LN–8 IDLE MIND SOLUTIONS

1. $k_1 = Ae^{-E_A/RT_1}$

$$k_2 = 3k_1 = Ae^{-E_A/RT_2} \qquad \frac{1}{3} = e^{-\frac{E_A}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)}$$

$$\ln 3 = \frac{E_A}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$E_A = \frac{R \text{ x } \ln 3}{\frac{1}{293} - \frac{1}{313}} = 4.19 \text{ x } 10^4 = \boxed{41.9 \text{ kJ/mole}}$$

2. (a) $k = Ae^{-E_A/RT} = 1.7 \text{ x } 10^{14} \text{ x } e^{-\left(\frac{2.5 \text{ x } 10^5}{8.31 \text{ x } 10^{23}}\right)} = \boxed{28.8 \text{ s}^{-1}}$

(b) Requires knowledge of k_{600}:

$$k_{600} = 1.7 \text{ x } 10^{14} \, e^{-\left(\frac{2.5 \text{ x } 10^5}{8.31 \text{ x } 873}\right)} = 0.184$$

$c/c_o = e^{-kt} = e^{-0.184\text{x}600} = 1.3 \text{ x } 10^{-48} \rightarrow 0$

c = 0: **reaction complete to 100%**

(c) $k = 3 \text{ x } k_1 = 3 \text{ x } 28.8 = Ae^{-E_A/RT_x}$

$$\ln 86.4 = \ln(1.7 \text{ x } 10^{14}) - \frac{E_A}{RT_x}$$

$$T_x = \frac{E_A}{R[\ln 86.4 - \ln(1.7 \text{ x } 10^{14})]}$$

$T_x = 1063\text{K} = \boxed{790^o\text{C}}$

3. $\frac{c_o}{c} = \frac{0.035}{0.025} = 1.4 = e^{k \times 65}$

$$\ln 1.4 = k \times 65$$

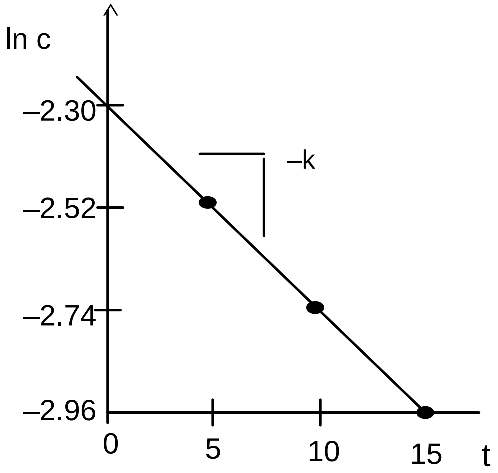
$$k = \ln 1.4/65 = 5.18 \times 10^{-3}\ s^{-1}$$

$$c = c_o e^{-kt}$$

$$= 0.035\ e^{-5.18 \times 10^{-3} \times 98} = \boxed{0.021\ M}$$

4. (a) A plot of ln c vs time places all points on a straight line, indicative for a **first order reaction**.

c	ln c	t
0.1000	–2.30	0
0.0804	–2.52	5
0.0648	–2.74	10
0.0519	–2.96	15



(b) We may obtain the rate constant from points (1) and (4).

$$-k = \frac{-2.3 + 2.96}{0 - 15} = -4.4 \times 10^{-2}\ m^{-1}$$

$$\boxed{k = 4.4 \times 10^{-2}\ m^{-1}}$$

(You may check the correctness of the results by applying the exponential form of the rate equation, $c/c_o = e^{-kt}$.)

5. $$D = D_o e^{-E_A/RT_x}$$

$$\ln \frac{D_o}{D} = \frac{E_A}{RT_x}$$

$$T_x = \frac{E_A}{R \times \ln \frac{D_o}{D}} = \frac{3.15 \times 10^5}{8.31 \times \ln \frac{1.7}{5 \times 10^{-11}}} = \boxed{1563\text{K} = 1290^o\text{C}}$$

6. $c_o/c = e^{kt}$ $(c = 0.06 \times c_o)$

$$\ln \frac{c_o}{0.06\ c_o} = kt_x$$

$$\ln 0.06 = -kt_x$$

$$t_x = -\frac{\ln 0.06}{\frac{\ln 2}{t_{1/2}}} = -\frac{\ln 0.06}{\frac{0.693}{12.5}} = \boxed{50.7 \text{ years}}$$

7. If 28% Ag* decays in 1.52 hours, then $c = (0.72\ c_o)$.

$$\frac{0.72\ c_o}{c_o} = e^{-kt}$$

$$\ln 0.72 = -kt$$

$$k = -\frac{\ln 0.72}{1.52} = 2.16\ (\text{hrs}^{-1})$$

$$t_{1/2} = \frac{0.693}{2.16} = \boxed{3.2 \text{ hours}}\ \ ({}^{112}\text{Ag}^*)$$

8. Decay is a 1st order reaction:

$$-\frac{dc}{dt} = kc$$

$$2.3 \times 10^{6} \text{ at/s} = k\,\frac{3.5 \times 10^{-6} \text{ g} \times 6.02 \times 10^{23}}{238 \text{ g}} = k \times 8.85 \times 10^{15}$$

$$k = \frac{2.3 \times 10^{6}}{8.85 \times 10^{15}} = \boxed{2.598 \times 10^{-10} \text{ s}^{-1}}$$

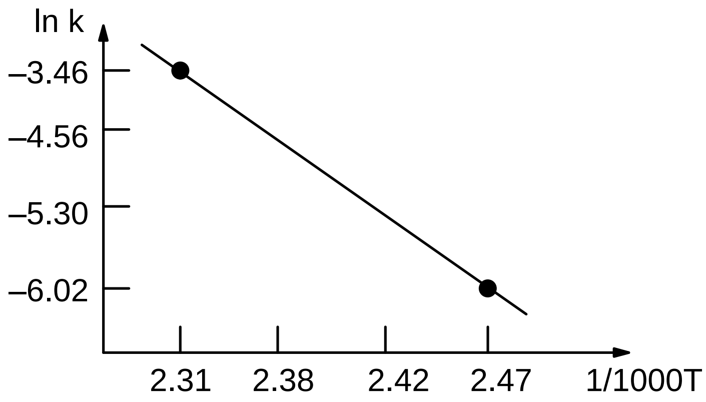
9. $\ln\frac{88}{53} = kt$

$$k = \frac{\ln\frac{88}{53}}{9.5} = 5.34 \times 10^{-2}\ (\text{h}^{-1})$$

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{5.34 \times 10^{-12}} = \boxed{12.9 \text{ hours}}$$

10.

T(°C)	1/T(1/°K)	k	ln k
131.5	$2.47\text{x}10^{-3}$	$02.44\text{x}10^{-3}$	–6.02
139.5	$2.42\text{x}10^{-3}$	$05.00\text{x}10^{-3}$	–5.3
147.5	$2.38\text{x}10^{-3}$	$10.57\text{x}10^{-3}$	–4.56
160.5	$2.31\text{x}10^{-3}$	$31.50\text{x}10^{-3}$	–3.46



(continued)

10. Continued.

Notice: the first and fourth points are on the slope. (Knowing this) we could forego the plotting:

$$\frac{2.44 \text{ x } 10^{-3}}{31.5 \text{ x } 10^{-3}} = \frac{A\ e^{-E_A/RT_1}}{A\ e^{-E_A/RT_2}} = e^{-\frac{E_A}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)}$$

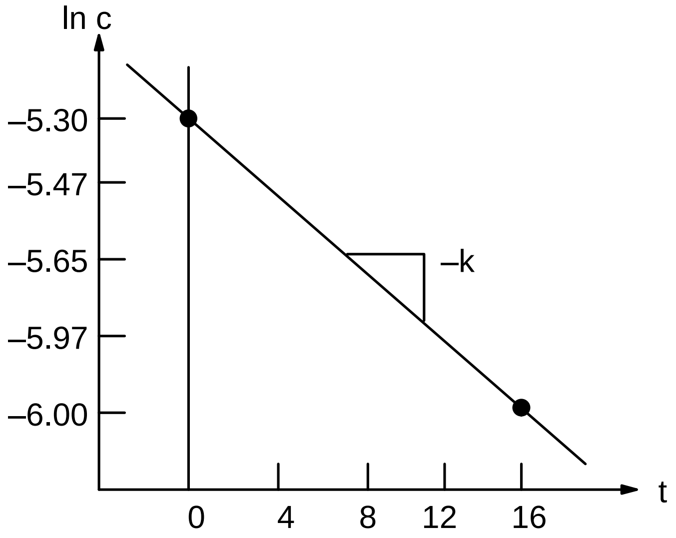
$$-\frac{E_A}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) = \ln(2.44 \text{ x } 10^{-3}) - \ln(31.5 \text{ x } 10^{-3})$$

$$-\frac{E_A}{R} = \frac{-6.02 + 3.46}{(2.47 \text{ x } 10^{-3}) - (2.31 \text{ x } 10^{-3})}$$

$$\boxed{E_A = 133 \text{ kJ/mole}}$$

11. If the reaction is first order, a plot of ln c vs time will yield a straight line. The shape will give –k, which allows calculation of the time required for 70% completion.

c	ln c	t
$5.00\text{x}10^{-3}$	–5.30	0
$4.20\text{x}10^{-3}$	–5.47	4
$3.53\text{x}10^{-3}$	–5.65	8
$2.56\text{x}10^{-3}$	–5.97	12
$2.48\text{x}10^{-3}$	–6.00	16



The plot indicates a **first order reaction**. However, one data point is erratic (presumably an error in recording since the last point is again on the straight line). We may take points (1) and (5) for the determination of the slope.

(continued)

11. Continued.

$$-k = \frac{-5.3 + 6.0}{0 - 16} = -4.4 \times 10^{-2}$$

$$\boxed{k = 4.4 \times 10^{-2}\ \text{min}^{-1}}$$

$$\left(t_{1/2} = \frac{\ln 2}{k} = 15.8\ \text{min}\right)$$

70% completion of the reaction means: $c/c_o = 0.3$; accordingly:

$$\ln\frac{c}{c_o} = -kt_x \qquad \boxed{t_x = -\frac{\ln 0.3}{k} = 27.4\ \text{min}}$$

12. (a) Knowing the half–life, we can determine the rate (decay) constant, k:

$$k = \frac{\ln 2}{t_{1/2}} = 3.46 \times 10^{-2}\ \text{min}^{-1}$$

According to $C = C_oe^{-kt}$:

$$\frac{C}{C_o} = e^{-3.46 \times 10^{-2} \times 3 \times 60} = 1.97 \times 10^{-3}$$

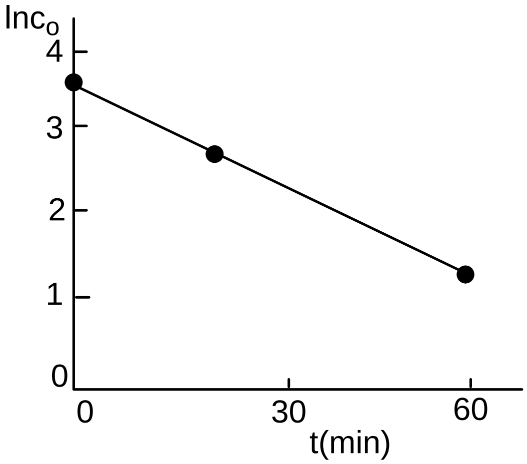
$C = 1.97 \times 10^{-3} \times C_o = \boxed{0.2\%}$ of original amount of C^{11} remains after 3 hours

(b) Since the half–life is independent of concentration (for first order reactions), the answer must be the same as in (a):

$$1.97 \times 10^{-3} \simeq \boxed{0.2\%}\ \text{remains after 3 hours}$$

13. In this question we are given a concentration of product (or rather, a volume proportional to a product). We want to convert the information given into quantities proportional to the original reactant (to be able to treat the problem in the familiar manner). We recognize that the volume of alkali for $t = \infty$ (29.7 ml) should be proportional to C_o, the concentration of the reactant at $t = 0$. The volume at $t = 27$ min, proportional to the remaining reactant concentration, is (29.7 – 18.1) ml and the volume at $t = 60$ min, proportional to the remaining reactant concentration, is (29.7 – 26.0) ml. We can now plot the data in terms proportional to reactant concentration vs time.

time (min)	0	27	60	∞
V (ml) prop. to product	0	18.1	26.0	29.7
V (ml) prop. to reactant	29.7	(29.7–18.1)	(29.7–26.0)	0
ln V (prop. to reactant)	3.39	2.45	1.31	



From the graph, the reaction is shown to be **first order**. For the slope determination, we may use t = 0 and t = 60 min.

$$-k = \frac{3.39 - 1.31}{0 - 60}$$

$$= -3.47 \times 10^{-2}\ \text{min}^{-1}$$

$$\boxed{t_{1/2} = \frac{\ln 2}{3.47 \times 10^{-2}} = 20\ \text{min}}$$

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

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

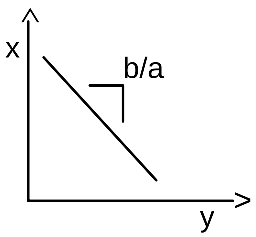
$$\ln 1.02 = \frac{E_A}{R}\,\frac{\Delta T}{T^2}$$

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

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

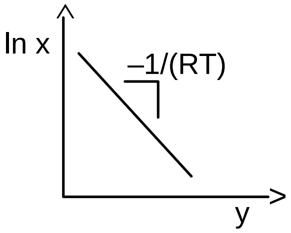
15. (1) $ax = by$

$$x = \frac{b}{a}y + \frac{c}{a}$$



(2) $x = Ae^{-y/RT}$

$$\ln x = \left(-\frac{1}{RT}\right)y + \ln A$$



(3) $xy = ax + by$

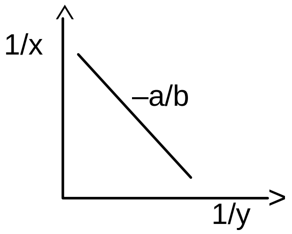
$$xy - ax = by$$

$$x(y-a) = by$$

$$\frac{y - a}{by} = \frac{1}{x}$$

$$\frac{1}{b} - \frac{a}{by} = \frac{1}{x}$$

$$\frac{1}{x} = -\frac{a}{by} + \frac{1}{b}$$



16. $$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{12.5\ a} = 5.54 \times 10^{-2}\ a^{-1}$$

$$\frac{c}{c_o} = e^{-kt} = \frac{0.14\ C_o}{C_o}$$

$$\ln 0.14 = -kt$$

$$t = \frac{-\ln 0.14}{5.54 \times 10^{-2}} = \boxed{35.5\ \text{years}}$$

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

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

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

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

18. T = 1600K $\quad$ 1/T = $6.25 \text{ x } 10^{-4}$

From the data in the problem:

D_{1600K} (In –> Si) = $8 \text{ x } 10^{-12}$ cm^2/sec

$$\frac{C}{C_2} = 1 - \text{erfc}\left(\frac{x}{2\sqrt{Dt}}\right)$$

C = 1/2 C_2

X = 10^{-3} cm

$$1 - \text{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) = 0.5$$

$$\text{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = 0.5$$

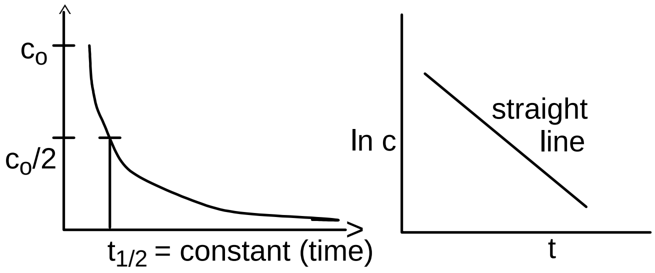
erf (Z) = 0.5 ; from tables, Z = 0.477

$$\left(\frac{x}{2\sqrt{Dt}}\right) = 0.477$$

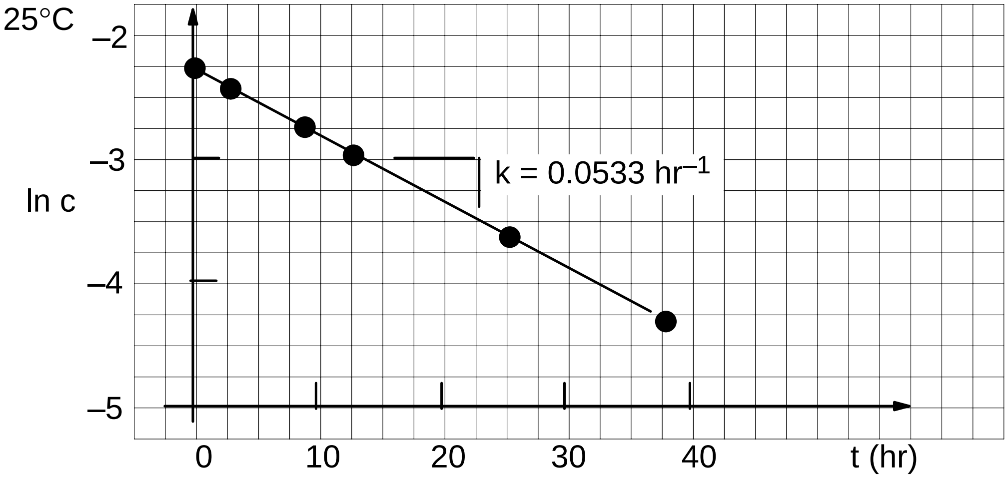
$$\left(\frac{x^2}{4Dt}\right) = 0.228$$

$$t = \frac{(10^{-3})^2}{0.228\ \text{x}\ 4D} = 1.37\ \text{x}\ 10^5\ \text{sec} = \boxed{1.59\ \text{days}}$$

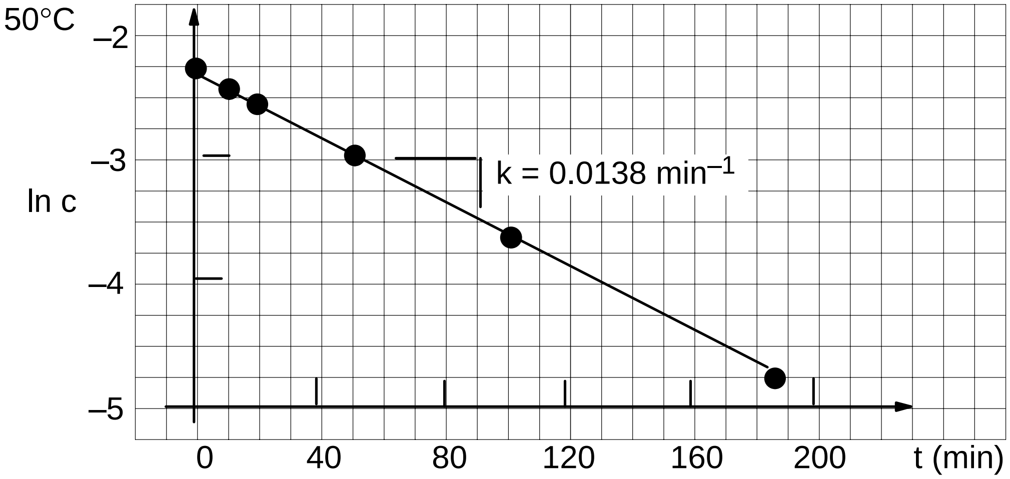
19. (a) For the first order reactions:



(b) at 25°C, k = 0.0533 hr^{-1}



at 50°C, k = 0.0138 min^{-1}



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

19. Continued.

(d)

$$k = A\ \exp\left(\frac{-E_a}{RT}\right)$$

We need to determine A (and E_a):

$$\frac{k_{25}}{k_{50}} = \exp\left(\frac{-E_a}{R}\right)\left(\frac{1}{T_{25}} - \frac{1}{T_{50}}\right) \qquad k_{25} = 0.0533\ \text{hr}^{-1} \times \frac{1\ \text{hr}}{60\ \text{min}}$$

$$= 8.88 \times 10^{-4}\ \text{min}^{-1}$$

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

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

At 25°C: $k = A\ \exp\text{–}(E_a/RT)$

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

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

So, at 70°C (= 343K):

$$k = A\ \exp - \left(\frac{E_a}{RT}\right) = (2.22 \times 10^{12})\ \exp - \left(\frac{8.77 \times 10^4}{8.31 \times 343}\right)$$

$k = 9.28 \times 10^{-2}\ \text{min}^{-1}$

and (finally!):

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

(continued)

19. (e)

$c = c_o e^{-kt}$

If reaction is 42% complete, then
58% of reactants remain.
Therefore, $c = 0.58\ c_o$.

$$\ln\frac{c}{c_o} = -kt$$

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

20. $t_{1/2} = (\ln 2)/k = 1590$ years

$k = 4.36 \times 10^{-4}\ \text{years}^{-1}$

$c/c_o = e^{-kt}$

$c/c_o = \exp -(4.36 \times 10^{-4})(15) = 0.993$

Hence, fraction decayed = 1 – 0.993 = $\boxed{0.007}$

21. $E_a = 50 \times 10^3$ J/mole

$$k = A\ \exp -\left(\frac{E_a}{RT}\right)$$

$$\frac{k_{25}}{k_{50}} = \exp -\left(\frac{E_a}{R}\right)\left(\frac{1}{298} - \frac{1}{283}\right)$$

$$\frac{k_{25}}{k_{10}} = 2.92 \quad ; \quad k_{10^o} = 0.342\ k_{25^o}$$

If we consider a “half–life” for tires, $t_{1/2} = (\ln 2)/k$:

$$\text{at } 10^oC,\ t_{1/2\ 10^o} = \frac{\ln 2}{t_{10}} = \frac{\ln 2}{0.342\ k_{25}} = 2.92\ t_{1/2\ 25^o}$$

$$\text{at } 25^oC,\ t_{1/2\ 25^o} = \frac{\ln 2}{k_{25}}$$

We have increased the life of the rubber by a factor of 2.92!

22. (a) Plot ln c vs t and 1/c vs t. If ln c vs t yields a straight line, then the reaction is first order and k equals the slope of the line. If 1/c vs t yields a straight line, then the reaction is second order and k equals the slope of the line.

(b) $$-k = \frac{-1.078 - 0.846}{3144 - 0} = -6.1 \times 10^{-4}\ \text{sec}^{-1}$$

$$\boxed{k = 6.1 \times 10^{-4}\ \text{sec}^{-1}}$$

See following graph. Realize: these data are same data as that of problem 29.

23. For a first order reaction we have:

$$k = \frac{\ln 2}{t_{1/2}} \quad \text{and} \quad k = \frac{\ln 2}{t_{1/2}} = Ae^{\frac{-E_A}{RT}}$$

(a) $k = Ae^{-E_A/RT}$ $\qquad$ $\ln k = \ln A - \frac{E_A}{RT}$

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

$$T = \frac{E_A}{R}\left(\ln \frac{A}{k}\right)^{-1} = \frac{E_A}{R}\left[\ln \frac{A}{\frac{\ln 2}{t_{1/2}}}\right]^{-1} = \frac{104 \text{ x } 10^3}{8.314}\left(\ln \frac{5 \text{ x } 10^{13}}{0.0115}\right)^{-1}$$

$$= \boxed{347^oK = 74.47^oC}$$

(b) $$T = \frac{E_A}{R}\left[\ln \frac{A}{\frac{\ln 2}{t_{1/2}}}\right]^{-1} = \frac{104 \text{ x } 10^3}{8.314}\left[\ln \frac{5 \text{ x } 10^{13}}{\frac{\ln 2}{30 \text{ x } 24 \text{ x } 3600}}\right]^{-1}$$

$$= \boxed{268^oK = 5.01^oC}$$

24. $$\frac{k_1}{k_3} = \frac{1}{3} = \frac{Ae^{-E_A/RT_1}}{Ae^{-E_A/RT_2}} = e^{\frac{-E_A}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

$$\ln \frac{1}{3} = -\frac{E_A}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$-\ln \frac{1}{3} = \ln 3 = \frac{E_A}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$E_A = \frac{\ln 3 \text{ x } R}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

(a) $$E_A = \frac{\ln 3 \text{ x } 8.314}{\left(\frac{1}{300} - \frac{1}{310}\right)} = \boxed{84.9 \text{ x } 10^3 \text{ J/mole}}$$

24. (b) $$E_A = \frac{\ln 3 \text{ x } 8.314}{\left(\frac{1}{1000} - \frac{1}{1010}\right)} = \boxed{922.5 \text{ x } 10^3 \text{ J/mole}}$$

25. $SO_2Cl_2 \rightarrow SO_2 + Cl_2$: $k = 2.2 \text{ x } 10^{-5} \text{ sec}^{-1}$ (at $T = 593^oK$)

$$\ln \frac{C}{C_o} = -kt$$

$$\frac{C}{C_o} = e^{-kt} = e^{-2.2 \text{ x } 10^{-5} \text{ x } 2 \text{ x } 3600} = 0.853$$

or: $\boxed{\text{14.7\% has decomposed}}$

26. $$k = 2 \text{ x } 10^{13}\ e^{-\frac{216.1 \text{ x } 10^3}{8.314 \text{ x } 700}} = 1.496 \text{ x } 10^{-3} \text{ sec}^{-1}$$

$$\boxed{t_{1/2} = \frac{\ln 2}{1.496 \text{ x } 10^{-3}} = 463 \text{ sec at } 700^oK = 7.72 \text{ min at } 700^oK}$$

27. At T_x, $k_A = k_B$ or: $10^{15}\ e^{\frac{-125 \text{ x } 10^3}{RT_x}} = 10^{13}\ e^{\frac{-83.6 \text{ x } 10^3}{RT_x}}$

$$\ln 10^{15} - \frac{125 \text{ x } 10^3}{RT_x} = \ln 10^{13} - \frac{83.6 \text{ x } 10^3}{RT_x}$$

$$\ln \frac{10^{15}}{10^{13}} = \frac{1}{RT_x}\left[(125 \text{ x } 10^3) - (83.6 \text{ x } 10^3)\right]$$

$$T_x = \frac{(125 \text{ x } 10^3) - (83.6 \text{ x } 10^3)}{R \text{ x } \ln \frac{10^{15}}{10^{13}}}$$

$$= \frac{41.4 \text{ x } 10^3}{8.314 \text{ x } \ln \frac{10^{15}}{10^{13}}} = \boxed{1081^oK = 808^oC}$$

28. $k = \dfrac{\ln 2}{t_{1/2}}$ $\qquad k_1 = k_{300^oC} = \dfrac{\ln 2}{100} = 6.9 \times 10^{-3}\ \text{sec}^{-1} \quad (T_1 = 573^oK)$

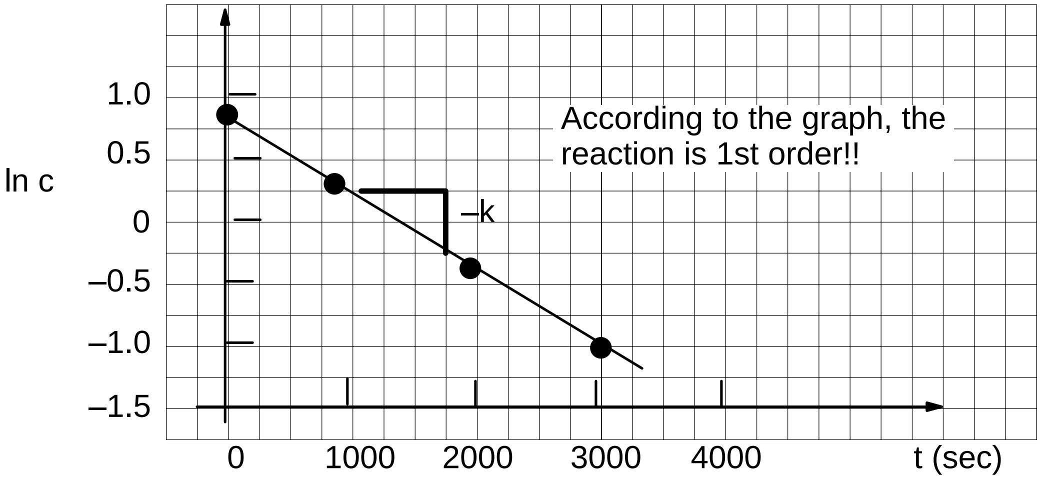
$$k_2 = k_{500^oC} = \frac{\ln 2}{20} = 3.5 \times 10^{-2}\ \text{sec}^{-1} \quad (T_2 = 773^oK)$$

$$\frac{k_1}{k_2} = \frac{6.9 \times 10^{-3}}{3.5 \times 10^{-2}} = 0.197 = e^{-\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

$$\ln 0.197 = -\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$E_a = -\frac{\ln 0.197 \times R}{\frac{1}{T_1} - \frac{1}{T_2}} = \boxed{29.9 \times 10^3\ \text{J/mole}}$$

29. (a) Plot ln c vs t and 1/c vs t. If ln c vs t yields a straight line, then the reaction is first order and –k equals the slope of the line. If 1/c vs t yields a straight line, then the reaction is second order and k equals the slope of the line.



According to the graph, the reaction is 1st order!!

$$-k = \frac{-1.078 - 0.846}{3144} = -6.1 \times 10^{-4}\ \text{sec}^{-1}$$

(b) $-k = \dfrac{-1.078 - 0.846}{3144}$

$$\boxed{k = 6.1 \times 10^{-4}\ \text{sec}^{-1}}$$

(continued)

29. Continued.

(c) $C = C_o\ e^{-kt}$ (for a first order reaction)

$$C = 2.33 \text{ x } e^{-6.1 \text{ x } 10^{-4} \text{ x } 4500}$$

$$\boxed{C = 0.15 \text{ moles/ltr}}$$

30. In this question the rate of disintegration (decay) is given (– dc/dt = 1.4 x 10^5/min). To determine $t_{1/2}$ (or k), we look at the rate equation:

$$-\frac{dc}{dt} = kc$$

We need to know the concentration (c) at t = 0; it is given through the data provided:

$$1\ \mu g = 10^{-6} \text{ g } Pu^{239}$$

The isotope Pu–239 has the atomic weight 239:

$$1\ \mu g = 10^{-6} \text{ g x } \frac{6.02 \text{ x } 10^{23} \text{ atoms mole}^{-1}}{239 \text{ g mole}^{-1}} = \boxed{2.52 \text{ x } 10^{15} \text{ atoms}}$$

Thus:

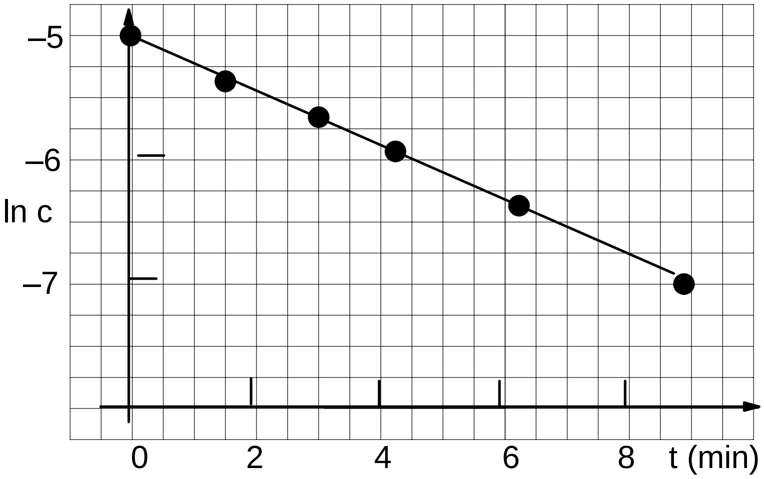
$$-\frac{dc}{dt} = kc \quad \text{and} \quad k = -\frac{\frac{dc}{dt}}{c} = \frac{1.4 \text{ x } 10^5}{2.52 \text{ x } 10^{15}} = 5.56 \text{ x } 10^{-11} \text{ min}^{-1}$$

$$= 2.92 \text{ x } 10^{-5} \text{ years}$$

$$t_{1/2} = \frac{0.693}{2.92 \text{ x } 10^{-5}} = \boxed{23,700 \text{ years}}$$

31. (a) A look at the data shows that after three minutes the concentration drops from 6.5 to 3.25 m–moles/ltr, and after 6.5 min c has decreased to 1.45 m–moles – a typical first order reaction behavior. (We could forego plotting the data and take $t_{1/2}$ = 3 min, test the validity of this value, and calculate the requested data.)

conc	ln c	time (min)
6.50	–5.03	0
4.61	–5.38	1.5
3.25	–5.73	3.0
2.50	–6.00	4.2
1.45	–6.54	6.5
0.85	–7.07	8.8



$$-k = \frac{-7.07 + 5.03}{8.8} = 0.232 \text{ min}^{-1}$$

(b) $k = 0.232 \text{ min}^{-1}$

(c) $$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{0.232} = 2.99 = \boxed{3.0 \text{ min}}$$

(d) $$c = c_o e^{-kt} = 6.5 \times 10^{-3} e^{-0.232 \times 11} = \boxed{0.506 \times 10^{-3} \text{ m–moles/ltr}}$$

32. First order reaction:

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

$$t_{1/2} = 30\text{d} = 30 \times 24 \times 3600 \text{ s} = 2.592 \times 10^6 \text{ s}$$

$$k = \frac{\ln 2}{2.6 \times 10^6} = 2.7 \times 10^{-7} \text{ s}^{-1}$$

$$k = Ae^{-E/RT_x} \quad ; \quad \ln k = \ln A - \frac{E}{RT_x}$$

$$T_x = \frac{E}{R(\ln A - \ln k)} = \boxed{324\text{K}}$$

33. We may solve the problem graphically: plot ln k_t vs 1/T, which yields –E/R as the slope which will permit us to determine the pre–exponential, A. Alternately we can take T_1 and T_4 (which are on the curve) and solve numerically:

$$\ln k_1 = \ln A - \frac{E}{RT_1}$$

$$\ln k_2 = \ln A - \frac{E}{RT_2}$$

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

for $T_1 = 273K$

$T_2 = 318K$

$$E = -\frac{\ln \frac{k_1}{k_2} \text{ x } R}{\frac{1}{T_1} - \frac{1}{T_2}}$$

$E = 9 \text{ x } 10^4$ J/mole

$A = k \text{ x } e^{E/RT} = \boxed{1.8 \text{ x } 10^{12} \text{ s}^{-1}}$

34.

$$\ln \frac{k_1}{k_2} = \ln \frac{1}{2} = -\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

for $T_1 = 300K$

$T_2 = 310K$

$$E = -\frac{\ln 0.5 \text{ x } R}{\frac{1}{300} - \frac{1}{310}}$$

$$\boxed{E = 53.6 \text{ kJ/mole}}$$

35. (a) $\frac{c}{c_o} = e^{-kt}$

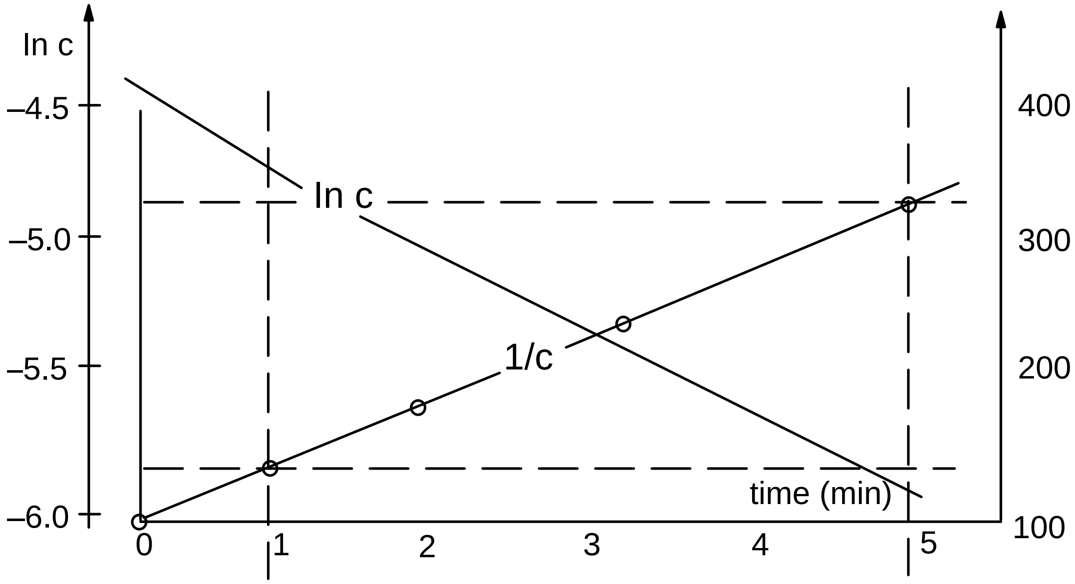
$$c = 1.65 \cdot 10^{-2} \cdot e^{-4.8 \cdot 10^{-4} \cdot 825} = \boxed{1.11 \text{x} 10^{-2} \text{ moles/L}}$$

(continued)

35. (b) $$\frac{1.0 \cdot 10^{-2}}{1.65 \cdot 10^{-2}} = e^{4.8 \cdot 10^{-4} \cdot t}$$

$$\ln 1.65 = 4.8\text{x}10^{-4} \text{ x } t \qquad \boxed{t = \frac{\ln\ 1.65}{4.8 \cdot 10^{-4}} = 1043 \text{ sec}}$$

36. (a)



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

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

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

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

$$\tau_{\frac{1}{2}} = \frac{1}{k \cdot C_o} = \frac{1}{46.5 \cdot 10^{-2}} = \boxed{2.15 \text{ min}}$$

37. $k = A \cdot e^{-\frac{E_A}{RT}}$

$$\frac{k_{T_1}}{k_{T_2}} = \frac{A \cdot e^{\frac{-E}{RT_1}}}{A \cdot e^{\frac{-E}{RT_2}}} = e^{-\frac{E}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]} = \frac{kT_1}{3 \cdot kT_1} = \frac{1}{3}$$

$$\ln \frac{1}{3} = -\ln 3 = -\frac{E_A}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$E_A = \frac{R \cdot \ln 3}{\left[\frac{1}{293} - \frac{1}{313}\right]} = \boxed{41.9 \ \frac{\text{kJ}}{\text{mole}}}$$

38. (a) $$\frac{k_{350}}{k_{400}} = e^{-\frac{E_A}{R}\left[\frac{1}{350} - \frac{1}{400}\right]} = \frac{9.3 \text{ x } 10^{-6}}{6.9 \text{ x } 10^{-4}} = \frac{1}{74.2}$$

$$E_A = \frac{[\ln 74.2] \cdot R}{\frac{1}{350} - \frac{1}{400}} = \boxed{100.3 \ \frac{\text{kJ}}{\text{mole}}}$$

(b) First we find A, then we determine (k).

$$6.9 \cdot 10^{-4} = A \cdot e^{\frac{-100300}{R \cdot 400}}$$

$$A = 6.9 \cdot 10^{-4} \cdot e^{\frac{100300}{R \cdot 400}} = 8.65 \cdot 10^{9}$$

$$k_{450} = 8.65 \cdot 10^{9} \cdot e^{\frac{-100300}{8.314 \cdot 450}} = \boxed{1.97 \cdot 10^{-2} \ \text{sec}^{-1}}$$