Biophysical chemistry

Part A
Chapter: 3
Chemical kinetics
Lecture - 6

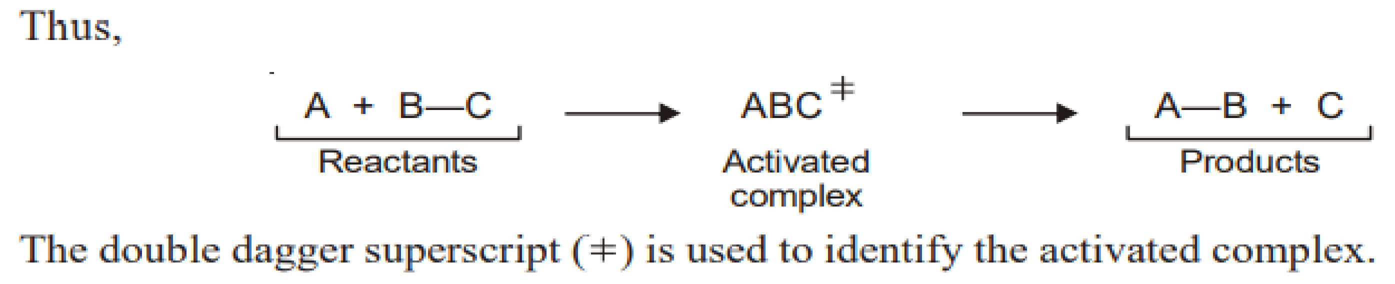
Fahmida Akter Lia
Department of Biochemistry
National Institute of Science and Technology(NIST)

ACTIVATED COMPLEX THEORY

activated complex theory or The transition state was developed by Henry Erying

Also called the absolute rate theory because with its help it is possible to get the absolute value of the rate constant.

The transition state theory assume the reactant molecules form a transition state or activated complex which decomposes to give the products



Thus,

$$\underbrace{A + B{-}C}_{\text{Reactants}} \longrightarrow \underset{\substack{\text{Activated}\\ \text{complex}}}{ABC^{\ddagger}} \longrightarrow \underbrace{A{-}B + C}_{\text{Products}}$$

The double dagger superscript (‡) is used to identify the activated complex.

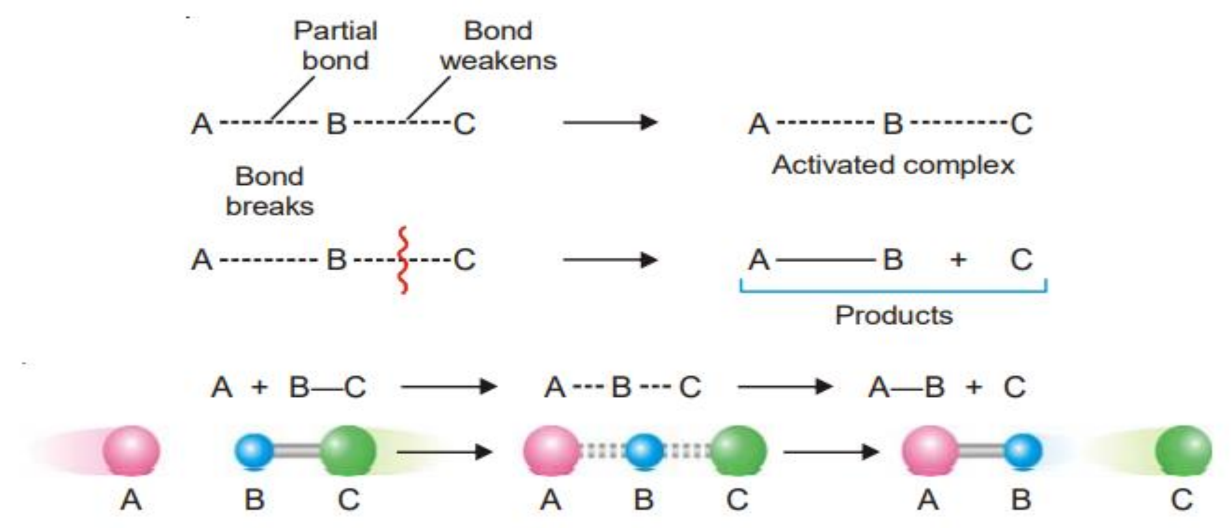
ACTIVATED COMPLEX THEORY

The transition state theory may be summarized as follows :

(1) In a collision, the fast approaching reactant molecules (A and BC) slow down due to gradual repulsion between their electron clouds. In the process the kinetic energy of the two molecules is converted into potential energy.

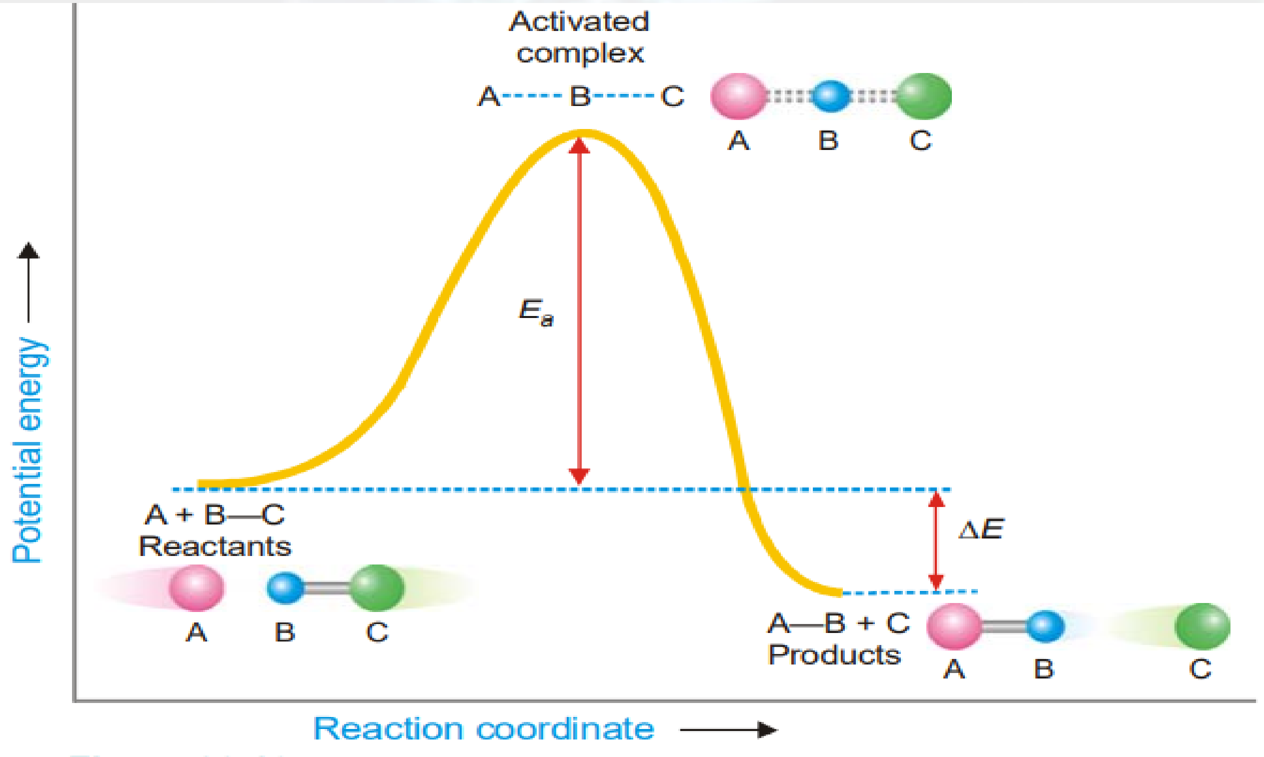
(2) As the molecules come close, the interpenetration of their electron clouds occurs which allows the rearrangement of valence electrons.

(3) A partial bond is formed between the atoms A and B with corresponding weakening of B – C bond. This leads to formation of an activated complex or transition state. The activated complex is momentary and decomposes to give the products (A–B + C)



ACTIVATED COMPLEX THEORY

The activated complex theory may be illustrated by the reaction energy diagram



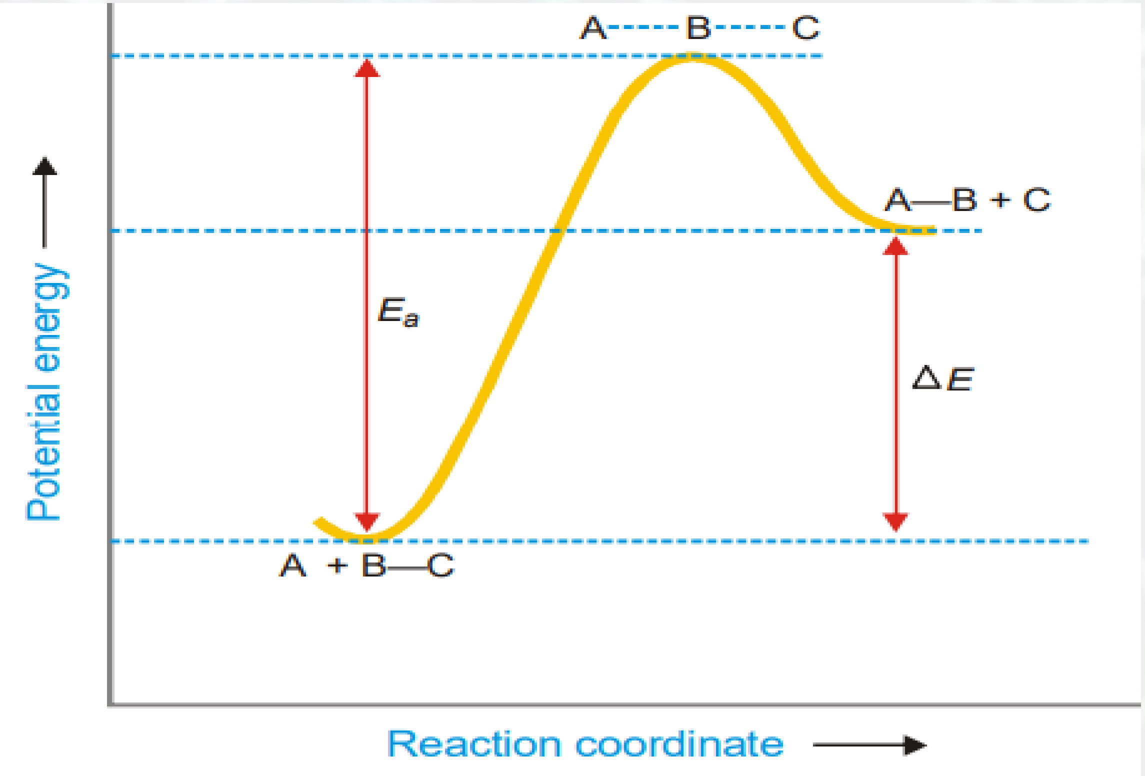
As evident from the energy diagram,

energy is required by the reactants to reach the transition state. Also, the energy is obtained in passing from the transition state to the products.

If the potential energy of the products is less than that of the reactants the energy obtained in going from the activated complex to products will be more than the activation energy (Ea). Thus such a reaction will be exothermic

ACTIVATED COMPLEX THEORY

On the other hand, if the potential energy of the products is greater than that of the reactants, the energy released in going from the activated complex to products will be less than the activation energy and the reaction will be endothermic

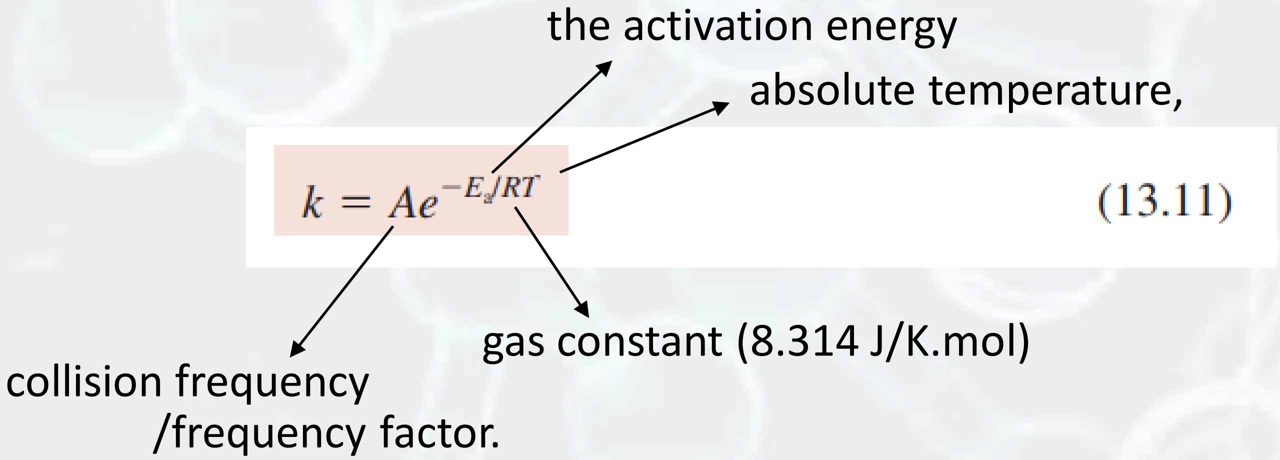


EFFECT OF INCREASE OF TEMPERATURE ON REACTION RATE

It has been found that generally an increase of temperature increases the rate of reaction. As a rule, an increase of temperature by 10°C doubles the reaction rate.

The Arrhenius Equation

The dependence of the rate constant of a reaction on temperature can be expressed by the following equation, known as the Arrhenius equation:



the activation energy

absolute temperature,

$$k = Ae^{-E_a/RT} \qquad (13.11)$$

gas constant (8.314 J/K.mol)

collision frequency
/frequency factor.

can be treated as a constant for a given reacting system over a fairly wide temperature range.

EFFECT OF INCREASE OF TEMPERATURE ON REACTION RATE

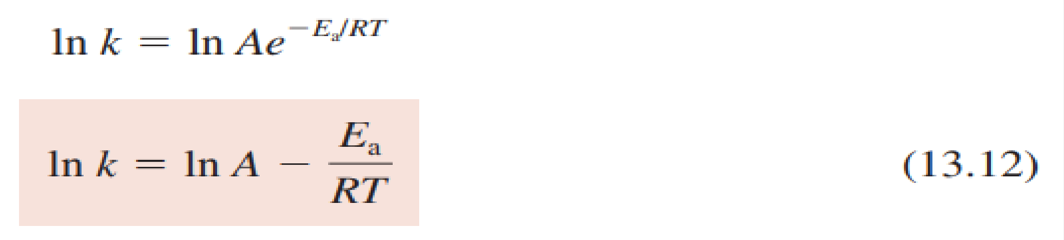
$$k = Ae^{-E_a/RT} \qquad (13.11)$$

Equation (13.11) shows that the rate constant is directly proportional to A and, therefore, to the collision frequency.

In addition, because of the minus sign associated with the exponent Ea/RT, the rate constant decreases with increasing activation energy and increases with increasing temperature.

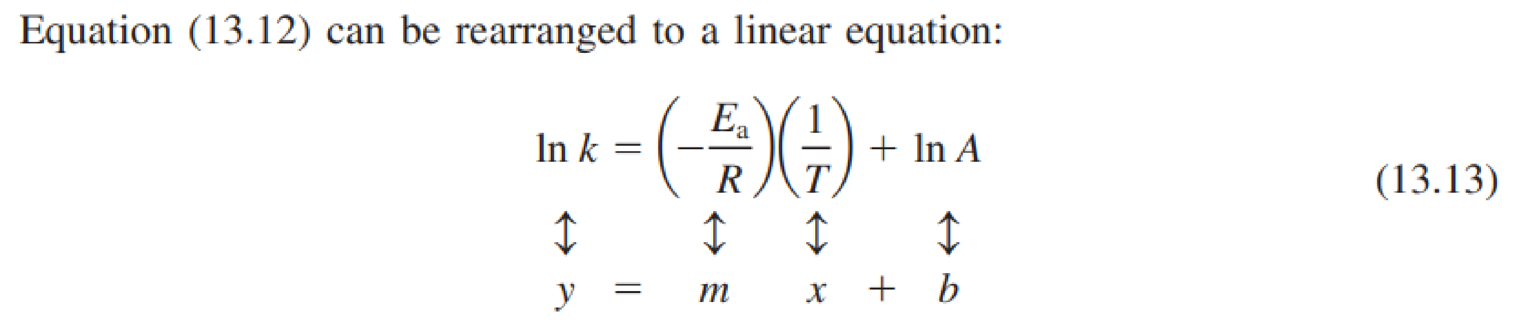
Calculation of Ea Using Arrhenius Equation

This equation can be expressed in a more useful form by taking the natural logarithm of both sides



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

$$\ln k = \ln A - \frac{E_a}{RT} \qquad (13.12)$$



Equation (13.12) can be rearranged to a linear equation:

$$\begin{array}{ccccccc} \ln k & = & \left(-\dfrac{E_a}{R}\right) & \left(\dfrac{1}{T}\right) & + & \ln A & \qquad (13.13) \\ \updownarrow & & \updownarrow & \updownarrow & & \updownarrow & \\ y & = & m & x & + & b & \end{array}$$

EFFECT OF INCREASE OF TEMPERATURE ON REACTION RATE

An equation relating the rate constants k1 and k2 at temperatures T1 and T2 can be used to calculate the activation energy or to find the rate constant at another

temperature if the activation energy is known.

To derive such an equation we start with Equation (13.12):

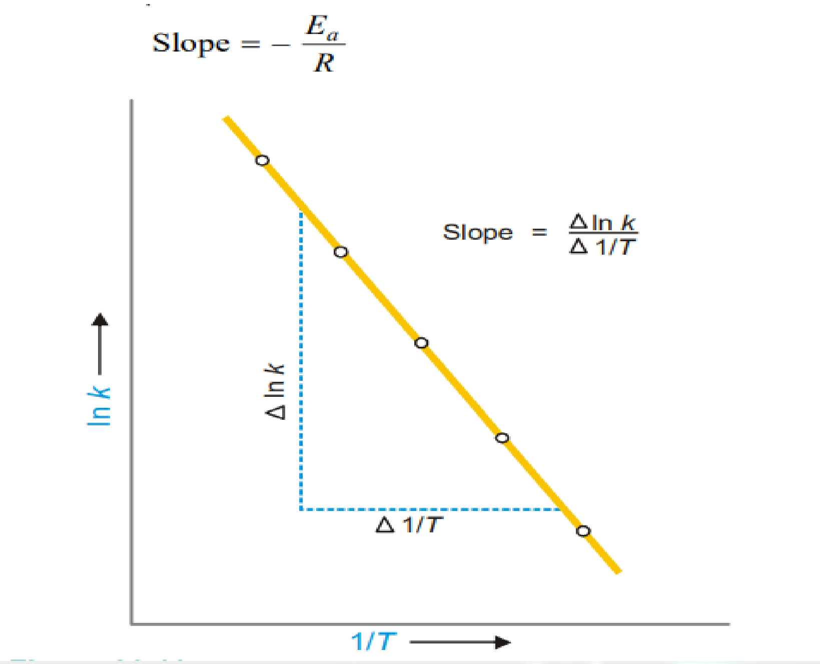
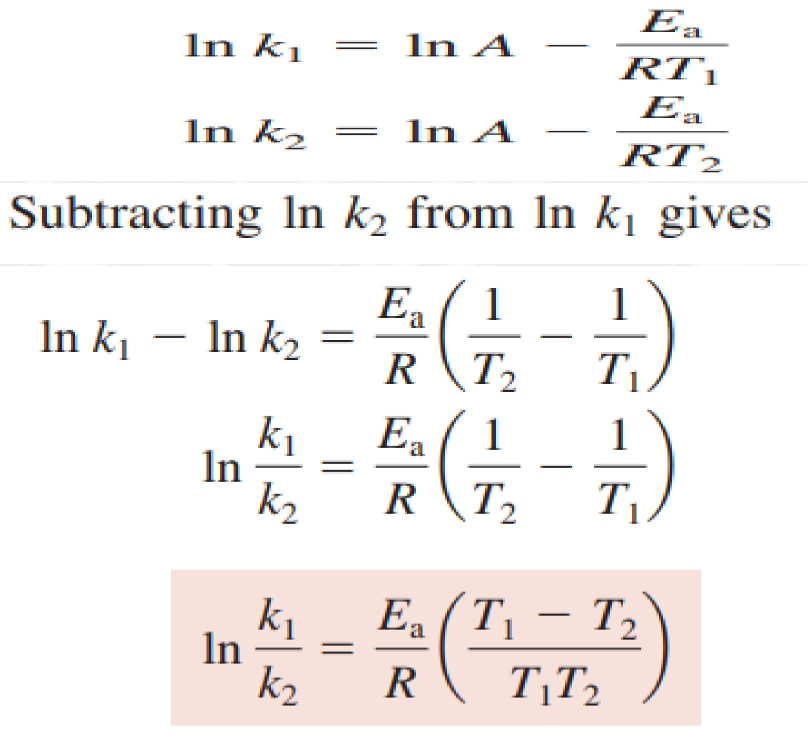


Figure 20.11
The plot of ln *k* versus l/*T* gives a straight line. The slope of line Δ ln *k* /Δ l/*T* gives E_a using the expression given above.



$$\ln k_1 = \ln A - \frac{E_a}{RT_1}$$

$$\ln k_2 = \ln A - \frac{E_a}{RT_2}$$

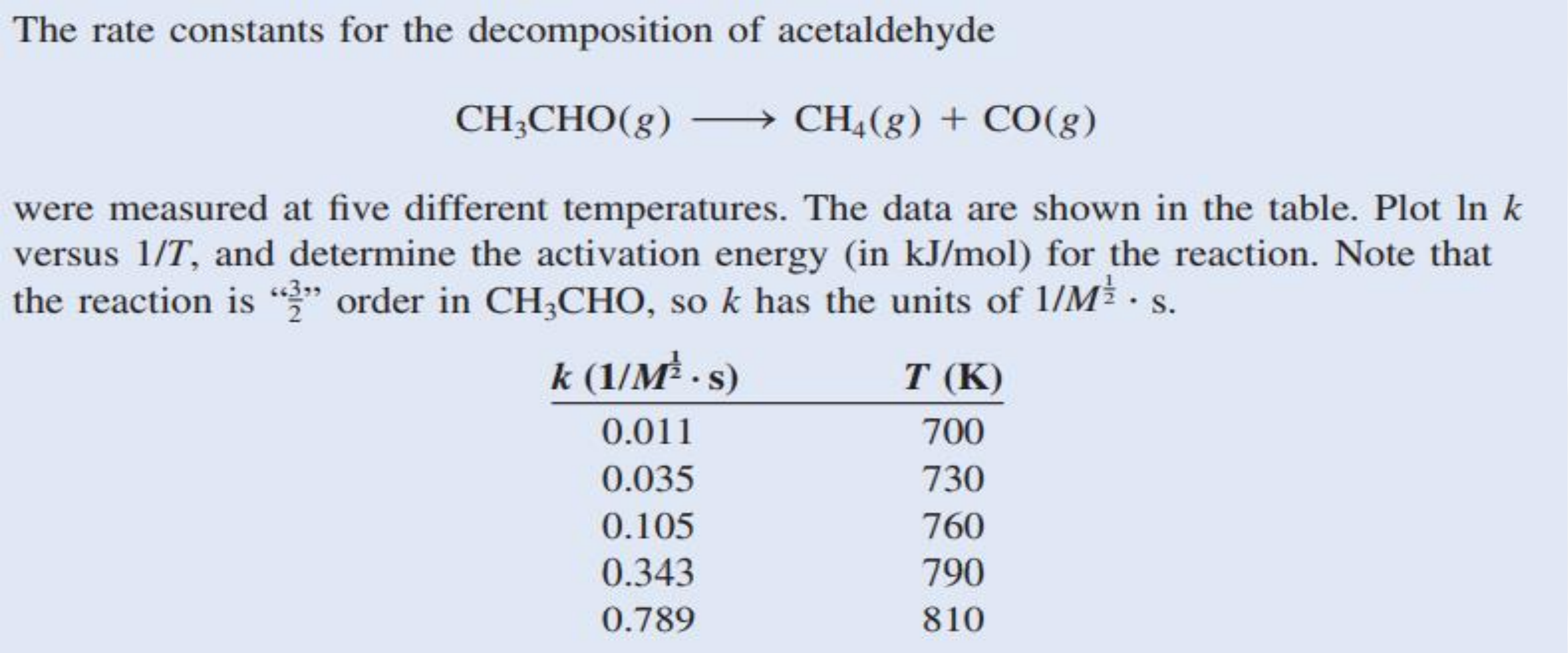
Subtracting $\ln k_2$ from $\ln k_1$ gives

$$\ln k_1 - \ln k_2 = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{T_1 - T_2}{T_1 T_2}\right)$$

EFFECT OF INCREASE OF TEMPERATURE ON REACTION RATE

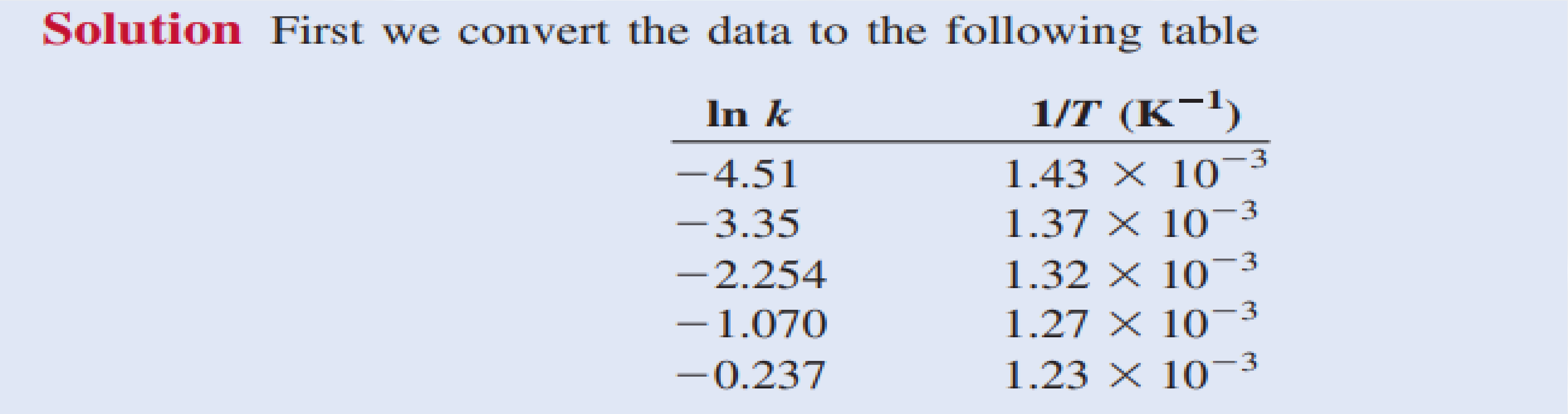


The rate constants for the decomposition of acetaldehyde

$$CH_3CHO(g) \longrightarrow CH_4(g) + CO(g)$$

were measured at five different temperatures. The data are shown in the table. Plot ln k versus $1/T$, and determine the activation energy (in kJ/mol) for the reaction. Note that the reaction is "$\frac{3}{2}$" order in CH_3CHO, so k has the units of $1/M^{\frac{1}{2}} \cdot s$.

k $(1/M^{\frac{1}{2}} \cdot s)$	T (K)
0.011	700
0.035	730
0.105	760
0.343	790
0.789	810



Solution First we convert the data to the following table

ln k	$1/T$ (K^{-1})
−4.51	1.43×10^{-3}
−3.35	1.37×10^{-3}
−2.254	1.32×10^{-3}
−1.070	1.27×10^{-3}
−0.237	1.23×10^{-3}

EFFECT OF INCREASE OF TEMPERATURE ON REACTION RATE

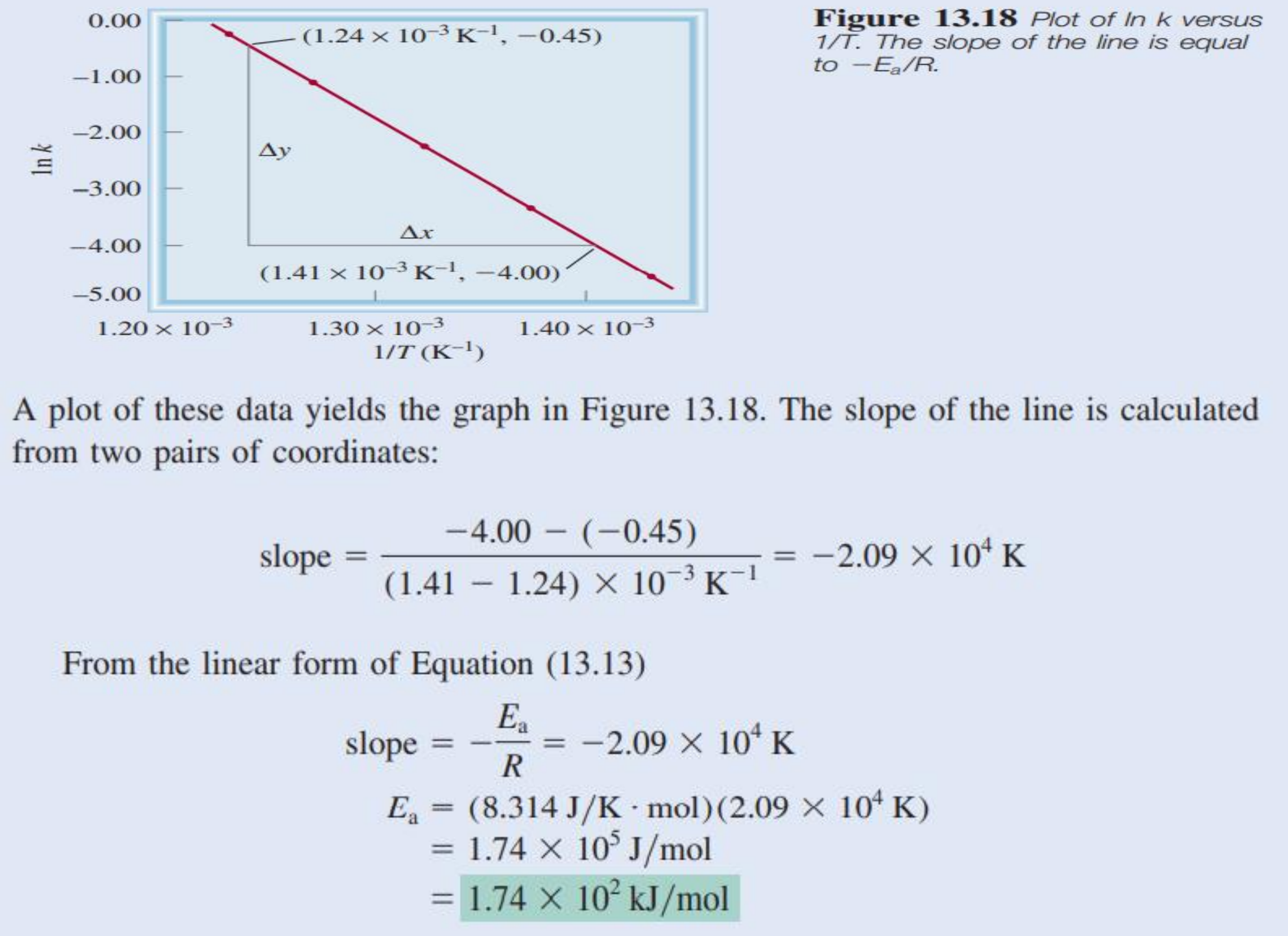


Figure 13.18 *Plot of ln k versus 1/T. The slope of the line is equal to $-E_a/R$.*

A plot of these data yields the graph in Figure 13.18. The slope of the line is calculated from two pairs of coordinates:

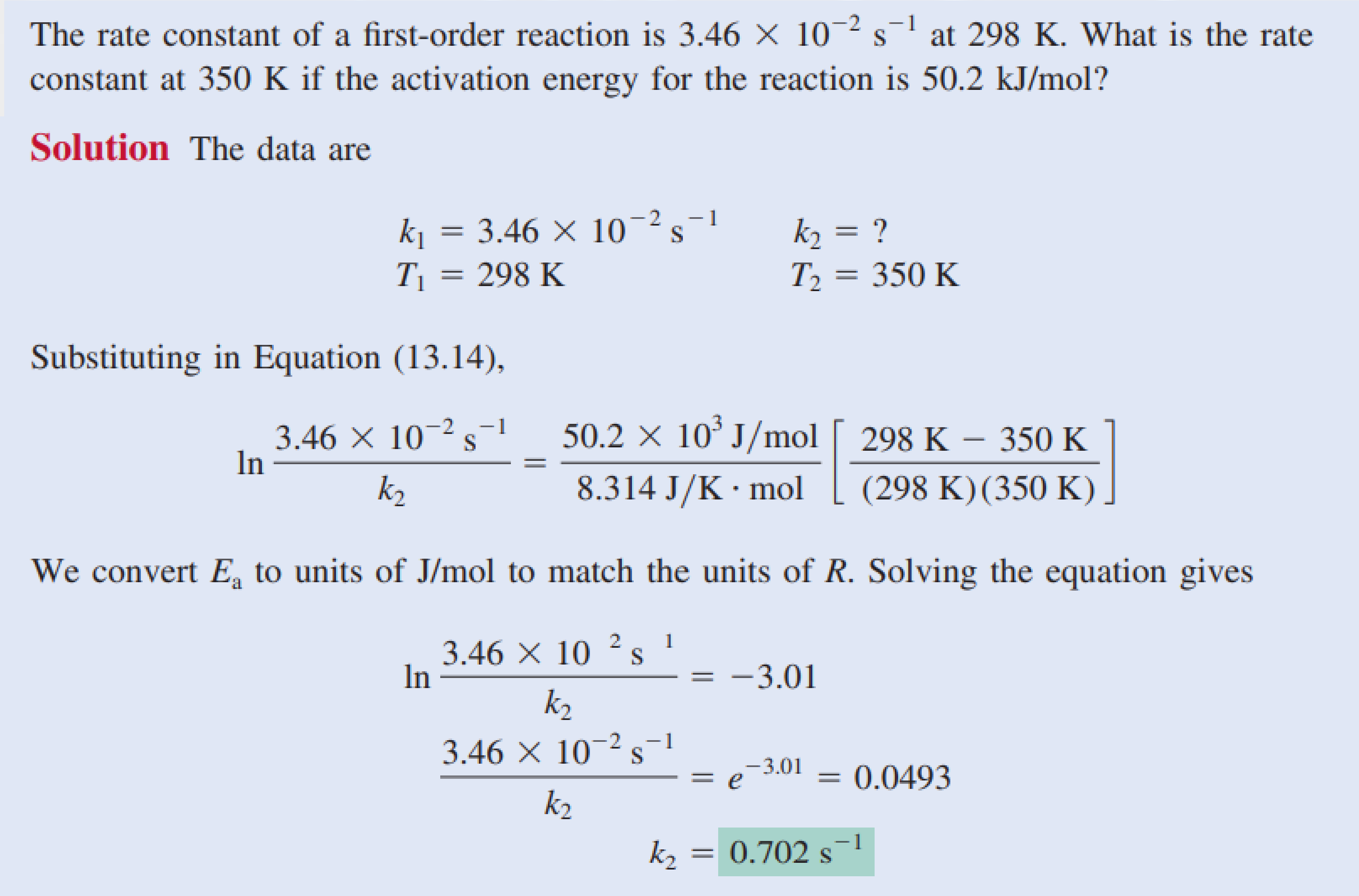
$$\text{slope} = \frac{-4.00 - (-0.45)}{(1.41 - 1.24) \times 10^{-3}\ \text{K}^{-1}} = -2.09 \times 10^{4}\ \text{K}$$

From the linear form of Equation (13.13)

$$\text{slope} = -\frac{E_a}{R} = -2.09 \times 10^{4}\ \text{K}$$

$$\begin{aligned} E_a &= (8.314\ \text{J/K} \cdot \text{mol})(2.09 \times 10^{4}\ \text{K}) \\ &= 1.74 \times 10^{5}\ \text{J/mol} \\ &= 1.74 \times 10^{2}\ \text{kJ/mol} \end{aligned}$$

EFFECT OF INCREASE OF TEMPERATURE ON REACTION RATE



The rate constant of a first-order reaction is $3.46 \times 10^{-2}\ s^{-1}$ at 298 K. What is the rate constant at 350 K if the activation energy for the reaction is 50.2 kJ/mol?

Solution The data are

$$k_1 = 3.46 \times 10^{-2}\ s^{-1} \qquad k_2 = ?$$
$$T_1 = 298\ K \qquad T_2 = 350\ K$$

Substituting in Equation (13.14),

$$\ln \frac{3.46 \times 10^{-2}\ s^{-1}}{k_2} = \frac{50.2 \times 10^3\ J/mol}{8.314\ J/K \cdot mol}\left[\frac{298\ K - 350\ K}{(298\ K)(350\ K)}\right]$$

We convert E_a to units of J/mol to match the units of R. Solving the equation gives

$$\ln \frac{3.46 \times 10^{\ 2}\ s^{\ 1}}{k_2} = -3.01$$

$$\frac{3.46 \times 10^{-2}\ s^{-1}}{k_2} = e^{-3.01} = 0.0493$$

$$k_2 = 0.702\ s^{-1}$$

CATALYSIS

is the process of increasing the rate of a chemical reaction by lowering the activation energy by adding a substance known as a **catalyst**

It does so by providing an alternative reaction pathway.
The catalyst may react to form an intermediate with the reactant, but it is regenerated in a subsequent step so it is not consumed in the reaction

In the laboratory preparation of molecular oxygen, a sample of potassium chlorate is heated,

$$2KClO_3(s) \longrightarrow 2KCl(s) + 3O_2(g)$$

However, this thermal decomposition process is very slow in the absence of a catalyst.
The rate of decomposition can be increased dramatically by adding a small amount of the catalyst manganese(IV) dioxide (MnO_2), a black powdery substance. All of the MnO_2 can be recovered at the end of the reaction

CATALYSIS

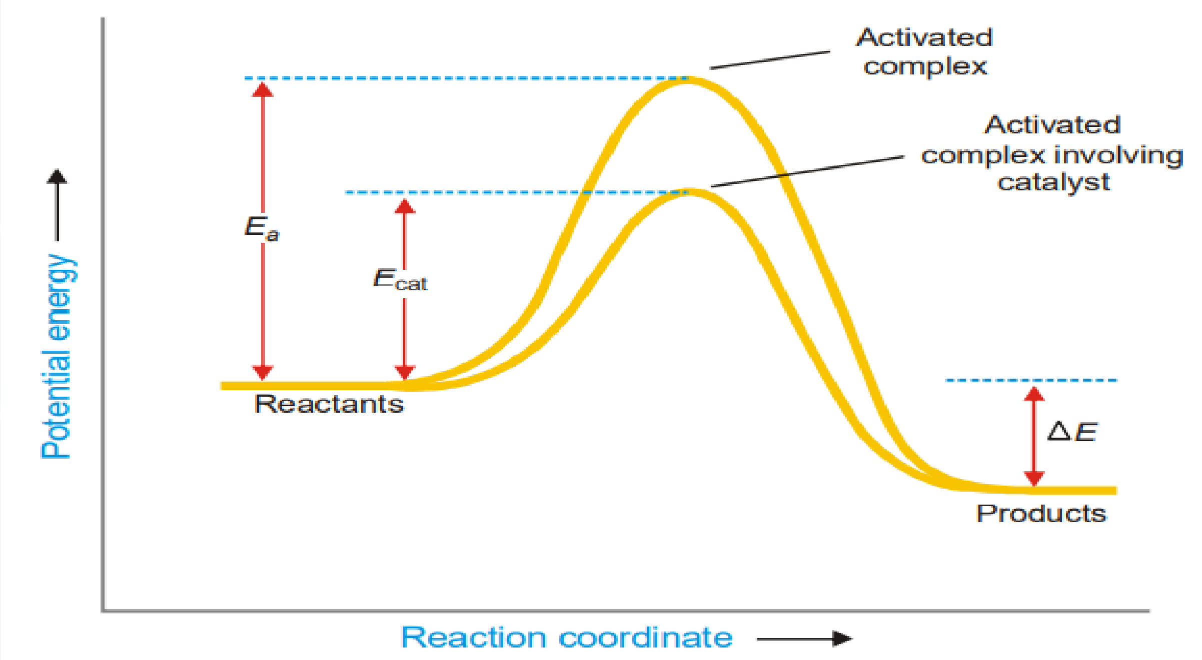
Characteristics of Catalyst

- Catalyst may undergo physical changes but not chemical
- Small quantities of catalyst are sufficient for catalysis.
- Catalyst activates the rate of reaction but cannot initiate it
- Catalytic activity is maximum at optimum temperature
- Catalyst lowers the activation energy of forward and backward reaction and also lowers threshold energy
- It provides a new mechanism for the reaction
- It does not change the energy and extent of reaction

CATALYSIS

ACTIVATION ENERGY AND CATALYSIS

We know that for each reaction a certain energy barrier must be surmounted the reactant molecules must possess the activation energy, Ea, for the reaction to occur.



The catalyst functions by providing another pathway with lower activation energy, Ecat. Thus a much large number of collisions becomes effective at a given temperature.

Since the rate of reaction is proportional to effective collisions, the presence of a catalyst makes the reaction go faster, other conditions remaining the same.

The energy difference, ΔE, between products and reactants remains the same.

CATALYSIS

There are three general types of catalysis, depending on the nature of the rate increasing substance: heterogeneous catalysis, homogeneous catalysis, and enzyme catalysis.

Heterogeneous Catalysis

In heterogeneous catalysis, the reactants and the catalyst are in different phases. Usually the catalyst is a solid and the reactants are either gases or liquids.

Heterogeneous catalysis is by far the most important type of catalysis in industrial chemistry

Examples: The Haber Synthesis of Ammonia

Homogeneous Catalysis

In homogeneous catalysis the reactants and catalyst are dispersed in a single phase, usually liquid. Acid and base catalyses are the most important types of homogeneous catalysis in liquid solution.

For example, the reaction of ethyl acetate with water to form acetic acid and ethanol normally occurs too slowly to be measured

CATALYSIS

Enzyme Catalysis

Enzymes are biological catalysts.

The amazing fact about enzymes is that not only can they increase the rate of biochemical reactions by factors ranging from 10^6 to 10^{18}, but they are also highly specific.

An enzyme acts only on certain molecules, called substrates (that is, reactants), while leaving the rest of the system unaffected.

An enzyme is typically a large protein molecule that contains one or more active sites where interactions with substrates take place.

Enzyme catalysis is usually homogeneous because the substrate and enzyme are present in aqueous solution.