Chemistry 225 Semester 01-2013
Homework for Submission #2

Answer the following questions and submit them for marking on or before 5 pm on Wednesday 13th February 2013 at the beginning of class. Only answers showing full working may attract full marks. Careless and sloppy work will be penalised. Express your answers to the correct number of significant figures. Make sure you include correct units where appropriate. *Answers showing evidence of copying will attract zero marks.*

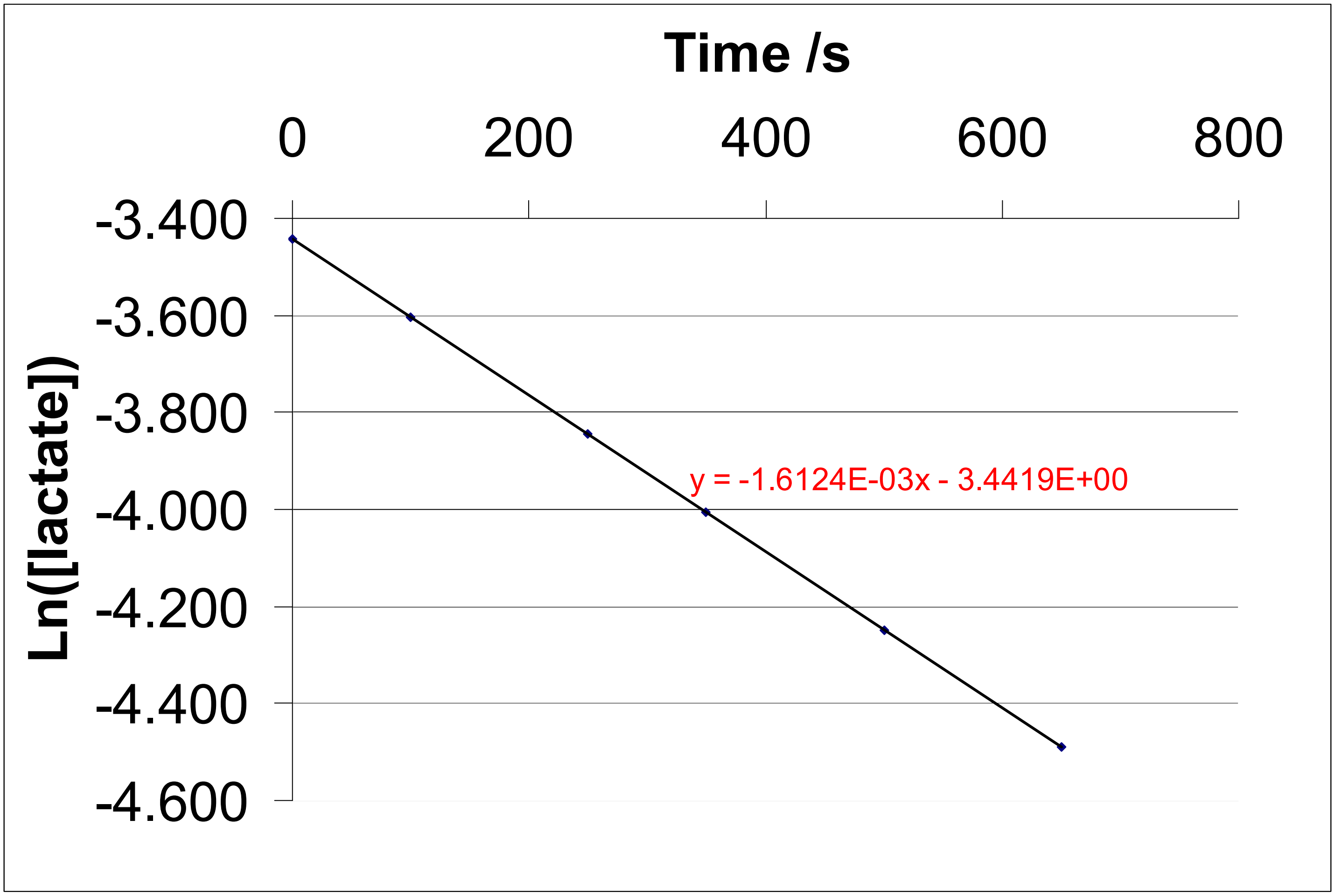
1) Lactate, ($CH_3CH(OH)COO^-$) is oxidised to pyruvate (CH_3COCOO^-) in the presence of a suitable enzyme. The following table gives the concentration of lactate at various times.

t/s	0	100	250	350	500	650
[lactate]/M	3.200×10^{-2}	2.724×10^{-2}	2.138×10^{-2}	1.821×10^{-2}	1.429×10^{-2}	1.122×10^{-2}

Use a spread-sheet program to plot the natural logarithm of the concentration of lactate against time

Solution

t/s	0	100	250	350	500	650
[lactate]/M	3.20E-02	2.72E-02	2.14E-02	1.82E-02	1.43E-02	1.12E-02
Ln([lactate])	-3.442	-3.603	-3.845	-4.006	-4.248	-4.490



and hence (a) suggest the order of reaction with respect to lactate giving your reasoning,

Solution

Since the graph of ln[reactant] against time is a straight line, the reaction is first order.

and (b) on this basis determine the rate constant for the reaction. (Submit your graph and full working.)

Solution

If the reactant is designated A, then the logarithmic form of the integrated rate equation is

$$\ln[A]_t = \ln[A]_0 - kt$$

which is the equation of a straight line if $\ln[A]_t$ is plotted against t.
The slope of the line in the graph is therefore –k. Hence $k = 1.6124\times10^{-3} \approx \underline{\underline{1.61\times10^{-3}\ s^{-1}\ \text{to 3.s.f.}}}$

c) Calculate the half-life for the reaction.

Solution

For a first order reaction

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

$$\therefore t_{\frac{1}{2}} = \frac{\ln 2}{1.6124\times10^{-3}} = 429.885\ldots \approx \underline{\underline{430\ s}}\ \text{to 3 s.f.}$$

d) Calculate the fraction of the original lactate remaining after 3 half-life periods from the start of the reaction.

Solution

After one half-life period, half of the original reactant remains. After a second half-life period, half of this remains. Since ½×½ = ¼, after two half-life periods, ¼ of the original reactant remains. After a third half life period, ½ of this remains. Since ½ of ¼ is ⅛, after three half-life periods, one eighth of the original reactant remains. (In general, the fraction remaining is given by $\{½\}^n$ where n is the number of half-life periods. $\{½\}^3 = ⅛$.)

e) Calculate the time taken for 10% of the lactate to decompose.

Solution

Since $\ln[A]_t = \ln[A]_0 - kt$

$$\ln[A]_t - \ln[A]_0 = -kt$$

$$\therefore \ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$$

If $[A]_0$ decreases by 10%, $[A]_t$ = 90% of $[A]_0$ = 0.9

$$[A]_t = 0.9\times[A]_0$$

$$\therefore \ln\left(\frac{0.9\times[A]_0}{[A]_0}\right) = -kt$$

$$\therefore \ln(0.9) = -kt$$

$$\therefore t = \frac{-\ln(0.9)}{k} = \frac{-\ln(0.9)}{1.6124\times10^{-3}}$$

$\therefore$ Time taken for 10% of original lactate to decompose $\underline{\underline{= 65.3\,s}}$

2) The half-life of carbon-14 is 5600 years. It gradually decays into nitrogen-14 by a first-order process, and each atomic disintegration gives rise to a β-particle which may be counted by a suitable counter. The

number of disintegrations per minute (cpm) as recorded by such a counter is proportional to the concentration of carbon-14 in a sample of wood. The wood from an Egyptian mummy case gives a reading of 9.5 cpm as compared with a fresh sample of wood which gives 15.0 cpm. Calculate the age of the case.

Solution

Since the decay process is first order, it is described by the first-order integrated rate equation:

$[A]_t = [A]_0 e^{-kt}$ which may also be written $\ln[A]_t = \ln[A]_0 - kt$

We may use either form, but if we start with the first, we first write

$$\frac{[A]_t}{[A]_0} = e^{-kt}$$

We note that if the counts-per-minute, cpm are proportional to the concentration of reactant (here carbon-14), then

$$\frac{[A]_t}{[A]_0} = \frac{9.5}{15} = 0.63333...$$

and since

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

$$k = \ln 2 / t_{1/2} = \frac{0.693147}{5600} = 1.23776 \times 10^{-4} ... yr^{-1}$$

$$\therefore 0.63333... = e^{-kt}$$

$$and \ \ln(0.63333...) = \ln(e^{-1.23776 \times 10^{-4} ... t})$$

$$\therefore -0.456758... = -1.23776 \times 10^{-4} ... t$$

$$\therefore t = \frac{-0.456758...}{-1.23776 \times 10^{-4} ...} = 3690.19... yr \approx \underline{\underline{3700\, yr}}\ to\ 2\ s.f.$$

This is the age of the mummy case.

3) The anti-cancer drug cisplatin, $Pt(NH_3)_2Cl_2$, is hydrolysed in aqueous solution according to the equation:

$$Pt(NH_3)_2Cl_2(aq) + H_2O(l) \rightarrow Pt(NH_3)_2(H_2O)Cl^+(aq) + Cl^-(aq)$$

The rate of the reaction increases by a factor of 15 on increasing the temperature from 25°C to 50°C. Estimate the activation energy for the reaction in kJ mol^{-1}.

Solution

At two different temperatures, T_1 and T_2, we may write

$$\ln k = \ln A - \frac{E_A}{RT}$$

$$\ln k_1 = \ln A - \frac{E_A}{RT_1} \ and \ \ln k_2 = \ln A - \frac{E_A}{RT_2}$$

$$Subtracting\ gives:$$

$$\ln k_1 - \ln k_2 = \ln A - \frac{E_A}{RT_1} - \ln A - \frac{E_A}{RT_2}$$

$$giving:$$

as

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

where k_1 is the rate constant at T_1 and k_2 is the rate constant at T_2. Note that the term in *A* disappears. Since the rate at the higher temperature is 15 times that at the lower temperature, and the variation of rate with temperature is concentrated in the rate constant, k_2 is 15 times larger than k_1. Therefore:

$$\frac{k_2}{k_1} = 15, \text{ and}$$

$$\frac{k_1}{k_2} = \frac{1}{15}$$

And so

$$\ln\left(\frac{1}{15}\right) = \frac{E_A}{8.31}\left(\frac{1}{273+50} - \frac{1}{273+25}\right)$$

$$\therefore E_A = 8.31 \times \ln\left(\frac{1}{15}\right) \div \left(\frac{1}{273+50} - \frac{1}{273+25}\right)$$

$$= 8.31 \times (-2.70805...) \div (-2.597295... \times 10^{-4})$$

$$= 8.66436... \times 10^4\ J\ mol^{-1} = 8.66436 \times 10^1\ kJ\ mol^{-1}$$

$$\approx \underline{\underline{87\ \text{kJ mol}^{-1}}} \text{ to 2 s.f.}$$

This is an estimate of the activation energy.

4) The reaction

$$\text{A} + \text{B} \rightarrow \text{C} + \text{D}$$

has the rate law:

$$\text{Rate} = \text{k[A][B]}$$

A student proposes the following mechanism:

i. $\text{A} + \text{B} \rightarrow \text{AB}$ … fast
ii. $\text{AB} \rightarrow \text{A} + \text{B}$ … fast
iii. $\text{AB} + \text{D} \rightarrow \text{CD} + \text{D}$ … slow
iv. $\text{CD} \rightarrow \text{C} + \text{D}$ … fast

The rate constants for the successive steps may be called k_i, k_{ii}, k_{iii}, and k_{iv}.

a) Determine the overall reaction suggested by the mechanism.
b) Derive the rate law suggested by the mechanism.
c) Identify a catalyst.
d) Identify a reactive intermediate.
e) Explain why the suggested mechanism is incorrect.

Solutions

a) The overall reaction is obtained by adding the forward steps of the mechanism. Since (ii) is a backward step, reversing (i), we ignore it. This gives

$$\text{A} + \text{B} + \text{AB} + \text{D} + \text{CD} \rightarrow \text{AB} + \text{CD} + \text{D} + \text{C} + \text{D}$$

Cancelling like terms gives:

$$\underline{\text{A} + \text{B} \rightarrow \text{C} + \text{D}}$$

b) Recall that the slow step in the mechanism is the rate-determining step, and so controls the rate of the overall reaction. Since it is an elementary step, the rate law corresponds to the stoichiometry: it is bimolecular, and so second order with rate law:

$$R_{iii} = k_{iii}[\text{AB}][\text{D}] \ \ldots (1)$$

But AB is not a reactant for the overall reaction, and so this is not a rate law for it. It is necessary to express [AB] in terms of the concentrations of the reactants of the overall reaction. We assume that since steps (i) and (ii) are almost in balance, so that $R_i \simeq R_{ii}$ but since these are elementary steps, we may write:

$$R_i = k_i[A][B] \text{ and } R_{ii} = k_{ii}[AB] \text{ and so}$$
$$k_i[A][B] = k_{ii}[AB]$$
$$[AB] = \frac{k_i[A][B]}{k_{ii}}$$

Substituting for [AB] in (1) above gives:

$$R_{iii} = k_{iii}\frac{k_i[A][B]}{k_{ii}}[D]$$

Recalling that R_{iii} is the rate of the overall reaction and substituting k for $k_{iii}\frac{k_i}{k_{ii}}$, we have:

$$\text{Rate} = k[A][B][D]$$

as the rate law suggested by the mechanism.

c) D is a catalyst. (D is also a product: such reactions are designated “autocatalytic”. They are slow at first, and then get faster as the product/catalyst is formed.)

d) AB is a reactive intermediate.

e) Since the observed rate law is not the same as the one suggested by the mechanism, the mechanism must be incorrect.