

EXAMPLES OF EVALUATION OF RATE FORMS FROM KINETIC DATA IN BATCH SYSTEMS

EXAMPLE 1: Determine the reaction order and the rate constant for a single reaction of the type $A \rightarrow$ products based on the following experimental information obtained at isothermal conditions at $V = \text{const}$.

$t(\text{min})$	0	5	10	15	20	25	30	35	40	∞
$C_A \left(\frac{\text{mol}}{\text{lit}} \right)$	1	0.58	0.41	0.32	0.25	0.22	0.19	0.16	0.14	≈ 0

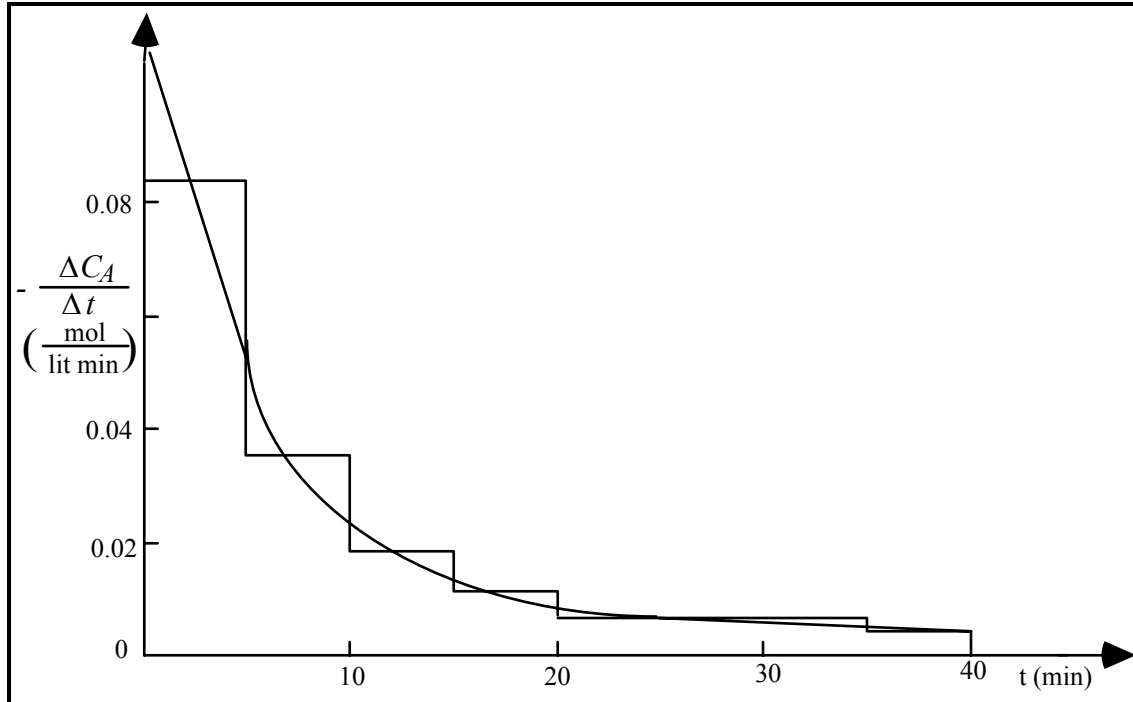
The last data point simply indicates that after a very long time (several hours as compared to minutes) practically no A is found. Thus, at the experimental conditions used the reaction is practically irreversible.

A. Differential Analysis:

We can form Δt_i and $-\Delta C_{A_i} = C_{A_i} - C_{A_{i+1}}$ from the table, and $-\frac{\Delta C_{A_i}}{\Delta t_i}$

$\Delta t = 5$	0-5	5-10	10-15	15-20	20-25	25-30	30-35	35-40
$-\frac{\Delta C_{A_i}}{\Delta t_i}$	0.084	0.034	0.018	0.014	0.006	0.006	0.006	0.004

We can plot now $-\frac{\Delta C_{A_i}}{\Delta t}$ vs. t_i as a stepwise curve shown below. Now we have to pass a smooth curve so that



the area under the stepwise curve and the smooth curve are approximately equal. From the smooth curve we now read off the corresponding values of $-\frac{dC_A}{dt}$ at desired measured concentrations C_{Ai} .

t	5	10	15	20	25	30	35
C_{Ai}	0.58	0.41	0.32	0.25	0.22	0.19	0.16
$-\frac{dC_A}{dt}$	0.055	0.024	0.015	0.0105	0.0065	0.005	0.004

Now we can plot

$$\log \left(-\frac{dC_A}{dt} \right) = \log k + \alpha \log C_A \text{ i.e. we plot } -\frac{dC_A}{dt} \text{ vs. } C_A \text{ on a log-log plot.}$$

From the slope of the straight line that we managed to pass through the data points we find that $\alpha = 2.05$. From any point of the line now we could determine k . For example:

$$\log (0.0014) = \log k + 2.05 \log 0.1$$

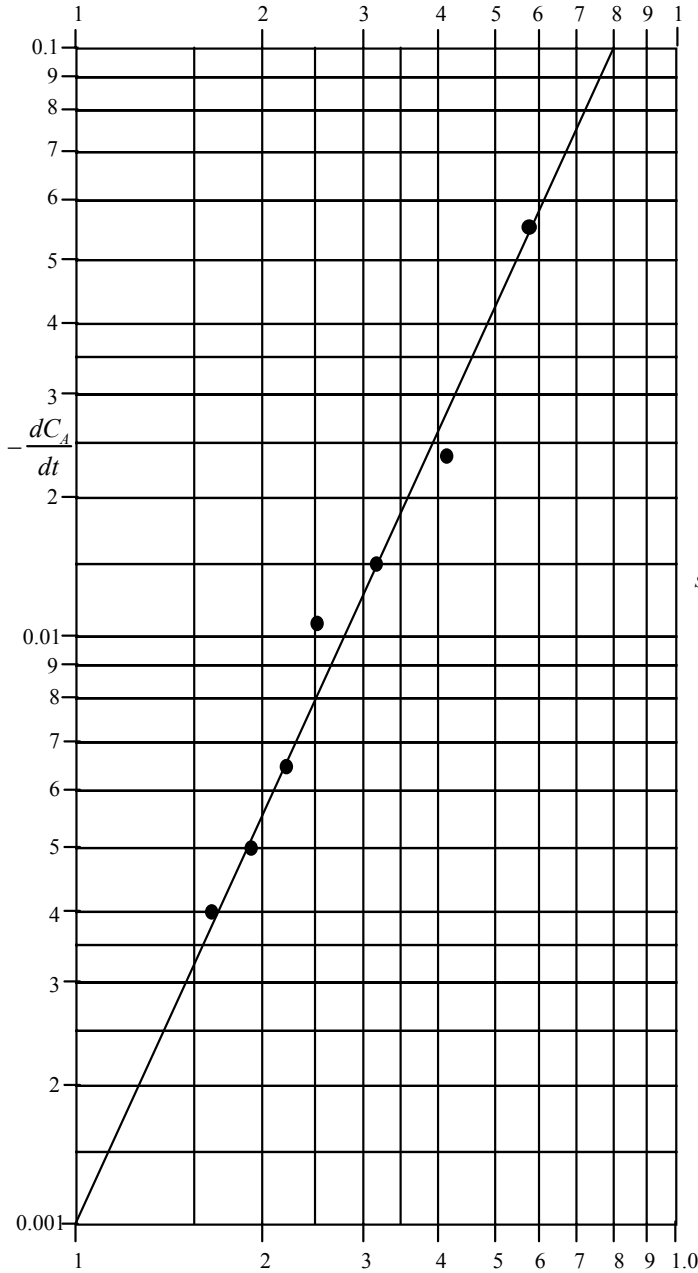
$$\log k = \log (0.0014) - 2.05 \log 0.1$$

$$\underline{\underline{k = 10^{-0.8039} = 0.157 \left(\frac{\text{lit}}{\text{mol min}} \right)}}$$

However, we should quickly realize that the estimated order is only 2.5% from 2nd order and, thus, most likely the reaction is of order two. $\alpha \equiv 2$. $-\frac{dC_A}{dt} = k C_A^2$.

We can now evaluate k for every data point and then average them out.

$$k = \frac{-\frac{dC_A}{dt}}{C_A^2} \quad \begin{array}{c|c|c|c|c|c|c|c} C_A & 0.58 & 0.41 & 0.32 & 0.25 & 0.22 & 0.19 & 0.16 \\ \hline k & 0.163 & 0.143 & 0.146 & 0.168 & 0.134 & 0.139 & 0.156 \end{array}$$



$$slope = \frac{\log\left(\frac{0.1}{0.0014}\right)}{\log\left(\frac{0.8}{0.1}\right)} = 2.05$$

The mean value of k turns out to be $k = 0.150 \left(\frac{\text{lit}}{\text{mol min}} \right)$. Thus at the temperature of the experiment we have determined

$$-r_A \left(\frac{\text{mol}}{\text{lit min}} \right) = 0.150 C_A^2$$

Note: Although the values of the rate constants calculated from various data points vary considerably, the variation is random and shows no trend with concentration level indicating that the selected order is correct.

Integral Method:

Suppose that we have attempted to solve the same problem by the integral method. Since the stoichiometry is $A \rightarrow$ products, we will try first whether a first order rate form can fit the data (hoping for an elementary reaction).

Assume $\alpha = 1$:

$$- \frac{dC_A}{dt} = k C_A$$

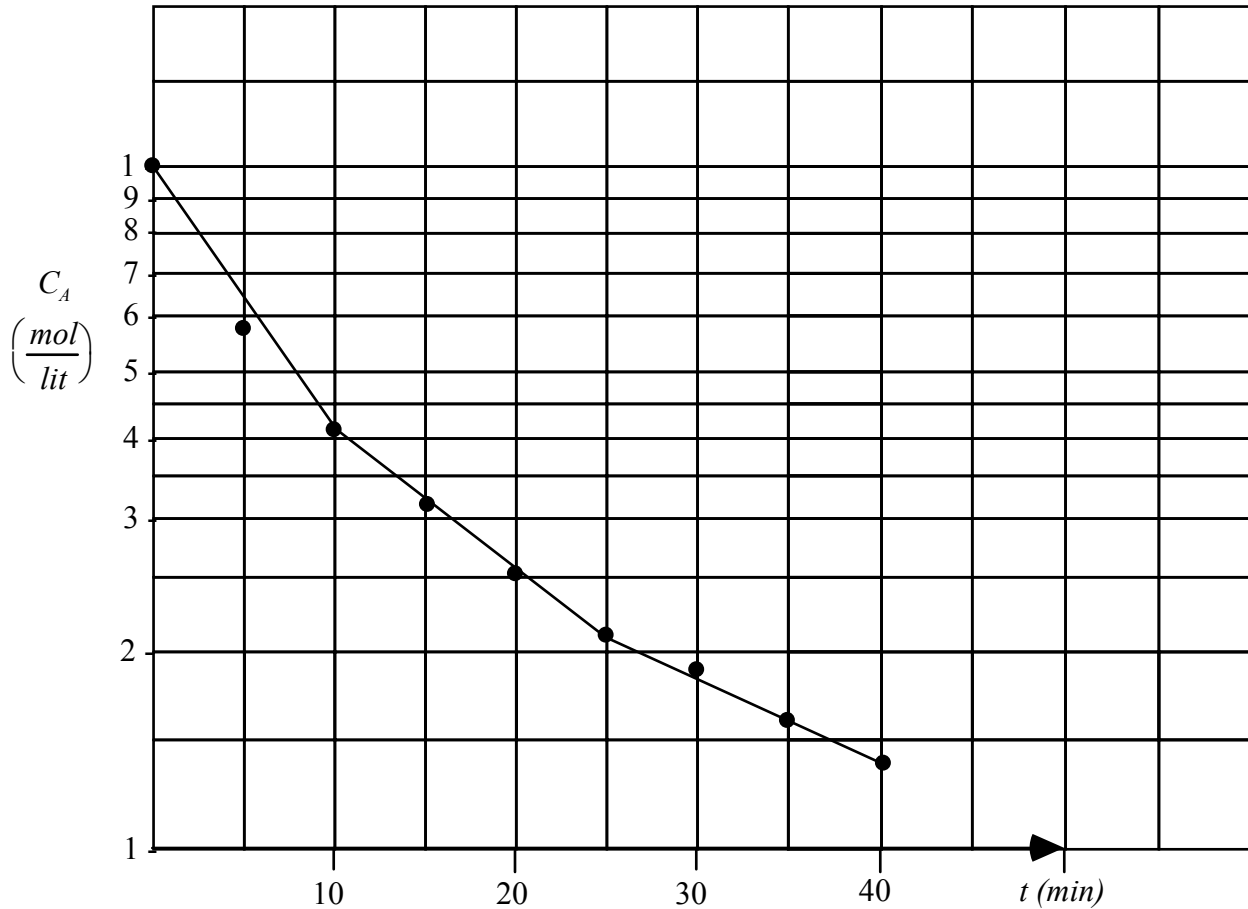
$$- \int_{C_{Ao}}^{C_A} \frac{dC_A}{C_A} = k \int_0^t dt$$

$$\ln \frac{C_{Ao}}{C_A} = kt$$

$$\log \frac{C_{Ao}}{C_A} = (2.3026)^{-1} k t$$

$$\log C_A = \log C_{Ao} - (2.3026)^{-1} k t$$

We should then plot the experimental data on a semi log plot (C_A on the log scale and t on the linear scale). If the assumed order of one is correct we should be able to obtain a straight line through the data points. It is clear from the enclosed figure that a straight line cannot be obtained since the data show a definite curve here - convex towards the bottom. If we connect the first and the last data point by a straight line all the other data are below the line indicating that the concentration drop is faster than predicted by first order behavior.



Try 2nd order $\alpha = 2$

$$-\frac{dC_A}{dt} = k C_A^2$$

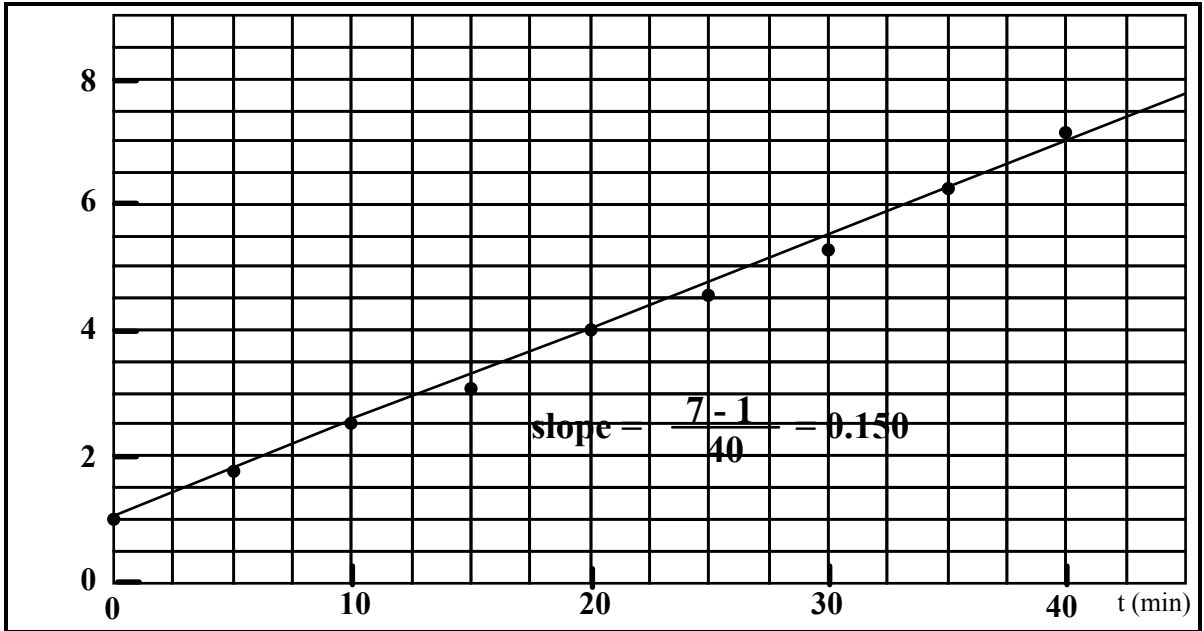
$$\frac{1}{C_A} = \frac{1}{C_{A0}} + kt$$

Plot $\frac{1}{C_A}$ vs. t on a linear plot.

This time a straight line is obtained which properly intersects the ordinate at $1 \left(\frac{1}{C_{A0}} = 1 \right)$. From the slope of the line we get $k = 0.150 \left(\frac{\text{lit}}{\text{mol min}} \right)$.

It is instructive again to evaluate k 's from the individual data points.

$$k = \frac{\frac{1}{C_A} - \frac{1}{C_{A0}}}{t} \quad \begin{array}{c|c|c|c|c|c|c|c|c|} C_A & 0.58 & 0.41 & 0.32 & 0.25 & 0.22 & 0.19 & 0.16 & 0.14 \\ \hline k & 0.145 & 0.144 & 0.142 & 0.150 & 0.142 & 0.142 & 0.150 & 0.154 \end{array}$$



The mean value of k turns to be $\bar{k} = 0.146 \left(\frac{\text{lit}}{\text{mol min}} \right)$ the difference between this mean value and the one obtained by "eye fitting" the line through data points is 2.7% and is negligible as far as engineering applications are concerned. Notice that the difference between the largest $k = 0.154$ and smallest $k = 0.142$ is only 0.012 or less than 8.5% based on the smallest k -value. For the same data the k 's evaluated by the differential method varied between a low of 0.134 and a high of 0.168, the difference being 0.034 or 25% based on the smallest k .

Thus, for the same quality data the integral method tends to smooth out the errors and give more consistent estimates for the rate constant.

Here by integral method we have determined also:

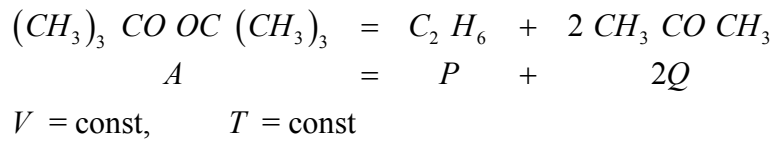
$$-r_A \left(\frac{\text{mol}}{\text{lit min}} \right) = 0.150 C_A^2$$

EXAMPLE 2:

Gas phase decomposition of di-t-butyl peroxide is monitored in a batch reactor of constant volume at isothermal conditions of 170°C. The run is started with pure di-t-butyl peroxide and the change of total pressure of the system was recorded in time. From the data below find the rate expression and the rate constant.

time (min)	0.0	2.5	5.0	10.0	15.0	20.0
$P(\text{mm Hg})$	7.5	10.5	12.5	15.8	17.9	19.4

The reaction is:



The hypothesized rate is of the form:

$$-r_A \left(\frac{\text{mol}}{\text{lit min}} \right) = k C_A^\alpha$$

We have seen before that we can also express the rate in terms of change of the partial pressure:

$$-\tilde{r}_A \left(\frac{\text{mm Hg}}{\text{min}} \right) = k_p P_A^\alpha$$

where

$$k_p = k (RT)^{1-\alpha}$$

In a batch system of constant volume:

$$-\tilde{r}_A = - \frac{dP_A}{dt} = k_p P_A^\alpha$$

We have shown before that

$$\begin{aligned} C_A &= C_{A0} - \xi = \frac{P_A}{RT} \\ C_T &= C_{T0} + \left(\sum_{j=1}^s \nu_j \right) \xi = \frac{P_T}{RT} \quad \frac{\text{here}}{\sum \nu_j = 3 - 1 = 2} \\ P_A &= P_{A0} - \frac{P_T - P_{T0}}{2} \end{aligned}$$

Since in this case $P_{A0} = P_{T0}$

$$P_A = \frac{3P_{T0} - P_T}{2}$$

$$\frac{1}{2} \frac{dP_T}{dt} = k_p \left(\frac{3P_{T0} - P_T}{2} \right)^\alpha$$

$$\boxed{\frac{dP_T}{dt} = (2^{1-\alpha} k_p) [3P_{T0} - P_T]^\alpha}$$

DIFFERENTIAL ANALYSIS:

Evaluate $\frac{\Delta P_T}{\Delta t}$, plot vs. t a stepwise curve, from a smooth curve that has the same area underneath as the stepwise curve. Evaluate $\frac{dP_T}{dt}$ and calculate the corresponding $3 P_{T_0} - P_T$. Plot $\frac{dP_T}{dt}$ vs. $3 P_{T_0} - P_T$ on a log-log scale. The slope gives α ; from the data find k_p and k and their mean value.

The augmented table is shown below as well as the two figures (next page)

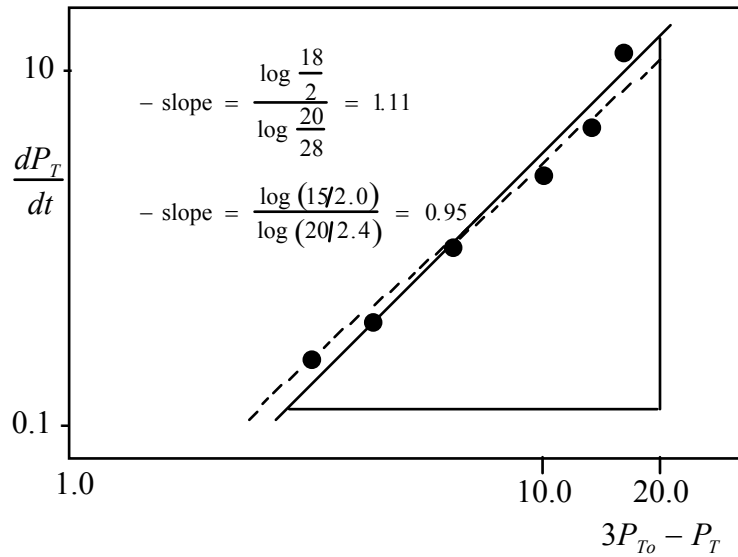
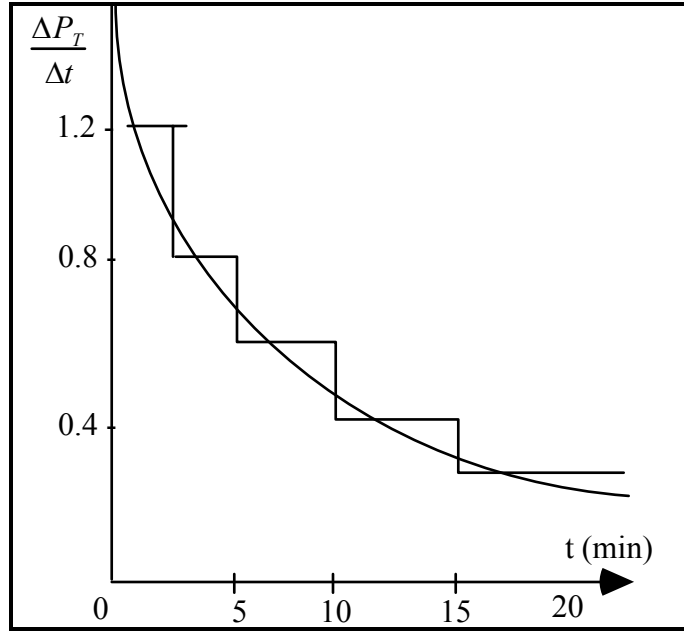
t	P_T	$\frac{\Delta P_T}{\Delta t}$	$\frac{dP_T}{dt}$	$3 P_{T_0} - P_T$	k_p
0	7.5		1.48	15.0	0.0987
2.5	10.5	1.20	0.95	12.0	0.0792
5.0	12.5	0.80	0.75	10.0	0.0750
10.0	15.8	0.66	0.52	6.7	0.0776
15.0	17.9	0.42	0.35	4.6	0.0761
20.0	19.4	0.30	0.25	3.1	0.0806

$\bar{k}_p = 0.0812(\text{min}^{-1})$

It seems that more than one straight line can be passed through the points on the log $\frac{dP_T}{dt}$ vs. $(3 P_{T_0} - P_T)$ plot. The maximum slope seems to be 1.11 and the minimum 0.95. This indicates that probably $\alpha = 1.0$.

$$k_p = \frac{\frac{dP_T}{dt}}{3P_{T_0} - P_T}$$

These values are given in the last column of the above table.



From the above figures and table we find

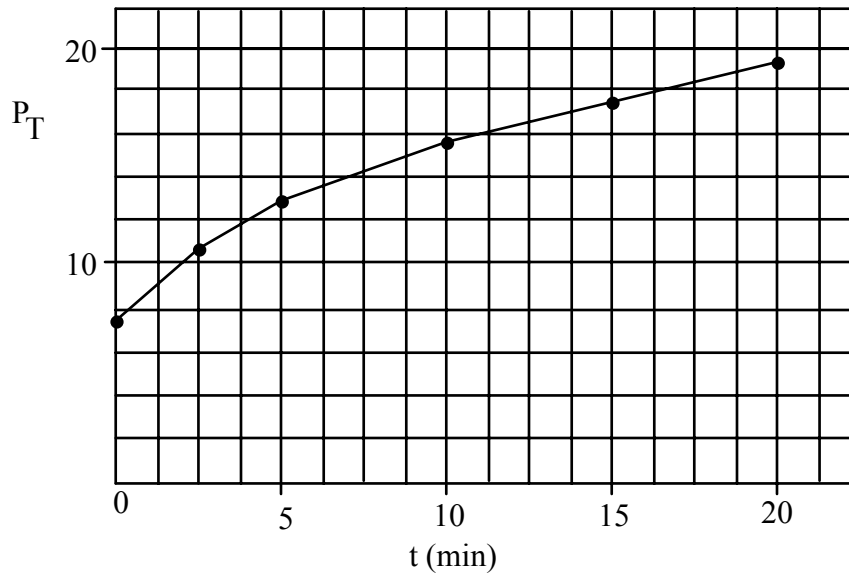
$$-\tilde{r}_A \left(\frac{\text{mm Hg}}{\text{min}} \right) = 0.0812 P_A = 0.08 P_A \text{ or } -r_A \left(\frac{\text{mol}}{\text{lit min}} \right) = 0.0812 C_A = 0.0022 P_A$$

INTEGRAL METHOD:

Suppose we assumed zero-th order

$$\frac{dP_T}{dt} = k'' \quad P_T = P_{T_0} + k'' t$$

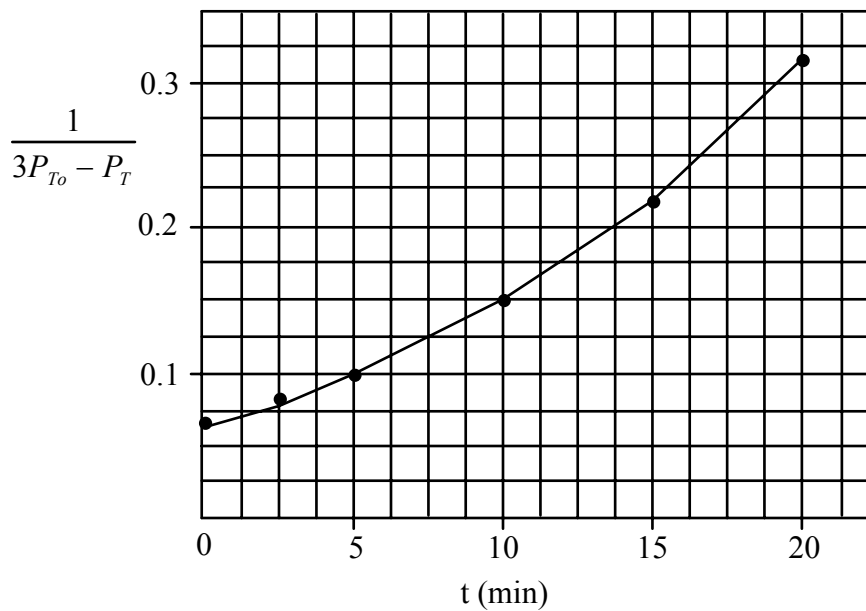
Data shows definite curvature and reaction is not zero-th order.



Assume 2nd order:

$$\frac{dP_T}{dt} = k'' (3P_{To} - P_T)^2$$

$$\frac{1}{\underbrace{3P_{To} - P_T}_y} = \frac{1}{2P_{To}} + k'' \frac{t}{x}$$



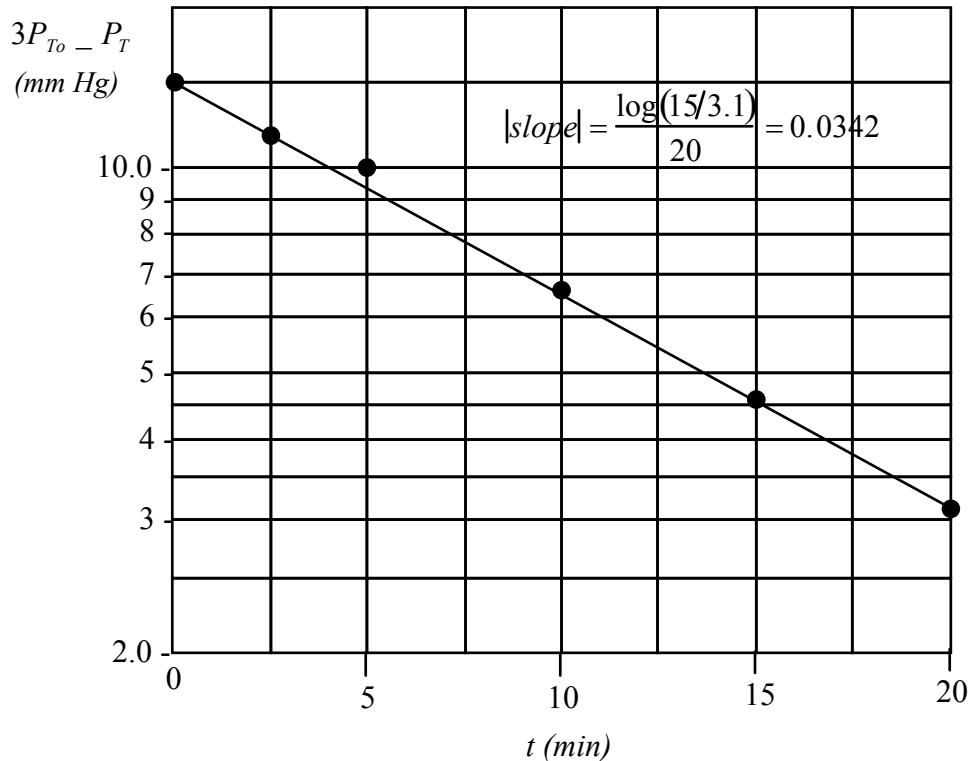
Again data show a definite curvature and the reaction is not 2nd order.
Assume 1st order

$$\frac{dP_T}{dt} = k'' (3 P_{T_0} - P_T)$$

$$\ln \left(\frac{2 P_{T_0}}{3 P_{T_0} - P_T} \right) = k'' t$$

$$\log (3 P_{T_0} - P_T) = \log (2 P_{T_0}) - (2.3026)^{-1} k'' t$$

$$|slope| = \frac{\log(15/3.1)}{20} = 0.0342$$



Now we do get a straight line.

$$k'' = 2.3026 |slope| = 2.3026 \times 0.0342 = 0.0787 \text{ (min}^{-1}\text{)}$$

Directly from data

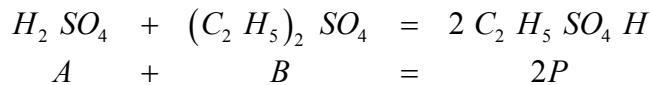
$$k_p = \frac{1}{t} \ln \frac{2 P_{T_0}}{3 P_{T_0} - P_T} = \begin{cases} 0.0893 \\ 0.0811 \\ 0.0806 \\ 0.0788 \\ 0.0788 \end{cases} \quad \bar{k}_p = 0.0817 \text{ min}^{-1}$$

$$-r_A \left(\frac{\text{mol}}{\text{lit min}} \right) = 0.08 C_A = 0.0022 P_A$$

$$-\tilde{r}_A \left(\frac{\text{mm Hg}}{\text{min}} \right) = 0.08 P_A$$

Notice again that the variation in the rate constant based on integral method is much less than if differential method is used.

Example 3: Consider the reaction between sulfuric acid and diethylsulfate in aqueous solution



At isothermal conditions ($T = 22.9^\circ C$) starting with equimolar mixture of the reactants and with no product the data presented below were obtained. Initial reactant concentration was 5.5 (mol/lit) for each of them. Find the rate expression.

$t(\text{min})$	0	41	48	55	75	96	127	146	162
$C_p \left(\frac{\text{mol}}{\text{lit}} \right)$	0	1.18	1.38	1.63	2.24	2.75	3.31	3.76	3.81

$t(\text{min})$	180	194	212	267	318	368	379	410	several days
$C_p \left(\frac{\text{mol}}{\text{lit}} \right)$	4.11	4.31	4.45	4.86	5.15	5.32	5.35	5.42	5.80

Since for each mole of A reacted one gets two moles of P if the reaction went to completion one would find 11 (mol/lit) of P . Since only 5.80 (mol/lit) of P are found this indicates that the reaction is reversible.

$$C_{P_{eq}} = 5.80 \quad C_{A_{eq}} = C_{B_{eq}} = C_{A_0} - \frac{C_{P_{eq}}}{2} = 2.6$$

$$\frac{C_{A_0} - C_{A_{eq}}}{1} = \frac{C_{P_{eq}}}{2}$$

$$x_{A_e} = \frac{C_{A_0} - C_{A_{eq}}}{C_{A_0}} = \frac{C_{P_{eq}}}{2 C_{A_0}} = \frac{5.8}{2 \times 5.5} = 0.527$$

Let us assume that the reaction is 2nd order in both directions

$$R_p = \frac{dC_p}{dt} = k_f C_A C_B - k_b C_p^2$$

Since we start in stoichiometric ratio

$$C_{A_0} = C_{B_0} \text{ therefore } C_A = C_B = C_{A_0} - \frac{C_p}{2}$$

$$\frac{dC_p}{dt} = k_f \left(C_{A_0} - \frac{C_p}{2} \right)^2 - k_b C_p^2 ; t = 0 \quad C_p = 0$$

Let us use integral analysis. From the above rate expression at equilibrium

$$\left(\frac{C_p^2}{C_A C_B} \right)_{eq} = \frac{k_f}{k_b} = K = \frac{4 x_{A_e}^2}{(1 - x_{A_e})^2} = 4.98$$

We can separate the variables in the above differential equation:

$$\int_0^{C_p} \frac{dC_p}{\left(C_{A_0} - \frac{C_p}{2} \right)^2 - \frac{k_b}{k_f} C_p^2} = k_f \int_0^t dt$$

The integral on the left hand side can be promptly evaluated by using a set of integration tables. For an exercise we will integrate it here:

$$\frac{k_b}{k_f} = \frac{1}{K}$$

$$\left(\frac{1}{4} - \frac{1}{K} \right) C_p^2 - C_{A_0} C_p + C_{A_0}^2 = 0$$

Find the roots of the denominator:

$$C_{p_{1,2}} = \frac{2 C_{A_0}}{1 \mp \sqrt{\frac{4}{K}}}$$

The integrand can now be written as:

$$\frac{1}{\left(\frac{1}{4} - \frac{1}{K} \right) \left(C_p - \frac{2 C_{A_0}}{1 - \sqrt{\frac{4}{K}}} \right) \left(C_p - \frac{2 C_{A_0}}{1 + \sqrt{\frac{4}{K}}} \right)} = \frac{A}{C_p - \frac{2 C_{A_0}}{1 - \sqrt{\frac{4}{K}}}} + \frac{B}{C_p - \frac{2 C_{A_0}}{1 + \sqrt{\frac{4}{K}}}}$$

Using partial fractions and evaluating for A and B we get:

$$A = \frac{1}{C_{A_0} \sqrt{\frac{4}{K}}} = -B$$

Thus:

$$\int_0^{C_p} \frac{dC_p}{\left(\frac{1}{4} - \frac{1}{K}\right) C_p^2 - C_{Ao} C_p + C_{Ao}^2} = \frac{1}{C_{Ao} \sqrt{4/K}} \left\{ \int_0^{C_p} \frac{dC_p}{C_p - \frac{2 C_{Ao}}{1 - \sqrt{4/K}}} - \int_0^{C_p} \frac{dC_p}{C_p - \frac{2 C_{Ao}}{1 + \sqrt{4/K}}} \right\}$$

$$= \frac{1}{C_{Ao} \sqrt{4/K}} \ln \left\{ \frac{\left(C_p - \frac{2 C_{Ao}}{1 - \sqrt{4/K}} \right) \frac{1}{1 + \sqrt{4/K}}}{\left(C_p - \frac{2 C_{Ao}}{1 + \sqrt{4/K}} \right) \frac{1}{1 - \sqrt{4/K}}} \right\} = k_f t$$

After some reorganization we get:

$$\ln \left\{ \frac{(\sqrt{K} - 2) C_p - 2 \sqrt{K} C_{Ao}}{(\sqrt{K} + 2) C_p - 2 \sqrt{K} C_{Ao}} \right\} = \frac{2 k_f C_{Ao}}{\sqrt{K}} t$$

Using the previously established relationship

$$K = \frac{4 x_{Ae}^2}{(1 - x_{Ae})^2}$$

We can rewrite this in the form:

$$\ln \left[\frac{x_{Ae} - (2 x_{Ae} - 1) x_A}{x_{Ae} - x_A} \right] = k_f C_{Ao} \frac{1 - x_{Ae}}{x_{Ae}} t$$

Using the already evaluated value of K and known C_{Ao} we should plot

$$\ln \left\{ \frac{0.232 C_p - 24.548}{4.232 C_p - 24.548} \right\} = 4.929 k_f t$$

i.e. $y = \frac{0.232 C_p - 24.548}{4.232 C_p - 24.548}$ vs. t on a semi-log plot.

t	0	41	48	55	75	96	127	146	162
y	1	1.240	1.295	1.369	1.595	1.853	2.256	2.742	2.809
y^1	1	1.255	1.311	1.390	1.627	1.897	2.322	2.831	2.901
t	180	194	212	267	318	368	379	410	
y	3.298	3.733	4.114	5.884	8.482	11.46	12.22	14.46	
y^1	3.412	3.877	4.263	6.095	8.757	11.77	12.53	14.76	

Suppose that we have assumed a first order reversible reaction:

$$\frac{dC_p}{dt} = k_f^1 C_A - k_b^1 C_p \qquad \frac{k_f^1}{k_b^1} = K^1 = \frac{C_{p_{eq}}}{C_{A_{eq}}} = \frac{2 x_{Ae}}{1 - x_{Ae}}$$

upon integration $K^1 = 2.23$

$$\ln \left[\frac{C_{A_0}}{C_{A_0} - \left(\frac{1}{2} + \frac{1}{K^1} \right) C_p} \right] = k_f^1 \left(\frac{1}{2} + \frac{1}{K^1} \right) t$$

$$\ln \left(\frac{1}{1 - 0.172 C_p} \right) = 0.948 k_f^1 t$$

or in alternative form:

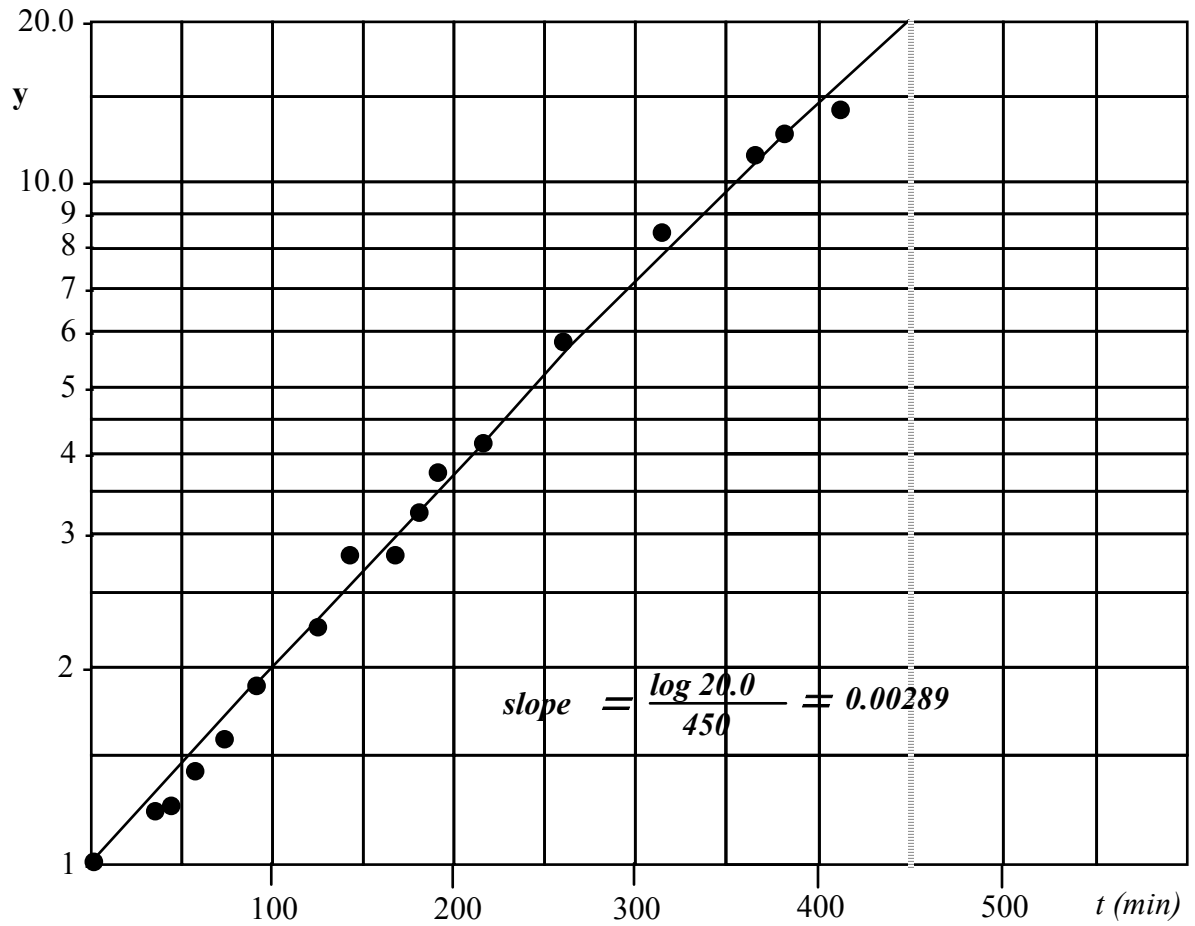
$$\ln \left(\frac{x_{Ae}}{x_{Ae} - x_A} \right) = \frac{k_f^1}{2 x_{Ae}} t$$

Now if we expect this rate form to hold we should also get a straight line on a semi-log plot of $y^1 = \frac{1}{1 - 0.172 C_p}$ vs. t . The values of y^1 are also calculated in the table on the previous page.

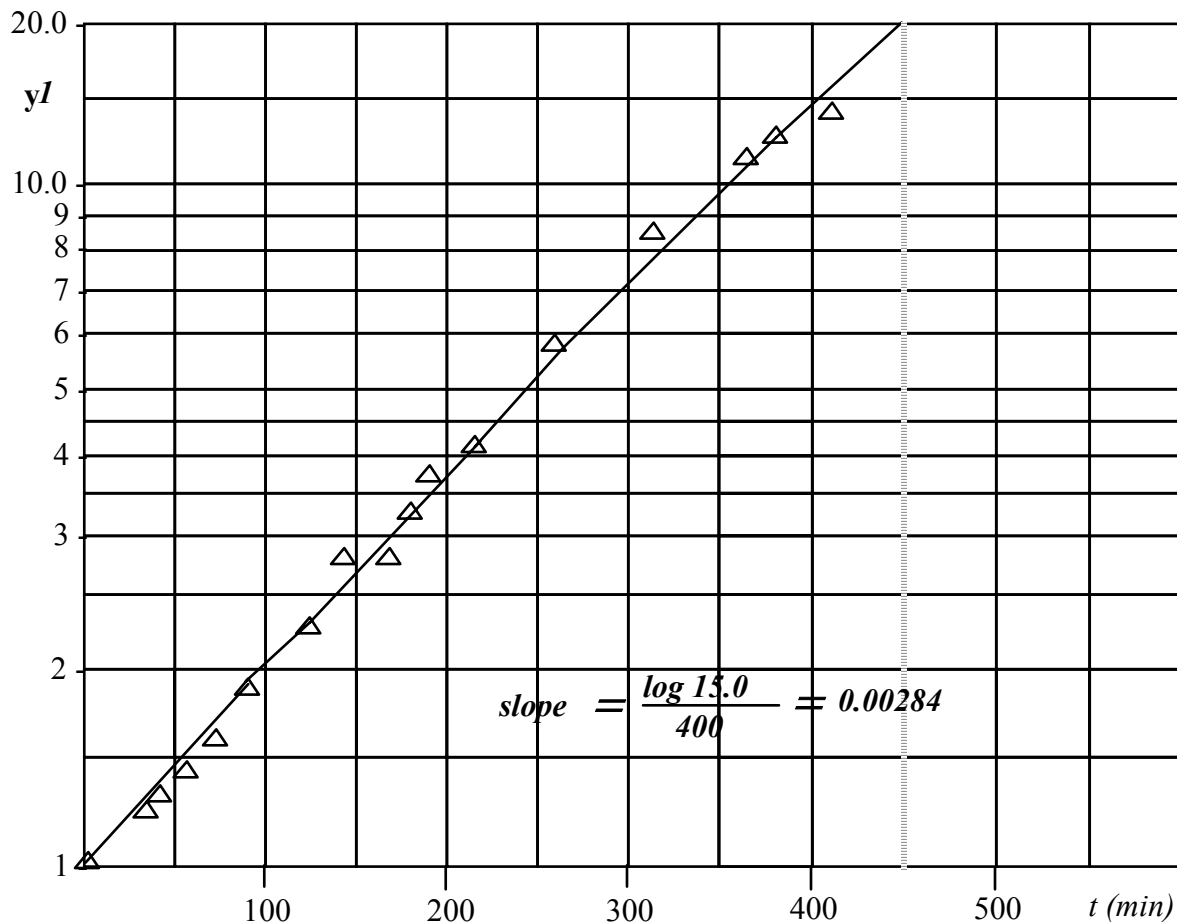
Both forms are plotted on semi-log paper on the next page and both yield a reasonable straight line! Apparently from the experimental data given we are unable to distinguish between a reversible 2nd order reaction in both directions and a reversible first order reaction in both directions. If we consider again the two integrated forms written in terms of conversion we can readily see that when $x_{Ae} = 0.5$ the two forms become identical and indistinguishable from each other. Since under the conditions of the experiment equilibrium conversion was $x_{Ae} = 0.527$, which is close to 0.5, due to experimental scatter we cannot distinguish between the two forms.

If we performed the experiments at different T so that x_{Ae} is far from 0.5; or if we used nonstoichiometric ratio of reactants, we would find that the rate indeed is 2nd order in each direction. It is important to determine the proper order since when designing a larger reactor we may be operating at conditions when $x_{Ae} \gg 0.5$ and the predictions of the reactor size for a desired production rate will differ vastly based on the rate form.

Plot for 2nd order reversible:



Plot for 1st order reversible:



From the slope for the 2nd order rate form we get the value of the rate constant k_f .

$$\frac{4.929}{2.3026} k_f = \text{slope} = 0.00289$$

$$k_f = \frac{0.00289 \times 2.3026}{4.929} = 1.35 \times 10^{-3} \left(\frac{\text{lit}}{\text{mol min}} \right)$$

Then $\frac{k_f}{k_b} = K$

$$k_b = \frac{k_f}{K} = \frac{1.35 \times 10^{-3}}{4.98} = 2.71 \times 10^{-3} \left(\frac{\text{lit}}{\text{mol min}} \right)$$

The rate in (mol/lit min) is given by the above expression at $T = 22.9^\circ\text{C}$. The temperature dependence of the constants would have to be found by performing experiments at different temperatures.

Caution: A note of caution is here in order. The integrated expression that we used for a reversible 2nd order reaction of the type $A + B = 2P$ was:

$$\ln \left[\frac{x_{Ae} - (2x_{Ae} - 1)x_A}{x_{Ae} - x_A} \right] = k_f \frac{1 - x_{Ae}}{x_{Ae}} C_{Ao} t$$

Note 1: This expression is only valid when the experiment is performed with stoichiometric ratio of A and B . It is not valid when $C_{Ao} \neq C_{Bo}$.

Note 2: The expression for the same reaction type is reported by Levenspiel (page 63, equation 56) and it looks almost exactly the same as the one above except that it has an extra factor of 2 on the right hand side.

Question: Did I make a mistake or did he make a mistake? Note that my k_f and his k_1 (which are rate constants for the reaction forward) will differ by a factor of two!!?

Answer: Neither of us made a mistake but k_f is based on production of P while k_1 is based on disappearance of A . Since due to stoichiometry $\frac{-r_A}{1} = \frac{r_P}{2}$ this implies $k_1 = \frac{k_f}{2} k_f = 2k_1$ which indeed is the case.

Potential

Trouble: The choice of the subscript f or 1 etc. does not indicate on which component the rate constant is based. Thus, if one has only an integrated form to work with, one has no way of knowing whether k_1 is based on reactant or product, etc. Clarify that whenever possible.

Note 3: Since the above mentioned ambiguity about rate constants always exists try to:

- use integrated forms only when you know what the k 's are based on;
- develop your own integrated forms by the help of integral tables.

This last choice after all is not that difficult. In the problem that we just solved we had to integrate

$$\int_0^{C_p} \frac{dC_p}{\left(C_{Ao} - \frac{C_p}{2}\right)^2 - \frac{1}{K} C_p^2} = \int_0^{C_p} \frac{dC_p}{\left(\frac{1}{4} - \frac{1}{K}\right) C_p^2 - C_{Ao} C_p + C_{Ao}^2} = k_f t$$

A quick look in the CRC Mathematical Tables shows that we have a problem of the type

$$\int \frac{dx}{y} \quad \text{where } x = C_p$$

$$y = a + bx + cx^2$$

$$a = C_{A_0}^2$$

$$b = -C_{A_0}$$

$$c = \frac{1}{4} - \frac{1}{K}$$

The answer is:

$$\int \frac{dx}{y} = \frac{1}{\sqrt{-q}} \ln \frac{2cx + b - \sqrt{-q}}{2cx + b + \sqrt{-q}}$$

where $q = 4ac - b^2$

Thus in our case $q = -\frac{4 C_{A_0}^2}{K}$.

Substitute proper terms for q , c , a , b and x in the above expression.

Caution: Do not forget to evaluate the above expression at the upper and lower limit of integration (expression at upper limit - expression of lower limit) since you started with a definite integral and CRC Tables gives you the answer for an indefinite one. You should get the expression used in the problem.