Activation energy and temperature dependence of rate constant
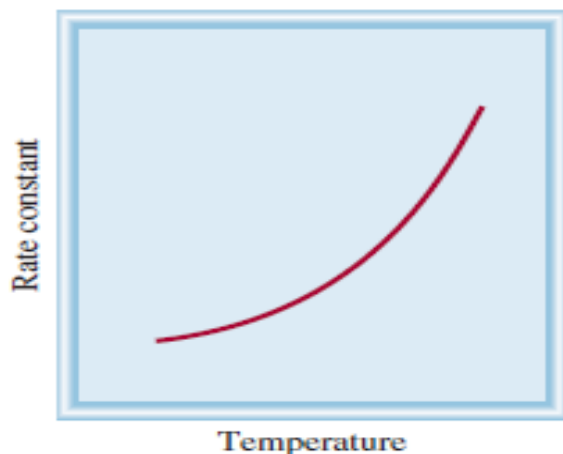
❖ Reaction rate increase with increasing temperature.

Rate constant

Temperature

→ This figure shows atypical example of the relationship between the rate constant of a reaction and temperature.

Dependence of rate constant on temperature. The rate constants of most reactions increase with increasing Temperature.

❖ The collision theory of chemical kinetics

Kinetic molecular theory of gases: → postulates that gas molecules frequently collide with one another.

Collision theory of chemical kinetics: → chemical reactions occur as a result of collisions between reacting molecules.

- Calculations based on the kinetic molecular theory shows that, at ordinary pressure (say, 1Atm) and temperatures (say, 298K) there are about $(1*10^{27})$ binary collisions (collisions between two molecules) in 1ml of volume every second in the gas phase.

- Even more collisions per second occur in liquid.

☒ Any molecules in motion pass kinetic energy.

☒ The faster it moves, the greater the kinetic energy.

☒ For a molecule to react, it must collide with another molecule.

☒ When molecules collide, part of their kinetic energy is converted to vibrational energy.

After molecules collides there are two cases

☒ If the initial kinetic energies are large.
- The colliding molecules will vibrate so strongly as to break some of the chemical bonds.
- This bond fracture in the first step toward product formation.

☒ If the initial kinetic energies are small.
- There is some minimum collision energy below which no reaction occurs.
- Lacking this energy, the molecules remain intact, and no change result from the collision.

Conclusion: →in order to react, the colliding molecules must have a total kinetic energy equal to or greater than the activation energy.
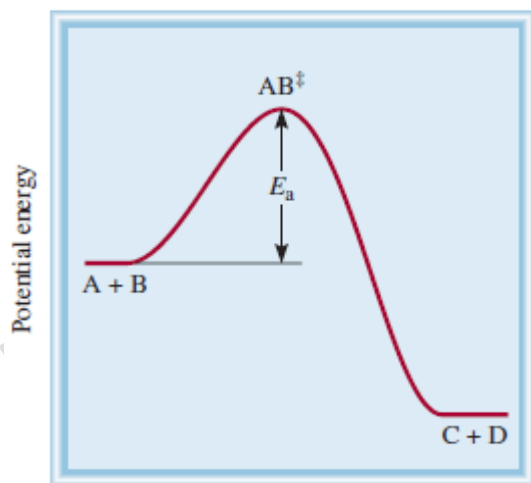
Activation energy (E_a):→ is the minimum amount of energy required to initiate a chemical reaction → (KJ/mol)

Activated complex "transition state":→ a temporary species formed by the reactant molecules as a result of the collision before they from the product.

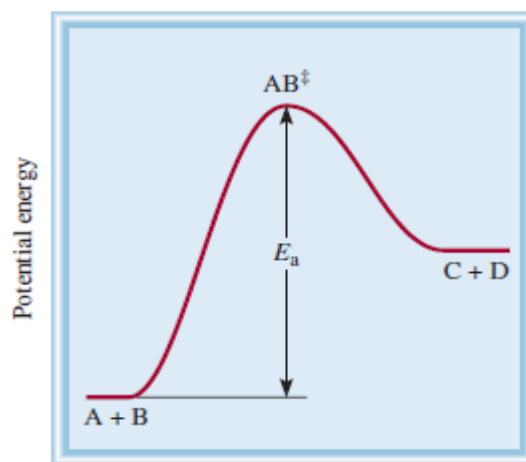Two different potential energy profiles for the reaction

A+B→AB →C+D

Exothermic   Endothermic

If the products are more stable than the reactants, then the reaction will be accompanied by a release of heat to the surroundings.

If the products are less stable than the reactants, then heat will be absorbed by the reacting mixture from the surroundings.

The Arrhenius equation :→ The dependence of the rate constant of a reaction on temperature.

$$K = Ae^{-Ea/RT}$$

Ea :→ activation energy of the reaction (KJ/mol).

R :→ gas constant (8.314 J/K.mol).

T:→ the absolute temperature.

e :→ The base of the natural logarithm.

A:→ The frequency factor.

A → is constant for a given reacting system over a fairly wide temperature range.

From the above equation we note that:

- The rate constant is directly proportional to A and, therefore, to the collision frequency.
- The minus sign indicate that, the rate constant decreases with increasing activation energy and increase with increasing temp.
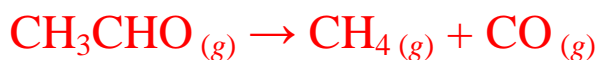
$$K = Ae^{-Ea/RT}$$

$$lnK = lnA - \frac{Ea}{RT}$$

The above equation can be rearranged as follow:

$$lnK = -\frac{Ea}{R}\left(\frac{1}{T}\right) + lnA$$

If we plot lnK versus $\left(\frac{1}{T}\right)$, this give a straight line whose slope is equal to $-\frac{Ea}{R}$ and whose intercept is lnA
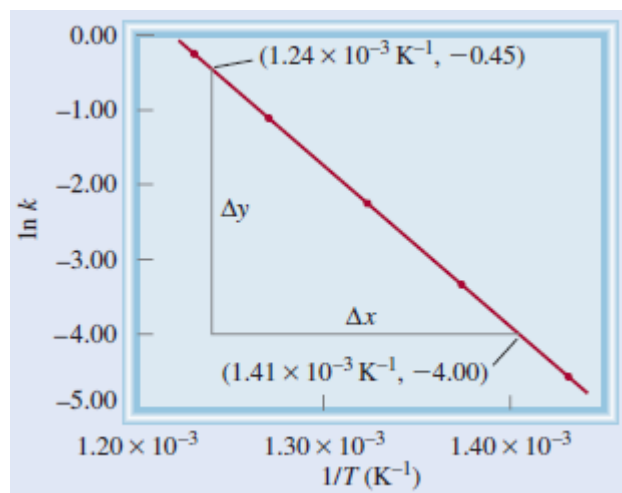
Example

The rate constants for the decomposition of acetaldehyde
$$CH_3CHO_{(g)} \rightarrow CH_{4\,(g)} + CO_{(g)}$$

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 $1/M^{1/2}.S$

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

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}

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

From the linear form of Equation

$$slope = \frac{Ea}{R} = -2.09 * 10^4 K$$

Ea = (8.134J/K.mol)(2.09*10⁴K)
    $=1.74*10^5$ J/mol $=1.74*10^2$ KJ/mol

☒ An equation relating the rate constant K_1 , K_2 at temperature T_1 , T_2 can be used to calculate the activation energy.

$$\ln\frac{K_1}{K_2} = \frac{Ea}{R}\left(\frac{T_1 - T_2}{T_1 T_2}\right)$$

Example

The rate constant of a first-order reaction is $3.46 * 10^{-2}$ 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

$k_1 = 3.46 *10^{-2}$ s^{-1} $k_2 = ?$

$T_1 = 298$ K $T_2 = 350$ K

$$\ln\frac{K_1}{K_2} = \frac{Ea}{R}\left(\frac{T_1 - T_2}{T_1 T_2}\right)$$

$$\ln\frac{3.46 * 10^{-2}}{K_2} = \frac{50.2 * 10^3}{8.314}\left[\frac{298 - 350}{(298)(350)}\right]$$

$$\ln\frac{3.46 * 10^{-2}}{K_2} = -3.01$$

$$\frac{3.46 * 10^{-2}}{K_2} = e^{-3.01} = 0.0493$$

$$K_2 = 0.702 \; S^{-1}$$

Example

The activation energy of a certain reaction is 76.7 Kl/mole, How many times faster will the reaction occur at 50°C than at 0°C?!

Solution

$$\ln\frac{K_2}{K_1} = \frac{Ea}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\ln\frac{K_2}{K_1} = \frac{76.7 * 1000}{8.314}\left(\frac{323 - 273}{323 * 273}\right)$$

$$\ln\frac{K_2}{K_1} = 5.23$$

$$\frac{K_2}{K_1} = 187$$

$$K_2 = 187K_1$$

Choose

1) ……… is the minimum amount of energy required to initiate a chemical reaction.

   A) Heat of formation   C) <u>Activation energy</u>

   B) Heat of decomposition   D) Thermal energy

2) ……… is a temporary species formed by the reactant molecules as a result of the collision before they form the product.

   A) intermediate   C) Activated complex

   B) Transition state   D) <u>Both B and C</u>

3) If the products are more stable than the reactants, then the reaction will be accompanied by……… of heat……. The surroundings

   A) absorbed-form   C) <u>Release-to</u>

   B) Increase- form   D) None of them

4) The expression of Arrhenius equation is……...

   A) $K = Ae^{-Rt}$ C) $A = Ke^{-Ea/Rt}$

   B) <u>$K = Ae^{-Ea/Rt}$</u>   D) $K = e^{-Ea/Rt}$

5) The Arrhenius equation is $K = Ae^{-Ea/Rt}$, the slope of a plot of lnK vs. 1/T is equal to…..

   A) $-K$ C) Ea

   B) K   D) <u>-Ea/R</u>

6) The activation energy for the reaction

$CH_3CO \rightarrow CH_3 + CO$ is 71KJ/mol.

How many times greater is the rate constant for this reaction at 170°C than at 150°C ?

A) <u>2.5</u>   C) 0.40

B) 1.1   D) 4.0

Solution

$Ea = 71*1000$ J/mol

$T_1 = 170+273 = 443°K$

$T_2 = 150+273 = 423°K$

$$\ln \frac{K_1}{K_2} = \frac{71*1000}{8.314}\left(\frac{443-423}{443*423}\right) = 0.91$$

$$\frac{K_1}{K_2} = e^{0.91} = 2.48$$

7) If Ea for a certain biological reaction is 50 KJ/mol, by what factor will the rate of this reaction increase when body temperature increases from 37°C to 40°C?!

A) <u>1.20</u>

C) $2*10^5$

B) 1.15

D) 1.0002

Solution

Ea = 50*1000 J/mol

T_1 = 37+273 = 310°K

T_2 = 40+273 = 313°K

$$\ln \frac{K_1}{K_2} = \frac{50 * 1000}{8.314}\left(\frac{310 - 313}{310 * 313}\right) = 0.185$$

$$\frac{K_1}{K_2} = e^{0.185} = 1.20$$

8) The isomerization of cyclopropane follows first order Kinetics. The rate constant at 700K is $6.2*10^{-4}$ min^{-1}, and the half-life at 760°K is 29.0min. Calculate the activation energy for this rxn.

A) 27.0 KJ/mol

C) 270 KJ/mol

B) 5.07 KJ/mole

D) 160 KJ/mol

Solution

$T_1 = 700°K$ $K_1 = 6.2 * 10^{-4}$ min^{-1}.

$T_2 = 760°K$ $K_2 = ?$ min^{-1}.

$t_{1/2} = 29$

$K_2 = \dfrac{ln2}{t_{1/2}} = \dfrac{ln2}{29} = 23.9 * 10^{-3}$ min^{-1}.

$\ln \dfrac{K_1}{K_2} = \dfrac{Ea}{R}\left(\dfrac{T_1 - T_2}{T_1 T_2}\right)$

$\ln \dfrac{6.2 * 10^{-4}}{23.9 * 10^{-3}} = \dfrac{Ea}{8.314}\left(\dfrac{700 - 760}{700 * 760}\right)$

$Ea = 270$ KJ/mole

9) The isomerization of methyl isocyanides, $CH_3NC \rightarrow CH_3CN$ follows first-order kinetics. The half-lives were found to be 161min at 199°C and 12.5min at 230°C. Calculate the activation energy for this reaction.

A) $6.17*10^{-3}$ KJ/mol

C) 124 KJ/mol

B) 31.4 KJ/mol

D) <u>163 KJ/mol</u>

Solution

$T_1 = 199 + 273 = 472$ °K

$K_1 = \dfrac{ln2}{t_{1/2}} = \dfrac{ln2}{161} = 4.3 * 10^{-3}$ min^{-1}.

$T_2 = 230 + 273 = 503$ °K

$K_2 = \dfrac{ln2}{t_{1/2}} = \dfrac{ln2}{12.5} = 55 * 10^{-3}$ min^{-1}.

$$\ln\dfrac{K_1}{K_2} = \dfrac{Ea}{R}\left(\dfrac{T_1 - T_2}{T_1 T_2}\right)$$

$$\ln\dfrac{4.3 * 10^{-3} \text{ min.}^{-1}}{55 * 10^{-3} \text{ min.}^{-1}} = \dfrac{Ea}{8.314}\left(\dfrac{472 - 503}{472 * 503}\right)$$

$Ea = 162.5 = 163$ KJ/mole