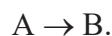


***Kinetics in Materials Science and Engineering 1st
edition Readey Solutions Manual***

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Chapter 2. Introduction to Kinetic Processes in Materials

- 2.1 The reaction rate constant for a zero order reaction for the decomposition of another liquid dissolved in water is given by $k = k_0 e^{-\frac{Q}{RT}}$ for the reaction



- a. Write the equation for the reaction rate for the decomposition of A .

Solution

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

- b. Give the units of k_0 if the units of the reactant concentration $[A]$ are millimol/cm³.

Solution

$$\text{units}[k_0] = \text{units}[k] = \text{units}\left[\frac{d[A]}{dt}\right]$$

$$\boxed{\text{units}[k_0] = \frac{\text{millimol}}{\text{cm}^3 \cdot \text{s}}}$$

- c. If $Q = 30$ kJ/mole and $k_0 = 10^{-2}$, calculate the reaction rate constant in millimol/liter at 25°F.

Solution

$$25^\circ\text{F} = (25 - 32) \times \frac{5}{9} = -3.9^\circ\text{C} = 273.15 - 3.9 = \boxed{269.25\text{K}}$$

$$\text{and } 1 \text{ millimol/cm}^3 = 1000 \text{ millimol/} \text{ or } \frac{\text{millimol}}{\text{cm}^3} \times \frac{1000 \text{cm}^3}{1} = 1000 \frac{\text{millimol}}{1}$$

$$\text{so } k_0 = 10 \frac{\text{millimol}}{1}. \text{ Therefore, } k = k_0 e^{-\frac{Q}{RT}} = 10 \times e^{-\frac{30,000}{8.314 \times 269.25}}$$

$$\text{or } \boxed{k = 1.51 \times 10^{-5} \text{ millimol/l}}$$

- d. Calculate how long it takes for the reaction to go to completion if $[A]_0$, the reactant concentration at time zero is one mole per liter.

Solution

For a zero order reaction, $[A] = [A]_0 - kt$ and one mole/liter = 1000 millimol/liter

so

$$t = \frac{[A]_0}{k} = \frac{1000 \text{ millimol/l}}{1.51 \times 10^{-5} \text{ millimol/l} \cdot \text{s}}$$

$$\boxed{t = 6.62 \times 10^7 \text{ s}}$$

Now the number of seconds in a year is approximately:

$$24 \text{ hr/day} \times 3600 \text{ s/hr} \times 365 \text{ day/yr} = \boxed{3.15 \times 10^7 \text{ s/yr}}$$

so it would take about two years for the reaction to go to completion.

- e. Neglecting any temperature effects on the density of water, which can be assumed to be 1.0 g/cm^3 , calculate the number of moles per cm^3 of water in pure water.

Solution

$$\frac{\rho(\text{g/cm}^3)}{M(\text{g/mol})} = \frac{1}{(2 \times 1.008 + 15.999)} = \boxed{5.55 \times 10^{-2} \text{ mol/cm}^3}$$

- f. Assuming that the molar volumes of water and the reactant are the same, calculate the m/o, w/o, and, v/o of A in water at 25°F at the start of the reaction if the molecular weight of the reactant is 60 g/mol.

Solution

From part e. above, the molar volume of water is

$$\frac{1}{5.55 \times 10^{-2} \text{ mol/cm}^3} = \boxed{18.02 \text{ cm}^3/\text{mol} = \bar{V}_{\text{H}_2\text{O}}}$$

and the molar volume of A is the same, $\bar{V}_A = 18.02 \text{ cm}^3/\text{mol}$. So the total volume stays the same with A is solution so

$$1 = n_A \bar{V}_A + n_{\text{H}_2\text{O}} \bar{V}_{\text{H}_2\text{O}}$$

and since $n_A = 0.001$, $n_{\text{H}_2\text{O}} = \frac{1}{18.02} - 0.001 = 0.0545$ moles and the total number of moles is $0.001 + 0.0545 = 0.0555$ moles. So,

$$\begin{aligned} (\text{m/o})_A &= \frac{0.001}{0.0555} \times 100 = \boxed{1.80} \\ (\text{m/o})_{\text{H}_2\text{O}} &= \frac{0.0545}{0.0555} \times 100 = \boxed{98.20} \end{aligned}$$

The results for the v/o are essentially the same since for 10^{-3} mol/cm^3 of A there is 0.018 cm^3 of A and $1 - 0.018 = 0.982 \text{ cm}^3$ of H_2O and the total volume is 1.0 cm^3 . So,

$$\begin{aligned} (\text{v/o})_A &= \frac{0.018}{1} \times 100 = \boxed{1.80} \\ (\text{v/o})_{\text{H}_2\text{O}} &= \frac{0.982}{1} \times 100 = \boxed{98.20} \end{aligned}$$

The results for the w/o are different due to the differences in molecular weights between water and A . In one cm^3 , there is $0.001 \times 60 \text{ g/mol} = 0.060 \text{ g}$. And weight

of water is the same 0.982 g for a total weight of 1.042 g. Therefore

$$(w/o)_A = \frac{0.060}{1.042} \times 100 = \boxed{5.76}$$

$$(w/o)_{H_2O} = \frac{0.982}{1.042} \times 100 = \boxed{94.24}$$

- 2.2 a. The reaction rate constant k ($k = k_0 e^{-\frac{Q}{RT}}$) for a first order reaction is $5.00 \times 10^{-3} \text{ s}^{-1}$ at 500°C and is 10.00 s^{-1} at 1000°C . Calculate the activation energy for this reaction.

Solution

There are several methods that can be used to solve this problem but,

since $k = k_0 e^{-\frac{Q}{RT}}$ a particularly simple method is to take the ratio of the two k values to eliminate k_0 :

$$\frac{k_1}{k_2} = \frac{k_0 e^{-\frac{Q}{RT_1}}}{k_0 e^{-\frac{Q}{RT_2}}} = e^{-\frac{Q}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)}.$$

Taking the natural logarithm of both sides of the equation and cancelling the k_0 s,

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

and rearranging, gives the result

$$Q = -\frac{R \ln \left(\frac{k_1}{k_2} \right)}{\left(\frac{1}{T_1} - \frac{1}{T_2} \right)} = -\frac{-8.314 \ln \left(\frac{5 \times 10^{-3}}{10} \right)}{\left(\frac{1}{773} - \frac{1}{1273} \right)}$$

$$\boxed{Q = 124.4 \text{ kJ / mole}}$$

- b. Calculate the pre-exponential term, k_0 , for the reaction rate constant and give its units.

Solution

$$k_0 = k_1 e^{\frac{Q}{RT}} = 5 \times 10^{-3} e^{\frac{124,400}{8.314 \times 773}}$$

$$\boxed{k_0 = 1.27 \times 10^6 \text{ s}^{-1}}$$

or

$$k_0 = k_2 e^{\frac{Q}{RT}} = 10 \times e^{\frac{124,400}{8.314 \times 1273}}$$

$$\boxed{k_0 = 1.27 \times 10^6 \text{ s}^{-1}}$$

- c. Calculate k at 750°C .

Solution

$$750^\circ\text{C} = 750 + 273 = 1023 \text{ K}$$

$$k = k_0 e^{-\frac{Q}{RT}} = 1.27 \times 10^{-6} e^{-\frac{124,400}{8.314 \times 1023}}$$

$$\boxed{k = 1.009 \text{ s}^{-1}}$$

- d. Calculate the relaxation time for this reaction at 750°C .

Solution

$$\text{The relaxation time, } \tau, \text{ is defined as } 1/k \text{ so } \tau = \frac{1}{k} = \frac{1}{1.009} = \boxed{0.991 \text{ s}}$$

- e. Calculate the half-life of this reaction.

Solution

The "half-life," $t_{1/2}$, is defined by $\frac{[A]}{[A]_0} = 0.5 = e^{-kt_{1/2}}$ so

$$t_{1/2} = -\frac{\ln 0.5}{k} = \frac{0.6931}{1.009}$$

$$t_{1/2} = 0.687\text{s}$$

f. Make a plot of $\log_{10}(\text{rate})$ vs $10^3/T$ (K^{-1}) from 100 °C to 1200 °C.

Solution

See Figure 2.1.

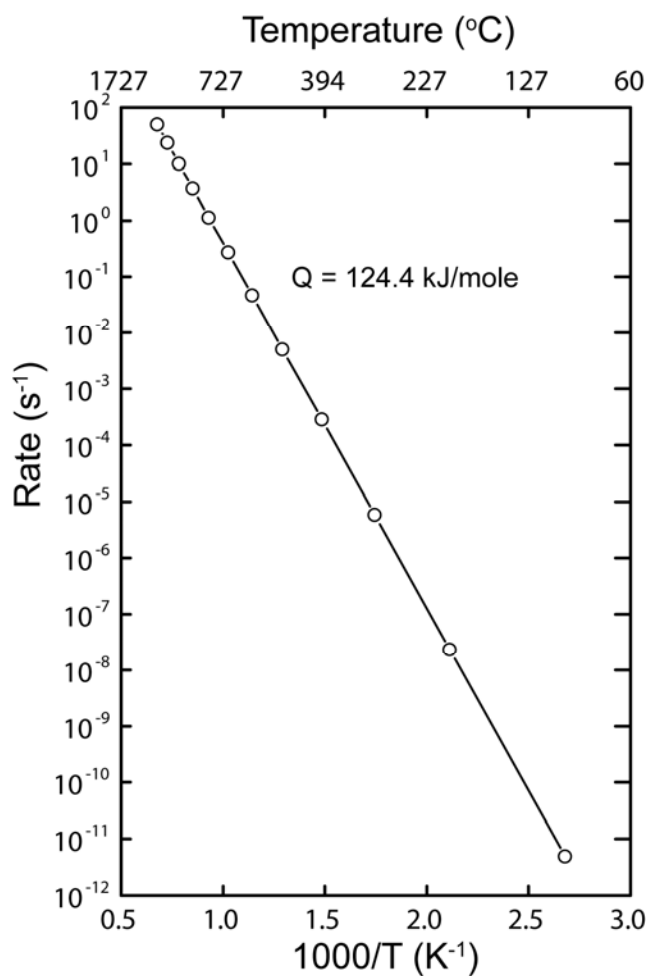


Figure 2.1 $\log_{10}(\text{rate})$ versus $1000/T$

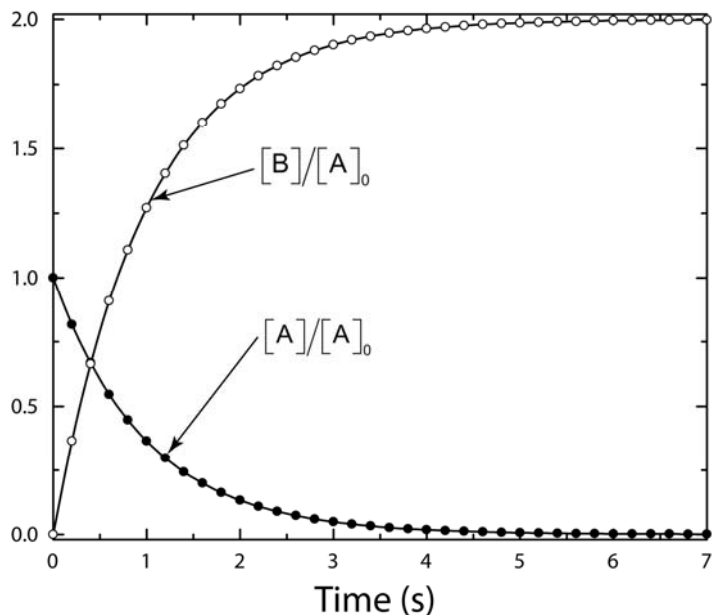


Figure 2.2 The amounts of reactant A and products B for a first order reaction at 750 °C

- g. Calculate how long it takes (hours) at 750°C for the unreacted fraction to be 0.001.

Solution

From part e. above,

$$t_{0.001} = -\frac{\ln 0.001}{k} = \frac{6.908}{1.009}$$

$$\boxed{t_{0.001} = 6.846\text{s} = 1.902 \times 10^{-3}\text{hr}}$$

- h. If the reaction is $A \rightarrow 2B$, plot the concentrations of A and B versus time from time zero up to the time that was calculated in g. above.

Solution

From the stoichiometry, $[B] = 2([A]_0 - [A]) = 2[A]_0(1 - e^{-kt})$. See Figure 2.2 for the plots of $[A]$ and $[B]$.

2.3 A well-known generalization (for back of the envelope calculations) for biochemical first order reactions near room temperature (300 K) is that their rates double for every 10 K rise in temperature.

a. Determine the activation energy (J/mol) for such reactions implied by this rule.

Solution

1. Take $\Delta T = T_1 - T_2 = 310 - 300 = 10$ K. So,

$$\frac{k_1}{k_2} = 2 = \frac{k_0 e^{-\frac{Q}{RT_1}}}{k_0 e^{-\frac{Q}{RT_2}}} = e^{-\frac{Q}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)}$$

and

$$Q = -\frac{R \ln 2}{\left(\frac{1}{T_1} - \frac{1}{T_2} \right)} = -\frac{8.314 \times \ln 2}{\left(\frac{1}{310} - \frac{1}{300} \right)}$$

$$\boxed{Q_1 = 53.6 \text{ kJ/mol}}$$

2. Take $\Delta T = T_1 - T_2 = 300 - 290 = 10$ K. In this case

$$Q = -\frac{8.314 \times \ln 2}{\left(\frac{1}{300} - \frac{1}{290} \right)}$$

$$\boxed{Q_2 = 50.1 \text{ kJ/mol}}$$

3. Finally, take $\Delta T = T_1 - T_2 = 305 - 295 = 10$ K and

$$Q = - \frac{8.314 \times \ln 2}{\left(\frac{1}{305} - \frac{1}{295} \right)}$$

$$\boxed{Q_3 = 51.9 \text{ kJ/mol}}$$

Obviously, the value of $\boxed{Q \cong 52 \text{ kJ/mole}}$ is about correct. Why not

take $\frac{dk}{dT} = k_0 e^{-\frac{Q}{RT}} \left(\frac{Q}{RT^2} \right) = k \left(\frac{Q}{RT^2} \right) \cong \frac{\Delta k}{\Delta T} = \frac{2k}{10}$? Solving this for Q ,

$$Q = \frac{2RT^2}{10} = \frac{2 \times 8.314 \times 300^2}{10} \cong 149 \text{ kJ/mol}$$

which is about a factor of three too

large because Δk is not small. However, if the natural logarithm of k were taken,

$$\ln k = \ln k_0 - \frac{Q}{RT}$$

$$\frac{d \ln k}{dT} = \frac{Q}{RT^2} \cong \frac{\Delta \ln k}{\Delta T} = \frac{\ln k_1 - \ln k_2}{\Delta T} = \frac{\ln(k_1/k_2)}{\Delta T}$$

then,

$$Q = \frac{RT^2 \Delta \ln k}{\Delta T} = \frac{8.314 \times 300^2 \times \ln 2}{10}$$

$$\boxed{Q = 51.9 \text{ kJ/mol}}$$

which is the same as in 1., 2., and 3.

- b. Calculate the value of the activation energy in eV/molecule.

Solution

Remember that $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J/atom}$ and $N_A = 6.022 \times 10^{23} \text{ atoms/mol}$,

so

$$1 \text{ eV} = 1.602 \times 10^{-19} (6.022 \times 10^{23})$$

$$\boxed{1 \text{ eV} = 96,472 \text{ J/mol}}$$

and

$$Q \cong \frac{51,900}{96,472}$$

$$\boxed{Q \cong 0.54\text{eV}}$$

roughly one-half of an electron volt.

- 2.4 a. The half-life for a first order reaction is 1000 seconds. Calculate the reaction rate constant (s^{-1}) for this reaction.

Solution

$$0.5 = e^{-kt_{1/2}} \text{ or } k = -\frac{\ln 0.5}{t_{1/2}} = \frac{0.693}{1000} \text{ and } \boxed{k = 6.93 \times 10^{-4} \text{s}^{-1}}$$

- b. Calculate the relaxation time (s) for this reaction.

Solution

$$\tau = 1/k = 1/(6.93 \times 10^{-4}) = \boxed{1.44 \times 10^3 \text{s}}$$

- 2.5 a. The half-life for a first order reaction is 1200 seconds. Calculate the reaction rate constant (s^{-1}) for this reaction.

Solution

$$0.5 = e^{-kt_{1/2}} \text{ or } k = -\frac{\ln 0.5}{t_{1/2}} = \frac{0.693}{1200} \text{ and } \boxed{k = 5.77 \times 10^{-4} \text{s}^{-1}}$$

- b. Calculate the relaxation time (s) for this reaction.

Solution

$$\tau = 1/k = 1/(5.77 \times 10^{-4}) = \boxed{1.73 \times 10^3 \text{ s}}$$

- c. Plot the fraction unreacted versus time for 0 to 10,000 seconds. Indicate the half-life and the relaxation time on your plot.

Solution

$$[A] = [A]_0 e^{-kt} \text{ so the fraction unreacted is given by } f_u = \frac{[A]}{[A]_0} = e^{-kt} = e^{-5.77 \times 10^{-4} t}.$$

The fraction unreacted versus time was calculated with a spreadsheet and is plotted in Figure 2.3.

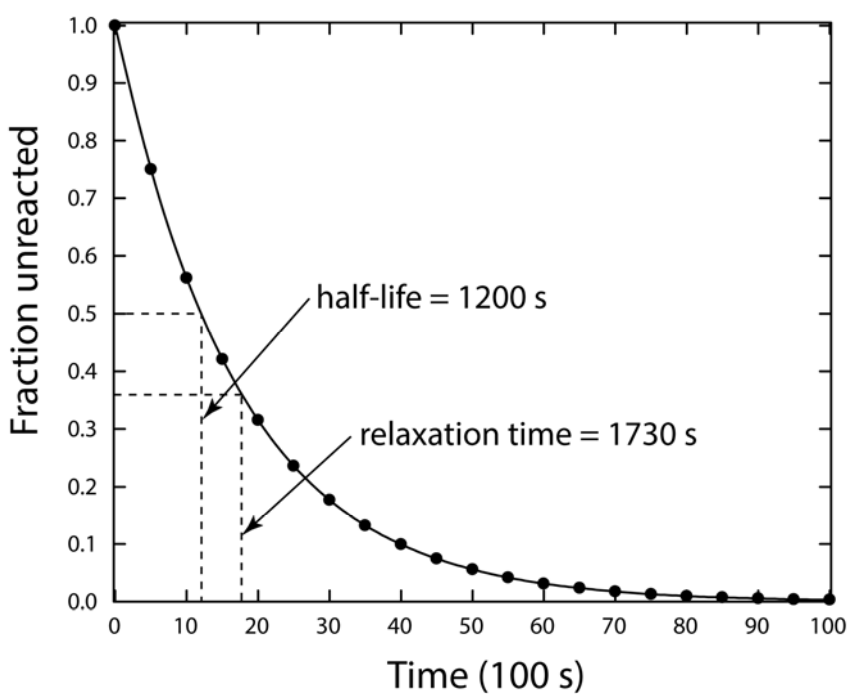
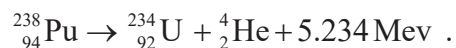


Figure 2.3 Fraction unreacted versus time for a first order reaction showing both the half-life and relaxation time.

- 2.6 a. Plutonium-238, $^{238}_{94}\text{Pu}$, spontaneously decays by alpha particle, ^4_2He , emission with a half-life of 86 years. The nuclear disintegration reaction is:



This disintegration rate is sufficiently fast to produce enough heat to be used as a power source in satellites. Calculate the first order reaction rate constant for the nuclear disintegration of plutonium-238.

Solution

$$k = -\frac{\ln 0.5}{t_{1/2}} = -\frac{\ln 0.5}{86} = 8.06 \times 10^{-3} \text{ yr}^{-1} \quad \text{However, the number of seconds per year}$$

$$\text{is } \text{s/yr} = 365 \text{ day/yr} \times 24 \text{ hr/day} \times 3600 \text{ s/hr} = \boxed{3.15 \times 10^7} . \quad \text{So } k \text{ is}$$

$$k = \frac{8.06 \times 10^{-3} \text{ yr}^{-1}}{3.15 \times 10^7 \text{ s} \cdot \text{yr}^{-1}} = \boxed{2.55 \times 10^{-10} \text{ s}^{-1}}$$

- b. Calculate the number of becquerels at time = 0 with one mole of plutonium-238.

Solution

1 becquerel = 1 disintegration/s so

$$kN_A = (2.55 \times 10^{-10} \text{ s}^{-1})(6.022 \times 10^{23} \text{ atom}) = \boxed{1.54 \times 10^{14} \text{ Bq}}$$

- c. Calculate the number of curies at time zero in one mole of pure $^{238}_{94}\text{Pu}$.

Solution

$$1 \text{ Ci} = 3.7 \times 10^{10} \text{ Bq} \quad \text{so the number of curies is } \frac{1.54 \times 10^{14} \text{ Bq}}{3.7 \times 10^{10} \text{ Bq/Ci}} = \boxed{4.16 \times 10^3 \text{ Ci}}$$

- d. Calculate the rate of energy generated in the plutonium-238 (watts) for one mole of plutonium-238 at time zero.

Solution

The energy per disintegration is 5.592 MeV. The rate of energy generation is therefore $(5.592 \times 10^6 \text{ eV})(1.602 \times 10^{-19} \text{ J/eV})(1.54 \times 10^{14} \text{ s}^{-1}) = \boxed{138 \text{ W}}$

- e. Calculate how long (years) it will take for the rate of energy generation to drop to 10 percent of its initial value.

Solution

The fraction unreacted is given by $f_u = e^{-kt}$ so

$$t = -\frac{\ln 0.9}{(2.55 \times 10^{-10} \text{ s}^{-1})(3.15 \times 10^7 \text{ s} \cdot \text{yr}^{-1})} = \boxed{13.1 \text{ yr}}$$

- f. If the $^{238}_{94}\text{Pu}$ were in the form of PuO_2 rather than pure plutonium, calculate the number of curies in 5 cm^3 of PuO_2 at time zero if the density of PuO_2 is 11.5 g/cm^3 .

Solution

The molecular weight of PuO_2 is $M = 238 + 2 \times 16 = 270 \text{ g/mol}$. The weight of 5 cm^3 of PuO_2 is $5 \text{ cm}^3 \times 11.5 \text{ g/cm}^3 = 57.5 \text{ g}$ which is $\frac{57.5 \text{ g}}{270 \text{ g/mol}} = 0.213 \text{ mol}$. Now

there is one mole of Pu per mole of PuO_2 so that, from part b., the number of disintegrations per mole per second is 1.54×10^{14} . So the number of curies in the 5 cm^3 of PuO_2 is $(1.54 \times 10^{14} \text{ Bq/mol})(0.213 \text{ mol})(1/3.7 \times 10^{10} \text{ Bq/Ci}) = \boxed{886.5 \text{ Ci}}$

- g. Calculate the number of watts that this 5 cm^3 of $^{238}_{94}\text{Pu}$ -containing PuO_2 generates.

Solution

From part d., the number of watts per mole is 138 W so the number of watts from 5 cm^3 of PuO_2 is $138 \text{ W/mol} \times 0.213 \text{ mol} = \boxed{29.4 \text{ W}}$

- h. If this 5 cm^3 of PuO_2 were perfectly insulated, calculate how long it takes (hours) for the 5 cm^3 of PuO_2 to reach its melting point of 2390°C if its molar heat capacity is $75 \text{ J/mole}\cdot\text{K}$.

Solution

$P(\text{W})t(\text{s}) = n(\text{mol})C_p(\text{J/mol}\cdot\text{K})\Delta T(\text{K})$ Assume that the starting temperature is

$$25^\circ\text{C} = 298 \text{ K so that } t = \frac{(0.213 \text{ mol})(75 \text{ J/mol}\cdot\text{K})(2390 - 278) \text{ K}}{(29.4 \text{ W})(3600 \text{ s/hr})} = \boxed{0.316 \text{ hr}}$$

not much time at all! Of course, heat will be lost by convection, conduction, and radiation and some steady-state temperature will be reached well below the melting point of PuO_2 .

- 2.7 A reaction obeys the stoichiometric equation:



The rates of formation of Z at various concentrations of A and B are given in the following table.

<u>[A] (mol/l)</u>	<u>[B] (mol/l)</u>	<u>rate (mol/l-s)</u>
2.00×10^{-2}	4.20×10^{-2}	3.53×10^{-9}
6.50×10^{-2}	4.80×10^{-2}	4.87×10^{-8}
1.10×10^{-1}	1.22×10^{-1}	9.00×10^{-7}

Determine the values of α , β , and k in the rate equation: $\text{rate} = k [A]^\alpha [B]^\beta$. Give the units for k as well. You may use programs such as Excel, Mathematica, etc., or by hand to get the solution. Just clearly indicate what operations were performed: i.e. copy that part of the Excel spreadsheet or the Mathematica page that shows the calculations.

Solution

There are three nonlinear equations and three unknowns, α , β , and R ($R = \text{rate}$) in the form of $R = k [A]^\alpha [B]^\beta$. Taking the logarithm of both sides of each equation gives three linear equations $\ln R_i = \ln k + \alpha \ln [A]_i + \beta \ln [B]_i$ with $i = 1, 2$, and 3 and these are

$$\begin{aligned}\ln(3.53 \times 10^{-9}) &= \ln k + \alpha \ln(2.00 \times 10^{-2}) + \beta \ln(4.20 \times 10^{-2}) \\ \ln(4.87 \times 10^{-8}) &= \ln k + \alpha \ln(6.50 \times 10^{-2}) + \beta \ln(4.80 \times 10^{-2}) \\ \ln(9.00 \times 10^{-7}) &= \ln k + \alpha \ln(1.10 \times 10^{-1}) + \beta \ln(1.22 \times 10^{-1})\end{aligned}$$

and become the following by taking the logarithms and letting $\gamma = -\ln k$

$$\begin{aligned}19.462 &= \gamma + 3.912\alpha + 3.170\beta \\ 16.838 &= \gamma + 2.733\alpha + 3.037\beta \\ 13.921 &= \gamma + 2.207\alpha + 2.104\beta\end{aligned}\tag{2.1}$$

and these three equations can be solved in a number of ways.

The Hard Way to Solve

Subtracting the second equation from the first gives

$$2.624 = 1.179\alpha + 0.133\beta \quad (2.2)$$

and the third from the second

$$2.917 = 0.526\alpha + 0.933\beta$$

and multiplying the last equation by 2.624 and dividing by 2.917 gives

$$2.624 = 0.473\alpha + 0.839\beta \quad (2.3)$$

and subtracting Eq.(2.3) from Eq. (2.2) gives

$$0 = 0.706\alpha - .706\beta$$

or $\boxed{\alpha = \beta}$. Substitution in Eq. (2.2) gives $\boxed{\alpha = \beta = 2.0}$ and substitution in Eq.

(2.3) also gives $\boxed{\alpha = \beta = 2.0}$. The value of k can be obtained from any one of the

three equations in Eq.(2.1)

$$19.462 = \gamma + (3.912 + 3.170)2$$

$$16.838 = \gamma + (2.733 + 3.037)2$$

$$13.921 = \gamma + (2.207 + 2.104)2$$

which give

$$\gamma = 5.298$$

$$\gamma = 5.298$$

$$\gamma = 5.299$$

$$\text{so } k = e^{-5.298} = \boxed{5.00 \times 10^{-3} \text{ mol}^3/\text{l}^3 \cdot \text{s}}.$$

Easier Way: Matrix Inversion in Excel®

Solution by Matrix Inversion in Excel

The natural logarithms of the equations must be taken to linearize:

ie. $\alpha \ln[A] + \beta \ln[B] + z \ln k = \ln(\text{rate})$

3.91202	-3.17009	1	-19.4625	2.00	alpha
2.73337	-3.03655	1	-16.8382	2.00	beta
2.20727	-2.10373	1	-13.9203	-5.29832	lnk
Determinant			1.029223	≠ 0	so OK
alpha =	2				
beta =	2				
k =	5.00E-03				

Easiest Way: solve with Mathematica®

```
In[1]:= Solve[{-3.912023 α - 3.170086 β + z = -19.46253, -2.733368 α - 3.036554 β + z = -16.83816,
-2.207275 α - 2.103734 β + z = -13.92034}, {α, β, z}]
```

```
Out[1]= {{α → 2., β → 2., z → -5.29834}}
```

```
In[2]:= e^(-5.29834)
```

```
Out[2]= 0.00499989 = k
```

- 2.8 In 2012, what were thought to be the bones of King Richard III of England were found under a parking lot in England and later confirmed by DNA evidence in 2014 that the bones were indeed his. The bones were dated by radiocarbon dating and confirmed that the date of death of the skeleton was 1485, the date of death of the king. Calculate the ratio of carbon-14 remaining in the bones.

Solution

For radiocarbon dating,

$$\frac{\left[{}^{14}_6\text{C} \right]}{\left[{}^{14}_6\text{C} \right]_0} = e^{-1.21 \times 10^{-4} t}$$

where Units(t) = yr. So $(2016 - 1485) = 531 \text{ yr}$. Therefore,

$$\frac{\left[{}^{14}_6\text{C} \right]}{\left[{}^{14}_6\text{C} \right]_0} = e^{-1.21 \times 10^{-4} \times 531} = \boxed{0.938}$$

- 2.9 If the number of disintegrations per minute per gram of carbon produced by pyrolyzing a piece of recently cut wood is 12.5 dis/min-g, calculate the fraction of ^{14}C in carbon of age zero if the half-life of ^{14}C is 5730 years. (The wood is assumed to have an age of zero.)

Solution

The number of disintegrations per second is given by,

$$\frac{dm^*}{dt} = km^*$$

where m^* is the amount of radioactive carbon. Now

$$k = \frac{1.21 \times 10^{-4} \text{ yr}^{-1}}{(365 \text{ day/yr})(24 \text{ hr/day})(60 \text{ min/hr})} = 2.302 \times 10^{-10} \text{ min}^{-1} \quad \text{So}$$

$$m^* = \left(\frac{dm^*}{dt} \right) \left(\frac{1}{k} \right) = \frac{12.5}{2.302 \times 10^{-10}} = 5.30 \times 10^{10}$$

^{14}C atoms per gram. Now, $M(\text{C}) = 12.01 \text{ g/mol}$ so 1 gram of carbon contains $1/12.01 = 8.33 \times 10^{-2} \text{ mol}$ of carbon or

$$N_A \times 8.33 \times 10^{-2} = (6.022 \times 10^{23})(8.33 \times 10^{-2}) = 5.014 \times 10^{22} \text{ atom/g}$$

so the fraction of ^{14}C is $\frac{5.30 \times 10^{10}}{5.014 \times 10^{22}} = \boxed{1.06 \times 10^{-12}}$ or about one part per trillion!