Section 80 – Collision Theory

80-1. Chemical reactions occur when reactants collide. What are two factors that may prevent a collision from producing a chemical reaction?

Solution

The reactants either may be moving too slowly to have enough kinetic energy to exceed the activation energy for the reaction, or the orientation of the molecules when they collide may prevent the reaction from occurring.

80-2. When every collision between reactants leads to a reaction, what determines the rate at which the reaction occurs?

Solution

diffusion; in this example, since every collision between reactants leads to a reaction, the activation energy has been exceeded

80-3. What is the activation energy of a reaction, and how is this energy related to the activated complex of the reaction?

Solution

The activation energy is the minimum amount of energy necessary to form the activated complex in a reaction. It is usually expressed as the energy necessary to form one mole of activated complex.

80-4. Account for the relationship between the rate of a reaction and its activation energy.

Solution

The rate of reaction will increase as the activation energy decreases. This relationship is reasonable because a large activation energy that requires a large amount of energy is a hindrance to reaction.

80-5. In terms of collision theory, to which of the following is the rate of a chemical reaction proportional?

(a) the change in free energy per second

(b) the change in temperature per second

(c) the number of collisions per second

(d) the number of product molecules

Solution
(c) the number of collisions per second

80-6. How does an increase in temperature affect rate of reaction? Explain this effect in terms of the collision theory of the reaction rate.
Solution
It increases the rate of reaction by increasing the average kinetic energy of the molecules involved. This results in a larger fraction of collisions resulting in the molecules having the energy to overcome the activation energy barrier to form activated complexes.

80-7. The rate of a certain reaction doubles for every 10 °C rise in temperature.
(a) How much faster does the reaction proceed at 45 °C than at 25 °C?
(b) How much faster does the reaction proceed at 95 °C than at 25 °C?
Solution
(a) The rate doubles for each 10 °C rise in temperature; 45 °C is a 20 °C increases over 25 °C. Thus, the rate doubles two times, or 2^2 (rate at 25 °C) = 4-times faster. (b) 95 °C is a 70 °C increases over 25 °C. Thus the rate doubles seven times, or 2^7 (rate at 25 °C) = 128-times faster.

80-8. Describe how graphical methods can be used to determine the activation energy of a reaction from a series of data that includes the rate of reaction at varying temperatures.
Solution

After finding k at several different temperatures, a plot of ln k versus $\frac{1}{T}$ gives a straight line with the slope $\frac{-E_a}{R}$, from which E_a may be determined.

80-9. In an experiment, a sample of $NaClO_3$ was 90% decomposed in 48 min. Approximately how long would this decomposition have taken if the sample had been heated 20 °C higher? (Hint: Assume the rate doubles for each 10 °C rise in temperature.)
Solution
The rate doubles for each 10 °C rise in temperature. Thus, an increase of 20 °C would increase the rate four times, thereby decreasing the time required to one-fourth its original value:

$$\frac{48\text{ min}}{4} = 12\text{ min}.$$

80-10. The rate constant at 325 °C for the decomposition reaction $C_4H_8 \longrightarrow 2C_2H_4$ is 6.1×10^{-8} s^{-1}, and the activation energy is 261 kJ per mole of C_4H_8. Determine the frequency factor for the reaction.

Solution

The rate constant k is related to the activation energy E_a by a relationship known as the Arrhenius equation. Its form is:

$$k = A \times 10^{-(E_a/2.303RT)} = A \times e^{-(E_a/RT)}$$

where A is the frequency factor. Using the data provided, and converting kilojoules to joules:

$$\begin{aligned} 6.1 \times 10^{-8}\ s^{-1} &= A \times 10^{-\left[+261.000\ J/2.303(8.314\ J\ K^{-1})(325+273)K\right]} \\ &= A \times 10^{-22.8} \end{aligned}$$

$$A = \frac{6.1 \times 10^{-8}\ s^{-1}}{1.58 \times 10^{-23}} = 3.9 \times 10^{15}\ s^{-1}$$

80-11. The rate constant for the decomposition of acetaldehyde, CH_3CHO, to methane, CH_4, and carbon monoxide, CO, in the gas phase is 1.1×10^{-2} L mol^{-1} s^{-1} at 703 K and 4.95 L mol^{-1} s^{-1} at 865 K. Determine the activation energy for this decomposition.

Solution

In the text, a graphical method was used to determine activation energies, but we are only given two data points in this problem. With only two data points available, it is not necessary to plot the points to calculate the slope of the line that would be generated if more points were plotted:

T (K)	$\frac{1}{T}$ (K^{-1})	k (L mol^{-1} s^{-1})	Lnk
703	1.422×10^{-3}	1.1×10^{-2}	–4.50986
865	1.156×10^{-3}	4.95	1.59939

$$\begin{aligned} \text{Slope} &= \frac{\Delta(\ln\ k)}{\Delta\left(\frac{1}{T}\right)} \\ &= \frac{(-4.50986) - (1.599388)}{(1.422 \times 10^{-3}\ K^{-1}) - (1.156 \times 16^{-3}\ K^{-1})} \\ &= \frac{-6.109248}{0.266 \times 10^{-3}\ K^{-1}} \\ &= -2.297 \times 10^{4}\ K \end{aligned}$$

Also, the $\text{slope} = \frac{-E_a}{R}$, so

E_a = slope × RE_a = slope R

= –(–2.297 × 10^4 K)(8.314 J/mol/K)

= 1.91 × 10^5 J/mol $\longrightarrow$ 1.91 × 10^2 kJ/mol

80-12. An elevated level of the enzyme alkaline phosphatase (ALP) in human serum is an indication of possible liver or bone disorder. The level of serum ALP is so low that it is very difficult to measure directly. However, ALP catalyzes a number of reactions, and its relative concentration can be determined by measuring the rate of one of these reactions under controlled conditions. One such reaction is the conversion of p-nitrophenyl phosphate (PNPP) to p-nitrophenoxide ion (PNP) and phosphate ion. Control of temperature during the test is very important; the rate of the reaction increases 1.47 times if the temperature changes from 30 °C to 37 °C. What is the activation energy for the ALP–catalyzed conversion of PNPP to PNP and phosphate?

Solution

Note that $e^{-x} = 10^{-x/2.303}$. Changes in rate brought about by temperature changes are governed by the Arrhenius equation: $k = A \times 10^{-E_a/2.303RT}$. In this particular reaction, k increases by 1.47 as T changes from 30 °C (303 K). The Arrhenius equation may be solved for A under both sets of conditions and then A can be eliminated between the two equations. Eliminating k from both sides, taking logs, and rearranging gives:

$$\frac{-E_a}{2.303 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1}(310 \text{ K})} = \log 1.47 - \frac{E_a}{2.303 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1}(303 \text{ K})}$$

$$\frac{-E_a}{5935.6 \text{ J mol}^{-1}} = 0.1673 - \frac{E_a}{5801.6 \text{ J mol}^{-1}}$$

$$\frac{E_a}{5801.6} - \frac{E_a}{5935.6} = 0.1673 \text{ J mol}^{-1}$$

$E_a(1.72366 \times 10^{-4} - 1.68474 \times 10^{-4}) = 0.1673$ J/mol

$3.892 \times 10^{-6} E_a = 0.1673$ J/mol

E_a= 42986 J/mol = 43.0 kJ/mol

80-13. Hydrogen iodide, HI, decomposes in the gas phase to produce hydrogen, H_2, and iodine, I_2. The value of the rate constant, k, for the reaction was measured at several different temperatures and the data are shown here:

Temperature (K)	k (L mol^{-1} s^{-1})
555	6.23×10^{-7}
575	2.42×10^{-6}
645	1.44×10^{-4}
700	2.01×10^{-3}

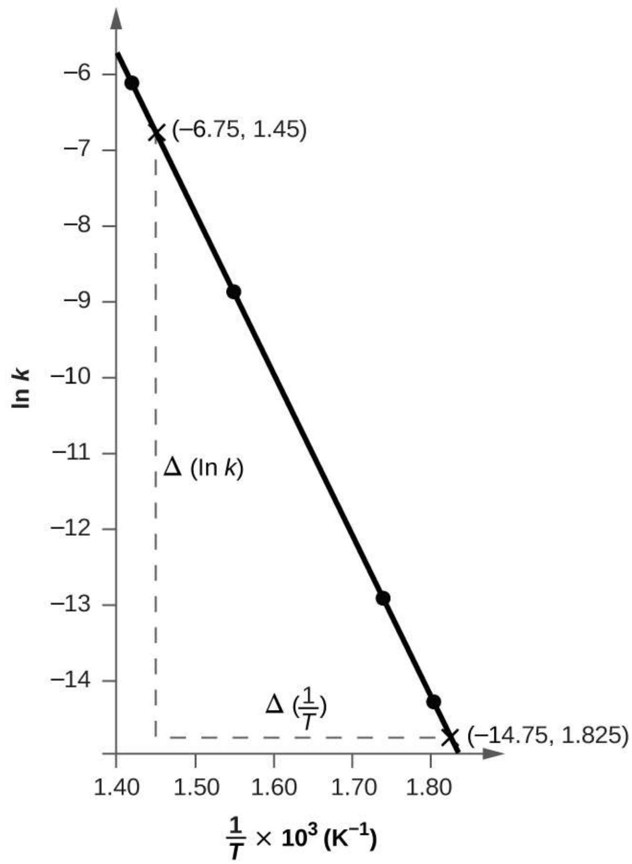
What is the value of the activation energy (in kJ/mol) for this reaction?

Solution

E_a may be determined from a plot of ln k against $\frac{1}{T}$ that gives a straight line whose slope is $\frac{-E_a}{R}$:

T (K)	$\frac{1}{T} \times 10^3$	k (L mol^{-1} s^{-1})	ln k
555	1.802	6.23×10^{-7}	−14.289
575	1.739	2.42×10^{-6}	−12.932
645	1.550	1.44×10^{-4}	−8.846
700	1.429	2.42×10^{-3}	−6.210

A plot of this data shows a straight line. Two points marked by an X are picked for convenience of reading and are used to determine the slope of the line:



$$\text{slope} = \frac{-14.750 - (-6.750)}{1.825 \times 10^{-3} - 1.450 \times 10^{-3}} = \frac{-8.000}{3.75 \times 10^{-4}} = -2.13 \times 10^{4}$$

$$\frac{-E_a}{R} = -2.13 \times 10^{4}$$

$E_a = –2.13 \times 10^4 \times 8.314$ J/mol = 177 kJ/mol

80-14. The element Co exists in two oxidation states, Co(II) and Co(III), and the ions form many complexes. The rate at which one of the complexes of Co(III) was reduced by Fe(II) in water was measured. Determine the activation energy of the reaction from the following data:

T (K)	k (s^{-1})
293	0.054
298	0.100

Solution

For only two data points, the Arrhenius equation:

$$k = A \times e^{-E_a/RT}$$

may be used in an analytical solution for E_a. This approach is possible because the value of A will be constant throughout the course of the reaction. Once the value of E_a is determined, the value of A may be determined from either Equation (1) or (2). At 293 K or 298 K, the value of k may be determined using the value of E_a and A so determined. The procedure is as follows:

At 293 K:

$$k = A \times e^{-E_a/2.303RT}$$
$$0.054\ \text{s}^{-1} = A \times e^{-E_a(8.314\ \text{J K}^{-1})(293\ \text{K})} \qquad \text{(equation 1)}$$
$$0.100\ \text{s}^{-1} = A \times e^{-E_a(8.314\ \text{J K}^{-1})(293\ \text{K})} \qquad \text{(equation 2)}$$

Equating the values of A as calculated from equations (1) and (2), we have:

$$0.054 \times e^{E_a/(8.314\ \text{J})(293)} = 0.100 \times e^{E_a/(8.314\ \text{J})(298)} \text{ or } 0.054 \times e^{E_a/2436} = 0.100 \times e^{E_a/2478}.$$

Taking natural logarithms of both sides gives:

$$\begin{aligned}
\ln 0.054 + \frac{E_a}{2436} &= \ln 0.100 + \frac{E_a}{2478} \\
-2919 + \frac{E_a}{2436} &= -2.303 + \frac{E_a}{2478} \\
-0.616 &= E_a\left(\frac{1}{2478} - \frac{1}{2436}\right) \\
&= E_a(4.0355 \times 10^{-4} - 4.1051 \times 10^{-4}) \\
&= E_a(-6.96 \times 10^{-6}) \\
E_a &= 89 \times 10^{4}\ \text{J or } 8.9 \times 10^{1}\ \text{kJ}
\end{aligned}$$

80-15. The hydrolysis of the sugar sucrose to the sugars glucose and fructose,

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

follows a first-order rate law for the disappearance of sucrose: rate = $k[C_{12}H_{22}O_{11}]$. (The products of the reaction, glucose and fructose, have the same molecular formulas but differ in the arrangement of the atoms in their molecules.)
(a) In neutral solution, $k = 2.1 \times 10^{-11}\ \text{s}^{-1}$ at 27 °C and $8.5 \times 10^{-11}\ \text{s}^{-1}$ at 37 °C. Determine the activation energy, the frequency factor, and the rate constant for this equation at 47 °C (assuming the kinetics remain consistent with the Arrhenius equation at this temperature).
(b) When a solution of sucrose with an initial concentration of 0.150 M reaches equilibrium, the concentration of sucrose is $1.65 \times 10^{-7}\ M$. How long will it take the solution to reach equilibrium at 27 °C in the absence of a catalyst? Because the concentration of sucrose at equilibrium is so low, assume that the reaction is irreversible.

(c) Why does assuming that the reaction is irreversible simplify the calculation in part (b)?

Solution

(a) The text demonstrates that the value of E_a may be determined from a plot of log k against $\frac{1}{T}$ that gives a straight line whose slope is $\frac{-E_a}{2.303R}$. This relationship is based on the equation $\ln k = \ln A - \frac{E_a}{RT}$ or $\log k = \log A - \frac{E_a}{2.303RT}$ where $\ln k = 2.303 \log k$. Only two data points are given, and these must determine a straight line when log k is plotted against $1/T$. The values needed are:

$k_1 = 2.1 \times 10^{-11}$

$\log k_1 = -10.6778$

$k_2 = 8.5 \times 10^{-11}$

$\log k_2 = -10.0706$

$T_1 = 27\ °C = 300\ K$

$\frac{1}{T_1} = 3.3333 \times 10^{-3}$

$T_2 = 37\ °C = 310\ K$

$\frac{1}{T_2} = 3.2258 \times 10^{-3}$

The slope of the line determined by these points is given by:

$$\text{Slope} = \frac{\Delta(\log k)}{\Delta\frac{1}{T}} = \frac{(-10.0706) - (-10.6778)}{(3.2258 \times 10^{-3}) - (3.3333 \times 10^{-3})}$$

$$= \frac{0.6072}{-0.1075 \times 10^{-3}} = -5648$$

$E_a = 2.303(8.314\ J/mol)(–5648) = 108{,}100\ J = 108\ kJ$

Whenever differences of very small numbers are taken, such as the reciprocals of T provided, an inherent problem occurs. To have accurate differences, a larger number of significant figures than justified by the data must be used. Thus five figures were used to obtain the value $E_a = 108$ kJ. This difficulty may be alleviated by the following approach.

For only two data points, the Arrhenius equation $k = A \times 10^{-E_a/2.303RT}$ may be used in an equally accurate, analytical solution for E_a. This application is possible because the value of A will be the same throughout the course of the reaction. Once the value of E_a is determined, the value of A may be determined from either Equation (1) or (2). Then k at 47 °C may be determined using the value of E_a and A so determined. The procedure is as follows:

$$k = A \times 10^{-E_a/2.303RT}$$
$$2.1 \times 10^{-11}\ \text{s}^{-1} = A \times 10^{-E_a/2.303(8.314\ \text{J K}^{-1})(300\ \text{K})} \qquad \text{(equation 1)}$$
$$8.5 \times 10^{-11}\ \text{s}^{-1} = A \times 10^{-E_a/2.303(8.314\ \text{J K}^{-1})(300\ \text{K})} \qquad \text{(equation 2)}$$

Equating the values of A as solved from equations (1) and (2):

$$2.1 \times 10^{-11}\ \text{s}^{-1} \times 10^{+E_a/2.303(8.314\ \text{J K}^{-1})(300\ \text{K})} = 8.5 \times 10^{-11}\ \text{s}^{-1} \times 10^{+E_a/2.303(8.314\ \text{J K}^{-1})(300\ \text{K})} \quad \text{or}$$
$$2.1 \times 10^{-11}\ \text{s}^{-1} \times 10^{+E_a/5744} = 8.5 \times 10^{-11}\ \text{s}^{-1} \times 10^{+E_a/5936}.$$

Taking common logs of both sides gives:

$$(\log 2.1 \times 10^{-11}) + \frac{E_a}{5744} = (\log 8.5 \times 10^{-11}) + \frac{E_a}{5936} \quad -10.68 + \frac{E_a}{5744} = -10.07 + \frac{E_a}{5936}$$
$$E_a\left(\frac{1}{5744} - \frac{1}{5936}\right) = -10.07 + 10.68$$
$$E_a(1.741 \times 10^{-4} - 1.685 \times 10^{-4}) = 0.61$$
$$E_a = \frac{0.61}{0.056 \times 10^{-4}} = 109\ \text{kJ}$$

The value of A may be found from either equation (1) or (2). Using equation (1):

$$2.1 \times 10^{-11}\ \text{s}^{-1} = A \times 10^{-109{,}000/2.303(8.314)(300)} = A \times 10^{-18.98}$$

$$A = 2.1 \times 10^{-11}\ \text{s}^{-1} \times 10^{+18.91} = 2.1 \times 10^{-11}(9.55 \times 10^{18}\ \text{s}^{-1}) = 2.0 \times 10^{8}\ \text{s}^{-1}$$

The value of k at 47°C may be determined from the Arrhenius equation now that the values of E_a and A have been calculated:

$$k = A \times 10^{-E_a/2.303RT}$$
$$= 2.0 \times 10^{8}\ \text{s}^{-1} \times 10^{-109{,}000\ \text{J}/2.303(8.314\ \text{J K}^{-1})(320\ \text{K})}$$

$$= 2.0 \times 10^{8}\ \text{s}^{-1} \times 10^{-17.79} = 2.0 \times 10^{8}\ \text{s}^{-1}(1.62 \times 10^{-18}) = 3.2 \times 10^{-10}\ \text{s}^{-1}$$

Using the earlier value of $E_a = 108$ kJ, the calculated value of A is $1.3 \times 10^{8}\ \text{s}^{-1}$, and $k = 3.1 \times 10^{-10}\ \text{s}^{-1}$. Either answer is acceptable.

(b) Since this is a first-order reaction we can use the integrated form of the rate law to calculate the time that it takes for a reactant to fall from an initial concentration $[A]_0$ to some final concentration $[A]$:

$$\ln \frac{[A]_0}{[A]} - kt$$

At 27 °C.

$k = 2.1 \times 10^{-11}\ s^{-1}$.

In this case, the initial concentration is 0.150 M and the final concentration is $1.65 \times 10^{-7} M$. We can now solve for the time t:

$$\ln \frac{[0.150\ M]}{[1.65 \times 10^{-7}\ M]} = (2.1 \times 10^{-11}\ s^{-1})(t)$$

$$t = \frac{13.720}{2.1 \times 10^{-11}\ s^{-1}} = 6.5 \times 10^{11}\ s$$

or 1.81×10^{8} h or 7.6×10^{6} day. (c) Assuming that the reaction is irreversible simplifies the calculation because we do not have to account for any reactant that, having been converted to product, returns to the original state.