Problem Set 7 Solutions

CHM 3400, Dr. Chatfield, Fall 2011

1. (Atkins 10.9)

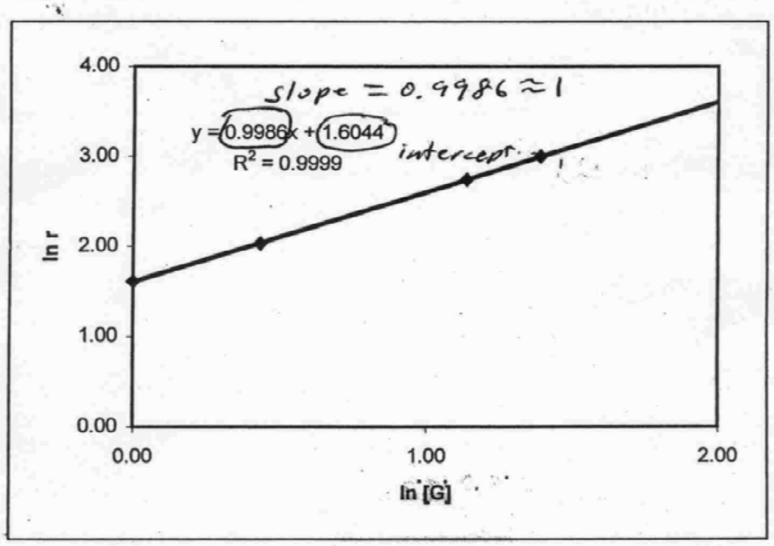
enzyme glucose

$E + G \rightarrow EG$ rate $= r = k[G]^a$

$\ln r = \ln k + a \ln[G] \Rightarrow$ Plot $\ln r$ vs $\ln[G]$

• slope $= a$

[G] (mmol L^{-1})	r (mol L^{-1} s^{-1})	ln [G]	ln r
1.00	5.00	0.00	1.61
1.54	7.60	0.43	2.03
3.12	15.50	1.14	2.74
4.02	20.00	1.39	3.00



(a) order of reaction with respect to glucose is 1

(b) Plug into 1st data point:

$5.0 \text{ mol } L^{-1} s^{-1} = k(1.00 \times 10^{-3} \text{ mol } L^{-1})$

$k = \frac{5}{10^{-3}} s^{-1} = 5 \times 10^{3} s^{-1}$

2. (Atkins 10.11)

For 1^{st}-order reaction, $t_{1/2} = \frac{\ln 2}{k} = 2.04 \times 10^{4}\,s$

$k = 3.38 \times 10^{-5}\,s^{-1}$

$[N_2O_5] = [N_2O_5]_0 e^{-kt} \Rightarrow p_{N_2O_5} = p_{N_2O_5,\,init.}\, e^{-kt}$

assuming closed container

a) $p_{N_2O_5} = (78.4\,kPa)\, e^{-kt} = 78.387\,kPa$, $t = 5.0\,s$

$2N_2O_5$	$\longrightarrow 4NO_2$	$+\ O_2$	
78.4	0	0	$78.4 - 2x = 78.387$
$-2x$	$4x$	x	$x = 0.0066$
$78.4-2x$	$4x$	x	

$p_{total} = 78.387 + 4(0.0066) + 0.0066 = 78.420\ kPa$

b) $p_{N_2O_5} = (78.4\,kPa)\, e^{-kt} = 77.61\,kPa$, $t = 5\,min = 300\,s$

$x = \frac{1}{2}(78.4 - 77.61) = 0.39\,kPa$

$p_{total} = 77.61 + 4(0.39) + 0.39 = 79.59\ kPa$

3. (Atkins 10.18)

$2ICl(g) + H_2(g) \longrightarrow I_2(s) + 2HCl(g)$

Will assume that the rate law only involves ICl and H_2 since the data only include those species. In ~~you~~ principle, though, I_2 and HCl could be important if the mechanism is complicated.

a) $r = k[ICl]^a[H_2]^b \Rightarrow \ln r = \ln k + a\ln[ICl] + b\ln[H_2]$

From experiment 1+2, we determine a:

$$\ln \frac{7.4\times10^{-7}}{3.7\times10^{-7}} = a \ln \frac{3.0}{1.5} \Rightarrow a = 1$$

From experiment 2+3, we determine b:

$$\ln \frac{22\times10^{-7}}{7.4\times10^{-7}} = b \ln \frac{4.5}{1.5} \Rightarrow b = 1$$

b) Plugging into the rate equation for experiment 1 gives k:

$$3.7\times10^{-7}\,\mathrm{mol\,L^{-1}\,s^{-1}} = k(1.5\times10^{-3}\,\mathrm{mol/L})^1(1.5\times10^{-3}\,\mathrm{mol/L})^1$$

$$k = 0.16\ \mathrm{s^{-1}\,mol^{-1}\,L}$$

c) Plugging in for experiment 4 gives

$$\text{rate} = (0.16\,\mathrm{s^{-1}\,mol^{-1}\,L})(4.7\times10^{-3}\,\mathrm{mol/L})^1(2.7\times10^{-3}\,\mathrm{mol/L}) = 2.0\times10^{-6}\,\mathrm{mol\ldots}$$

4. (Atkins 10.24)

$2A \rightarrow B$

There are several ways to determine rate laws. These include the isolation method and the method of initial rates. Another method, which is most convenient in this case, is to compare the data with integrated rate laws.

Reactions with simple mechanisms often have rate laws that depend only on the concentrations of reactants (that is, the rate law is zeroth order with respect to all product species). This may not be true of reactions with more complicated mechanisms. But a sensible approach is to begin by testing whether the data fit a simple rate law well. If they do not, it becomes necessary to consider more complicated rate laws.

Therefore we begin by assuming that the rate of this reaction depends only on the reactant, A. The simplest cases are 1st order and 2nd order.

1st order: $[A] = [A]_o e^{-kt}$ → $\ln[A] = \ln[A]_o - kt$ → Plot of ln[A] vs t linear with slope –k

2nd order: $\frac{1}{[A]} = \frac{1}{[A]_o} + kt$ → Plot of $\frac{1}{[A]}$ vs t linear with slope +k

Similar relationships can be derived for other orders, and plotting $[A]^s$ vs t, where s is the appropriate power, will be linear.

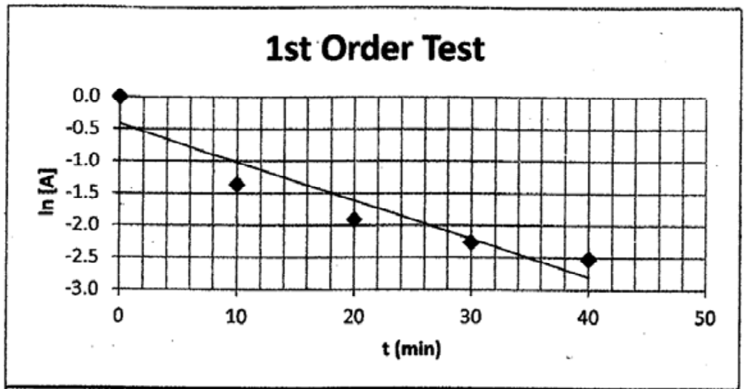
We will begin by assuming 1st or 2nd order and test which relationship gives a straight line using the data.

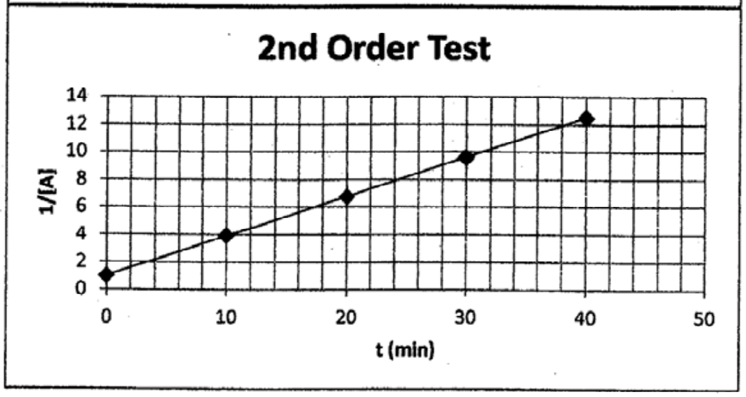
Note in the table below that the [A] can be determined from [B] and the stoichiometry. Since the initial concentration of B is zero ($[B]_o=0$), $[A]=[A]_o-2[B]$ at all times. Furthermore, since eventually all of A is converted to B, $[A]_o=2[B]_\infty$.

t (min)	[B]*	[A]*	ln [A]	1/[A]
0	0.000	1.000	0.000	1.000
10	0.372	0.256	-1.363	3.906
20	0.426	0.148	-1.911	6.757
30	0.448	0.104	-2.263	9.615
40	0.460	0.080	-2.526	12.500
∞	0.500	0.000		

*All concentration units are mol/L

On the next page, graphs are shown testing the data for each kind of rate law.





Straight-line (linear) fits to the data are shown on each graph. It is clear that the data fit a 2nd order rate law well, but not a 1st order rate law. With this known, we can determine the rate constant, *k*. For a 2nd order rate law, *k* is equal to the slope:

$$k = slope = \frac{12.5-1}{40-0} = 0.288 \text{ L mol}^{-1} \text{ min}^{-1}$$

Order of reaction is 2 with respect to A (and 2 overall)

Note: the value of *k* above what you get if the rate law is defined as

$$v = -\frac{d[A]}{dt} = k[A]^2 \rightarrow \frac{1}{[A]} - \frac{1}{[A]_o} = kt \rightarrow k = 0.288 \text{ L mol}^{-1} \text{ min}^{-1}$$

It is more proper to define the rate slightly differently, as below. If we do that, the value of *k* will differ from the value above by a factor of 2. Both answers for *k* are correct, but each must be paired with the appropriate definition of rate. The second way of looking at it is more consistent with the presentation in the text.

$$v = -\frac{1}{2}\frac{d[A]}{dt} = k[A]^2 \rightarrow k = 0.144 \text{ L mol}^{-1} \text{ min}^{-1}$$

5. (Atkins 10.27)

1^{st}-order: $k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{5730\,y} = 1.21\times10^{-4}\ y^{-1}$

$[^{14}C] = [^{14}C]_0\, e^{-kt}$

$e^{-kt} = \frac{[^{14}C]}{[^{14}C]_0} = 0.69$

$kt = -\ln 0.69 = 0.371$

$t = \frac{0.371}{1.21\times10^{-4}\,y^{-1}} = 3066\,y$

6. (Atkins 10.33)

$k = A e^{-E_a/RT} \Rightarrow \ln k = \ln A - \frac{E_a}{RT}$

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

$T_1 = 19^\circ C = 292\,K \quad k(T_1) = 2.78\times10^{-4}\ dm^3\,mol^{-1}\,s^{-1}$

$T_2 = 37^\circ C = 310\,K \quad k(T_2) = 3.38\times10^{-3}\ dm^3\,mol^{-1}\,s^{-1}$

$\underset{\uparrow\,2.498}{\ln(12.16)} = \frac{E_a}{R}\left(\frac{1}{292K} - \frac{1}{310K}\right) = E_a\,(2.392\times10^{-5}\ mol\ J^{-1})$

$\boxed{E_a = 104500\ J\,mol^{-1} = 104.5\ kJ/mol}$

Plug into Arrhenius eq. for either temperature (choose T_1)

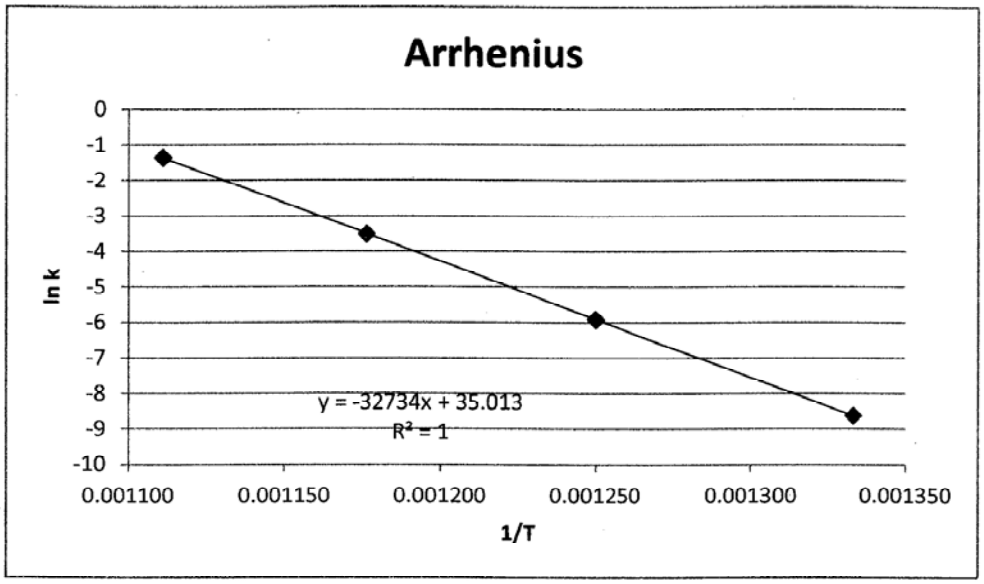
$A = \underset{k(T_1)}{k}\, e^{+E_a/RT}\ (T_1 = 292K) = 1.3\times10^{15}\ dm^3\,mol^{-1}\,s^{-1}$

7. (Atkins 10.37)

$k = A e^{-E_a/RT} \Rightarrow \ln k = \ln A - \frac{E_a}{R}\left(\frac{1}{T}\right)$

Plot $\ln k$ vs $\frac{1}{T}$ $\Rightarrow$ slope $= -\frac{E_a}{R}$, intercept $= \ln A$

T (K)	1/T (K^{-1})	k (s^{-1})	ln k
750	0.001333	1.80E-04	-8.62255
800	0.001250	2.70E-03	-5.91450
850	0.001176	3.00E-02	-3.50656
900	0.001111	2.60E-01	-1.34707



From linear fit, slope $= -32734$ K

intercept $= 35.013$

$E_a = -R \cdot \text{slope} = 272200$ J/mol $= 272.2$ kJ/mol

same units as k

$\ln A = \text{intercept} = 35.013 \Rightarrow A = e^{35.013} = 1.6 \times 10^{15}\ s^{-1}$