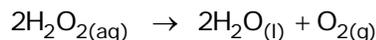


Session #23: Homework Solutions

Problem #1

The decomposition of hydrogen peroxide, H_2O_2 , can be represented by the following reaction:



The table below reports data taken at room temperature (300 K).

Table 1. Decomposition of $\text{H}_2\text{O}_{2(\text{aq})}$ at 300 K.

conc H_2O_2 (mol/liter)	time (seconds)
2.32	0
2.01	200
1.72	400
1.49	600
0.98	1200
0.62	1800
0.25	3000

- Show that the reaction is first order.
- Calculate the value of the half-life of this reaction.
- Suppose that the initial concentration of H_2O_2 were 3.5 M. How long would it take at 300 K to reduce the concentration of H_2O_2 to 25% of its initial value?

Solution

- (a) To show that the reaction is first order, try fitting the logarithm of concentration versus time. Least-squares analysis gives:

$$\ln c = 0.831 - 7.21 \times 10^{-4} t$$

with a correlation coefficient of 0.998.

(b) The half-life is given by $t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{7.21 \times 10^{-4}} = 961 \text{ s}$

- (c) To decrease the concentration to 25% of initial value would take 2 half-lives, since after $t_{1/2}$ the concentration would be 50% and after $2t_{1/2}$ it would be 50% of 50%. So the answer is $2 \times 961 \text{ s} = 1922 \text{ s}$.

Problem #2

A chemical reaction which has an activation energy of 167.0 kJ/mole is to proceed at $T = 450$ K with a very constant rate; the rate is allowed to vary at most by $\pm 1\%$. How constant must the temperature be to achieve this required rate stability? (For $T \gg \Delta T$, $T_1 \times T_2 = T^2$)

Solution

$$\frac{k_1}{k_2} = 1.02 = e^{\frac{E_A}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)}$$

$$\ln 1.02 = \frac{E_A}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) = \frac{E_A}{R} \left(\frac{T_1 - T_2}{T_1 \times T_2} \right) = \frac{E_A}{R} \left(\frac{\Delta T}{T^2} \right)$$

$$\ln 1.02 = \frac{E_A \Delta T}{RT^2}$$

$$\Delta T = \frac{R \times T^2 \times \ln 1.02}{E_A} = 2.0 \times 10^{-1} \text{ K} = \pm 0.1 \text{ K}$$

The required temperature stability is beyond the capabilities of conventional thermostats.

Problem #3

Determine the diffusivity D of lithium (Li) in silicon (Si) at 1200°C , knowing that $D_{1100^\circ\text{C}} = 10^{-5} \text{ cm}^2/\text{s}$ and $D_{695^\circ\text{C}} = 10^{-6} \text{ cm}^2/\text{s}$.

Solution

$$\frac{D_1}{D_2} = \frac{10^{-6}}{10^{-5}} = 10^{-1} = e^{-\frac{E_A}{R} \left(\frac{1}{968} - \frac{1}{1373} \right)}$$

$$E_A = \frac{R \ln 10}{\frac{1}{968} - \frac{1}{1373}} = 62.8 \text{ kJ/mole}$$

$$\frac{D_{1100}}{D_{1200}} = e^{-\frac{E_A}{R} \left(\frac{1}{1373} - \frac{1}{1473} \right)}$$

$$D_{1200} = 10^{-5} \times e^{\frac{E_A}{R} \left(\frac{1}{1373} - \frac{1}{1473} \right)} = 1.45 \times 10^{-5} \text{ cm}^2 / \text{sec}$$

Problem #4

For a chemical reaction, the concentrations of reactant as a function of time are given below for 25°C and for 50°C.

at 25°C

time (h)	conc. (mole/L)
.00	0.1039
3.15	0.0896
10.00	0.0639
13.50	0.0529
26.00	0.0270
37.30	0.0142

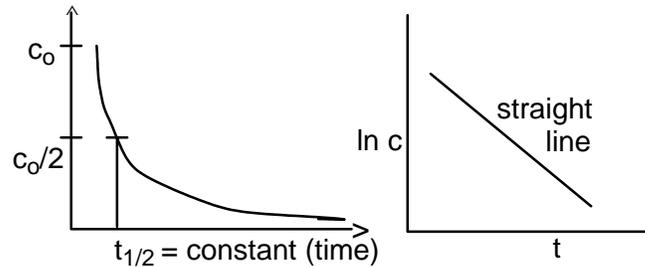
at 50°C

time (min)	conc. (mole/L)
0	0.1056
9	0.0961
18	0.0856
54	0.0536
105	0.0270
180	0.0089

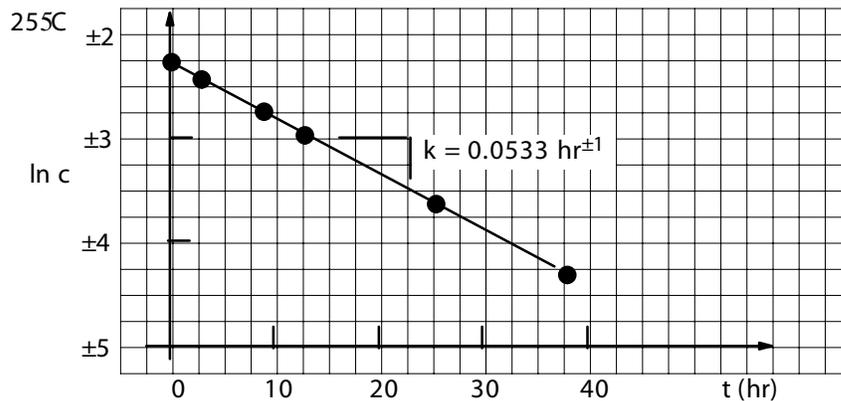
- (a) Indicate schematically (in two different graphic presentations) how you could prove, given concentration data at certain times, that a reaction is of first order.
- (b) Determine, from graphic presentations, the rate constants (k) for the given reaction at 25°C and 50°C.
- (c) Determine the half-life ($t_{1/2}$) for the reaction at 50°C.
- (d) Determine the half-life ($t_{1/2}$) for the reaction at 70°C.
- (e) What is the time required for the reaction at 25°C to be completed to the extent of 42%?

Solution

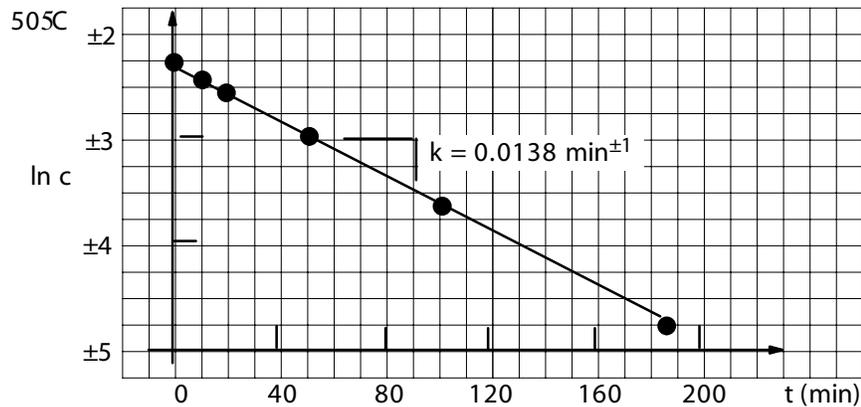
- (a) For the first order reactions:



- (b) at 25°C, $k = 0.0533 \text{ hr}^{-1}$



at 50°C, $k = 0.0138 \text{ min}^{-1}$



$$(c) t_{1/2} = \frac{\ln 2}{k} = \frac{\ln 2}{0.0138} = 50.2 \text{ min}$$

$$(d) k = A e^{\frac{-E_A}{RT}}$$

We need to determine A (and E_A):

$$\frac{k_{25}}{k_{50}} = e^{\frac{-E_A}{R} \left(\frac{1}{T_{25}} - \frac{1}{T_{50}} \right)}$$

$$k_{25} = 0.0533 \text{ hr}^{-1} \times \frac{1 \text{ hr}}{60 \text{ min}} = 8.88 \times 10^{-4} \text{ min}^{-1}$$

$$\ln \frac{k_{25}}{k_{50}} = \left(-\frac{E_A}{R} \right) \left(\frac{1}{T_{25}} - \frac{1}{T_{50}} \right)$$

$$E_A = \frac{-R \ln \left(\frac{k_{25}}{k_{50}} \right)}{\left(\frac{1}{T_{25}} - \frac{1}{T_{50}} \right)} = \frac{-8.3 \ln \left(\frac{8.88 \times 10^{-4}}{1.38 \times 10^{-2}} \right)}{\left(\frac{1}{298} - \frac{1}{323} \right)} = 87.7 \times 10^3 \text{ J/mole}$$

$$\text{At } 25^\circ\text{C: } k = A e^{\frac{-E_A}{RT}}$$

$$A = k e^{\frac{E_A}{RT}} = (8.88 \times 10^{-4}) e^{\left(\frac{8.77 \times 10^4}{8.31 \times 298} \right)}$$

$$A = 2.22 \times 10^{12} \text{ min}^{-1}$$

So, at 70°C (343 K):

$$k = A e^{\frac{-E_A}{RT}} = (2.22 \times 10^{12}) e^{\left(-\frac{8.77 \times 10^4}{8.31 \times 343} \right)} = 9.28 \times 10^{-2} \text{ min}^{-1}$$

and (finally!):

$$t_{1/2} = \frac{\ln 2}{k} = \frac{\ln 2}{9.28 \times 10^{-2} \text{ min}^{-1}} = 7.47 \text{ min}$$

(e) If the reaction is 42% complete, then 58% of the reactants remain. Therefore, $c = 0.58 c_0$.

$$c = c_0 e^{-kt} \rightarrow \ln \frac{c}{c_0} = -kt$$

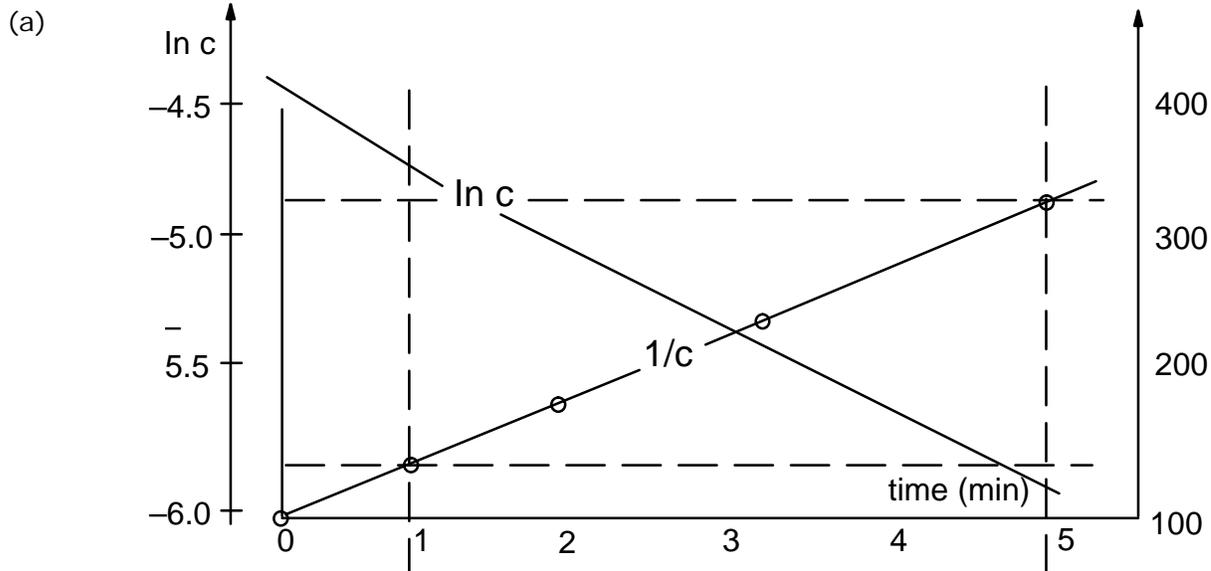
$$t = -\frac{\ln \frac{c}{c_0}}{k} = -\frac{\ln \left(0.58 \frac{c_0}{c_0} \right)}{0.0533 \text{ hr}^{-1}} = 10.22 \text{ hr} = 10 \text{ hr}, 13 \text{ min}, 12.1 \text{ sec}$$

Problem #5

In a chemical reaction the concentration of a rate-determining component is measured (in moles) at one minute intervals from zero to 5 minutes. The data are: 1.0×10^{-2} , 0.683×10^{-2} , 0.518×10^{-2} , 0.418×10^{-2} , 0.350×10^{-2} , and 0.301×10^{-2} .

- Determine the order (n) of this reaction.
- Determine the rate constant (k).
- Determine the half-life of this reaction.

Solution



The graph indicates that the $\ln c$ vs time plot yields almost a straight line, but the $1/c$ plot does yield a straight line. This identifies the reaction as a 2nd order reaction.

(b) The rate constant (k) is given by the slope of the $1/c$ vs time plot:

$$k = \frac{332-146}{5-1} = 46.5 \frac{1}{\text{mole} \times \text{min}}$$

(c) The half life of a second-order reaction (given in class) can be simply obtained from the second order rate equation. It is:

$$\tau_{1/2} = \frac{1}{k \times c_0} = \frac{1}{46.5 \times 10^{-2}} = 2.15 \text{ min}$$

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