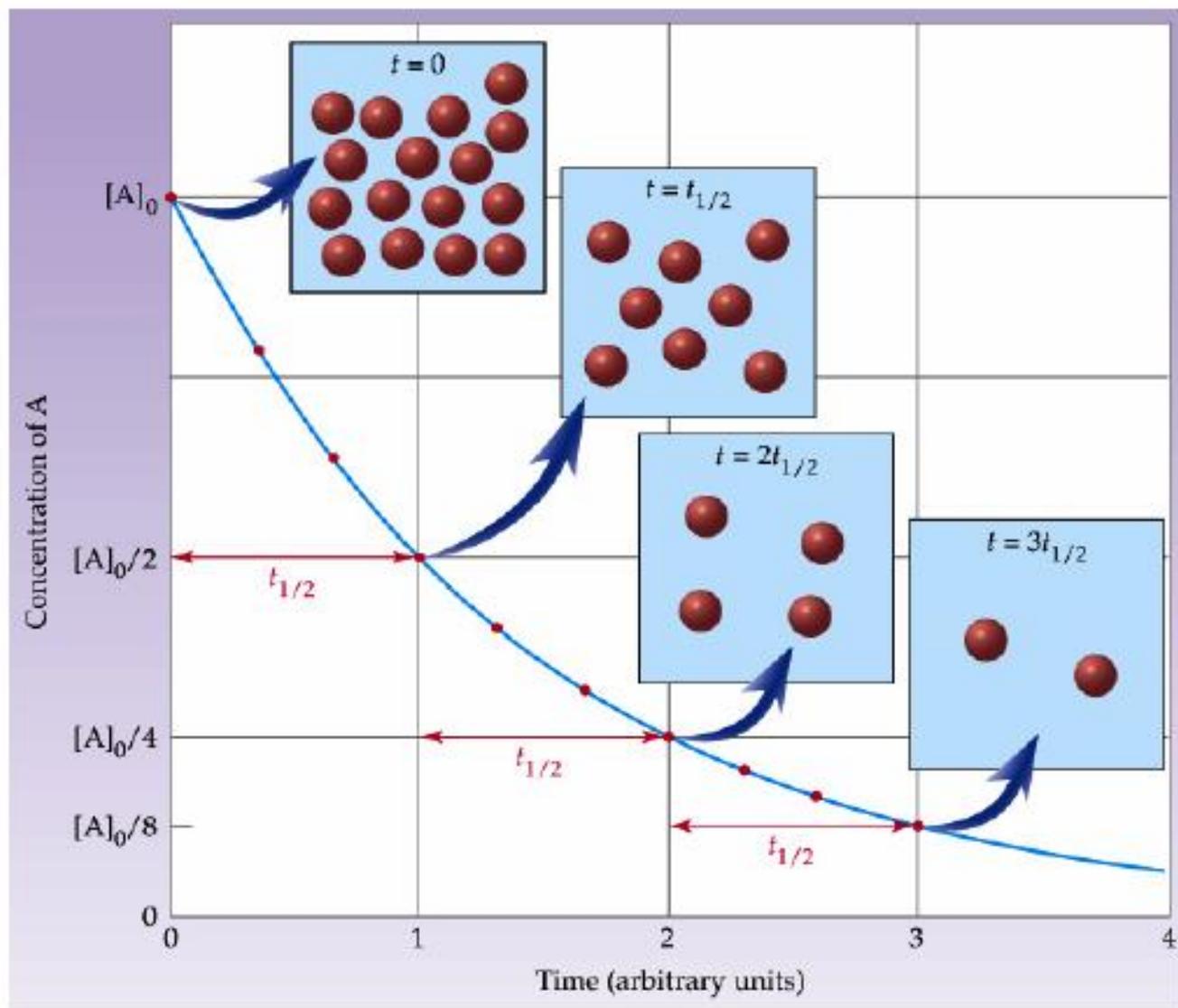
Calculate the rate constant for the reaction.

Time (s)	P (mmHg)	ln (P)
0	284	5.65
100	220	5.39
150	193	5.26
200	170	5.14
250	150	5.01

$$k = 2.6 \times 10^{-3} s^{-1}$$



Reaction Half-Life



Reaction Half-life:

Half-life is the time taken for the concentration of a reactant to drop to half its original value.

$$[A] = \frac{[A]_0}{2}$$

For a first order process the half life ($t_{1/2}$) is found mathematically from:

$$(1) \ln[A] = -kt + \ln[A]_0$$

$$(2) \ln[A] - \ln[A]_0 = -kt$$

$$(3) \ln\left(\frac{[A]}{[A]_0}\right) = -kt$$

$$(4) \ln\left(\frac{[A]_0}{[A]}\right) = kt$$

$$(5) \ln\left(\frac{[A]_0}{[A]_0/2}\right) = kt_{1/2}$$

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

Or with the other Method

Half-Life - 1st order

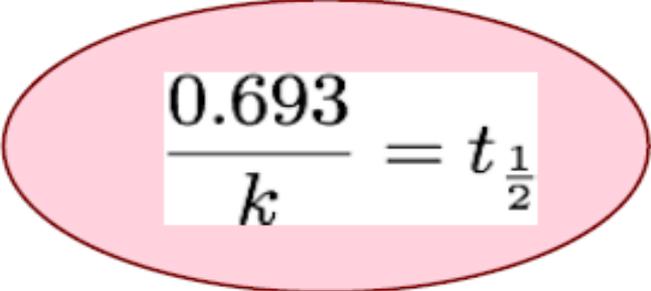
For a **first-order** process, set $[A]_t = 0.5 [A]_0$ in integrated rate equation:

$$\ln[A] = \ln[A]_0 - kt$$

$$\ln \frac{0.5 [A]_0}{[A]_0} = -kt_{\frac{1}{2}}$$

$$\ln(0.5) = -kt_{\frac{1}{2}}$$

$$\ln(2) = 0.693 = +kt_{\frac{1}{2}}$$


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

A certain reaction proceeds through t first order kinetics.

The half-life of the reaction is 180 s.

What percent of the initial concentration remains after 900s?

Step 1: Determine the magnitude of the rate constant, k.

$$t_{\frac{1}{2}} = \frac{\ln 2}{k} = \frac{0.693}{k} \qquad k = \frac{\ln 2}{t_{\frac{1}{2}}} = \frac{\ln 2}{180\text{s}} = 0.00385\text{s}^{-1}$$

Using the integrated rate law, substituting in the value of k and 900s we find:

$$\frac{[A]}{[A]_0} = e^{-kt} \longrightarrow \frac{[A]}{[A]_0} = e^{-0.00385\text{ s}^{-1} \times 900\text{ s}} \quad = 0.0312$$

Since the ratio of [A] to [A]₀ represents the fraction of [A]₀ that remains, the % is given by:

$$100 \times 0.0312 = 3.12\%$$

Q A solution of a drug contained 500 units/mL when prepared. It was analyzed after 40 days and was found to contain 300 units/mL. Assuming the decomposition is first order, at what time will the drug have decomposed to one-half of its original concentration?

We have

$$k = \frac{2.303}{40} \log \frac{500}{300} = 0.0128 \text{ day}^{-1}$$

$$t = \frac{2.303}{0.0128} \log \frac{500}{250} = 54.3 \text{ days}$$

Second-Order Reactions

The rates of bimolecular reactions, which occur when two molecules come together,



are frequently described by the second-order equation.

- When the speed of the reaction depends on the concentrations of A and B with each term raised to the first power, the rate of decomposition of A is equal to the rate of decomposition of B , and both are proportional to the product of the concentrations of the reactants:

$$-\frac{d[A]}{dt} = \frac{d[B]}{dt} = k[A][B] \quad (14-19)$$

If a and b are the initial concentrations of A and B , respectively, and x is the concentration of each species reacting in time t , the rate law can be written as

$$\frac{dx}{dt} = k(a - x)(b - x) \quad (14-20)$$

where dx/dt is the rate of reaction and $a - x$ and $b - x$ are the concentrations of A and B , respectively, remaining at time t .

□ When, in the simplest case, both A and B are present in the same concentration so that $a = b$,

$$\frac{dx}{dt} = k(a - x)^2 \quad (14-21)$$

Equation (14-21) is integrated, using the conditions that $x = 0$ at $t = 0$ and $x = x$ at $t = t$.

$$\int_0^x \frac{dx}{(a - x)^2} = k \int_0^t dt$$
$$\left(\frac{1}{a - x} \right) - \left(\frac{1}{a - 0} \right) = kt$$
$$\frac{x}{a(a - x)} = kt \quad (14-22)$$

or

$$k = \frac{1}{at} \left(\frac{x}{a - x} \right) \quad (14-23)$$

□ When, in the general case, A and B are not present in equal concentrations, integration of equation (14-20) yields

$$\frac{2.303}{a-b} \log \frac{b(a-x)}{a(b-x)} = kt \quad (14-24)$$

$$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)} \quad (14-25)$$

For a Second Order Process:

A → Products

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

$$\text{Rate}(\text{Ms}^{-1}) = -\frac{d[A]}{dt} = k[A]^2$$

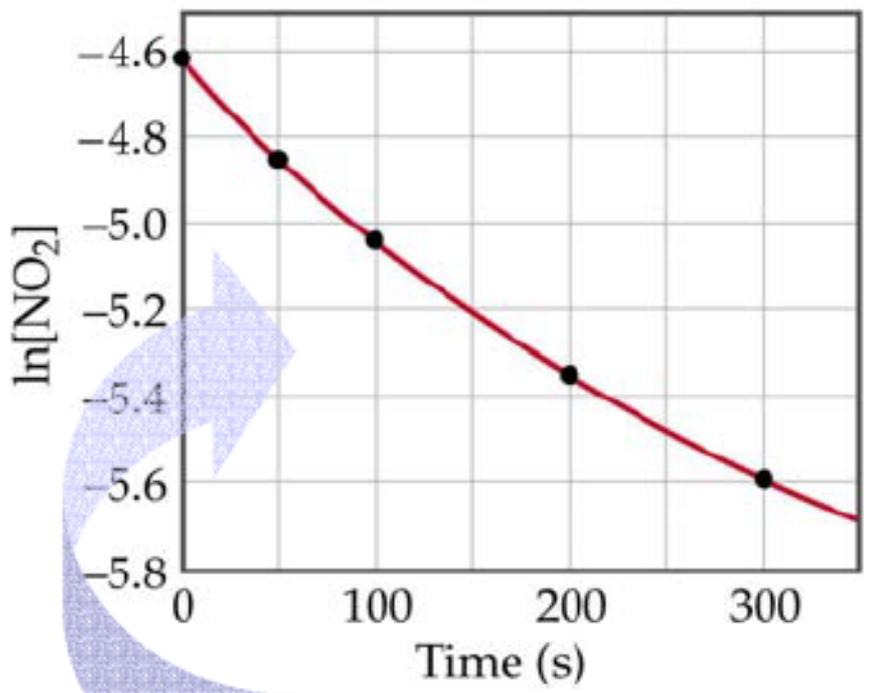
Integrating as before we find:

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

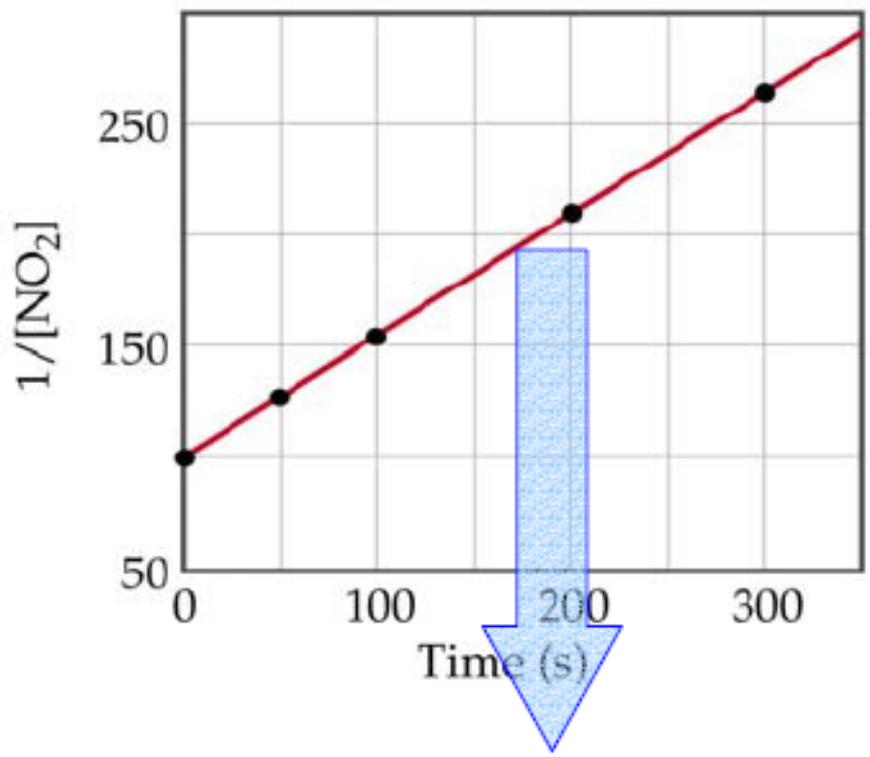
A plot of $1/[A]$ versus t is a straight line with slope k and intercept $1/[A]_0$

For a second order reaction, a plot of $\ln[A]$ vs. t is **not linear**.

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$



Non-linearity indicates that the reaction is not first order.



Slope = k (rate constant)

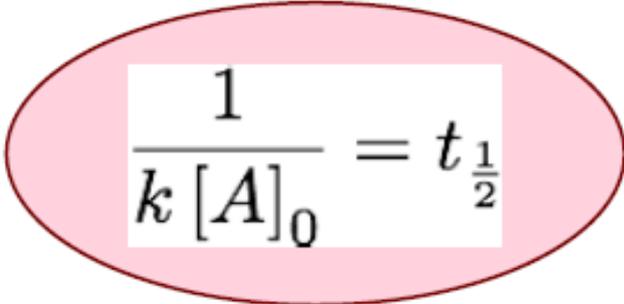
Half-Life - 2nd order

For a **second-order** process, set $[A]_t = 0.5 [A]_0$ in 2nd order equation: $\frac{1}{[A]} = \frac{1}{[A]_0} + 2kt$

$$\frac{1}{0.5 [A]_0} = kt_{\frac{1}{2}} + \frac{1}{[A]_0}$$

$$\frac{2}{[A]_0} = kt_{\frac{1}{2}} + \frac{1}{[A]_0}$$

$$\frac{2}{[A]_0} - \frac{1}{[A]_0} = kt_{\frac{1}{2}}$$


$$\frac{1}{k [A]_0} = t_{\frac{1}{2}}$$

Q\ The saponification of ethyl acetate at 25°C:



The initial concentrations of both ethyl acetate and sodium hydroxide in the mixture were 0.01000 M. The change in concentration, x , of alkali during 20 min was 0.00566 mole/liter; therefore, $(a - x) = 0.01000 - 0.00566 = 0.00434$.

Compute (a) the rate constant and (b) the half-life of the reaction.

a. Using equation (14-23), we obtain

$$k = \frac{1}{0.01 \times 20} \frac{0.00566}{0.00434} = 6.52 \text{ liter mole}^{-1} \text{ min}^{-1}$$

b. The half-life of a second-order reaction is

$$t_{1/2} = \frac{1}{ak} \quad (14-26)$$

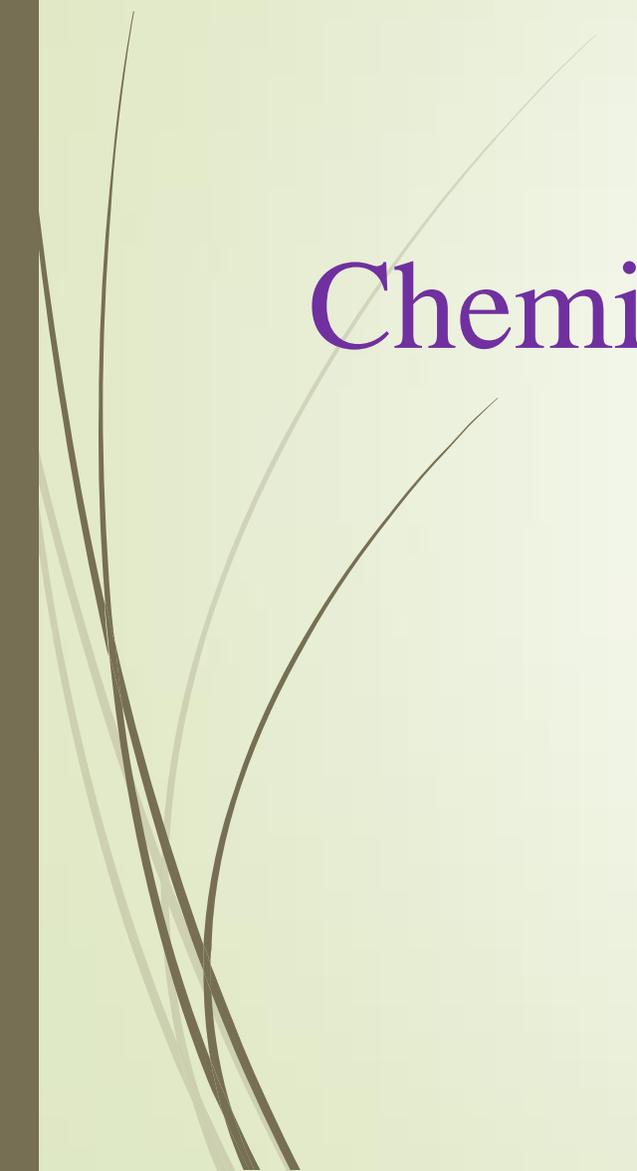
It can be computed for the reaction only when the initial concentrations of the reactants are identical. In the present example,

$$t_{1/2} = \frac{1}{0.01 \times 6.52} = 15.3 \text{ min}$$



Physical pharmacy II

Chemical kinetic and stability / المحاضرة الثانية ➤

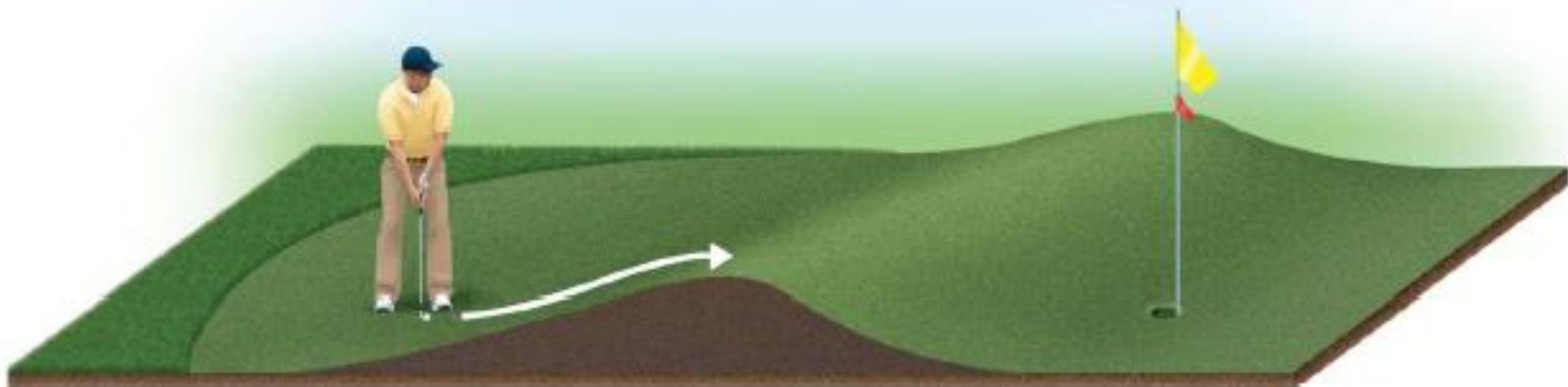
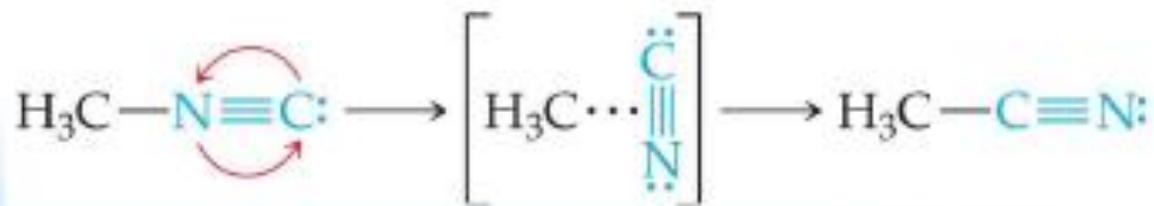


Summary of the Kinetics of Zero-Order, First-Order and Second-Order Reactions

Order	Rate Law	Concentration-Time Equation	Half-Life
0	rate = k	$[A] - [A]_0 = -kt$	$t_{1/2} = \frac{[A]_0}{2k}$
1	rate = $k[A]$	$\ln[A] - \ln[A]_0 = -kt$	$t_{1/2} = \frac{\ln 2}{k}$
2	rate = $k[A]^2$	$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$	$t_{1/2} = \frac{1}{k[A]_0}$

Activation Energy

- ❖ There is a minimum amount of energy required for a reaction: the activation energy, E_a .
- ❖ Just as a ball cannot get over a hill if it does not roll up the hill with enough energy, a reaction cannot occur unless the molecules possess sufficient energy to get over the activation energy barrier.



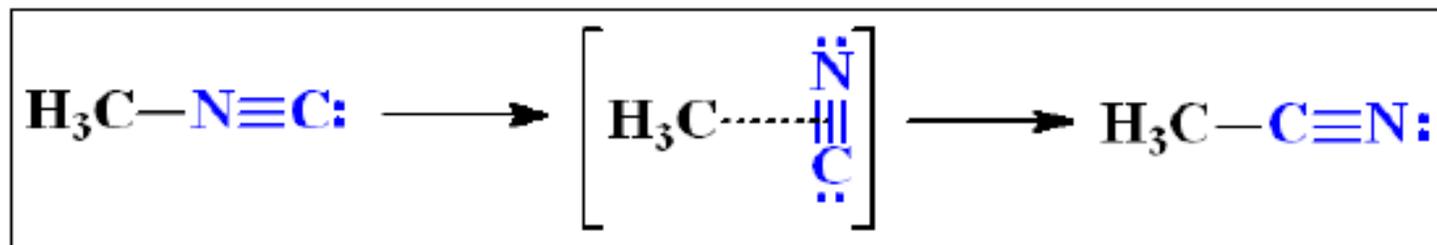
Activation Energy

- ❑ Molecules must possess a minimum amount of energy to react. Why?
 - ✓ In order to form products, bonds must be broken in the reactants.
 - ✓ Bond breakage requires energy.
 - ✓ Molecules moving too slowly, with too little kinetic energy, don't react when they collide.
- ❑ Activation energy, E_a , is the minimum energy required to initiate a chemical reaction.
 - ✓ E_a will vary with the reaction.

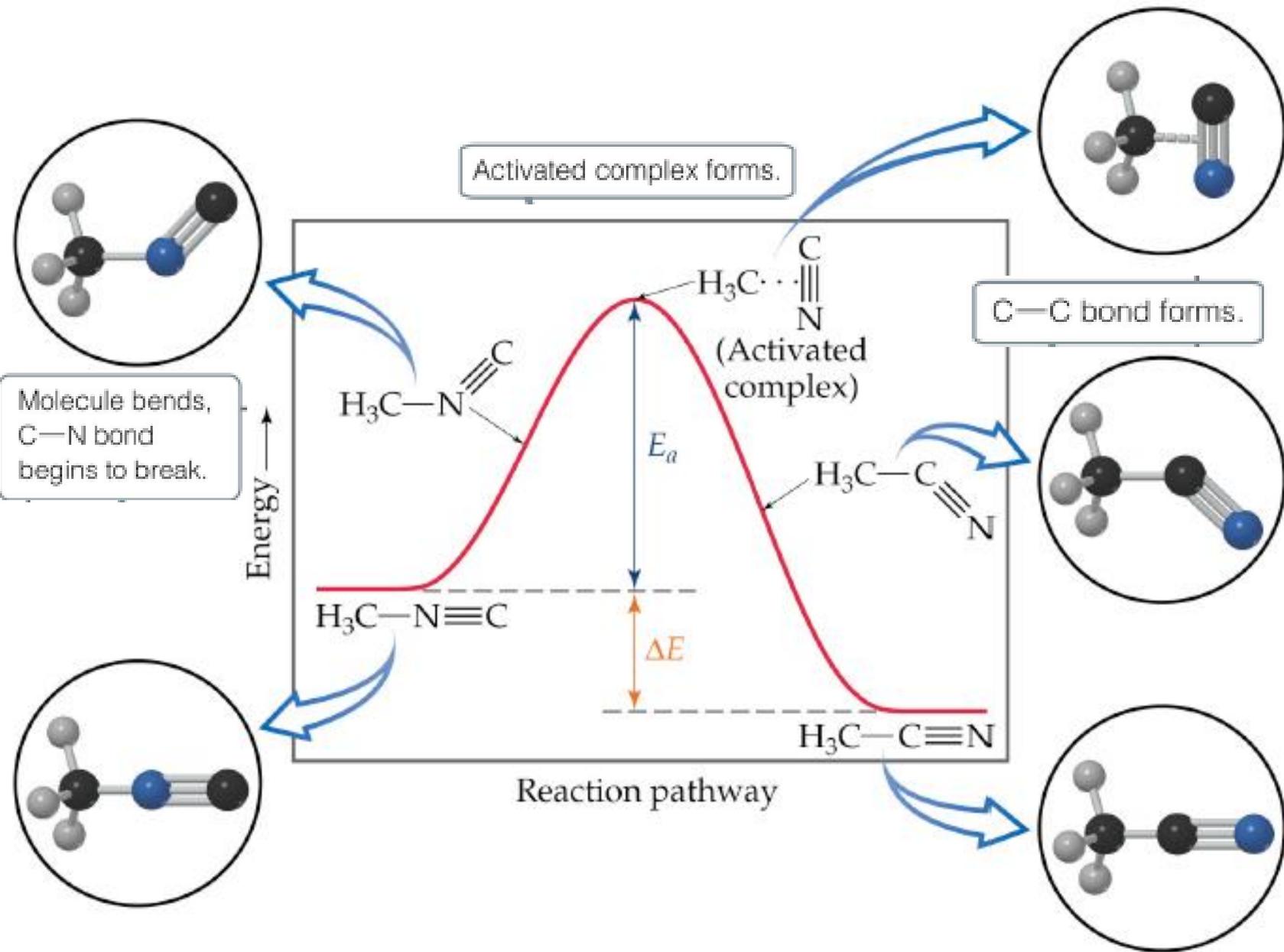
Next we will look at an example of E_a .

Activation Energy

- Consider the rearrangement of methyl isonitrile:

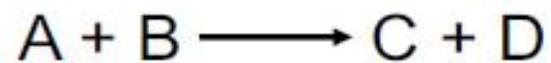


- In $\text{H}_3\text{C}-\text{N}\equiv\text{C}$, the $\text{C}-\text{N}\equiv\text{C}$ bond bends until the $\text{C}\equiv\text{N}$ bond breaks and the $\text{N}\equiv\text{C}$ portion is perpendicular to the H_3C portion. This structure is called the **activated complex** or **transition state**.
 - The energy required for the above twist and break is the **activation energy**, E_a .
 - Once the $\text{C}-\text{N}$ bond is broken, the $\text{N}\equiv\text{C}$ portion can continue to rotate forming a $\text{C}-\text{C}\equiv\text{N}$ bond.
- * Here's what the reaction looks like in terms of a graph of the energies that are involved in the process...

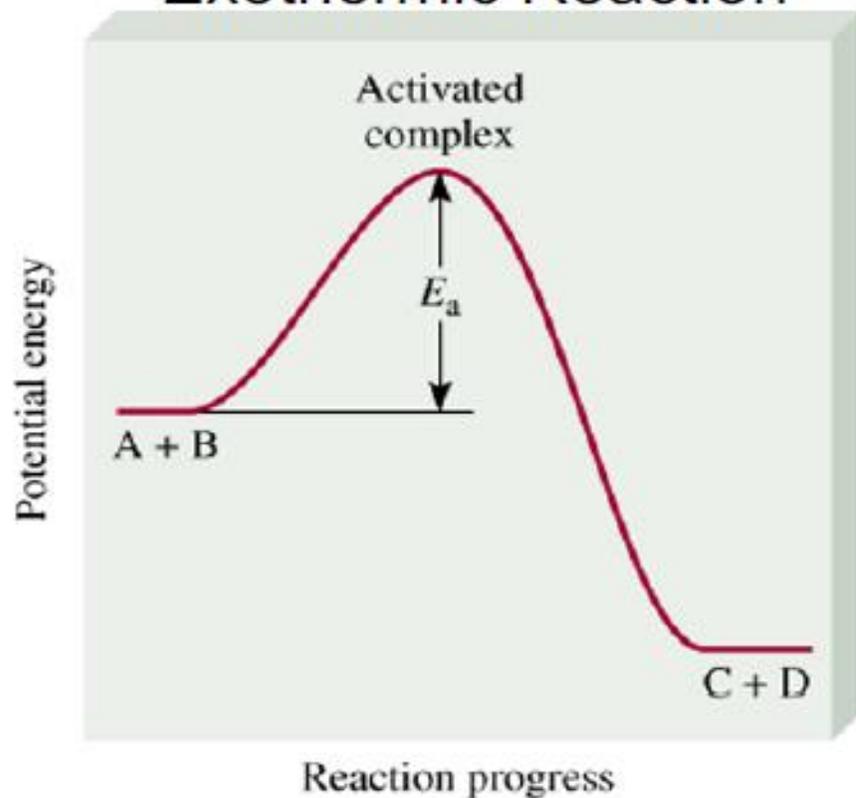


Activation Energy

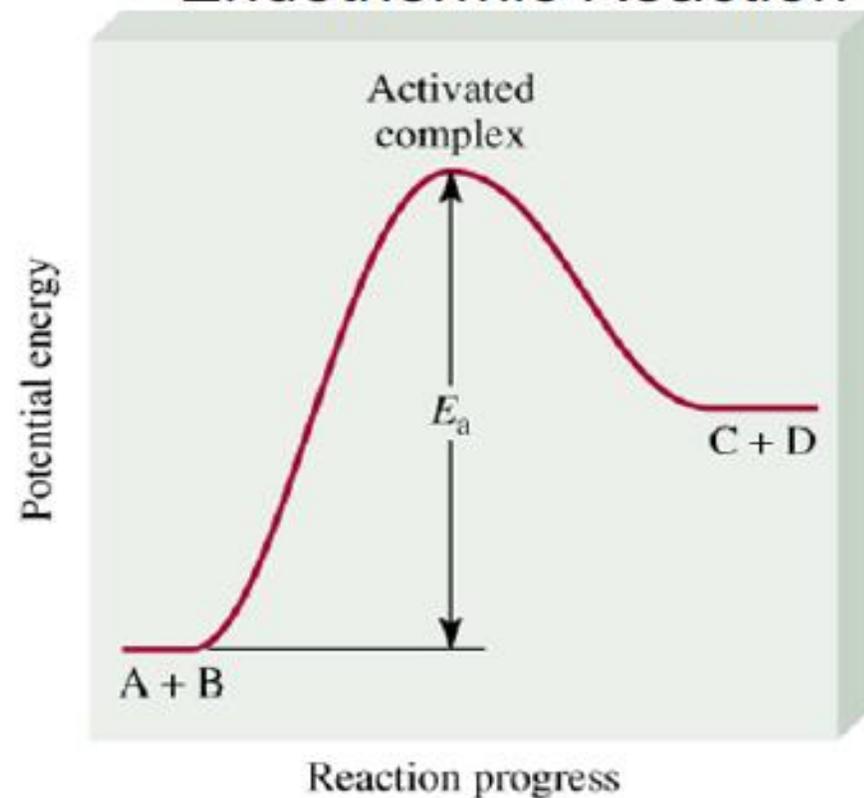
- The change in energy ΔE for the reaction is the difference in energy between CH_3NC (reactant) and CH_3CN (product).
- The **activation energy** E_a is the difference in energy between reactants, CH_3NC , and the transition state.
- The rate depends on E_a . If the “hill” is taller, the reaction rate is slower. If the “hill” is shorter the rate is faster.
- Notice that if a forward reaction is exothermic... ($\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$), then the reverse reaction is endothermic... ($\text{CH}_3\text{CN} \rightarrow \text{CH}_3\text{NC}$).
- The methyl isonitrile molecule needs to gain enough energy to overcome the activation energy barrier.
- From kinetic molecular theory, we know that as temperature increases, the total kinetic energy increases and the number of molecules with energy greater than E_a increases.
- So as long as the temperature is high enough, the reaction can make it “over the hill” and proceed.



Exothermic Reaction

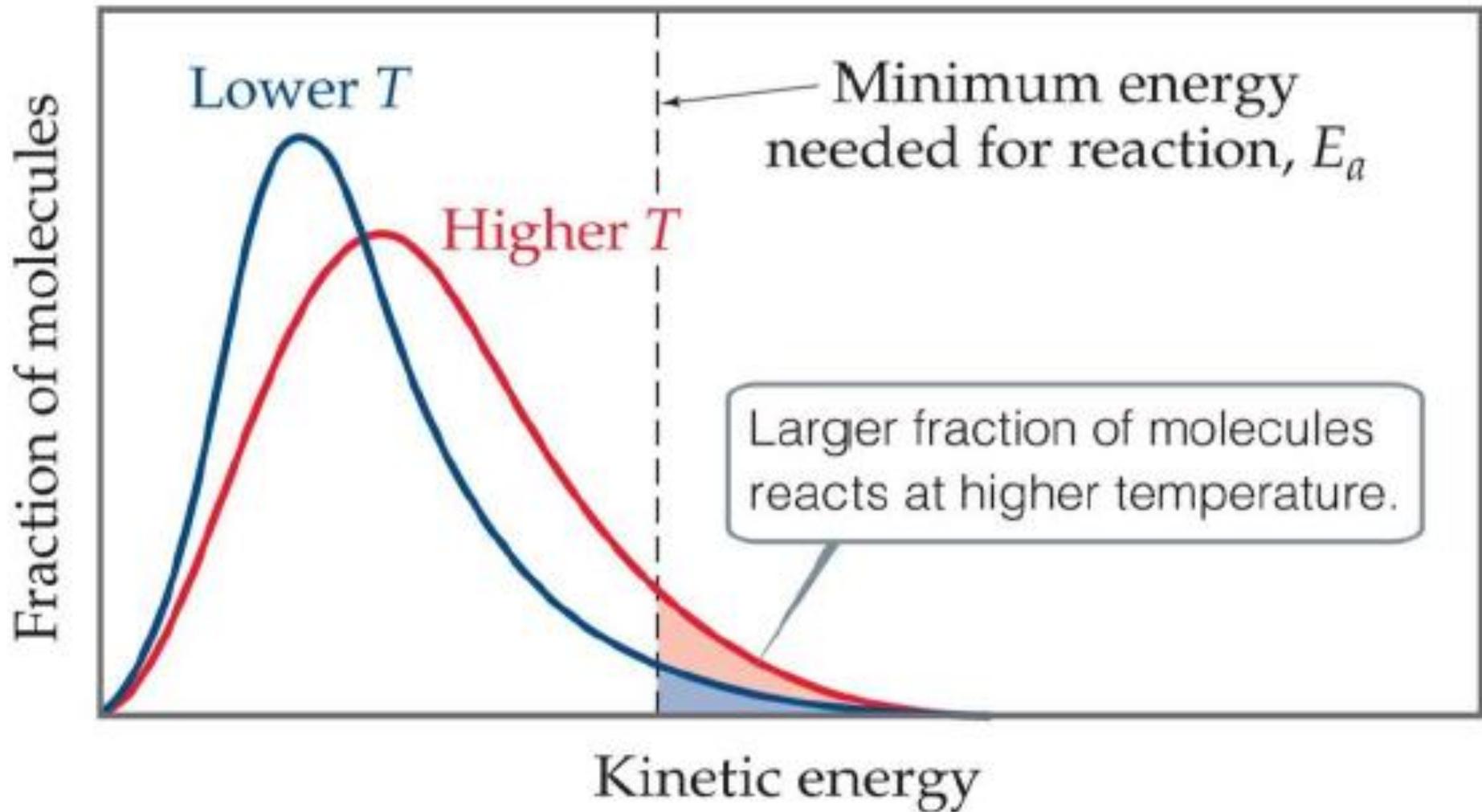


Endothermic Reaction



The **activation energy (E_a)** is the minimum amount of energy required to **initiate** a chemical reaction.

Energy Distributions



The Arrhenius Equation

Arrhenius discovered that most reaction-rate data obeyed an equation based on three factors:

- (1) The number of collisions per unit time.
- (2) The fraction of collisions that occur with the correct orientation.
- (3) The fraction of the colliding molecules that have an energy greater than or equal to *E_a*. From these observations Arrhenius developed the aptly named

Arrhenius equation.

Arrhenius equation

$$k = Ae^{\frac{-E_a}{RT}}$$

k is the rate constant

T is the temperature in K

E_a is the activation energy

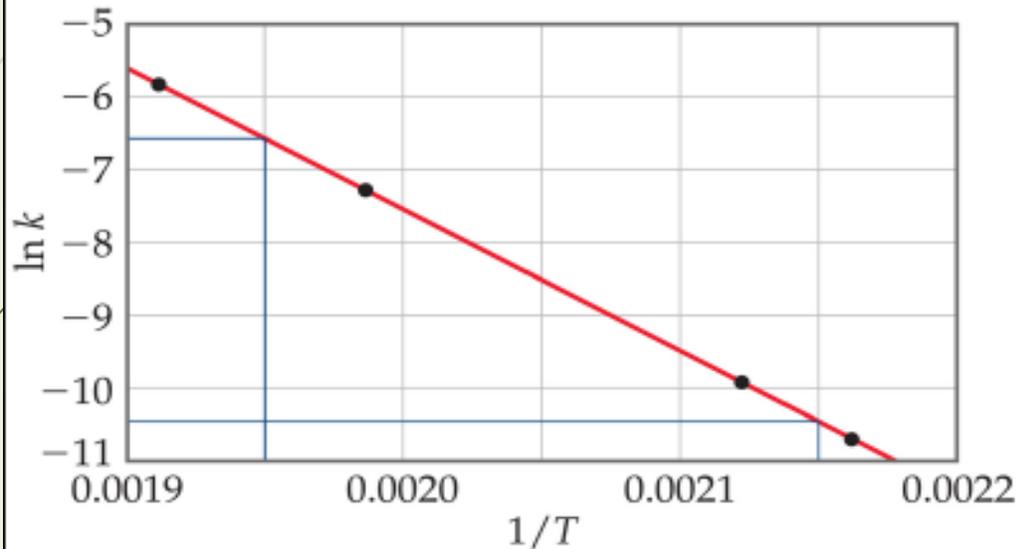
R is the ideal-gas
constant (8.314 J/Kmol)

A is known the *frequency or pre-exponential factor*

In addition to carrying the units of the rate constant, “**A**” relates to the frequency of collisions and the orientation of a favorable collision probability

Both A and E_a are *specific to a given reaction*.

Arrhenius Equation



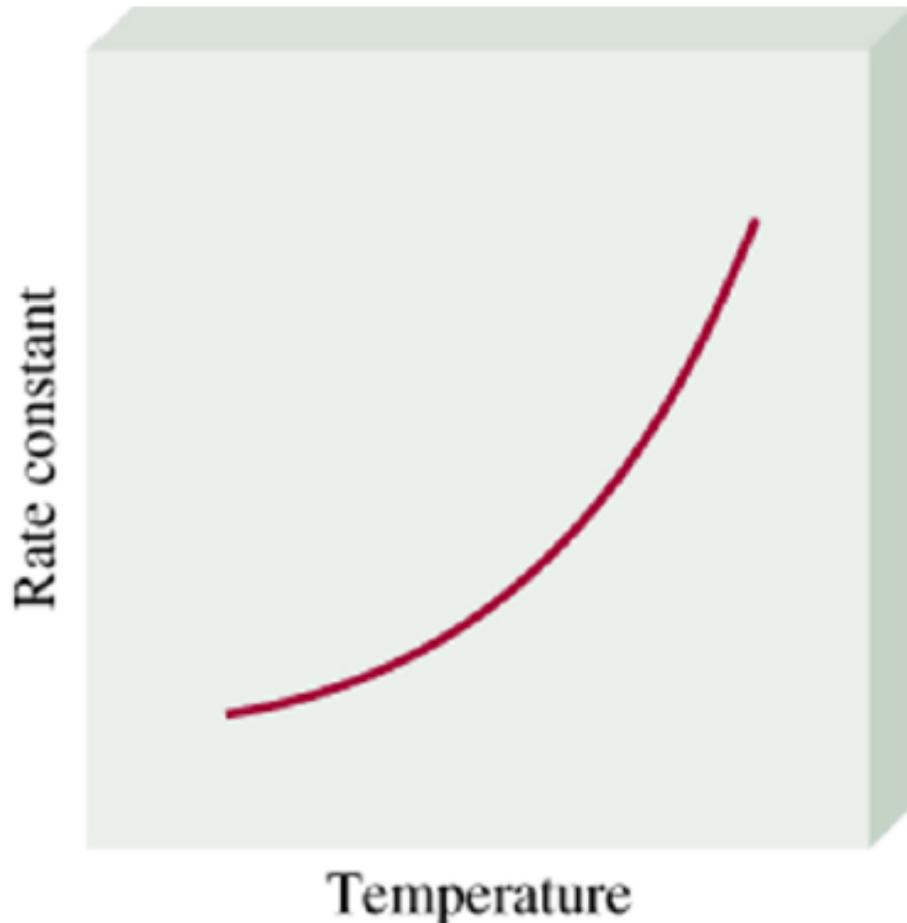
Taking the natural logarithm of both sides, the equation becomes

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

$$y = mx + b$$

When k is determined experimentally at several temperatures, E_a can be calculated from the slope of a plot of $\ln(k)$ vs. $1/T$.

Temperature Dependence of the Rate Constant



$$k = A \cdot \exp(-E_a/RT)$$

(Arrhenius equation)

k is the rate constant

E_a is the activation energy (J/mol)

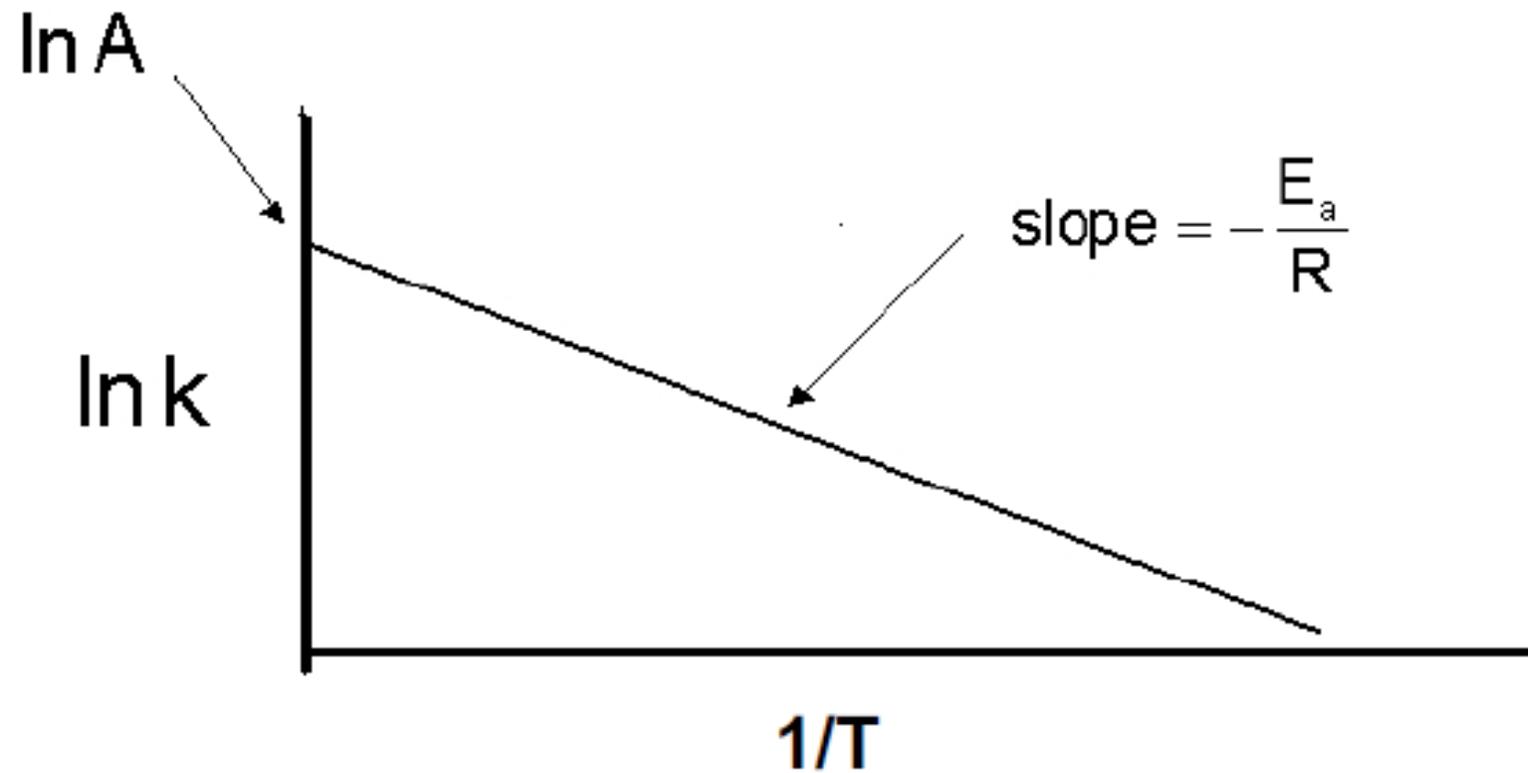
R is the gas constant (8.314 J/K•mol)

T is the Kelvin temperature

A is the frequency factor

$$\ln k = \frac{-E_a}{R} \frac{1}{T} + \ln A$$

Plot of Arrhenius Equation

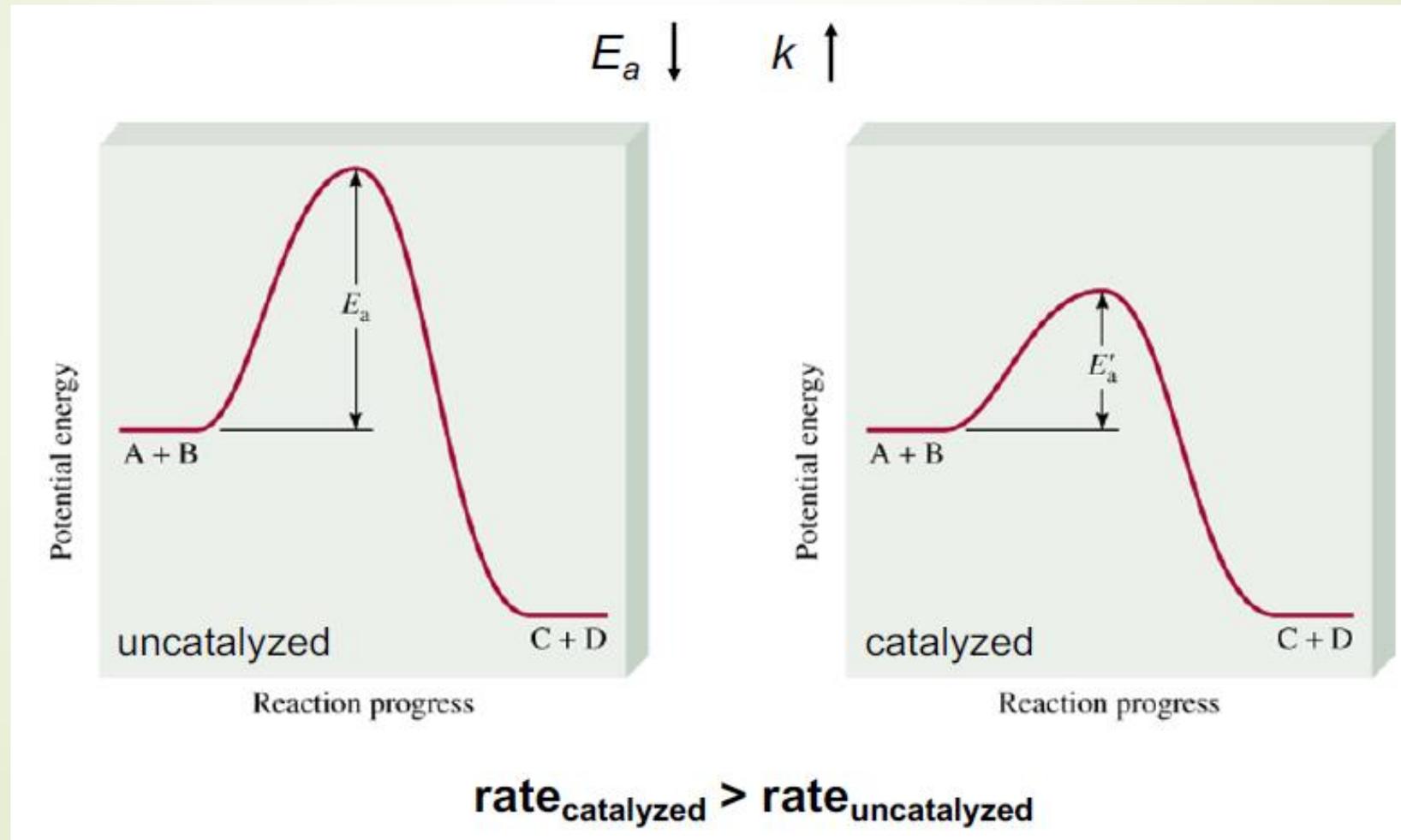


Summary of Kinetics

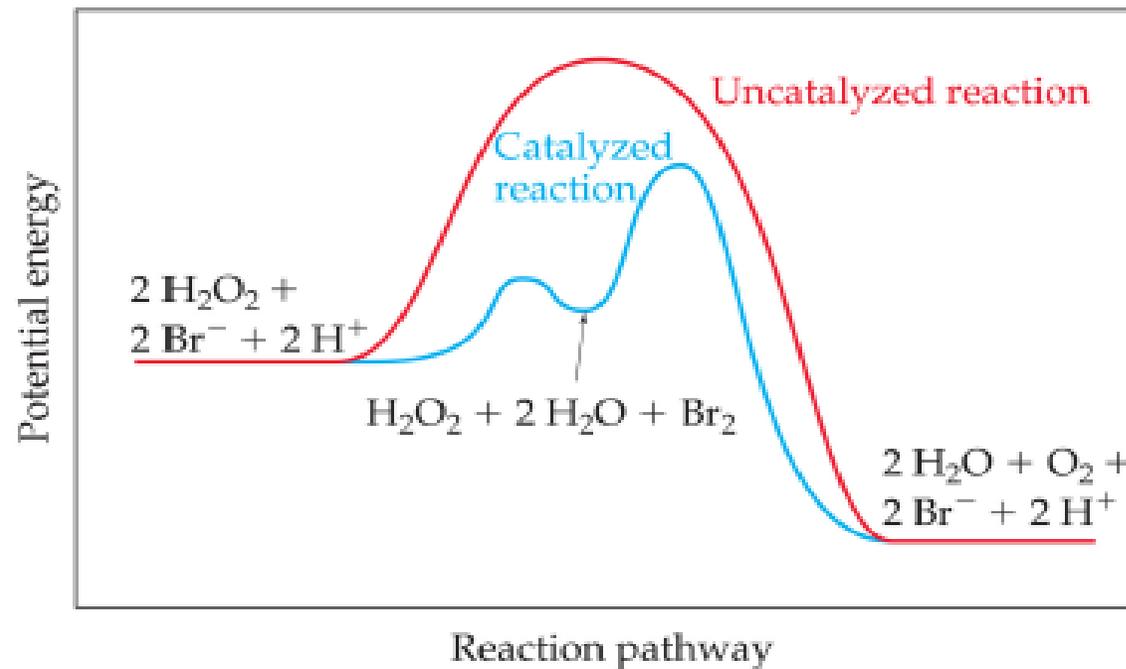
	First order	Second order (1 reactant)	General Second order
Rate Laws	$rate = -k [A]$	$rate = -k [A]^2$	$rate = -k [A] [B]$
Integrate d Rate Laws	$\ln \frac{[A]_t}{[A]_0} = -kt$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	complicated
Half-life	$\frac{0.693}{k} = t_{\frac{1}{2}}$	$\frac{1}{k [A]_0} = t_{\frac{1}{2}}$	complicated
$k(T)$	$k = Ae^{-\frac{E_a}{RT}}$		$\ln(k) = -\frac{E_a}{RT} + \ln A$

Catalyst

A **catalyst** is a substance that increases the rate of a chemical reaction without itself being consumed.

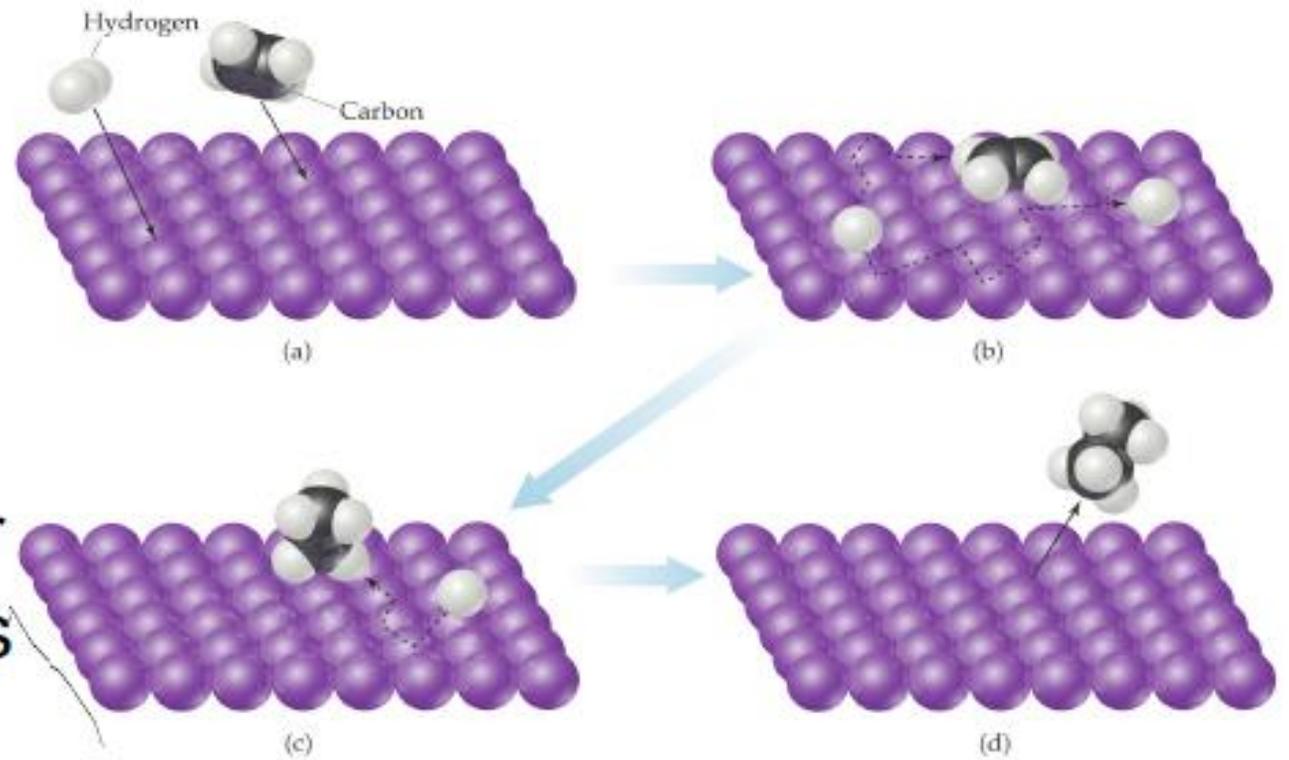


- Catalysts increase the rate of a reaction by **decreasing the activation energy** of the reaction.
- Catalysts **change the mechanism** by which the process occurs.



Catalysts

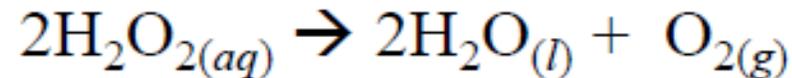
One way a catalyst can speed up a reaction is by holding the reactants together and helping bonds to break.



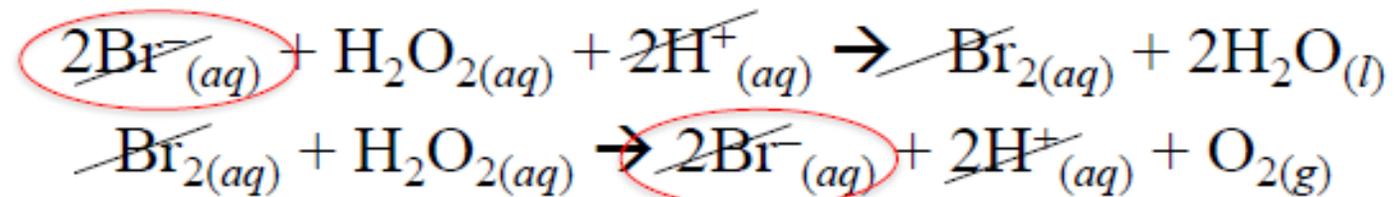
Catalysts

There are two types of catalyst: Heterogeneous – one that is present in a different **phase** as the reacting molecules. Homogeneous – one that is present in the same phase as the reacting molecules.

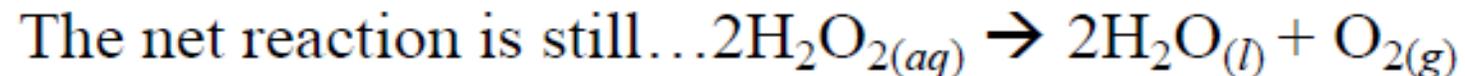
Example: Hydrogen peroxide decomposes very slowly in the absence of a catalyst:



In the presence of bromide ions, the decomposition occurs rapidly in an acidic environment:



Br^- is a homogeneous catalyst because it is regenerated at the end of the reaction.



Catalysts and Reaction Rates

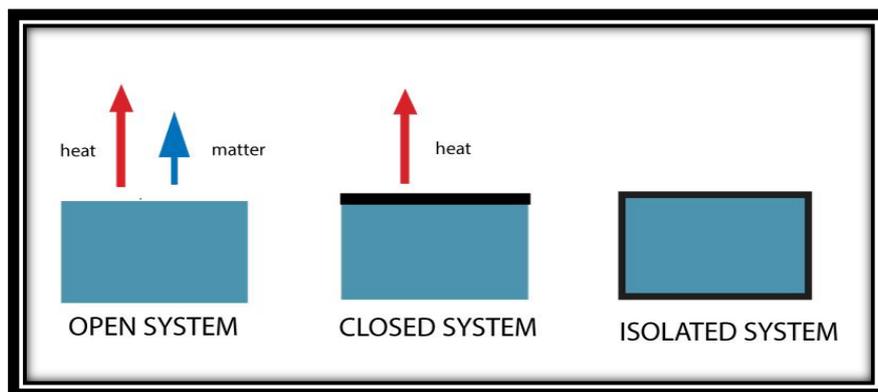
How do catalysts increase reaction rates?

- In general, catalysts operate by lowering the overall activation energy, E_a , for a reaction. (It lowers the “hill”.)
- However, catalysts can operate by increasing the number of effective collisions.
- A catalyst usually provides a completely different mechanism for the reaction.
- In the preceding peroxide decomposition example, in the absence of a catalyst, H_2O_2 decomposes directly to water and oxygen.
- In the presence of Br^- , $\text{Br}_{2(aq)}$ is generated as an **intermediate**.
- When a catalyst adds an intermediate, the activation energies for *both* steps must be lower than the activation energy for the uncatalyzed reaction.

Thermodynamics

Thermodynamics deals with the quantitative relationships of interconversion of the various forms of *energy*, including mechanical, chemical, electric, and radiant energy.

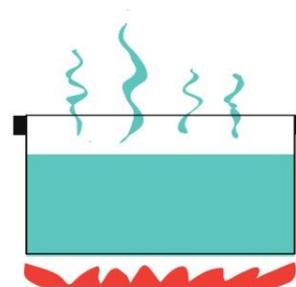
- Types of Thermodynamic Systems



1. Open Systems

Open systems is one that freely allows energy and matter to be transferred in and out of a system.

For example boiling water without a lid Heat escape into the air. At the same time steam (which is matter) also escapes into the air.



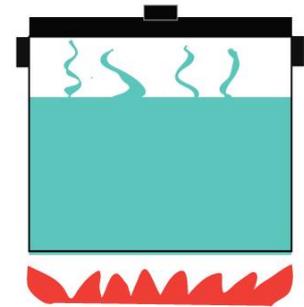
2. Closed Systems

A closed system, on the other hand, does not allow the exchange of matter but allows energy to be transferred.

- It allows heat to be transferred from the stove to the water
- Heat is also transferred to the surroundings

- Steam is not allowed to escape

Example of a closed system – a pressure cooker.



3. Isolated Systems

This system is completely sealed.

- Matter is not allowed to be exchanged with the surroundings.
- Heat cannot transfer to the surroundings.

Example – A thermoflask is an isolated system



The first thermodynamics law

The first law is a statement of the conservation of energy. It states that, although energy can be transformed from one kind into another, it cannot be created or destroyed. Put in another way, the total energy of a system and its immediate surroundings remains constant during any operation. The relativistic picture of the universe expressed by Einstein's equation:

$$E = m \times c^2$$

According to the first law, the effects Q and W in a given system during a transformation from an initial thermodynamic state to a final thermodynamic state are related to an intrinsic property of the system called the internal energy, defined as:

$$\Delta E = E_2 - E_1 = Q + W \quad (1)$$

Where E_2 is the internal energy of the system in its final state and E_1 is the internal energy of the system in its initial state, Q is the heat, and W is the work. The change in internal energy ΔE is related to Q and W transferred between the system and its surroundings. The internal energy is related to the microscopic motion of the atom, ion, or molecules of which the system is composed. Knowledge of its absolute value would tell us something about the microscopic motion of the vibrational, rotational, and translational components. In addition, the absolute value would also provide information about the kinetic and potential energies of their electrons and nuclear element, which in practice is extremely difficult to attain.

By using equation(1) (the first law), one can evaluate the change of internal energy by measuring Q and W during the change of state .However, it is useful to relate the change of internal energy to the measurable properties of the system: P, V and T Any two of these variables must be specified to define the internal energy. For an infinitesimal change in the energy dE , equation (1) is written as

$$dE = dq + dw \quad (2)$$

Where dq is the heat absorbed and dw is the work done during the infinitesimal change of the system. Capital letters Q and W are used for heat and work in equation (1) to signify finite changes in these quantities. The symbol d in equation (2) signifies infinitesimal changes of properties that depend on the "path," also called inexact differentials. Hence, dq and dw are not in these circumstances thermodynamic properties. The infinitesimal change of any state property like dE , also called an exact differential, can be generally written, for

instance, as a function of T and V as in the following equation for a closed system (i.e., constant mass):

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV \quad (3)$$

The partial derivatives of the energy in equation (3) are important properties of the system and show the rate of change in energy with the change in T at constant volume or with the change of V at constant temperature. Therefore, it is useful to find their expression in terms of measurable properties. This can be done by combining equations (2) and (3) into

$$dq + dw = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV \quad (4)$$

This equation will be used later to describe properties of E as a function of T and V .

Isothermal and Adiabatic processes

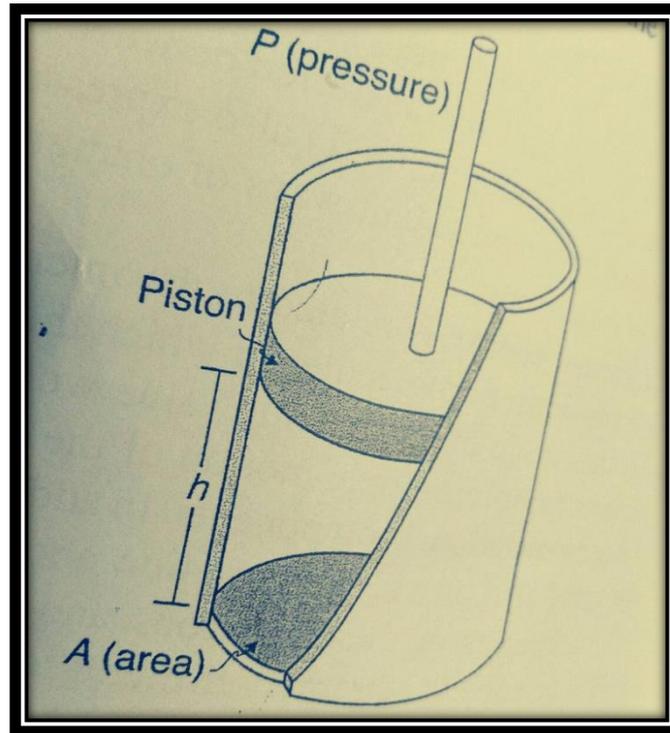
When the temperature is kept constant during a process, the reaction is said to be conducted *isothermally*. An isothermal reaction may be carried out by placing the system in a large constant – temperature bath so that heat is drawn from or returned to it without affecting the temperature significantly. When heat is neither lost nor gained during a process, the reaction is said to occur *adiabatically*. A reaction carried on inside a sealed Dewar flask or "vacuum bottle" is adiabatic because the system is thermally insulated from its surroundings. In thermodynamic terms, it can be said that an adiabatic process is one in which $dq=0$, and the first law under adiabatic conditions reduces to

$$dw = dE \quad (5)$$

According to equation (5), when work is done by the system, the internal energy decreases, and because heat cannot be absorbed in an adiabatic process,

the temperature must fall. Here, the work done becomes a thermodynamic property dependent only on the initial and final states of the system.

Work of Expansion Against a constant pressure



We first discuss the work term. Because of its importance in thermodynamics, initial focus is on the work produced by varying the volume of a system (i.e., expansion work or compression work) against a *constant* opposing external pressure, P_{ex} . Imagine a vapor confined in a hypothetical cylinder fitted with a weightless, frictionless piston of area A , as shown in figure (1). If a constant external pressure P_{ex} is exerted on the piston, the total force is $P_{ex} \times A$ because $P = \text{Force}/\text{Area}$. The vapor in the cylinder is now made to expand by increasing the temperature, and the piston moves a distance h . the work done against the opposing pressure in one single stage is

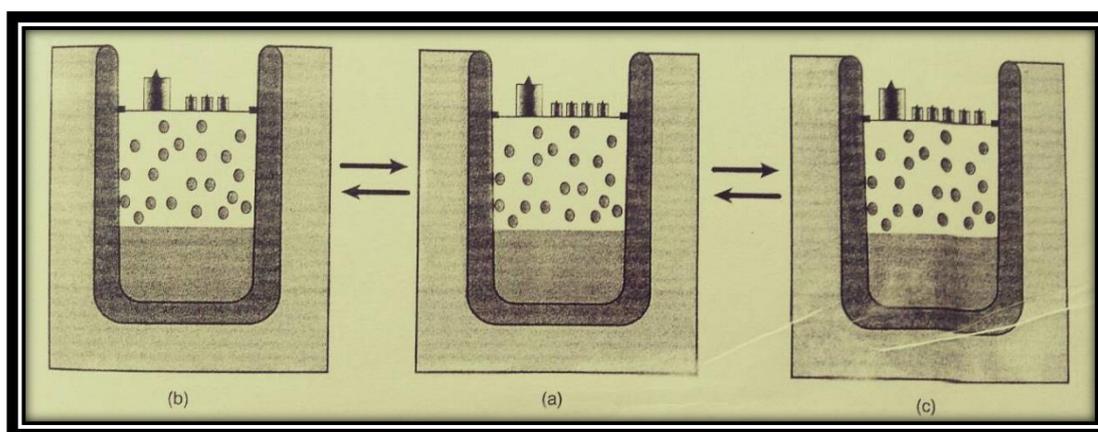
$$W = -P_{ex} \times A \times h \quad (6)$$

Now $A \times h$ is the increase in volume, $\Delta V = V_2 - V_1$, so that, at constant pressure,

$$W = -P_{ex} \Delta V = -P_{ex} (V_2 - V_1) \quad (7)$$

Reversible Processes

Now let us imagine the hypothetical case of water at its boiling point contained in a cylinder fitted with a weightless and frictionless piston fig(a). The apparatus is immersed in a constant- temperature bath maintained at the same temperature as the water in the cylinder. By definition, the vapor pressure of water at its boiling point is equal to the atmospheric pressure, represented in fig(2) by a set of weights equivalent to the atmospheric pressure of 1 atm; therefore, the temperature is $100^\circ C$. The process is an isothermal one, that is, it is carried out at constant temperature. Now, if the external pressure is decreased slightly by removing one of the infinitesimally small weights (b), the volume of the system increases and the vapor pressure fall infinitesimally. Water then a evaporates to maintain the vapor pressure constant at its original value, and heat is extracted from the bath to keep the temperature constant and bring about the vaporization. During this process, a heat exchange between the system and the temperature bath will occur.



On the other hand, if the external pressure is increased slightly by adding an infinitesimally small weight (c) the system is compressed and the vapor

pressure also rises infinitesimally. Some of the water condenses to reestablish the equilibrium vapor pressure, and the liberated heat is absorbed by the constant –temperature bath. If the process could be conducted infinity slowly so that no work is expended in supplying kinetic energy to the piston, and if the piston is considered to be frictionless so that no work is done against the force of friction, all the work is used to expand or compress the vapor. ***Then, because this process is always in a state of virtual thermodynamic equilibrium, being reversed by an infinitesimal change of pressure, it is said to be reversible. If the pressure on the system is increased or decreased rapidly or if the temperature of the bath cannot adjust instantaneously to the change in the system, the system is not in the same thermodynamic state at each moment, and the process is irreversible.***

Maximum Work

The work done by a system in an isothermal expansion process is at a maximum when it is done reversibly. This statement can be shown to be true by the following argument. No work is accomplished if an ideal gas expands freely into a vacuum, where $P=0$, because any work accomplished depends on the external pressure. As the external pressure becomes greater. More work is done by the system, and it rises to a maximum when the external pressure is infinitesimally less than the pressure of the gas, that is, when the process is reversible. Of course, if the external pressure is continually increased, the gas is compressed rather than expanded, and work is done *on* the system rather than by the system in an isothermal reversible process.

Then the maximum work done for a system that is expanded in reversible fashion is

$$W = \int_1^2 dw = - \int_{V_1}^{V_2} PdV \quad (8)$$

Where P_{ex} was replaced by P because the external pressure is only infinitesimally smaller than the pressure of the system. In similar fashion, it can

be deduced that the minimum work in a reversible compression of the system will also lead to equation (8) , because at each stage P_{ex} is only infinitesimally large than P . the right term in equation (8) is depicted in the shaded area in fig(), which represents the maximum expansion work or the minimum compression work in a reversible process.

Example/ A gas expands by 0.5 liter against a constant pressure of 0.5 atm at 25 ° C. what is the work in ergs and in joules done by the system ?

$$W = P\Delta V$$

$$1 atm = 1.013 \times 10^6 \text{ dynes / cm}^2$$

$$W = (0.507 \times 10^6 \text{ dynes / cm}^2) \times 500 \text{ cm}^2$$

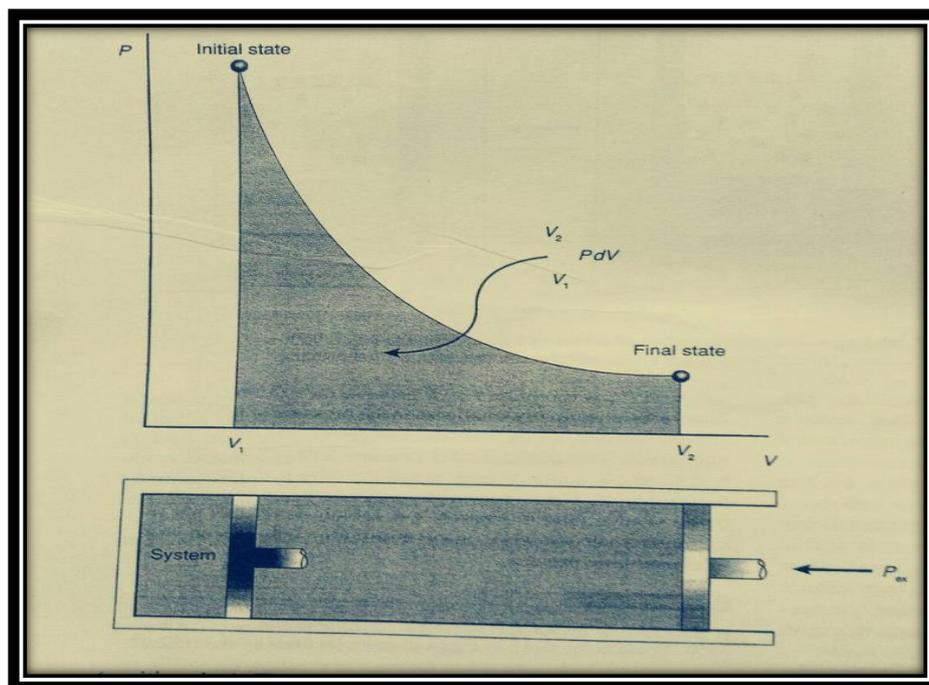
$$= 2.53 \times 10^6 \text{ ergs} = 25.3 \text{ joules}$$

The external pressure in equation(8) can be replaced by the pressure of an ideal gas, $P = nRT / V$, and by ensuring that the temperature of the gas remains constant during the change of state (isothermal process); then one can take nRT outside the integral, the equation

$$W_{\max} = \int dW_{\max} = -nRT \int_{V_1}^{V_2} \frac{dV}{V} \quad (9)$$

$$W_{\max} = -nRT \ln \frac{V_2}{V_1} \quad (10)$$

Note that in expansion, $V_2 > V_1$, and $\ln\left(\frac{V_2}{V_1}\right)$ is a positive quantity; therefore, the work is done by the system, so that its energy decreases (negative sign). When the opposite is true, $V_2 < V_1$, and $\ln\left(\frac{V_2}{V_1}\right)$ is negative due to gas compression, work is done by the system, so that its energy increases (positive sign). The process itself determines the sign of W and ΔE . Equation (10) gives the



maximum work done in the expansion as well as the heat absorbed, because $Q = \Delta E - W$, and, as will be shown later, ΔE is equal to zero for an ideal gas in an isothermal process. The maximum work in an isothermal reversible expansion may also be expressed in terms of pressure because, from Boyle's law, $V_2 / V_1 = P_1 / P_2$ at a constant temperature. Therefore, equation(10) can be written as

$$W_{\max} = -nRT \ln \frac{P_1}{P_2} \quad (11)$$

Q / Calculate the final volume of one mole of an ideal gas initially at 0°C and 1 atm pressure. If it absorbs 2000 Cal of heat during reversible isothermal expansion. Where $V_1 = 22.4 \text{ dm}^3$, Where universal gas constant = 8.3143 J/K mole

Solv./ The gas is in the standard temperature and pressure condition i.e. at S.T.P

Hence $V_1 = 22.4 \text{ dm}^3$ and V_2 have to be calculated.

As given expansion is isothermal and reversible therefore, $\Delta E = 0$

We know that $\Delta E = Q + W$

But $\Delta E = 0$

Hence $Q = -W = 2000 \text{ cal}$

But $1 \text{ cal} = 4.184 \text{ J}$

$$Q = 2000 \times 4.184 \text{ J} = 8368 \text{ J}$$

As work done in reversible isothermal expansion is given by:

$$W = -nRT \ln (V_2 / V_1)$$

Therefore $nRT \ln (V_2 / V_1) = -W = 8368 \text{ J}$

$$\ln V_2 / 22.4 = 3.6866$$

$$V_2 / 22.4 = e^{3.68667} \rightarrow V_2 = 10.02 \times 22.4 \rightarrow V_2 = 242.50 \text{ dm}^3$$

Hence the final volume of one mole of an ideal gas initially at 0°C and 1 atm pressure is equal to 242.50 dm^3 .

Q/ What is the maximum work done in the isothermal reversible expansion of 1 mole of an ideal gas from 1 to 1.5 liters at 25°C ?

SOL//

$$W = -(1 \text{ mole})(8.3143 \text{ joules/K mole})(298.15\text{K}) \ln(1.5/1.0)$$

$$W = -1005.3 \text{ joules}$$

Changes of state at constant volume

If the volume of the system is kept constant during a change of state, $dV=0$, the first law can be expressed as

$$dE = dQ_v \quad (12)$$

where the subscript v indicates that volume is constant. Similarly, under these conditions the combined equation (4) is reduced to

$$dq_v = \left(\frac{\partial E}{\partial T} \right)_v dT \quad (13)$$

This equation relates the heat transferred during the process at constant volume, dQ_v , with the change in temperature, dT . The ratio between these quantities defines the molar heat capacity at constant volume

$$\bar{C}_v \equiv \frac{dq_v}{dT} \left(\frac{\partial E}{\partial T} \right)_v \quad (14)$$

Ideal Gases and the First Law

An ideal gas has no internal pressure, and hence no work needs be performed to separate the molecules from their cohesive force when the gas expands. Therefore, $dw=0$, and the first law becomes

$$dE = dq \quad (15)$$

the process is done isothermally, there is no temperature change in the surroundings, $dT=0$, and $q=0$. equation (4) is reduced to

$$dE = \left(\frac{\partial E}{\partial V} \right)_v dV = 0 \quad (16)$$

In this equation, $dV \neq 0$ because has been expansion,

$$\therefore \left(\frac{\partial E}{\partial V} \right)_v = 0 \quad (17)$$

Equation (17) suggests that the internal energy of a n ideal is a function of the *temperature* only.

Changes of State at Constant Pressure

When the work of expansion is done at constant pressure,

$W = -P\Delta V = -P(V_2 - V_1)$ by equation (7), the first law can be written as

$$\Delta E = Q_p - P(V_2 - V_1) \quad (18)$$

Where Q_p is the heat absorbed at constant pressure.

$$\begin{aligned} Q_p &= E_2 - E_1 + P(V_2 - V_1) \\ &= (E_2 + PV_2) - (E_1 + PV_1) \end{aligned} \quad (19)$$

Where $E + PV$ is called *enthalpy*, H . By substituting H in equation (19)

$$Q_p = H_2 - H_1 = \Delta H \quad (20)$$

And writing equation (18) as

$$\Delta H = \Delta E + P\Delta V \quad (21)$$

For an infinitesimal change, one can write as

$$dq_p = dH \quad (22)$$

If T and P are chosen as variables, dH can be written as

$$dH = \left(\frac{\partial H}{\partial T} \right)_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP \quad (23)$$

When the pressure is held constant, as, for example, a reaction proceeds in an open container in the laboratory at essentially constant atmospheric pressure, equation (23) becomes

$$dH = \left(\frac{\partial H}{\partial T} \right)_P dT \quad (24)$$

Because $dq_p = dH$ at constant pressure according to equation (22), **the molar heat capacity C_p at constant pressure** is define as

$$\bar{C}_P = \frac{dq_P}{dT} = \left(\frac{\partial H}{\partial T} \right)_P \quad (25)$$

And for a change in enthalpy between products and reactants,

$\Delta H = H_{products} - H_{reactants}$, equation (25) written as

$$\left[\frac{\partial(\Delta H)}{\partial T} \right]_P = \Delta \bar{C}_P \quad (26)$$

Where $\Delta \bar{C}_P = (C_P)_{products} - (C_P)_{reactants}$. Equation (26) is known as the *Kirchhoff equation*.

Table: Modified First-Law Equations for Processes Occurring Under Various Conditions

Specific condition		Process	Common means for establishing the condition	Modification for the first law $dE=dq + dw$ under the stated condition
Constant heat	$dq = 0$	Adiabatic	Insulated vessel	$dE = dw$
Reversible process at constant temperature	$dT = 0$	isothermal	Constant temp bath	$dW = W_{max}$
Constant volume	$dV = 0$	Isometric (isochoric)	Closed vessel of constant volume	$dW = -pdV = 0$ $dE = Q_v$
Constant pressure	$dP = 0$	isobaric	Reaction occurring in an open container at constant atmospheric pressure	$dH = Q_p$ $dE = dH - PdV$

Thermochemistry

Thermochemistry deals with the heat changes accompanying isothermal chemical reactions at constant pressure or volume, from which values of ΔH Or ΔE can be obtained.

Most chemical and physical processes of interest are carried out at constant pressure.

- A negative ΔH and Q_p means that heat is released (*exothermic*).
- A positive value of ΔH and Q_p means that heat is absorbed (*endothermic*).

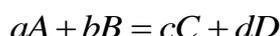
It is also possible that a reaction takes place in a closed container; in such (*i.e.* $\Delta E = Q_v$).

Heat of Formation

The formation enthalpy of reaction (ΔH_f°) is the enthalpy of reaction carried out at formation condition of (25°C) and 1atm pressure.

Unit: Cal/mole

For any reaction represented by the chemical equation



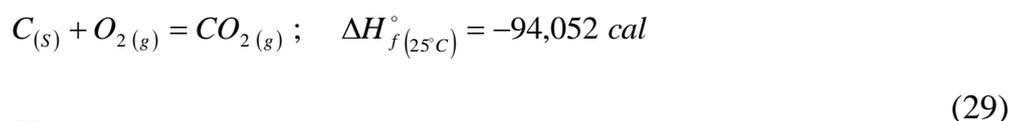
The enthalpy change can be written as

$$\Delta H = \sum \bar{H}_{\text{Products}} - \sum \bar{H}_{\text{Reactants}} \quad (27)$$

$$\Delta H = c\bar{H}_C + d\bar{H}_D + a\bar{H}_A + b\bar{H}_B \quad (28)$$

Where \bar{H} = enthalpy per mole (called the molar enthalpy), and a,b,c and d are stoichiometric coefficients.

One can, for instance, choose the reaction of formation of carbon dioxide from its elements,



Here

$$\Delta H_{f(25^\circ\text{C})}^\circ = \bar{H}(CO_2, g, 1 \text{ atm}) - \bar{H}(C, s, 1 \text{ atm}) - \bar{H}(O_2, g, 1 \text{ atm})$$

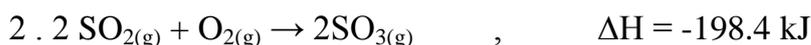
The subscripts represent the physical states,(s) standing for solid and (g) for gas.

$\Delta H_{f(25^{\circ}C)}^{\circ}$ = the standard heat of formation of gaseous carbon dioxide

Hess` s law and Heat of Combustion

It is not possible to directly measure the heats of formation of every known compound in equation (29). Incomplete or side reactions often complicate such determinations. Hess showed that because ΔH depends only on the initial and final states of system. Principle is known as Hess`s law of constant heat summation and is used to obtain heats of reaction that are not easily measured directly.

Ex.1/ Find ΔH for the reaction : $S_{(s)} + 3/2 O_{2(g)} \rightarrow SO_{3(g)}$, $\Delta H = ?$ from the following eqns.



Soln.

- eq.1 stay as it is because S(s) present in left for unknown eq.

- eq.2 multiply by 1/2 to get the same no. of mole in unknown eq.



Sum-----

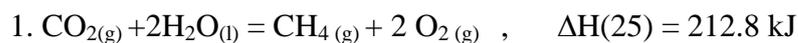


Ex.2/ Calculate ΔH for the reaction : $C_{(s)} + 2 H_{2(g)} = CH_{4(g)}$, $\Delta H(25) = ?$ from eqs.



Sol/

- eq.1 reverse , eq.2 multiple by 2 ,and eq.3 stay as it is.



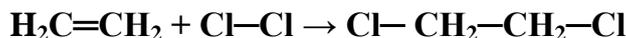
Sum.....



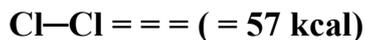
Heat of Reaction from Bond Energies.

In a chemical reaction , bonds may be broken and new bond may be formed during the reaction process.

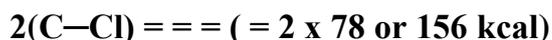
Ex.3 : Calculate ΔH for the following reaction:



from **C=C bond is broken(requiring 130 kcal).**



And C—C bond is formed (liberating 80 kcal)



$$\Delta H = \Sigma \Delta H_{\text{bond broken}} - \Sigma \Delta H_{\text{bond form}}$$

$$= [130 + 57] - [80 + 156] = -49 \text{ kcal.}$$

EX.4/A steam engine operates between the temperature 373 and 298 K.

- what is the theoretical efficiency of the engine ?
- If the engine is supplied with 1000 cal of Heat Q_{hot} ?
- What is the theoretical work in ergs

Sol/

a. Efficiency = $W/Q_{hot} = T_{hot} - T_{cold}/T_{hot} = 373-298/373=0.20$ or 20% .

b. $W=1000 \times 0.2 =200$ cal.

c. $2000 \times 4.184 \times 10^7$ ergs/cal= 8.36×10^9 ergs

The Second law of thermodynamics:

In second law of thermodynamic the entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process.

The Efficiency of a Heat Engine

An important consideration is that of the possibility of converting heat into work. The spontaneous character of natural processes and the limitations on the conversion of heat into work constitute the second law of thermodynamics. Falling water can be made to do work owing to the difference in the potential energy at two different levels, and electric work can be done because of the difference in electric potential. A heat engine (such as a steam engine) likewise can do useful work by using two heat reservoirs, a " **source**" and "**sink**" at two different temperatures. Only part of the heat at the source is converted into work, with the remainder being returned to the sink (which, in practical operations, is often the surroundings) at the lower temperature. The fraction of the heat, Q , at the source converted into work , W , is known as the efficiency of the engine:

$$Efficiency = \frac{W}{Q} \quad (30)$$

Imagine a hypothetical steam engine operating reversibly between an upper temperature T_{hot} and a lower temperature T_{cold} . It absorbs heat Q_{hot} from the hot boiler or source , and by means of the working substance, steam, it converts quantity W into work and returns heat Q_{cold} to cold reservoir or sink .

Carnot, proved that the efficiency of such an engine, operating reversibly at every stage and returning to its initial stage (cyclic process), could be given by the expression:

$$\frac{W}{Q_{hot}} = \frac{Q_{hot} - Q_{cold}}{Q_{hot}} \quad (31)$$

Lord Kelvin used the ratios of the two heat quantities Q_{hot} and Q_{cold} of the Carnot cycle to establish the kelvin temperature scale:

$$\frac{Q_{hot}}{Q_{cold}} = \frac{T_{hot}}{T_{cold}} \quad (32)$$

By combining equations (30) through (32), we can describe the efficiency by:

$$efficiency = \frac{Q_{hot} - Q_{cold}}{Q_{hot}} = \frac{T_{hot} - T_{cold}}{T_{hot}} \quad (33)$$

When T_{cold} reaches absolute zero on kelvin scale in reversible process ,that

$$\lim_{T_{cold} \rightarrow 0} \frac{W}{Q} = 1 \quad (34)$$

Entropy (S)

Entropy is a measure of randomness or disorder of a system. It consider as a quantitative measure of increasing the probability of spontaneous process. If the change from initial to final results in an increase in randomness.

$$\Delta S = S_f - S_i$$

Carnot recognized that when Q_{rev} , a path-dependent property, is divided by T , a **new** path-independent property is generated, called Entropy . It is defined as

$$\Delta S = \frac{Q_{rev.}}{T} \quad (1)$$

We note that if Q_{hot} is the heat absorbed by an engine at T_{hot} , then $-Q_{\text{hot}}$ must be the heat lost by the surroundings (the hot reservoir) at T_{hot} , and the entropy of the surroundings is

$$\Delta S_{\text{surr}} = -\frac{Q_{\text{hot}}}{T_{\text{hot}}} \quad (2)$$

Hence, for any system and its surroundings or universe,

$$\textit{in reversible process} \quad \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0 \quad (3)$$

Therefore there are two cases in which $\Delta S = 0$,

- (a) a system in a reversible cyclic process and
- (b) a system and its surroundings undergoing any reversible process.

In irreversible process, the entropy change of the total system or universe (a system and its surroundings) is always positive because ΔS_{sys} in irreversible process. In mathematical symbols, we write

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0 \quad (4)$$

EX.5/ What is entropy change for vaporization of 1 mole of water in equilibrium with its vapor at 25C, $\Delta H_v = 10500$ cal/mole ?

Sol/

At constant pressure, $Q_P = \Delta H_v$

$$\Delta S = \Delta H_v / T = 10500 / 298 = 35.2 \text{ cal/mole.deg.}$$

Entropy and disorder

Thermodynamic systems describe by macroscopic properties such as T , P , or composition can also be described in terms of microscopic quantities such as molecular random motions.

Disorder can be seen as the number of ways the inside of a system can be arranged so that from the outside the system looks the same.

$$S = k \ln O$$

Where k is the Boltzmann constant.

O is the number of microscopic states or configuration. The probability P for

$$P = (O_1/O_2) = (V_1/V_2)^N$$

$$\Delta S = S_2 - S_1 = k \ln(O_1/O_2) = k N_A \ln (V_1/V_2),$$

N =no. of particles.

The Third law of thermodynamics

The entropy of pure crystalline substance is Zero. A pure perfect crystal has only one possible configuration and according to eq. [$S = k \ln(1) = 0$] its entropy Zero.

The third law.

$$S_T = \sum \frac{dq_{rev,i}}{T_i} + S_0 \quad (1)$$

Where, S_0 is the molar entropy at absolute zero and ,

S_T is the molar entropy at any temperature.

Entropy changes during a phase change as the temperature rises from $0K$ to T . The following equation shows S_T for a substance that undergoes two phase changes ,melting (m) and vaporization (v).

from eq. $\bar{C}_p = \frac{dq_p}{dT} \Rightarrow dq = C_p dT$ (3)

In substitute (3) in eq.(1) we obtain

$$S_T = \int_0^{T_m} \frac{C_p dT}{T} + \frac{\Delta H_m}{T_m} + \int_{T_m}^{T_v} \frac{C_p dT}{T} + \frac{\Delta H_v}{T_v} + \int_{T_v}^T \frac{C_p dT}{T} \quad (2)$$

Where , $S_0 = 0$ has been omitted .

Free energy functions and applications

Consider an isolated system composed of a closed container (i.e., the system) in equilibrium with a temperature bath (i.e., the surrounding) then according to equations:

$$\Delta S_{isolatedsystem} = \Delta S_{syst} + \Delta S_{surr} \geq 0 \quad (1)$$

Equilibrium is a condition where the transfer of heat occurs reversibly: therefore, at constant temperature, $-\Delta S_{syst} = \Delta S_{surr}$ and

$$\Delta S = -\frac{Q_{rev}}{T} \quad (2)$$

Now , renaming $-\Delta S_{syst} = \Delta S_{surr}$ and $Q_{rev} = Q$, we write equation as

$$\Delta S - \frac{Q}{T} \geq 0 \quad (3)$$

which can also be written in the following way:

$$Q - T \Delta S \leq 0 \quad (\text{at } T=\text{const.}) \quad (4)$$

For a process at constant volume, $Q_v = \Delta E$, so eq.(4) become

$$\Delta E - T \Delta S \leq 0 \quad (\text{at } T=\text{const, } V=\text{const}) \quad (5)$$

In the case of a process at constant pressure, $Q_p = \Delta H$, and

$$\Delta H - T \Delta S \leq 0 \quad (\text{at } T=\text{const, } P=\text{const}) \quad (6)$$

- **The terms on the left of eq.5 and eq.6 define as:**

Helmholtz free energy or work function A ,

$$A = E - T S \quad (7)$$

And

Gibbs free energy, G

$$G = H - T S \quad (8)$$

Thus equilibrium and spontaneity conditions are reduced to only.

$$\Delta A = 0 \quad (\text{at } T= \text{constant. , } V= \text{constant}) \quad (9)$$

$$\Delta G = 0 \quad (\text{at } T=\text{constant , } P=\text{constant}) \quad (10)$$

Maximum Net Work.

$$q = \Delta E - W \dots\dots\dots(1) \quad \text{first law.}$$

$$\Delta E - W - T \Delta S = 0 \dots\dots\dots(2)$$

The system does maximum work (W_{\max}) when it is working under Reversible W conditions.

$$\Delta A - W_{\max} = 0 \quad \text{or} \quad \Delta A = W_{\max} \quad (3)$$

$$\Delta G - W_a = 0 \quad \text{or} \quad \Delta G = W_a \quad (4)$$

The main eq. for Gibbs eq.

$$\Delta G = \Delta H - T \Delta S \quad (5)$$

$$\Delta G = nRT \ln \frac{P_2}{P_1} \quad (6)$$

$$\Delta G = nRT \ln \frac{a_2}{a_1} \quad (7) \quad a_1 \text{ and } a_2 \text{ activities of solute.}$$