

- Suppose you are asked to measure the viscosity of a motor oil. You drop a steel ball (diameter 0.800 mm) into a vertical glass tube filled with the oil and observe the ball to sink 10.0 cm in 76 s. The densities of the oil and steel are 0.82 and 7.82 g cm⁻³, respectively. Calculate the viscosity of the oil. Why is the viscosity of motor oil of considerable practical importance?
- The importance of thermal conductivity is gruesomely illustrated by school children who lick metal objects during class recess on sub-zero winter days and find their tongues stuck firmly to the metal. Wood, brick, plastic, and other materials are less dangerous in this respect. Why?
- A current of 0.75 amps flows through a metal wire of cross-sectional area 0.020 cm². Calculate the charge flux density. How many electrons flow through a cross section of the wire in 1.0 s?
- An aqueous solution is analyzed for dissolved sodium chloride by measuring its conductivity. The electrical resistance of a conductivity cell (cell constant 1.03 cm⁻¹) filled with the solution is 39,700 ohms. Use 0.0050 and 0.0076 S m² mol⁻¹ for the molar conductivities of Na⁺ and Cl⁻ ions to calculate the concentration of sodium chloride.
- The conductivity reported for ultrapure water at 25 °C is 5.47 × 10⁻⁸ S cm⁻¹. Use 0.0350 and 0.0199 S m² mol⁻¹ for the molar conductivities of H⁺ and OH⁻ ions to calculate the equilibrium constant $K_w = [H^+][OH^-]$ for the dissociation of water: H₂O(l) = H⁺(aq) + OH⁻(aq).
- The molar conductivities of aqueous Li⁺ and Na⁺ ions at 25 °C are 0.00501 and 0.00398 S m² mol⁻¹, respectively. Use

$$\frac{N_{\text{Avogadro}} \lambda_{+m}}{(z_+ F)^2} \approx \frac{1}{6\pi\eta r}$$
 to estimate the diameters of the ions. The viscosity of water at 25 °C is 0.000891 Pa s.
 - The Li⁺ ion (1s²) is generally considered to be significantly smaller than the Na⁺ ion (1s²2s²2p⁶). Conductivity data indicate the opposite behavior. Why?
- The molar conductivity of aqueous ClO₄⁻ ions at 25 °C and infinite dilution is 67.2 S cm² mol⁻¹. Calculate the electric mobility (μ_-) of aqueous ClO₄⁻ ions at 25 °C and infinite dilution.
 - Calculate the drift speed of ClO₄⁻ ions in a 24 volt per centimeter electric field.

8. a) The molar conductivities of aqueous hydrochloric acid, sodium acetate, and sodium chloride at 25 °C and infinite dilution are: 0.042616, 0.009100 and 0.012645 S m² mol⁻¹. Calculate the molar conductivity of completely dissociated acetic acid.
- b) The molar conductivity measured for a 0.0001115 mol L⁻¹ aqueous acetic solution at 25 °C is 0.012775 S m² mol⁻¹. Estimate the extent of dissociation and the equilibrium constant for the reaction CH₃COOH(aq) = CH₃COO⁻(aq) + H⁺(aq).

9. The progress of the reaction SO₂Cl₂(g) → SO₂(g) + Cl₂(g) is monitored by following the total pressure *p* at fixed volume and fixed temperature. The following data are obtained:

time / hr	0	3	6	9	12	15
<i>p</i> / kPa	11.07	14.79	17.26	18.90	19.99	20.71

- a) Is the reaction first- or second-order with respect to SO₂Cl₂?
- b) Calculate the rate constant for the reaction.
10. Cobalt-60 is a convenient source of gamma rays for radiation chemistry research.



The half-life of cobalt-60 is 1900 days. Suppose you have a sample containing one micromole of cobalt-60. How long will you have to wait for the last gamma ray to be emitted?

11. The second-order reaction A + B → products with rate law $R = k_2[A][B]$ is 60 % complete in one minute when the initial concentrations of A and B are [A]₀ = 0.100 M and [B]₀ = 0.500 M.
- a) Calculate the rate constant k_2 .
- b) How long will it take for the reaction to reach 60 % completion of the initial concentrations are [A]₀ = 0.050 M and [B]₀ = 0.250 M?

12. Bacteriorhodopsin (B) is a protein found in certain bacteria that converts visible light into intermediates J and K used for ATP synthesis with the sequential first-order reactions



- a) Calculate the time at which the concentration of intermediate J reaches the maximum value. Data: [J]₀ = 0, [K]₀ = 0, $k_J = 2.0 \times 10^{12} \text{ s}^{-1}$, $k_K = 3.3 \times 10^{11} \text{ s}^{-1}$.
- b) Draw plots of [B], [J] and [K] as functions of time.

Q1. A steel ball (radius $r = 0.400 \text{ mm}$, density $\rho_{\text{steel}} = 7.82 \text{ g cm}^{-3}$)

sinks at the terminal velocity $v = -\frac{10.0 \text{ cm}}{76 \text{ s}} = -0.1316 \text{ cm s}^{-1}$ ("down")

through oil (density 0.82 g cm^{-3}). Oil viscosity?

terminal velocity $v = \frac{-1}{6\pi r \eta} \left[\left(\frac{4}{3} \pi r^3 \right) (\rho_{\text{steel}} - \rho_{\text{oil}}) \right] g$

in SI units: $v = -0.001316 \text{ m s}^{-1}$

$r = 0.000400 \text{ m}$

$\rho_{\text{steel}} = 7820 \text{ kg m}^{-3}$

$\rho_{\text{oil}} = 820 \text{ kg m}^{-3}$

$g = 9.8 \text{ m s}^{-2}$

$\eta = \frac{-1}{6\pi r v} \left[\left(\frac{4}{3} \pi r^3 \right) (\rho_{\text{steel}} - \rho_{\text{oil}}) \right] g$

$= \frac{-1}{6\pi (0.000400) (-0.001316)} \left[\left(\frac{4}{3} \pi (0.000400)^3 \right) (7820 - 820) \right] 9.8$

$\eta = 1.85 \text{ Pa s}$

(also removes heat, reduces corrosion, carries away particulate debris)

So what? ...
The "falling-sphere" method illustrated here is widely used to measure viscosities.

Motor oil lubricates moving parts inside engines.

The viscosity of motor oil must be low enough for the oil to flow through channels and tubes in the engine (and for engines to start on cold days),

but high enough for the oil to coat and lubricate metal parts (not "wash away"), especially at operating temperatures when the engines are "hot"

Who cares?
Well...

(i.e., Canada)

Q2. Metals have significantly higher thermal conductivities than wood, brick, and plastic.

As a result, heat is conducted away much more rapidly by metal, causing freezing (almost instantaneous) on cold winter days.

Q3. A current of 0.75 amperes flows through a metal wire (cross-sectional area 0.020 cm^2).

$$\begin{aligned} \text{charge flux density } J_x &= \frac{\text{current}}{\text{area}} = \frac{\text{electric charge per unit time}}{\text{area}} \\ &= \frac{0.75 \text{ C s}^{-1}}{(0.020 \text{ cm}^2)(10^{-4} \text{ m}^2 \text{ cm}^{-2})} \\ &= \frac{0.75 \text{ C s}^{-1}}{2.0 \times 10^{-6} \text{ m}^2} \end{aligned}$$

$$J_x = 3.75 \times 10^5 \text{ C m}^{-2} \text{ s}^{-1}$$

$$\begin{aligned} \text{moles of electrons} \\ \text{flowing through} \\ \text{the wire per second} \end{aligned} \frac{I}{F} = \frac{0.75 \text{ C s}^{-1}}{96485 \text{ C mol}^{-1}} = 7.77 \times 10^{-6} \frac{\text{mol}}{\text{s}}$$

$$\begin{aligned} \text{number of electrons} \\ \text{flowing per second} \end{aligned} N_{\text{Avogadro}} \frac{I}{F} = (6.022 \times 10^{23} \text{ mol}^{-1}) \left(7.77 \times 10^{-6} \frac{\text{mol}}{\text{s}} \right) \\ = 4.68 \times 10^{18} \text{ s}^{-1}$$

"analytical chemistry"!
from conductivity

Q4. A conductivity cell (cell constant $L/A = 1.03 \text{ cm}^{-1}$) filled with aqueous sodium chloride solution ($\lambda_{+m}(\text{Na}^+) = 0.0050 \text{ S m}^2 \text{ mol}^{-1}$ and $\lambda_{-m}(\text{Cl}^-) = 0.00765 \text{ S m}^2 \text{ mol}^{-1}$) has a resistance of $39,700 \text{ ohm}$ ($= 39,700 \text{ S}^{-1}$).

sodium chloride concentration?

$$\text{cell conductance} = \frac{1}{\text{cell resistance}} = \kappa \frac{A}{L}$$

$$\text{conductivity} = \kappa = (c_{+m} \lambda_{+m} + c_{-m} \lambda_{-m})$$

$$\kappa = c_m (\lambda_{+m} + \lambda_{-m})$$

$$\begin{aligned} c_m &= \text{molar concentration of NaCl} \\ &= c_{+m} \quad (\text{molar concentration of Na}^+) \\ &= c_{-m} \quad (\text{molar concentration of Cl}^-) \end{aligned} \left. \vphantom{\begin{aligned} c_m &= \text{molar concentration of NaCl} \\ &= c_{+m} \\ &= c_{-m} \end{aligned}} \right\} \text{electroneutrality}$$

cell constant $\left(\frac{L}{A} = 1.03 \text{ cm}^{-1} = 103 \text{ m}^{-1} \right)$

$$\text{cell resistance} = \frac{1}{\kappa} \left(\frac{L}{A} \right) = \frac{1}{c_m (\lambda_{+m} + \lambda_{-m})} \left(\frac{L}{A} \right)$$

$$c_m = \frac{1}{\text{cell resistance}} \frac{1}{\lambda_{+m} + \lambda_{-m}} \left(\frac{L}{A} \right)$$

$$= \frac{1}{39,700 \text{ S}^{-1}} \frac{1}{(0.0050 + 0.0076) \text{ S m}^2 \text{ mol}^{-1}} (103 \text{ m}^{-1})$$

$$c_m = 0.206 \text{ mol m}^{-3} = \boxed{0.000206 \text{ mol L}^{-1}}$$

($1 \text{ m}^3 = 1000 \text{ L}$)

not easily prepared

Q5. "Ultrapure" water has a small residual conductivity $\kappa = 5.47 \times 10^{-8} \text{ S cm}^{-1}$ due to the self-ionization equilibrium



Calculate the equilibrium constant K_w

$$K_w = [\text{H}^+][\text{OH}^-]$$

in terms of the molarities ($\frac{\text{mol}}{\text{L}}$) of H^+ and OH^- ions

$$\text{conductivity } \kappa = c_{+m} \lambda_{+m} + c_{-m} \lambda_{-m}$$

$\lambda_{+m}, \lambda_{-m} \Rightarrow$ molar conductivities of H^+ and OH^-

$c_{+m}, c_{-m} \Rightarrow$ molar concentrations of H^+ and OH^-

($c_{+m} = c_{-m}$ electroneutrality)

$$\text{data provided: } \left. \begin{array}{l} \lambda_{+m} = 0.0350 \text{ S m}^2 \text{ mol}^{-1} \\ \lambda_{-m} = 0.0199 \text{ S m}^2 \text{ mol}^{-1} \end{array} \right\} \text{ at } 25^\circ\text{C}$$

$$\kappa = 5.47 \times 10^{-8} \text{ S cm}^{-1} = 5.47 \times 10^{-6} \text{ S m}^{-1}$$

$$\kappa = c_{+m} \lambda_{+m} + c_{-m} \lambda_{-m} = c_{+m} (\lambda_{+m} + \lambda_{-m})$$

$$c_{+m} = \frac{\kappa}{\lambda_{+m} + \lambda_{-m}} = \frac{5.47 \times 10^{-6} \text{ S m}^{-1}}{0.0549 \text{ S m}^2 \text{ mol}^{-1}} = 9.96 \times 10^{-5} \frac{\text{mol}}{\text{m}^3}$$

$$[\text{H}^+] = [\text{OH}^-] = 9.96 \times 10^{-5} \frac{\text{mol}}{\text{m}^3} \left(\frac{10^{-3} \text{ m}^3}{\text{L}} \right) = 9.96 \times 10^{-8} \frac{\text{mol}}{\text{L}}$$

$$K_w = \left(9.96 \times 10^{-8} \frac{\text{mol}}{\text{L}} \right)^2 = [\text{H}^+][\text{OH}^-] = 9.92 \times 10^{-15} \frac{\text{mol}^2}{\text{L}^2}$$

$\approx 1.00 \times 10^{-14}$
commonly used

Q6. The size of ions in solution can be estimated from molar conductivities using the mobility $1/(6\pi\eta r)$ from Stokes law and

$$\frac{N_{\text{Avogadro}} \lambda_m}{(zF)^2} \approx \frac{1}{6\pi\eta r}$$

$$r \approx \frac{(zF)^2}{N_{\text{Avogadro}} \lambda_m} \frac{1}{6\pi\eta}$$

a)

aqueous Na^+ ion $\lambda_m = 0.00501 \text{ S m}^2 \text{ mol}^{-1}$
 (25°C, $\eta = 0.000891 \text{ Pas}$) $z = 1$
 for the viscosity of water

$$r \approx \frac{((1) 96485)^2}{6.022 \times 10^{23} (0.00501)} \frac{1}{6\pi (0.000891)} \quad (\text{all SI})$$

$$r_{\text{Na}^+} = 1.84 \times 10^{-10} \text{ m} = 0.184 \text{ nm}$$

aqueous Li^+ ion $\lambda_m = 0.00398 \text{ S m}^2 \text{ mol}^{-1}$
 $z = 1$

$$r \approx \frac{((1) 96485)^2}{6.022 \times 10^{23} (0.00398)} \frac{1}{6\pi (0.000891)}$$

$$r_{\text{Li}^+} = 2.31 \times 10^{-10} \text{ m} = 0.231 \text{ nm}$$

b) Li^+ is a smaller ion than Na^+ , but its small size produces a larger electric field, causing Li^+ ions to be more strongly hydrated (water electric dipoles more oriented around Li^+). The extra water molecules Li^+ "drags around" reduces λ_m for Li^+ , making it look larger.

Q7. The molar conductivity of aqueous ClO_4^- ions at 25 °C and infinite dilution is $67.2 \text{ S cm}^2 \text{ mol}^{-1}$. SI: $0.00672 \text{ S m}^2 \text{ mol}^{-1}$

a) electric mobility of ClO_4^- ions?

$$u_- = \frac{\lambda_{-m}}{|z_-| F} = \frac{\text{ion drift speed}}{\text{applied electric field}}$$

$$= \frac{0.00672 \text{ S m}^2 \text{ mol}^{-1}}{|-1| 96485 \text{ C mol}^{-1}} =$$

$u_- = 6.96 \times 10^{-8} \text{ S C}^{-1} \text{ m}^2$

? units? from current = $\frac{\text{voltage}}{\text{resistance}} = (\text{voltage})(\text{conductance})$

coulombs per second = voltage Siemens

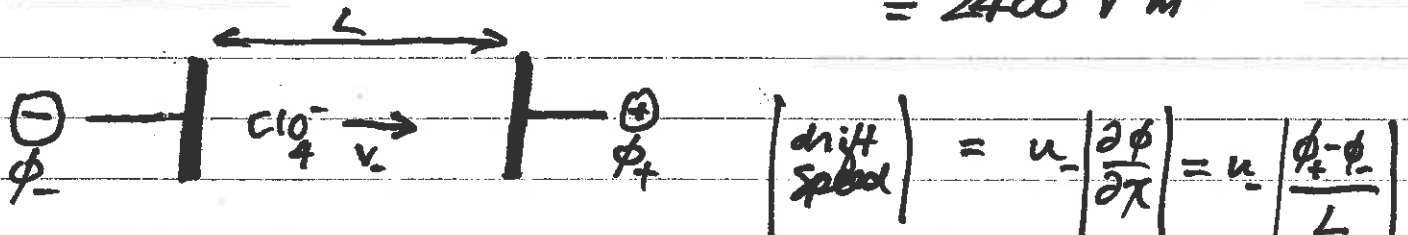
$$\text{C s}^{-1} = \text{V S}$$

$$\text{so } \text{S C}^{-1} = \text{s}^{-1} \text{V}^{-1}$$

$$\text{and } u_- = 6.96 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$$

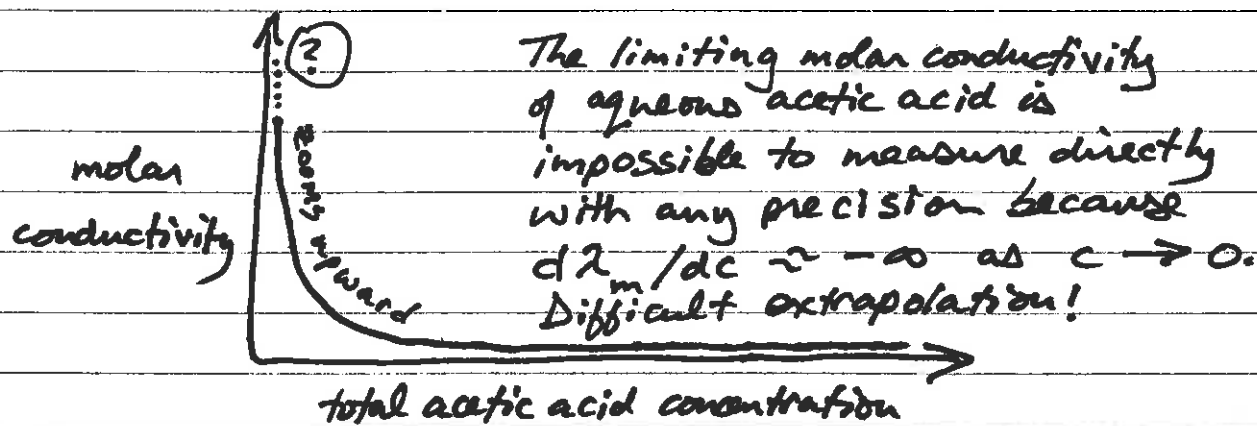
b) ClO_4^- ions in an aqueous solution "drift" toward the positive electrode.

The applied electric field is $24 \text{ V cm}^{-1} = 2400 \text{ V m}^{-1}$



$$v_d = u_- \left| \frac{\Delta \phi}{\Delta x} \right| = (6.96 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}) (2400 \text{ V m}^{-1}) = \boxed{1.67 \times 10^{-4} \text{ m s}^{-1}}$$

- Q8. a) The molar conductivity of aqueous acetic acid increases very sharply as the concentration of the acid is reduced, and a larger fraction of the total acid dissociates to form H^+ and CH_3COO^- ions. Why? Molecular CH_3COOH has zero conductivity.

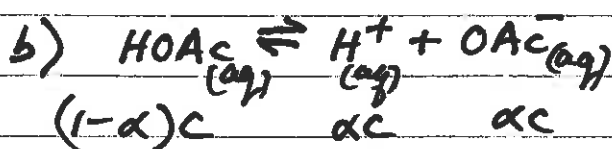


a)

Plan B: Ions migrate independently as the electrolyte concentration drops to zero. This means the "infinite dilution" molar conductivity of acetic acid (fully dissociated) is

$$\begin{aligned} \Lambda_m^0(\text{HOAc}) &= \lambda_m^0(H^+) + \lambda_m^0(\text{OAc}^-) \\ &= \lambda_m^0(H^+) + \lambda_m^0(\text{Cl}^-) + \lambda_m^0(\text{Na}^+) + \lambda_m^0(\text{OAc}^-) - \lambda_m^0(\text{Na}^+) - \lambda_m^0(\text{Cl}^-) \\ &= \Lambda_m^0(\text{HCl}) + \Lambda_m^0(\text{NaOAc}) - \Lambda_m^0(\text{NaCl}) \\ &= 0.042616 + 0.009100 - 0.012645 \end{aligned}$$

$$\boxed{\Lambda_m^0(\text{HOAc}) = 0.039071 \text{ S m}^2 \text{ mol}^{-1}}$$



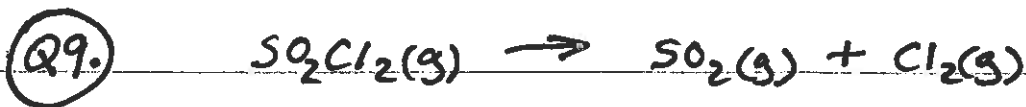
$c =$ total acid concentration

$$\alpha = \frac{[H^+]}{c} = \frac{[OAc^-]}{c} = \text{extent of dissociation}$$

$$K \approx \frac{(\alpha c)(\alpha c)}{(1-\alpha)c} = \frac{\alpha^2 c}{1-\alpha}$$

$$\alpha \approx \frac{\Lambda_m}{\Lambda_m^0} = \frac{0.012775}{0.039071} = 0.32697$$

$$\alpha \approx \frac{(0.32697)^2 \cdot 0.0001115}{1 - 0.32697} = \boxed{1.771 \times 10^{-5}}$$



$t=0$ $[\text{SO}_2\text{Cl}_2]_0$ 0 0

t $[\text{SO}_2\text{Cl}_2]_t$ $[\text{SO}_2]_t$ $[\text{Cl}_2]_t$

assume constant-volume reaction vessel

total concentration at time t $[\text{SO}_2\text{Cl}_2]_t + [\text{SO}_2]_t + [\text{Cl}_2]_t$

(from stoichiometry) = $[\text{SO}_2\text{Cl}_2]_0 + [\text{SO}_2]_t = [\text{SO}_2\text{Cl}_2]_0 + [\text{Cl}_2]_t$

First Order Reaction? If so, then $[\text{SO}_2\text{Cl}_2]_t = [\text{SO}_2\text{Cl}_2]_0 e^{-k_1 t}$

total concentration: $[\text{SO}_2\text{Cl}_2]_t + 2([\text{SO}_2\text{Cl}_2]_0 - [\text{SO}_2\text{Cl}_2]_t)$
 $= [\text{SO}_2\text{Cl}_2]_0 e^{-k_1 t} + 2([\text{SO}_2\text{Cl}_2]_0 - [\text{SO}_2\text{Cl}_2]_0 e^{-k_1 t}) = [\text{SO}_2\text{Cl}_2]_0 (2 - e^{-k_1 t})$

pressure p is proportional to the total concentration

$\therefore p(t) = \text{const.} (2 - e^{-k_1 t})$ $p(0) = \text{const.} (2 - 1)$

$p(t) = p(0)(2 - e^{-k_1 t})$ $p(0)e^{-k_1 t} = p(t)$

$2p(0) - p(t) = p(0)e^{-k_1 t}$

$\ln(2p(0) - p(t)) = -k_1 t$

* If 1st order, then $\ln(2p(0) - p(t))$ is linear *

t/hr	$p(t)/\text{kPa}$	$\ln(2p(0) - p(t))$	$\Delta \ln(2p(0) - p(t))$
0	11.07	2.404	
3	14.79	1.995	-0.409
6	17.26	1.585	-0.410
9	18.90	1.175	-0.410

constant slope = $-k_1$

yes!
 - Slope = k_1
 $= \frac{0.410}{3\text{hr}}$
 $= 0.137\text{hr}^{-1}$

radioactive decay obey 1st-order rate equations

(Q10) number of ^{60}Co atoms at time t : $N(t) = N(0)e^{-k_1 t}$

half-life: $N(t_{1/2}) = \frac{N(0)}{2} = N(0)e^{-k_1 t_{1/2}}$

$$\frac{1}{2} = e^{-k_1 t_{1/2}}$$

$$\ln\left(\frac{1}{2}\right) = -\ln 2 = -k_1 t_{1/2}$$

$$k_1 = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{1900 \text{ days}} = 3.65 \times 10^{-4} \text{ days}^{-1}$$

$$N(0) = (6.022 \times 10^{23} \text{ mol}^{-1}) (1 \times 10^{-6} \text{ mol}) = 6.02 \times 10^{17}$$

$$N(t) = (6.02 \times 10^{17}) e^{-(3.65 \times 10^{-4} \text{ days}^{-1})t}$$

the last ^{60}Co will have decayed when

$N(t)$ drops below about 1

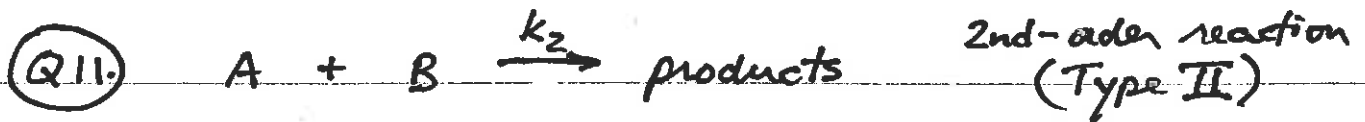
solve $1 = 6.02 \times 10^{17} e^{-(3.65 \times 10^{-4} \text{ days}^{-1})t}$

$$\ln(1) = \ln(6.02 \times 10^{17}) - (3.65 \times 10^{-4} \text{ days}^{-1})t$$

$$t = \frac{\ln(6.02 \times 10^{17})}{3.65 \times 10^{-4} \text{ days}^{-1}}$$

$$= 1.12 \times 10^5 \text{ days}$$

$$t = 307 \text{ years}$$



rate law $-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k_2[A][B]$

integrated to give $k_2 t = \frac{1}{[B]_0 - [A]_0} \ln \left(\frac{[B]_t/[B]_0}{[A]_t/[A]_0} \right)$

a) $[A]_0 = 0.100 \text{ M}$ $[B]_0 = 0.500 \text{ M}$
(limiting reactant)

reaction 60% complete at $t = 60 \text{ s}$

→ 40% of A remains: $[A]_t = 0.40[A]_0 = 0.40(0.100 \text{ M})$
 $[A]_t = 0.040 \text{ M}$

0.060 M of A has reacted
= amount of B reacted: $[B]_t = [B]_0 - 0.060 \text{ M}$
 $= (0.500 - 0.060) \text{ M}$

$[B]_t = 0.440 \text{ M}$

$$k_2 = \frac{1/t}{[B]_0 - [A]_0} \ln \left(\frac{[B]_t/[B]_0}{[A]_t/[A]_0} \right)$$

$$= \frac{1/60 \text{ s}}{(0.500 - 0.100) \frac{\text{mol}}{\text{L}}} \ln \left(\frac{0.440/0.500}{0.040/0.100} \right) = 0.0328 \frac{\text{L}}{\text{mol} \cdot \text{s}}$$

b) $[A]_0 = 0.050 \text{ M}$ $[B]_0 = 0.250 \text{ M}$ $k_2 = 0.0328 \frac{\text{L}}{\text{mol} \cdot \text{s}}$

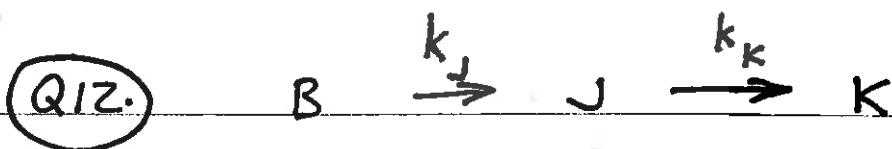
@ 60% completion $[A]_t = 0.40[A]_0 = 0.020 \text{ M}$

$[B]_t = [B]_0 - 0.030 \text{ M} = 0.220 \text{ M}$

time?

$$t = \frac{1/k_2}{[B]_0 - [A]_0} \ln \left(\frac{[B]_t/[B]_0}{[A]_t/[A]_0} \right) = \frac{(1/0.0328 \frac{\text{L}}{\text{mol} \cdot \text{s}})}{0.200 \text{ M}} \ln \left(\frac{0.220/0.250}{0.020/0.050} \right)$$

$t = 120 \text{ s}$

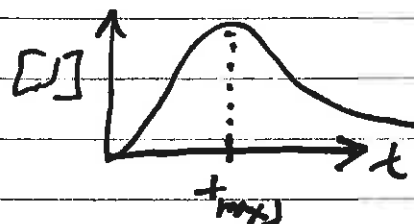


two consecutive first-order reactions

$$k_j = 2.0 \times 10^{12} \text{ s}^{-1} \quad k_k = 3.3 \times 10^{11} \text{ s}^{-1}$$

fast!

$$([J]_0 = 0 \quad [K]_0 = 0)$$



integrating the rate equations:

$$\frac{d[B]}{dt} = -k_j [B]$$

$$\frac{d[J]}{dt} = k_j [B] - k_k [J]$$

$$\frac{d[K]}{dt} = k_k [J]$$

gives $[J]_t = \frac{k_j}{k_k - k_j} [B]_0 (e^{-k_j t} - e^{-k_k t})$ for the concentration of intermediate J

the concentration of J reaches a maximum value when:

differentiate

$$\left. \frac{d[J]_t}{dt} \right|_{t_{max}} = 0$$

max [J] when this is zero

$$\frac{d[J]_t}{dt} = \frac{k_j}{k_k - k_j} [B]_0 (-k_j e^{-k_j t} - (-k_k) e^{-k_k t})$$

$$k_j e^{-k_j t_{max}} = k_k e^{-k_k t_{max}} \leftarrow \text{log this}$$

$$\ln k_j - k_j t_{max} = \ln k_k - k_k t_{max}$$

$$\ln k_j - \ln k_k = (k_j - k_k) t_{max} \Rightarrow t_{max} = \frac{\ln(k_j/k_k)}{k_j - k_k}$$

$$t_{max} = \frac{\ln(2.0 \times 10^{12} / 3.3 \times 10^{11})}{(2.0 \times 10^{12} - 3.3 \times 10^{11}) \text{ s}^{-1}} = 1.08 \times 10^{-12} \text{ s}$$

