CHM202

Energetics and dynamics of chemical reactions

Solutions Assignment –VIII

Q.1 The catalytic decomposition of H_2O_2 is followed by removing equal volume samples at various time intervals and titrating them with $KMnO_4$. The results are

Time (min)	0	5	10	20
Volume of $KMnO_4$ (ml)	46.2	37.1	29.8	19.6

Find the order and determine the half-life time.

Sol.:

Let us first see whether it is first order or not. For first order reaction $K = \frac{1}{t} \ln \frac{a}{a-x}$

Since it is the reactant (H_2O_2) that reacts with $KMnO_4$, so volume of $KMnO_4$ required at any time is proportional to conc. of H_2O_2 present.

So, initial volume $V_0 \propto a$

and Volume required at time 't' $V_t \propto (a-x)$

So, $K = \frac{1}{t} \ln \frac{V_0}{V_t}$; Here $V_0 = 46.2$ ml

Putting $t = 5$ mins $\quad V_t = 37.1$ ml $\quad K = 0.043$ min^{-1}

" $t = 10$ " $\quad V_t = 29.1$ ml $\quad K = 0.046$ "

$t = 20$ " $\quad V_t = 19.6$ ml $\quad K = 0.043$ "

Since constant values are coming, given data fit well in the first order rate equation. Hence, the reaction is of first order with average rate constant $= 0.044\ min^{-1}$

Hence $t_{1/2} = \frac{0.693}{0.044} = 15.75$ min

Q.2 At 127 °C, the rate of decomposition of a gaseous compound initially at a pressure of 12.6 kPa, was 9.71 Pa s^{-1} when 10% had reacted and7.67 Pa s^{-1} when 20% had reacted. Determine the order of the reaction.

Sol:

The rate law is

$$v = k[A]^a \propto p^a = \{p_0(1-f)\}^a$$

where a is the reaction order, and f the fraction reacted (so that $1-f$ is the fraction remaining). Thus

$$\frac{v_1}{v_2} = \frac{\{p_0(1-f_1)\}^a}{\{p_0(1-f_2)\}^a} = \left(\frac{1-f_1}{1-f_2}\right)^a \quad \text{and} \quad a = \frac{\ln(v_1/v_2)}{\ln\left(\frac{1-f_1}{1-f_2}\right)} = \frac{\ln(9.71/7.67)}{\ln\left(\frac{1-0.100}{1-0.200}\right)} = \boxed{2.00}$$

Q.3 The rate constant for the first-order decomposition of a compound A in the reaction 2A → P is k = 2.78 × 10^{-7} s^{-1} at 25 °C. What is the half-life of A? What will be the pressure, initially 32.1 kPa, at (a) 10 s, (b) 10 min after initiation of the reaction?

Sol.: The rate law is

$$v = -\frac{1}{2}\frac{d[A]}{dt} = k[A]$$

Since the half-life time formula ($t_{1/2} = \frac{\ln 2}{k}$) is based on the assumption that

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

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

Where

$$k' = 2k$$

So

$$t_{1/2} = \frac{\ln 2}{2 \times 2.78 \times 10^{-7}\ s^{-1}} = 1.8 \times 10^6 s$$

As we modify the integrated rate law ($\ln\left(\frac{[A]}{[A]_0}\right) = -kt$, or $[A] = [A]_0 e^{-kt}$), noting that pressure is proportional to concentration:

$$p = p_0 e^{-2kt}$$

(a) Therefore, after 10 h, we have

$$p = (32.1\ \text{kPa}) \exp[-2 \times (2.78 \times 10^{-7}\ s^{-1}) \times (3.6 \times 10^4\ s)] = \boxed{31.5\ \text{kPa}}$$

(b) After 50 h,

$$p = (32.1\ \text{kPa}) \exp[-2 \times (2.78 \times 10^{-7}\ \text{s}^{-1}) \times (1.8 \times 10^5\ \text{s})] = \boxed{29.0\ \text{kPa}}$$

Q.4 At 100 °C, the gaseous reaction A → 2B + C is observed to be first order. Starting with pure A, it is found that at the end of 10 min the total pressure of the system is 176 mm of Hg and after a long time 270 mm. From these data find (a) the initial pressure of A, (b) the pressure of A at the end of 10 min, (c) the rate constant of the reaction and (d) half-life time.

Sol.: (a) The initial pressure of A

For a first order reaction, expression for rate constant (k) is $k = \frac{1}{t} \ln \frac{a}{a-x}$

For the gaseous reaction $A \rightarrow 2B + C$; initial moles of reactant i.e. $a \propto$ initial pressure (p°).

Since here one mole reactant is giving 3 moles products; so after a long time where the reaction is supposed to be almost complete, pressure will be three times the initial pressure.

As this pressure = 270 mm, so initial pressure $= \frac{270}{3}$

$= 90$ mm

(b) The pressure of A at the end of 10 min:

Now let at any time 't', x mole A decomposes and pressure becomes P_t.

Then at this time, no. of moles of $A = (a-x)$; of $B = 2x$ and of $C = x$; so total moles $= (a+2x)$

and $(a+2x) \propto P_t$

After 10 mins $P_t = 176$ mm

As $a \propto P_0$

So, $2x \propto (P_t - P_0)$ or $x \propto \frac{P_t - P_0}{2}$

i.e. $x \propto \frac{176-90}{2}$

i.e. $x \propto 43$, so pressure due to $A = (90-43)$ mm $= 47$ mm

(c) rate constant of the reaction and (d) half-life time:

after 10 mins. It is proportional to $(a-x)$.

Now, $K = \frac{1}{t} \ln \frac{a}{a-x}$

$K = \frac{1}{10} \ln \frac{90}{47} = 0.065 \text{ min}^{-1}$

Hence $t_{1/2} = \frac{0.693}{K} = \frac{0.693}{0.065} = 10.7 \text{ min.}$

Q.5 A reaction 2 A → P has a third-order rate law with k = 3.50×10^{-4} dm^6 mol^{-2} s^{-1}. Calculate the time required for the concentration of A to change from 0.077 mol dm^{-3} to 0.021 mol dm^{-3}.

Sol.:

The rate law is

$$v = -\frac{1}{2}\frac{d[A]}{dt} = k[A]^3$$

which integrates to

$$2kt = \frac{1}{2}\left(\frac{1}{[A]^2} - \frac{1}{[A]_0^2}\right) \quad \text{so} \quad t = \frac{1}{4k}\left(\frac{1}{[A]^2} - \frac{1}{[A]_0^2}\right),$$

$$t = \left(\frac{1}{4(3.50 \times 10^{-4}\,\text{dm}^6\,\text{mol}^{-2}\,\text{s}^{-1})}\right) \times \left(\frac{1}{(0.021\,\text{mol}\,\text{dm}^{-3})^2} - \frac{1}{(0.077\,\text{mol}\,\text{dm}^{-3})^2}\right)$$

$$= \boxed{1.5 \times 10^6\ \text{s}}$$

Q.6 Deduce an expression for the time it takes for the concentration of a substance to fall to one-third its initial value in an nth-order reaction.

Sol.:

A reaction nth-order in A has the following rate law

$$-\frac{d[A]}{dt} = k[A]^n \quad \text{so} \quad \frac{d[A]}{[A]^n} = -k\,dt = [A]^{-n}\,d[A]$$

Integration yields

$$\frac{[A]^{1-n} - [A]_0^{1-n}}{1-n} = -kt$$

Let $t_{1/3}$ be the time at which $[A] = [A]_0/3$,

$$\text{so } -kt_{1/3} = \frac{(\frac{1}{3}[A]_0)^{1-n} - [A]_0^{1-n}}{1-n} = \frac{[A]_0^{1-n}[(\frac{1}{3})^{1-n} - 1]}{1-n}$$

$$\text{and } t_{1/3} = \boxed{\frac{3^{n-1} - 1}{k(n-1)}[A]_0^{1-n}}$$

Q.7 The rate constant for the decomposition of a certain substance is 1.70×10^{-2} dm3 mol^{-1} s^{-1} at 24 °C and 2.01×10^{-2} dm^3 mol^{-1} s^{-1} at 37 °C. Evaluate the Arrhenius parameters of the reaction.

Sol.:

The rate constant is given by

$$k = A\exp\left(\frac{-E_a}{RT}\right) \quad [22.31]$$

so at 24 °C it is

$$1.70 \times 10^{-2}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1} = A\exp\left(\frac{-E_a}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times [(24+273)\,\text{K}]}\right)$$

and at 37 °C it is

$$2.01 \times 10^{-2}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1} = A\exp\left(\frac{-E_a}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times [(37+273)\,\text{K}]}\right)$$

Dividing the two rate constants yields

$$\frac{1.70 \times 10^{-2}}{2.01 \times 10^{-2}} = \exp\left[\left(\frac{-E_a}{8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}}\right) \times \left(\frac{1}{297\,\text{K}} - \frac{1}{310\,\text{K}}\right)\right]$$

$$\text{so } \ln\left(\frac{1.70 \times 10^{-2}}{2.01 \times 10^{-2}}\right) = \left(\frac{-E_a}{8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}}\right) \times \left(\frac{1}{297\,\text{K}} - \frac{1}{310\,\text{K}}\right)$$

$$\text{and } E_a = -\left(\frac{1}{297\,\text{K}} - \frac{1}{310\,\text{K}}\right)^{-1} \ln\left(\frac{1.70 \times 10^{-2}}{2.01 \times 10^{-2}}\right) \times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})$$

$$= 9.9 \times 10^3\,\text{J mol}^{-1} = \boxed{9.9\,\text{kJ mol}^{-1}}$$

With the activation energy in hand, the prefactor can be computed from either rate constant value

$$A = k\exp\left(\frac{E_a}{RT}\right) = (1.70 \times 10^{-2}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}) \times \exp\left(\frac{9.9 \times 10^3\,\text{J mol}^{-1}}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (297\,\text{K})}\right)$$

$$= \boxed{0.94\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}}$$

Q.8 The activation energy of one of the reactions in a biochemical process is 87 kJ mol^{-1}. What is the change in rate constant when the temperature falls from 37 °C to 15 °C?

Sol.:

From the Arrhenius equation we know that

$$\ln \frac{K_{r,2}}{K_{r,1}} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

E_a = activation energy $= 87\ \text{KJ mol}^{-1}$

$T_1 = (273+37)\text{K} = 310\ \text{K}$

$T_2 = (273+15)\text{K} = 288\ \text{K}$

$R = 8.314\ \text{J K}^{-1}\text{mol}^{-1}$

$$= \frac{87\ \text{KJ mol}^{-1}}{8.314\ \text{J K}^{-1}\text{mol}^{-1}}\left(\frac{1}{310} - \frac{1}{288}\right)$$

$$= \frac{87\times 10^3\ \text{J mol}^{-1}}{8.314\ \text{J K}^{-1}\text{mol}^{-1}}\left(\frac{288-310}{310\times 288}\right)$$

$$= \frac{87\times 10^3}{8.314}\times(-0.24\times 10^{-3})$$

$$= -2.511$$

$$\ln \frac{K_{r,1}}{K_{r,2}} = 2.511$$

$$\therefore \frac{K_{r,1}}{K_{r,2}} = e^{2.511} = 6.8256 \approx 7$$

$$\therefore K_{r,2} = \frac{K_{r,1}}{7}$$

So, when temp falls from 37°c to 15°c, the rate constant decreases seven times of initial rate constant.