

9.E: Chemical Kinetics (Exercises)

9.1: Reaction Rates

Q9.1

Write the rate of reaction in terms of the rate of disappearance of reactant and the rate of formation of products:

- $NO_{(g)} + O_{3(g)} \rightarrow NO_{2(g)} + O_{2(g)}$
- $2C_2H_{6(g)} + 7O_{2(g)} \rightarrow 4CO_{2(g)} + 6H_2O_{(aq)}$
- $H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)}$
- $4OH_{(g)} + H_2S_{(g)} \rightarrow SO_{2(g)} + 2H_2O_{(aq)} + H_{2(g)}$

S9.1

- rate of reaction = $\frac{-\Delta[NO]}{\Delta t} = \frac{-\Delta[O_3]}{\Delta t} = \frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$
- rate of reaction = $\frac{-\Delta[C_2H_6]}{2\Delta t} = \frac{-\Delta[O_2]}{7\Delta t} = \frac{\Delta[CO_2]}{4\Delta t} = \frac{\Delta[H_2O]}{6\Delta t}$
- rate of reaction = $\frac{-\Delta[H_2]}{\Delta t} = \frac{-\Delta[I_2]}{\Delta t} = \frac{\Delta[HI]}{2\Delta t}$
- rate of reaction = $\frac{-\Delta[OH]}{4\Delta t} = \frac{-\Delta[H_2S]}{\Delta t} = \frac{\Delta[SO_2]}{\Delta t} = \frac{\Delta[H_2O]}{\Delta t} = \frac{\Delta[H_2]}{\Delta t}$

9.2: Reaction Order

Q9.2

Determine the value of the rate constant for the elementary reaction:



given that when $[Br_2]$ is 0.15 M and $[H_2]$ is 0.2M, the rate of reaction is 0.005 M s^{-1} at 298 K.

S9.2

$$\begin{aligned} \text{rate of reaction} &= k[Br_2][H_2] \\ 0.005 \text{ Ms}^{-1} &= k(0.15\text{M})^2(0.2\text{M}) \\ k &= 1.11 \text{ M}^{-1}\text{s}^{-1} \end{aligned}$$

Q9.3

Given the rate of the third order reaction:



is 0.05 Ms^{-1}

If the $[A] = 0.05 \text{ M}$, $[B] = 0.01\text{M}$, and $[C] = 0.25\text{M}$. What is the third order rate constant?

S9.3

$$\begin{aligned} \text{rate of reaction} &= k[A][B][C] \\ 0.05\text{Ms}^{-1} &= k(0.05\text{M})(0.01\text{M})(0.25\text{M}) \\ k &= 0.05\text{Ms}^{-1}/(0.05)(0.01)(0.25) \text{ M}^3 \\ k &= 400\text{M}^{-2}\text{s}^{-1} \end{aligned}$$

Q9.3

What are the units of the rate constant for a second-order reaction?

S9.3

The reaction rate:

$$Rate = \frac{d[A]}{dt} = -k[A]^2 \quad (9.E.3)$$

The rate constant of a second-order reaction, k , is $M^{-1}min^{-1}$ or $M^{-1}s^{-1}$

Q9.4

Calculate the fraction of the starting quantity of A that will be used up after 60 s. Given the reaction below which is found to be the first order in A and $t_{1/2} = 40 \text{ s}$



S9.4

with $(t_{1/2} = 40 \text{ s})$

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{40} = 0.0173s^{-1}$$

The remain of fraction A after 60 s:

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

$$\frac{[A]}{[A]_0} = e^{-(0.0173s^{-1})(60s)} = 0.354$$

The fraction will be used up after 60s:

$$1 - 0.354 = 0.646$$

Q9.5

Given the first order reaction is completed 90% in 30 mins at 298 K. Calculate the rate constant.

S9.5

$$90\% = 0.9$$

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

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

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

$$\ln 0.9 = -30k$$

$$k = -\frac{\ln 0.9}{30} = 0.00351min^{-1}$$

Q9.6

Assume the half life of the first order decay of radioactive isotope takes about 1 year (365 days). How long will it take the radioactivity of that isotope to decay by 60%?

S9.6

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

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{365} = 0.00189day^{-1}$$

60% is lost

100% - 60% = 40% is remained

$$40\% = 0.4$$

$$\frac{[A]}{[A]_0} = 0.4$$

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

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

$$t = \frac{-1}{k} \ln \frac{[A]}{[A]_0} = \frac{-1}{0.00189} \ln 0.4 = 484.81 \text{ days}$$

Q9.7a

The decomposition of dinitrogen peroxide (N_2O_5) is a first-order reaction with a rate constant of 0.045 min^{-1} at 300 K.



If there were initially 0.040 mol of N_2O_5 , calculate the moles of N_2O_5 remaining after 5 minutes.

S9.7a

The integrated rate equation of a first-order reaction is:

$$[A] = [A]_0 e^{-kt} \quad (9.E.6)$$

Substituting concentration for moles of reactant and plugging in the known values:

$$n_A = 0.040 e^{-0.045 \times 5} \quad (9.E.7)$$

$$n_A = 0.032 \quad (9.E.8)$$

Q9.7b

You forgot to do your lab assignment the day before and realize you only have 5 hours to reduce your initial concentration of your reactant by 90%. You know the half life is 2 hours and before you get out of bed, you wonder if you can even finish the lab on time. Assuming you have a first order reactant, will 5 hours be enough time for your compound to reduce by 90%?

S9.7b

First, you need to figure the half life of your compound. We do this by solving for **k**:

$$t_{1/2} = \frac{0.693}{k} \quad (9.E.9)$$

$$k = \frac{0.693}{t \frac{1}{2}} \quad (9.E.10)$$

$$k = \frac{0.693}{2 \text{ hrs}} = 0.3465 \quad (9.E.11)$$

with this half life, we can find the time it will take by solving for **t**:

$$\ln \frac{[A]}{[A]_0} = -kt \quad (9.E.12)$$

We do not have the initial and final concentration, but that is okay.

Assuming the initial concentration is 100 g, we can assume that the final concentration is 10 g because that would be reduced 90% as stated in the problem.

$$\ln \frac{[10]}{[100]} = -kt \quad (9.E.13)$$

$$\frac{\ln[0.1]}{-0.3465} = t = 6.65 \text{ hours} \quad (9.E.14)$$

So 5 hours will be definitely not enough time to reduce the compound

Q9.8a

Assume you are dealing with a first order reactant. You know your rate constant is $1.5 \times 10^{-4}/\text{min}$, but your employer wants to the half-life of the reactant?

S9.8a

$$t_{1/2} = \frac{0.693}{k} \quad (9.E.15)$$

$$t_{1/2} = \frac{0.693}{1.5 \times 10^{-4}} \quad (9.E.16)$$

$$= 4.62 \times 10^3 \text{ mins} \quad (9.E.17)$$

Q9.8b

The half-life of a second order reaction



is given by:

$$t_{1/2} = \frac{1}{k[A]_o} \quad (9.E.19)$$

Calculate the half-life of a reaction with initial reactant concentration $[A] = 0.90 \text{ M}$ and a rate constant of $0.20 \text{ M}^{-1} \text{ min}^{-1}$.

S9.8b

$$t_{1/2} = \frac{1}{0.20 \times 0.90} = 0.18 \text{ min}^{-1} \quad (9.E.20)$$

Q9.9a

A reaction



is observed. You do not know the stoichiometry of the reactants or products, but observe that when you increase the initial concentration of A from 0.4 M to 0.8 M, the half-life decreased from 10 minutes to 5 minutes. Determine the reaction order and the rate constant.

S9.9a

A reaction whose half-life changes when the reactant concentration is changed is a second-order reaction.

$$t_{1/2} = \frac{1}{k[A]_o} \quad (9.E.22)$$

$$k = \frac{1}{[A]_o t_{1/2}} \quad (9.E.23)$$

$$k = \frac{1}{(0.4 \text{ M})(5 \text{ min})} = 0.5 \text{ M}^{-1} \text{ min}^{-1} \quad (9.E.24)$$

Q9.9b

You notice the initial concentration has no affect on the half-life. From this information alone, what can you determine about the the order of the reactant?

S9.9b

You can determine from this information that it would be a first order reactant. The concentration of first order reactants has not affect on the rate or half-life of the reactant. This can be seen in the formula. $t_{1/2} = \frac{0.693}{k}$ This formula does not account for the initial concentration of the reactant.

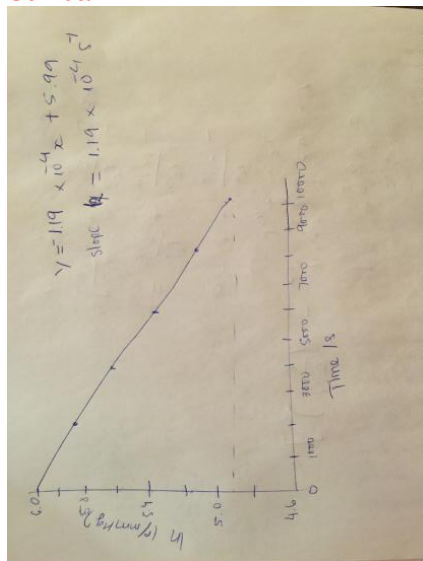
Q9.10a

Calculate the order of the reaction and the rate constant of Cytobutane decompose to ethylene based on equation



and temperature at 215°C, constant volume, the pressure 200, 158, 124, 98, 77.5, 61 mmHg.

S9.10a



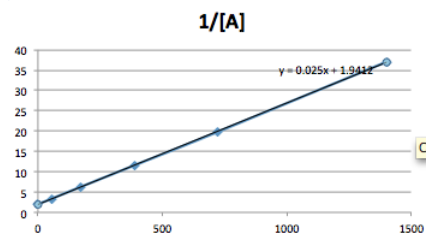
Q9.10b

Given the following data of concentration [A] over a period of time, decide if the data represents first order or second order. Solve for K. Show graphs.

| Time | [A] |
|------|-------|
| 0 | 0.5 |
| 54 | 0.3 |
| 171 | 0.16 |
| 390 | 0.08 |
| 720 | 0.05 |
| 1400 | 0.027 |

S9.10b

The data best fits a Second order graph.



The equation for a second order reaction is:

$$\frac{1}{[A]} = kt + \frac{1}{[A_0]}$$

When solving for K, the equation is rearranged to:

$$\frac{1}{[A]} - \frac{1}{[A_0]} = kt$$

t

Plug in the numbers given:

$$\frac{1}{[.3]} - \frac{1}{[.5]} = k$$

(0-54)

.025=k

One, can also obtain the slop of the graph and k=.025

Q9.11a

If a compound's $\frac{1}{2}$ life is 15.6 days. What is the value of k? How long will it take to decompose to 10%. Use first order reaction.

S9.11a

Equation for half-life of a First-Order Reaction is:

$$t_{\frac{1}{2}} = \frac{\ln(2)}{k} \quad (9.E.25)$$

If we plug in the information given:

$$15.6 \text{ days} = \frac{\ln(2)}{k} \quad (9.E.26)$$

$$k = 4.4 \times 10^{-2} \text{ day}^{-1} \quad (9.E.27)$$

The second equation needed is the first order reaction, which is:

$$\ln([A]/[A_0]) = -kt_{1/2}$$

so, $\ln([A]/[A_0]) = .1$

$t = -1/k \times \ln([A]/[A_0])$

$t = -1/(4.4 \times 10^{-2} \text{ day}^{-1}) \times (.1)$

$t = 52 \text{ days}$

12) In a second order reaction $2A \rightarrow \text{products}$, the final concentration is .28M. What is the initial concentration if $k = .32 \text{ M}^{-1}\text{s}^{-1}$ and the times is 5 seconds.

Solution:

Second order reaction equation is:

$$1/[A] = kt + 1/[A_0]$$

Filling the information given:

$$1/[\text{.28M}] = .32 \text{ M}^{-1}\text{s}^{-1}(5) + 1/[A_0]$$

$$1/[A_0] = 1.97$$

$$[A_0] = .50 \text{ M}$$

Q9.11b

Calculate the half life of a compound if 90% of a given sample of the compound decomposed in 30min

S9.11b

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

$$[A]_0 = 90\%$$

$$[A] = 10\%$$

$$t = 30 \text{ min} \times 60 \text{ s}/1 \text{ min} = 1800 \text{ s}$$

$$[10\%]/[90\%] = e^{-k \cdot 1800}$$

$$\ln[10\%/90\%]/1800 = k = 3.95 \times 10^{-4}$$

$$t_{1/2} = \ln(2)/k$$

$$t_{1/2} = .693/3.95 \times 10^{-4} = 1754 \text{ s}$$

$$1754s * 1\text{min}/60s = 29 \text{ min}$$

Q9.12

Given rate constant for second order reaction



is $1.08 \text{ M}^{-1}\text{s}^{-1}$ at 600°C . Find the time that would take for the concentration of NO_2 from 1.24 M to 0.56 M?

S9.12

$$\begin{aligned} 1/[A] - 1/[A]_0 &= kt \\ t &= 1/k (1/[A] - 1/[A]_0) \\ &= (1/1.08 \text{ M}^{-1}\text{s}^{-1}) (1/0.56 - 1/1.24) = 7.2 \text{ s} \end{aligned}$$

Q9.13a

Is which order of reaction half-life is independent of initial concentration?

S9.13a

First order because the half-life equation for first order is

$$t_{1/2} = \ln(2)/k, \text{ it does not have } [A]_0$$

Q9.13b

The decomposition of N_2O is the first order. At 365°C , $t_{1/2}$ is $1.79 \times 10^3 \text{ min}$. given initial pressure of 1.05 atm.. Calculate total pressure.

S9.13b

$$\begin{aligned} P &= P_{N_2O} + P_{N_2} + P_{O_2} \quad (9.E.29) \\ &= 0.525 + 0.525 + 0.2625 = 1.31 \text{ atm} \quad (9.E.30) \end{aligned}$$

Q9.14a

The integrated rate law for the zero-order reaction $A \rightarrow B$ is $[A]_t = [A]_0 - kt$

a) sketch the following plots:

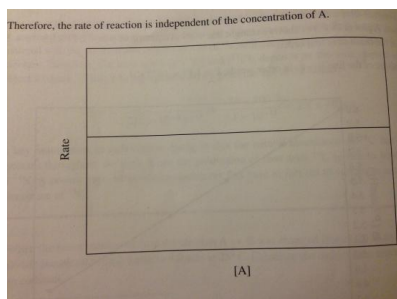
(i) rate vs. $[A]$

(ii) $[A]$ vs. t

S9.14a

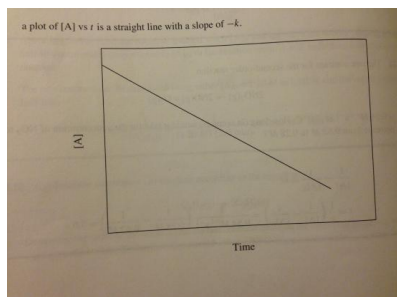
rate = k

rate is independent of $[A]$



(ii) $[A]$ vs. t

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



b) Derive an expression for the half-life of the reaction.

At $t = t_{1/2}$, $[A] = [A]_0/2$ so, $[A]_0/2 = [A]_0 - kt_{1/2}$

$$t_{1/2} = 1/2k [A]_0$$

c) Calculate the time in half-lives when the integrated rate law is no longer valid (that is, when $[A] = 0$)

$$[A]_t = 0 = [A]_0 - kt$$

$$t_{1/2} = 1/2k [A]_0 \Rightarrow k = 1/2t_{1/2} [A]_0$$

Therefore, to consume all of the reactants it takes

$$t = [A]_0/k = [A]_0/2 \text{ so, } [A]_0 / (1/(2t_{1/2})) [A]_0 = 2t_{1/2}$$

integrated rate law is no longer valid after 2 half-lives

Q9.14b

Jack, Jill, and you are in a physical chemistry class. The professor writes the following equations on the black board.



$$[A] = [A_0]e^{-kt} \quad (9.E.32)$$

a. The professor assigns you to derive the first-order reaction in front of the class.

b. Jack was assigned to find the rate constant if the reaction half-life is 10 hours. Since you are a good friend of Jack, you decide to help him double check his answer by solving for the rate constant.

S9.14b

a)

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = \int_0^t -k dt \quad (9.E.33)$$

$$\ln[A] \Big|_{[A]_0}^{[A]} = -kt \quad (9.E.34)$$

$$\ln[A] - \ln[A]_0 = -kt \quad (9.E.35)$$

$$\ln \frac{[A]}{[A]_0} = -kt \quad (9.E.36)$$

$$\frac{[A]}{[A]_0} = e^{-kt} \quad (9.E.37)$$

$$[A] = [A_0]e^{-kt} \quad (9.E.38)$$

b)

$$t_{1/2} = \frac{\ln 2}{k} \quad (9.E.39)$$

$$10\text{hours} = \frac{\ln 2}{k} \quad (9.E.40)$$

$$k = \frac{\ln 2}{10\text{hours}} \times \frac{1\text{hour}}{60\text{min}} \times \frac{1\text{min}}{60\text{secs}} \quad (9.E.41)$$

$$k = \quad (9.E.42)$$

Q9.15a

In the nuclear industry, workers use a rule of thumb that the radioactivity from any sample will be relatively harmless after 10 half-lives. Calculate the fraction of a radioactive sample that remains after this time period (hint: Radioactive decay obeys first-order kinetics)

S9.15a

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

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

$$[A] = (100)e^{-(1)(10)} = 0.00454$$

% remaining after 10 half-lives

Q9.15b

As a school field trip to apply what you learned in physical chemistry class, you and your class went to a nuclear power plant. The plant's manager, Mr. Setsaw gives the class a tour of the facilities. When the class reaches the simulation room, a meltdown simulation is offered to the class, but only if the class can answer his questions can the class experience it.

- Radioactive decay occurs in what order?
- The gas used in the simulation is harmless because the fraction of the original remaining is 0.004 and the time that passed 30 years. What is the rate constant?

S9.15b

- Radioactive decay occurs in first order.
-

$$\frac{[A]}{[A]_0} = e^{-kt} \quad (9.E.43)$$

$$0.004 = e^{-k \cdot 30\text{years}} \quad (9.E.44)$$

$$\ln[0.004] = -k \cdot 30\text{years} \quad (9.E.45)$$

$$k = \frac{-30}{\ln[0.004]} \quad (9.E.46)$$

$$k = \quad (9.E.47)$$

Q9.16a

Many reactions involving heterogeneous catalysis are zero order; that is, rate = k. An example is the decomposition of phosphine (PH_3) over tungsten (W):



The rate for this reaction is independent of $[\text{PH}_3]$ as long as phosphine's pressure is sufficiently high ($\geq 1 \text{ atm}$). Explain.

S9.16a

With sufficient PH_3 , all of the catalytic sites on the tungsten surface are occupied. Further increases in the amount of phosphine cannot affect the reaction, and the rate is independent of $[\text{PH}_3]$.

Q9.16b

Jill and you just went to an enzyme kinetic workshop. However, Jill is confused about why at high concentrations of substrates the reaction order is zero-order. Please explain to Jill in a way that anyone can understand.

S9.16b

At high concentrations of substrates, all the enzymes are working at their fastest rate. As soon as the enzyme is done converting one substrate to its product, another substrate comes into the active site. Therefore, the rate of the enzyme working is constant and this is the definition for zero-order reaction.

9.3: Molecularity of a Reaction

Q9.41a

A mixture of compounds M and N whose half-lives are 40 minutes and 17 minutes, respectively. They decompose by first-order kinetics. If their concentrations are equal initially, how long does concentration of N to be half that of M?

S9.41a

[I] is the initial concentration of M and N

$$\ln \frac{[M]}{[I]} = -k_M t \quad (1)$$

$$\ln \frac{[N]}{[I]} = -k_N t \quad (2)$$

$$(1) - (2) = \ln \frac{[M]}{[N]} = -t(k_M - k_N)$$

So, to have [N] equals half to [M], we have

$$\ln 2 = -t \left(\frac{\ln 2}{40} - \frac{\ln 2}{17} \right)$$

$$\rightarrow t = 30.1 \text{ min}$$

Q9.41b

Compounds A and B both decay by first-order kinetics. The half-life of A is 20 minutes and the half-life of B is 48 minutes. If a container initially contains equal concentrations of compounds A and B, after how long will the concentration of B be twice that of A?

S9.41b

1. Write, in mathematical terms, the information given in the problem and what the problem is asking for.

$$t_{1/2,A} = 20.0 \text{ min} \quad (9.E.49)$$

$$t_{1/2,B} = 48.0 \text{ min} \quad (9.E.50)$$

$$[A]_0 = [B]_0 \quad (9.E.51)$$

A and B decay by first-order, so

$$-\frac{d[A]}{dt} = k_A[A] \quad (9.E.52)$$

$$-\frac{d[B]}{dt} = k_B[B] \quad (9.E.53)$$

(Note: the rate constants for A and B are not equal, so indicate which is which with subscripts.)

Want find t at which the following is true:

$$[B] = 2[A] \quad (9.E.54)$$

2. Substitute the integrated rate equations for [A] and [B]

$$[B]_0 e^{-k_B t} = 2[A]_0 e^{-k_A t} \quad (9.E.55)$$

3. Write expressions for the rate constants in terms of half-lives, and substitute into the equation.

$$t_{1/2,A} = \frac{\ln 2}{k_A} \Rightarrow k_A = \frac{\ln 2}{t_{1/2,A}} \quad (9.E.56)$$

$$t_{1/2,B} = \frac{\ln 2}{k_B} \Rightarrow k_B = \frac{\ln 2}{t_{1/2,B}} \quad (9.E.57)$$

$$[B]_0 e^{-\frac{\ln 2}{t_{1/2,B}} t} = 2[A]_0 e^{-\frac{\ln 2}{t_{1/2,A}} t} \quad (9.E.58)$$

4. Solve for t

Since initial concentrations of A and B are equal:

$$e^{-\frac{\ln 2}{t_{1/2,B}} t} = 2e^{-\frac{\ln 2}{t_{1/2,A}} t} \quad (9.E.59)$$

Take natural log of both sides:

$$-\frac{t}{t_{1/2,B}} \ln 2 = \left(1 - \frac{t}{t_{1/2,A}}\right) \ln 2 \quad (9.E.60)$$

$$t = \frac{1}{\frac{1}{t_{1/2,A}} - \frac{1}{t_{1/2,B}}} \quad (9.E.61)$$

5. Plug in values for half-lives

$$t = \frac{1}{\frac{1}{20.0 \text{ min}} - \frac{1}{48.0 \text{ min}}} = 34.2 \text{ min}$$

Answer: 34.2 minutes

Q9.42a

In Q3 thermodynamics and in Q9 chemical kinetics, the term “reversible “ is used. How do you understand this term? (it has a same meaning in these two chapters)

S9.42a

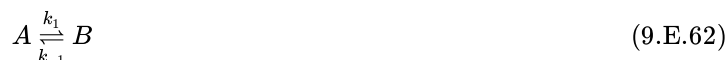
Actually, this word is used to describe a “reversible” reaction in which both forward and backward reactions can happen in kinetics. In thermodynamics, “reversible” is used to describe a process that is in equilibrium along the pathway from the initial to final states.

Q9.42b

If a reaction has come to thermodynamic equilibrium, can we say anything in particular about the system's kinetics?

S9.42b

Equilibrium occurs when all reactants and products are being consumed at the same rate that they are created. Take the simple example:



When the system is at equilibrium,

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = 0 \quad (9.E.63)$$

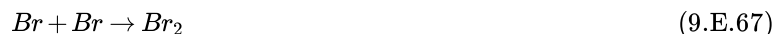
$$k_{-1}[A] = k_1[B] \quad (9.E.64)$$

$$\frac{k_{-1}}{k_1} = \frac{[B]}{[A]} \quad (9.E.65)$$

$$K_{eq} = \frac{k_{-1}}{k_1} \quad (9.E.66)$$

Q9.43a

The recombination of bromine atoms in an organic solvent, like carbon tetrafluoride, is considered as a diffusion-controlled process



we have the viscosity of CF₄ is 9.80 x 10⁻⁴ Nsm⁻² at 30°C, what is the rate of recombination at 30°C?

S9.43a

$$k_D = \frac{8RT}{3\eta}$$

$$= \frac{8(8.314 \text{ J/K-mol})(303.2 \text{ K}) \times 1000 \text{ L}}{(3 \times 9.8 \times 10^{-4} \text{ Nsm}^{-2}) \times (1 \text{ m}^3)}$$

$$= 6.86 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$$

Q9.43b

Calculate the rate constant of the diffusion-controlled reaction



in dichloromethane at 15°C, which has a viscosity of 0.449 mPa·s at 15°C.

S9.43b

1. Use equation 9.50 to calculate the rate constant.

$$k_D = \frac{8RT}{3\eta} \quad (9.E.69)$$

$$k_D = \frac{8}{3} \frac{8.314 \frac{\text{J}}{\text{mol K}} \times 288 \text{ K} \times \frac{\text{N m}}{\text{J}}}{0.449 \text{ mPa s} \times \frac{\text{Pa}}{1000 \text{ mPa}} \times \frac{\text{N/m}^2}{\text{Pa}}} \times \frac{1000 \text{ L}}{\text{m}^3} \quad (9.E.70)$$

Answer:

$$k_D = 1.42 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \quad (9.E.71)$$

Q9.52

Japanese survivors have been exposed to the risk of radiation after the atomic bomb. One man was measured to have iodine-131 levels at 9.7 mCi. Calculate the number of atoms of I-131 to which this radioactivity corresponds.

S9.52

First, convert the rate mCi s⁻¹

$$1 \text{ mCi} = 1.10 \times 10^{-3} \text{ Ci}$$

$$1 \text{ Ci} = 3.7 \times 10^{10} \text{ s}^{-1}$$

The rate (*r*) can be derived as such

$$r = (9.7 \text{ Ci}) \left(\frac{1 \text{ Ci}}{1000 \text{ mCi}} \right) \left(\frac{3.7 \times 10^{10} \text{ s}^{-1}}{1 \text{ Ci}} \right) = 3.59 \times 10^8 \text{ s}^{-1} \quad (9.E.72)$$

The accepted value for the half life of I-131 is 8.02 days. Using this information, the number of I-131 atoms can be calculated using the nuclear decay equation. Use the

Nuclear Decay Equation:

$$\lambda N = \frac{\ln 2}{t_{1/2}} N \quad (9.E.73)$$

or

$$N = \frac{\ln 2}{t_{1/2}} r \quad (9.E.74)$$

The half-life for the radioactive beta decay of iodine is 8.02 days



therefore, the rate is

$$r = 3.59 \times 10^8 \text{ s}^{-1} \quad (9.E.76)$$

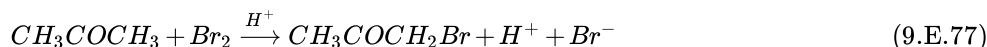
Plug into the equation and convert days to seconds.

$$(8.02 \text{ days}/\ln 2)(24 \text{ hours}/1 \text{ day})(3600 \text{ seconds}/1 \text{ hour})(3.59 \times 10^8) = 2.49 \times 10^{14} \text{ I-131 atoms.}$$

N= (

Q9.54

Calculate the rate law for the following acid-catalyzed reaction:



| Expt. # | $[\text{CH}_3\text{COCH}_3]_0 / \text{M}$ | $[\text{Br}_2]_0 / \text{M}$ | $[\text{H}^+]_0 / \text{M}$ | Rate of Disappearance $\text{Br}_2 / \text{M} \cdot \text{s}^{-1}$ |
|---------|---|------------------------------|-----------------------------|---|
| 1 | 0.3 | 0.05 | 0.05 | 5.7×10^{-5} |
| 2 | 0.3 | 0.1 | 0.05 | 5.7×10^{-5} |
| 3 | 0.3 | 0.05 | 0.05 | 1.2×10^{-4} |
| 4 | 0.4 | 0.05 | 0.2 | 3.1×10^{-4} |
| 5 | 0.4 | 0.05 | 0.05 | 7.6×10^{-5} |

S9.54

Find the rate law.

$$\text{rate} = k[\text{CH}_3\text{COCH}_3]^x [\text{Br}_2]^y [\text{H}^+]^z$$

[exp 1] / [exp 5]:

$$5.7\text{e-}5 / 7.6\text{e-}5 = (0.30/0.40)^x (0.050/0.050)^y (0.050/0.050)^z$$

$$3/4 = (3/4)^x$$

$$x = 1$$

[exp 1] / [exp 2]:

$$5.7\text{e-}5 / 5.7\text{e-}5 = (0.30/0.30) (0.050/0.10)^y (0.050/0.050)^z$$

$$1 = (1/2)^y$$

$$y = 0$$

[exp 1] / [exp 3]:

$$5.7\text{e-}5 / 1.2\text{e-}4 = (0.30/0.30) (0.050/0.10)^z$$

$$19/40 = (1/2)^z$$

$$z \approx 1$$

Use [exp 1] to find rate constant.

$$5.7 \times 10^{-5} \text{ M/s} = k(0.30 \text{ M})(0.050 \text{ M})$$

$$k = 3.8 \times 10^{-3} \text{ M}^{-1} \text{s}^{-1}$$

"calculate the rate of disappearance of bromine if the initial concentration are .600mol/L, 0.200 mol/L, and .10 mol/L for propanone, bromine and H+."

$$\text{rate} = (3.8 \times 10^{-3} \text{ M}^{-1} \text{s}^{-1})(0.600 \text{ M})(0.10 \text{ M})$$

$$\text{rate} = 2.28 \times 10^{-4} \text{ M/s}$$

Q9.55

Determine the rate law for the following reaction:



In addition, determine which of the following actions would alter the value of k ?

- Increase in pressure of N_2O_2
- Increase in volume size of container
- Increase in temperature
- Addition of catalyst to the container.
- None of the above ;a rate constant is always constant.

Q9.56

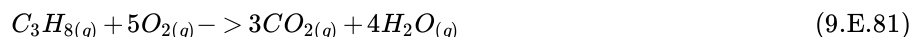
Consider the mechanism for the association of iodine atoms to create molecular iodine.



With the respect of the first step is at equilibrium, determine the expected rate law $(d/dt)[\text{I}_2(g)]$ in terms of k_1 , k_{-1} , k_2 , $[\text{I}]$, and $[\text{M}]$.

Q9.57

Consider the following reaction:



If propane (C_3H_8) is burning at a rate of 0.15 M/s^{-1} , calculate the rate of formation of CO_2 .

9.4: More Complex Reactions

S9.57

First, express the reaction with the differential rate equation for the reactants and products involved.

$$-(d/dt)[\text{C}_3\text{H}_8] = (1/3)(d/dt)[\text{CO}_2]$$

Then, use the given burning rate of propane and plug it into the differential equation.

$$(d/dt)[\text{CO}_2] = 3(0.15 \text{ M/s}^{-1})$$

$$(d/dt)[\text{CO}_2] = 0.45 \text{ M/s}^{-1}$$

9.5: The Effect of Temperature on Reaction Rates

Q9.26

If kept in a refrigerator, fresh fish will last for 3 days. If kept in a freezer, it will last for 6 months. Assuming that the temperature in the refrigerator is 5°C , and the temperature in the freezer is -10°C , calculate the activation energy for the bacterial spoiling of fish. Assume that the spoiling time is the $1/e$ lifetime instead of the half-life.

Q9.27

Find the activation energy of a reaction whose rate constant is multiplied by 6.50 when T is increased from 300.0 K to 310.0 K. For a reaction with $E_a = 19 \text{ kJ/mol}$, by what factor is k multiplied when T increases from 300.0 K to 310.0 K?

Q9.28

The kinetics of the browning of juice from Golden Delicious apples was studied; at 20°C $k=7.87 \times 10^{-3}/\text{week}$, and at 37°C $k=0.139/\text{week}$. What is the activation energy for the browning of Golden Delicious apple juice?

9.6: Potential Energy Surfaces

9.7: Theories of Reaction Rates

9.8: Isotope Effects in Chemical Reactions

9.9: Reactions in Solution

9.10: Fast Reactions in Solution

9.11: Oscillating Reactions

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