3.1 Since the reaction order, hence concentration dependency, is not known we are not given enough information to find the rate of reaction at the higher concentration ←—————————

3.3 For the 2nd order disappearance of a single reactant Eq 16, pg 49 gives

$$kt = \frac{1}{C_{A0}}\left(\frac{X_A}{1-X_A}\right) \quad \cdots \text{ or } \cdots \quad t = \frac{1}{kC_{A0}}\left(\frac{X_A}{1-X_A}\right)$$

Now for 50% conversion:
$$t_{50} = \frac{1}{kC_{A0}}\left(\frac{1/2}{1-1/2}\right) = \frac{1}{kC_{A0}} = 5 \text{ min}$$

For 75% conversion:
$$t_{75} = \frac{1}{kC_{A0}}\left(\frac{3/4}{1-3/4}\right) = \frac{3}{kC_{A0}} = 15 \text{ min}$$

∴ the extra time needed is 10 minutes ←—————————

3.5 Since the fractional disappearance is independent of initial concentration we have a first order rate, or

$$-\frac{dC}{dt} = kC \quad \cdots \text{ or } \cdots \quad \ln\frac{C_0}{C} = kt \quad \cdots \text{ where } C = \text{monomer concentration}$$

We also can find the rate constant. Thus replacing values

$$\ln\frac{C_0}{0.8C_0} = k(34 \text{ min}) \quad \cdots \text{ or } \quad k = \frac{-\ln 0.8}{34 \text{ min}} = 0.00657 \text{ min}^{-1}$$

Hence the rate of disappearance of monomer is given by

$$-r = -\frac{dC}{dt} = (0.00657 \text{ min}^{-1})C \quad ←—————————$$

3.7 Magoo's betting habits, and his losses, can be described by

$$-\frac{d\$}{dt} = k\$ \quad \cdots \text{ or } \quad \ln\frac{\$_0}{\$} = kt \quad \cdots \text{ where } \$ = \text{money at hand}$$

Now at t=0 $\cdots$ $\$_0 = 180$ } from which we can find his "paupacity" constant
t=2 hrs $\cdots$ $\$ = 135$

$$k = \frac{1}{t}\ln\frac{\$_0}{\$} = \frac{1}{2}\ln\frac{180}{135} = 0.144 \text{ hr}^{-1}$$

3.7
(Continued)

After his raise we have $\left.\begin{array}{l} t=0 \cdots \$_0 = ? \\ t = 3\,hrs \quad \$ = 135 \end{array}\right\}$ ... from this find $\$_0$

For unchanged betting habits

$$\ln \frac{\$_0}{135} = (0.144)(3) \cdots \text{ or } \$_0 = 208$$

Hence his raise is $208 - 180 \cdots$ or $\$28$

3.9 For a first order reversible reaction

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R \begin{cases} C_{A0} = 0.5\,mol/lit \\ C_{R0} = 0 \end{cases} \cdots X_{Ae} = 0.667$$
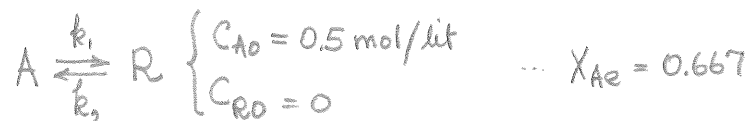
the integrated conversion equation in a batch reactor (constant volume because it is a liquid) is given by

$$-\ln\left(1 - \frac{X_A}{X_{Ae}}\right) = (k_1 + k_2)t$$

Replacing values we then find

$$-\ln\left(1 - \frac{1/3}{2/3}\right) = (k_1 + k_2)\,8\,min \quad \cdots \quad \therefore k_1 + k_2 = \frac{\ln 2}{8} = 0.086625 \; min^{-1} \cdots (i)$$

Now from thermodynamics we know that

$$K = \frac{C_{Re}}{C_{Ae}} = \frac{k_1}{k_2} = \frac{0.5 \times 2/3}{0.5 \times 1/3} = 2$$

equilibrium constant

Thus .... $\qquad k_1 = 2 k_2$ $\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (ii)

Solving (i) & (ii) gives $\begin{cases} k_2 = \dfrac{0.086625}{3} = 0.028875 \\ k_1 = 0.057750 \end{cases}$

Thus the rate expression for the disappearance of A

$$-r_A = 0.05775\, C_A - 0.028875\, C_R$$

$\underset{mol/lit\cdot min}{} \qquad \underset{min^{-1}}{} \quad \underset{mol/lit}{} \qquad \underset{min^{-1}}{} \quad \underset{mol/lit}{}$

3.11   From the table of data

at $C_A = 500$ $t = 100 \, min$

Thus

at $t = 5 \, hrs + 100 \, min = 400 \, min$

$C_A = 200 \, \dfrac{mol}{m^3}$ ... or $X_A = 0.6$ ⟵ _____

3.13

Let $A = \begin{smallmatrix} galloping \\ dominoes \end{smallmatrix}$. Then by this game alone $-\left(\dfrac{d\$}{dt}\right)_A = k_A \$$ -------- (i)

Let $B = $ chuk-a-luck. Then by this game alone $-\left(\dfrac{d\$}{dt}\right)_B = k_B \$$ ------- (ii)

Playing $A \& B$ simultaneously $-\dfrac{d\$}{dt} = -\left(\dfrac{d\$}{dt}\right)_A - \left(\dfrac{d\$}{dt}\right)_B = (k_A + k_B) \$$ ------ (iii)

From the problem statement we can find k_A from (i), k_B from (ii). We then use these in (iii) to see how long he can play both games simultaneously. This is our strategy

Integrating (i) we get $\ln \dfrac{\$_0}{\$} = k_A t$ ---or--- $k_A = \dfrac{1}{t} \ln \dfrac{\$_0}{\$}$

and with the data given. $k_A = \dfrac{1}{4} \ln 2$ -------- (iv)

Similarly with (ii) $k_B = \dfrac{1}{2} \ln 2$ ------- (v)

Integrating (iii) gives $\ln \dfrac{\$_0}{\$} = (k_A + k_B) t$ ---or--- $t = \dfrac{1}{k_A + k_B} \ln \dfrac{\$_0}{\$}$

and with (iv) & (v)

$$t = \dfrac{1}{\frac{3}{4} \ln 2} \ln \dfrac{1000}{10} = 8.87 \, hrs$$ ⟵

Note: This is simply a case of two "1st order reactions" in parallel, see pg. 49.
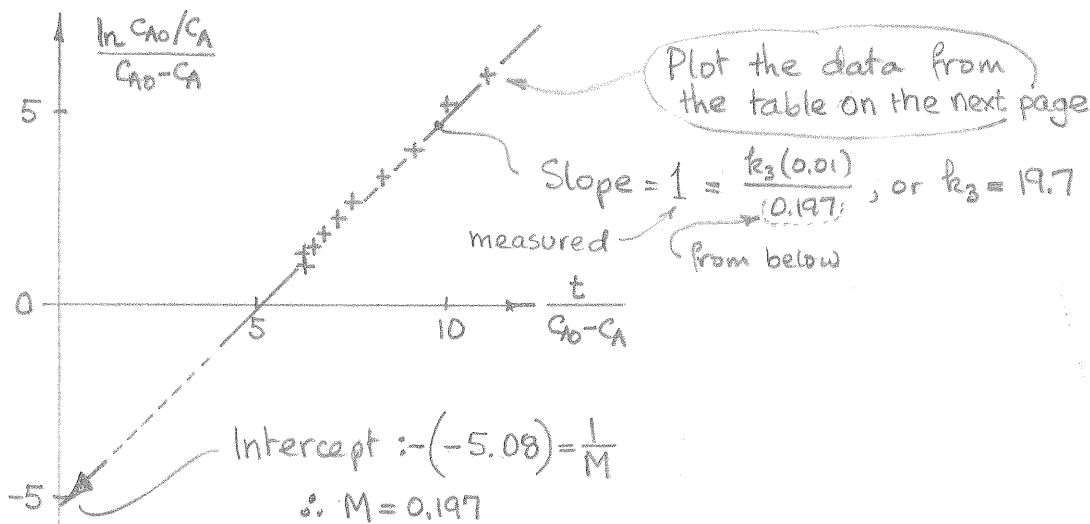

3.15 We can test the fit of the Michaelis-Menten type equation in many ways, integral or differential. We will sketch these different solutions in turn. But first let us transform the M-M equation into the following useful form

$$-r_A = \frac{k_3 C_{EO} C_A}{C_A + M} = \frac{k_4 C_A}{1 + k_5 C_A} \quad \cdots \text{where} \quad \begin{cases} k_4 = \dfrac{k_3 C_{EO}}{M} \\[2mm] k_5 = \dfrac{1}{M} \end{cases} \cdots\cdots\cdots(i)$$

use this form

Integral method Integrating (i) gives

$$\frac{\ln C_{AO}/C_A}{C_{AO} - C_A} = -k_5 + \frac{k_4 t}{C_{AO} - C_A} \quad \cdots \begin{cases} \text{slope:} \quad k_4 = \dfrac{k_3 C_{EO}}{M} \\[2mm] \text{intercept:} -k_5 = \dfrac{1}{M} \end{cases} \cdots\cdots(i)$$

Plot the data from the table on the next page

Slope = 1 = $\dfrac{k_3(0.01)}{(0.197)}$, or $k_3 = 19.7$

measured   from below

Intercept : $-(-5.08) = \dfrac{1}{M}$

∴ M = 0.197

From this figure the constants in Eq. (i) are

$$\left.\begin{array}{l} k_3 = 19.7 \ hr^{-1} \\[2mm] M = 0.197 \ \dfrac{millimol}{lit} \end{array}\right\} \ \text{thus} \quad r_A = \frac{19.7 \, C_A C_{EO}}{0.197 + C_A}$$

3.15
(continued)

t	C_A	$\dfrac{\ln C_{A0}/C_A}{C_{A0}-C_A}$	$\dfrac{t}{C_{A0}-C_A}$
1	0.84	1.09	6.25
2	0.68	1.2	6.25
3	0.53	1.35	6.39
4	0.38	1.56	6.45
5	0.27	1.80	6.85
6	0.16	2.18	7.15
7	0.09	2.65	7.7
8	0.04	3.36	8.34
9	0.018	4.08	9.17
10	0.006	5.15	10.1
11	0.0025	6.01	11.0

given   for integral method, above

3.17 For first order processes

$$k = \frac{0.6931}{t_{1/2}} = \frac{0.6931}{76 \text{ min}} = 9.12 \times 10^{-3} \text{ min}$$
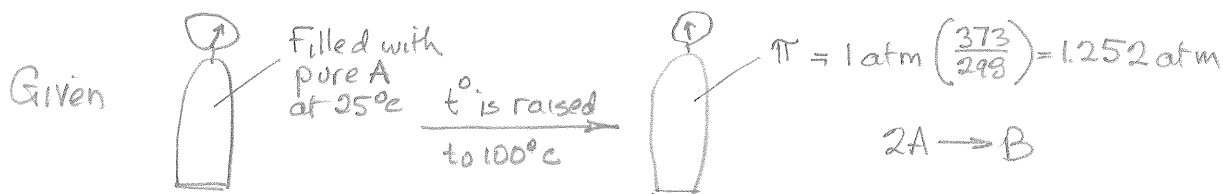
After one day

$$\frac{C_A}{C_{A0}} = e^{-kt} = e^{-(9.12 \times 10^{-3})(24 \times 60)} = 1.98 \times 10^{-6}$$

Thus the radioactivity drops to 2×10^{-6} of the original value.

3.19 The time for complete conversion of an nth order reaction from Eq. 29, is

$$t = \frac{C_{A0}^{1-n}}{(1-n)k} = \frac{(1)^{1-1/2}}{(1-1/2)3} = \frac{2}{3} \text{ hr}$$

Therefore after 1 hr $X_A = 1$, or $C_A = 0$

3.21

Given

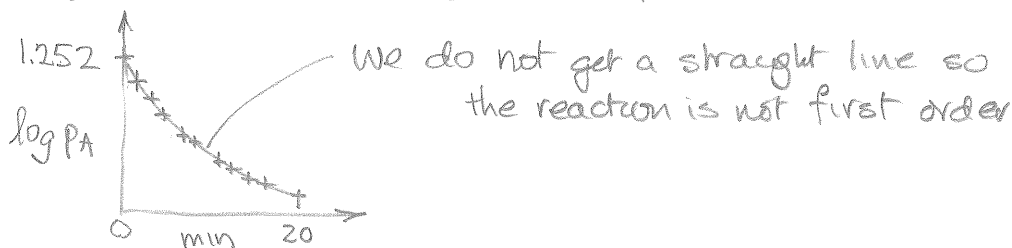Filled with pure A at 25°C, $t°$ is raised to 100°C

$\pi = 1\,atm\left(\frac{373}{298}\right) = 1.252\,atm$

$2A \longrightarrow B$

Tabulate

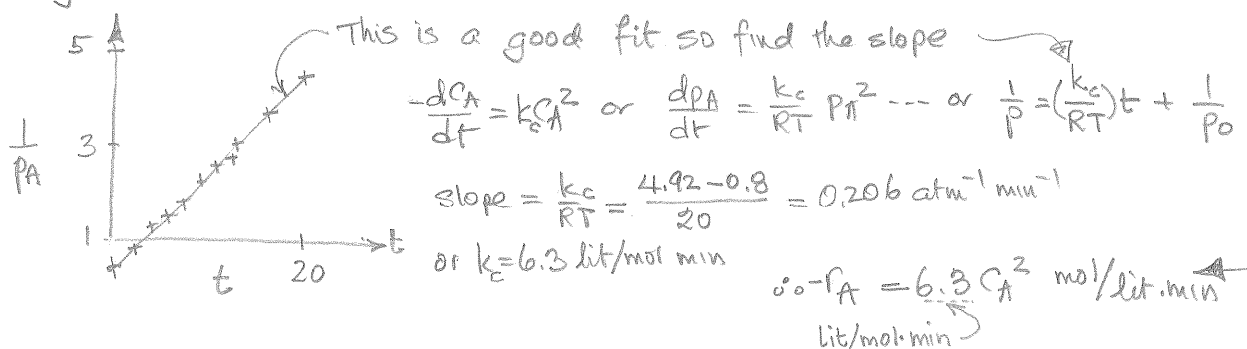| time (min) ①	π (atm) ②	p_A (atm) ③	$1/p_A$ (atm^{-1}) ④
0	(1.252)	(1.252)	(0.800)
1	1.14	1.028	0.975
2	1.04	0.828	1.208
3	0.982	0.712	1.404
4	0.940	0.628	1.592
5	0.905	0.558	1.792
6	0.870	0.488	2.049
7	0.850	0.448	2.232
8	0.832	0.412	2.427
9	0.815	0.378	2.646
10	0.800	0.348	2.873
15	0.754	0.256	3.90
20	0.728	0.204	4.90

given   calc^d.

Column ③ is obtained from Eq 5, or

$$p_A = p_{Ao} - \frac{a}{\Delta n}(\pi - \pi_o) = 1.252 - \frac{2}{(-1)}(\pi - 1.252) = 2\pi_A - 1.252$$

Try first order kinetics. For this plot as shown

We do not get a straight line so the reaction is not first order

Try second order kinetics. For this plot as shown

This is a good fit so find the slope

$$-\frac{dC_A}{dt} = k_c C_A^2 \quad or \quad \frac{dp_A}{dt} = \frac{k_c}{RT}p_\pi^2 \quad \cdots \quad or \quad \frac{1}{p} = \left(\frac{k_c}{RT}\right)t + \frac{1}{p_o}$$

$$slope = \frac{k_c}{RT} = \frac{4.92 - 0.8}{20} = 0.206\,atm^{-1}\,min^{-1}$$

or $k_c = 6.3\,lit/mol\cdot min$

$$\therefore -r_A = 6.3\,C_A^2 \;\; mol/lit\cdot min$$

lit/mol·min

3.23 Let us try n^{th} order kinetics. Then from Eq 33a, taking ratios, we get

$$\frac{(n-1)kt_2}{(n-1)kt_1} = \frac{C_{AO}\left[\left(\frac{C_{A2}}{C_{AO}}\right)^{1-n} - 1\right]}{C_{AO}\left[\left(\frac{C_{A1}}{C_{AO}}\right)^{1-n} - 1\right]} \quad \text{---(1)}$$

Replacing values give

$$2 = \frac{-1}{\left(\frac{1}{4}\right)^{1-n} - 1} \quad \text{---or} \quad n = \frac{1}{2} \longleftarrow$$

Replacing in Eq 33a gives

$$\left(\frac{1}{2} - 1\right)kt_2 = 1^{1-\frac{1}{2}}\left(\frac{mol}{lit}\right)^{1-\frac{1}{2}}\left[0-1\right]$$

or

$$k = 1 \frac{(mol)^{\frac{1}{2}}}{(lit)^{\frac{1}{2}}\cdot hr}$$

$$\therefore \quad -r_A = \left(1 \frac{mol^{\frac{1}{2}}}{lit^{\frac{1}{2}} hr}\right) C_A^{\frac{1}{2}}, \quad \frac{mol}{lit\cdot hr} \longleftarrow$$

3.25 Here we are given P_A vs t data, so we have two possible approaches

    (a) We could first transform at pressure readings into concentrations and then solve, or

    (b) We could stay with pressure readings and then transform our final equation into concentration units.

Let us stick with pressure units, and let us start by guessing first order reversible kinetics. Why reversible? Because at $t=\infty$ there is still some unreacted P_A. So the rate equation we will test is

$$A \underset{2}{\overset{1}{\rightleftarrows}} R, \quad \frac{dC_A}{dt} = k_1 C_A - k_2 C_R \quad \text{----}(53)$$

On integration we get

$$\ln\left(1 - \frac{X_A}{X_{Ae}}\right) = \frac{k_1 t}{X_{Ae}} \quad \text{-----}(54)$$
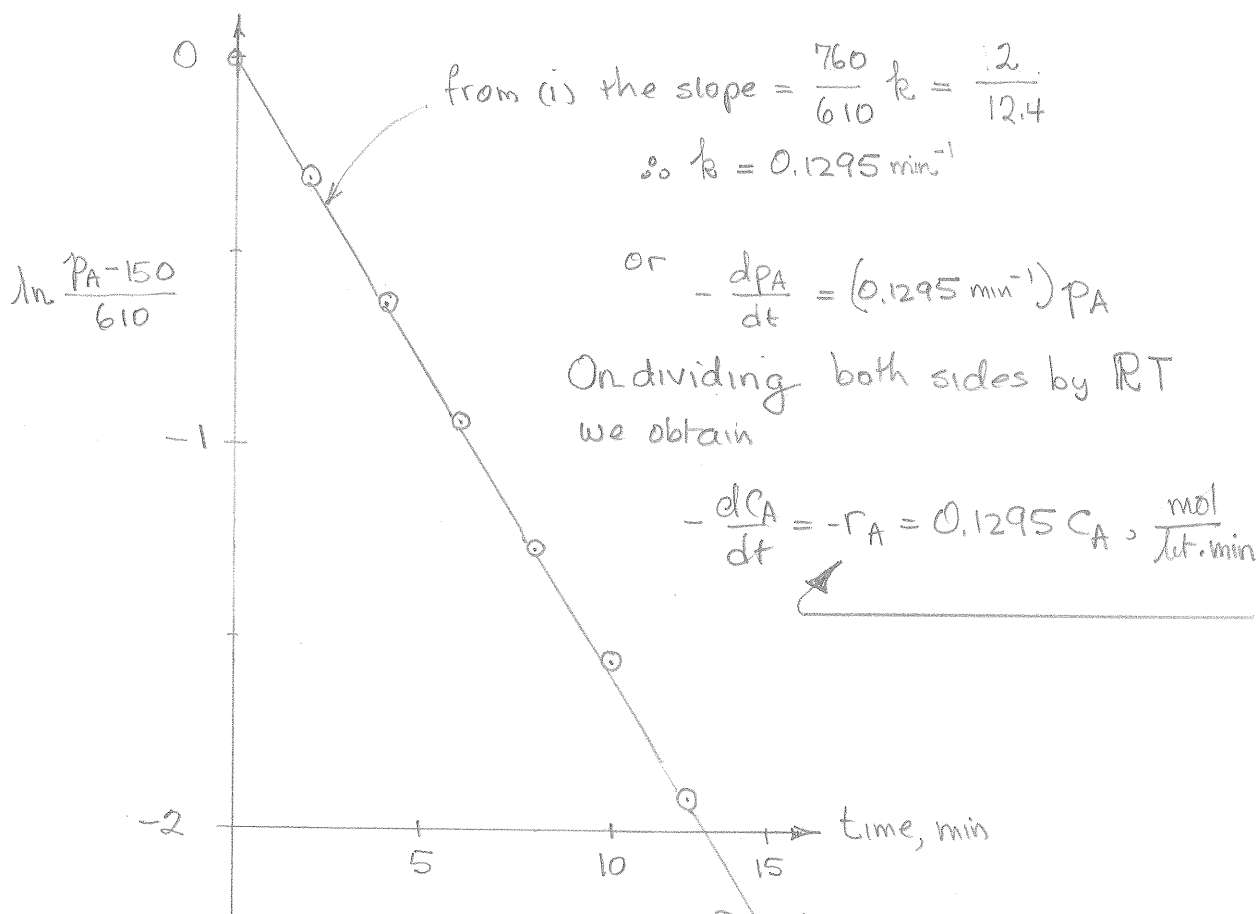
3.25
(continued)

In pressure units this integrated expression becomes

$$\ln \frac{p_A - p_{Ae}}{p_{Ao} - p_{Ae}} = \frac{k_1 t}{(p_{Ao} - p_{Ae})/p_{Ao}} \qquad \cdots (i)$$

Let us see whether this equation fits the facts. So tabulate & plot

t, min	p_A	$\frac{p_A - p_{Ae}}{p_{Ao} - p_{Ae}}$	$\ln \frac{p_A - p_{Ae}}{p_{Ao} - p_{Ae}}$
0	760	1	0
2	600	450/610	−0.3042
4	475	325/610	−0.6296
6	390	240/610	−0.9328
8	320	170/610	−1.2777
10	275	125/610	−1.5851
12	240	90/610	−1.9136
14	215	65/610	−2.2391
∞	150	0	−∞

Note: For 1st order rxs k_c and k_p have the same value, time^{-1}

from (i) the slope $= \frac{760}{610} k = \frac{.2}{12.4}$

∴ $k = 0.1295 \text{ min}^{-1}$

or $-\frac{dp_A}{dt} = (0.1295 \text{ min}^{-1}) p_A$

On dividing both sides by RT we obtain

$-\frac{dC_A}{dt} = -r_A = 0.1295 \, C_A , \frac{mol}{lit \cdot min}$

What this shows is that if we have isothermal 1st order kinetics we can use p_A or C_A without changing the rate constants

3.27 Since we are told that the reaction is elementary the stoichiometric equation shows that the reaction is 2nd order. So for a small relative concentration change we can write

$$-\frac{\Delta C_A}{\Delta t} = k\bar{C}_A^2$$

or

$$k = -\frac{\Delta C_A}{\Delta t}\frac{1}{\bar{C}_A^2} = \frac{-0.2\ \text{mol/lit}}{7\frac{2}{3}\ \text{hr}} \cdot \frac{1}{(19.9\ \text{mol/lit})^2} = 6.6\times10^{-5}\ \text{lit/mol·hr}$$

$$\therefore -r_{NH_2-CO-NH_2} = (6.6\times10^{-5})\ C_{NH_2-CO-NH_2}^2, \quad \frac{\text{mol}}{\text{lit·hr}} \quad \blacktriangleleft$$

3.29

	2A → B	
Amount of A or B :	0.8	0.4
Amount of inert :	0.2	0.2
Total :	1.0	0.6

$$\therefore \varepsilon_A = -0.4$$

For a first order reaction in a variable volume set-up, we have from Eq.79

$$-\ln\left(\frac{\varepsilon_A + 1 - V/V_0}{\varepsilon_A}\right) = kt \quad \cdots or \cdots \quad -\ln\left(\frac{-0.4+1-0.8}{-0.4}\right) = k\cdot 3\,min$$

$$\therefore k = \frac{\ln 2}{3} = 0.231\ min^{-1} \quad \blacktriangleleft$$

3.31 The units of the rate constant tells that this is a 2nd order reaction

$$-r_A = kC_A^2 = k_0 e^{-E/RT} C_A^2$$

Thus

$$k = k_0 e^{-E/RT}$$

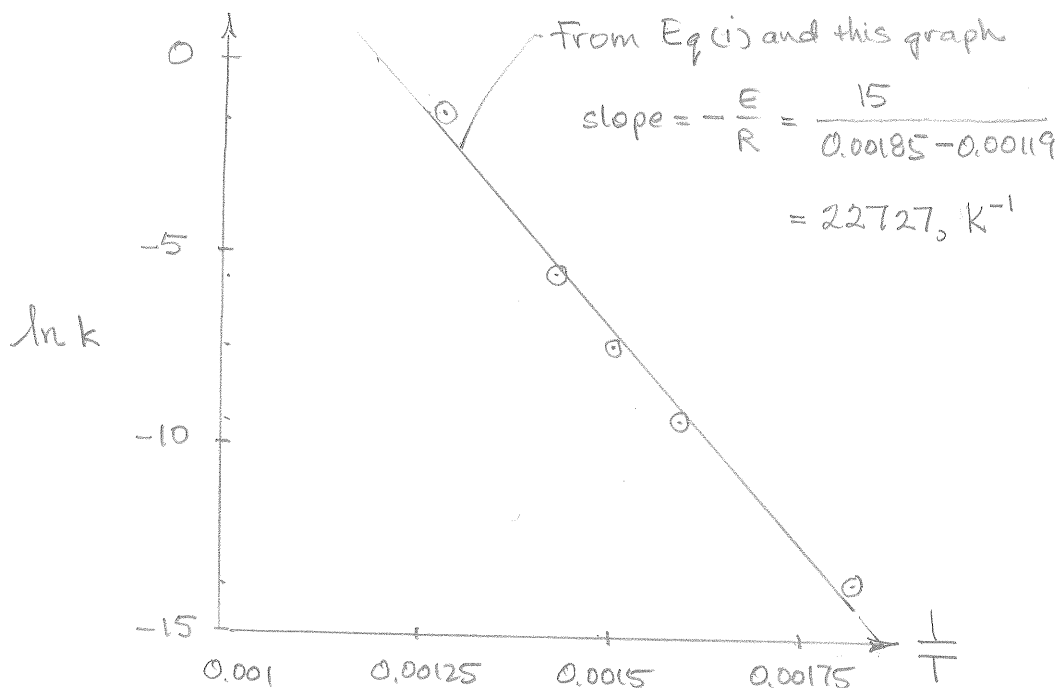or

$$\ln k = \ln k_0 - \frac{E}{R}\left(\frac{1}{T}\right)$$

So to find the value of the rate constant, or k_0 and E/R, we must plot $\ln k$ vs $1/T$. The slope gives E/R and the intercept gives k_0. Let us follow this procedure

3.31
(continued)

First let us tabulate

T, °C	T, K	1/T, K⁻¹	k	ln k
508	781	0.00128	0.1059	−1.6974
427	700	0.00143	0.0031	−5.7764
393	666	0.001502	0.000588	−7.4388
356	629	0.001590	80.9×10^{-6}	−9.4223
273	546	0.001832	0.942×10^{-6}	−13.8753

Next plot as shown below

From Eq (i) and this graph

$$\text{slope} = -\frac{E}{R} = \frac{15}{0.00185 - 0.00119}$$

$$= 22727, \text{K}^{-1}$$

To find the value of k_0 take the second data point.
From Eq (i)

$$\ln k_0 = \ln k - \frac{E}{R}\left(\frac{1}{T}\right)$$

$$= 5.7764 - 22727\left(\frac{1}{700}\right) = 38.2439$$

$$\text{or } k_0 = e^{38.2439} = 4.06 \times 10^{16}$$

So for the temperature range covered in the reported data

$$-r_{HI} = 4.06 \times 10^{16} \, e^{-22727/T} \, c_A^2, \quad {}^{mol}\!/_{cm^3 \cdot s}$$