Homework for Apr 28 (except graded problem for now)

9.30 The rate constants for the first-order decomposition of an organic compound in solution are measured at several temperatures:

k/s^{-1}	4.92×10^{-3}	0.0216	0.0950	0.326	1.15
t/° C	5.0	15	25	35	45

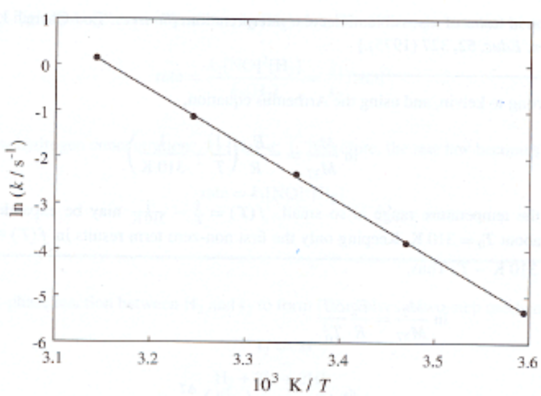
Determine graphically the pre-exponential factor and the energy of activation for the reaction.

Since

$$\ln k = \ln A - \frac{E_a}{RT}$$

A plot of $\ln k$ vs $1/T$ gives a slope of $-E_a/R$ and an intercept of $\ln A$. The following data are used for the plot:

10^3 K/T	3.595	3.470	3.353	3.245	3.143
$\ln(k/\text{s}^{-1})$	−5.314	−3.835	−2.354	−1.121	0.140

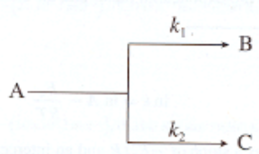


The equation for the line that best fits these points is $y = -1.207 \times 10^4 x + 38.06$. Therefore,

$$E_a = -\left(-1.207 \times 10^4\ \text{K}^{-1}\right)\left(8.314\ \text{J K}^{-1}\ \text{mol}^{-1}\right) = 1.00 \times 10^5\ \text{J mol}^{-1}$$

$$A = e^{38.06} = 3.38 \times 10^{16}\ \text{s}^{-1}$$

9.34 Consider the following parallel reactions



The activation energies are 45.3 kJ mol^{-1} for k_1 and 69.8 kJ mol^{-1} for k_2. If the rate constants are equal at 320 K, at what temperature will $k_1/k_2 = 2.00$?

The ratio of the rate constants is

$$\frac{k_1}{k_2} = \frac{A_1 e^{-E_{a1}/RT}}{A_2 e^{-E_{a2}/RT}}$$

$$= \frac{A_1}{A_2} e^{(E_{a2}-E_{a1})/RT} = \frac{A_1}{A_2} e^{\left(69.8\times10^3\ \mathrm{J\ mol^{-1}} - 45.3\times10^3\ \mathrm{J\ mol^{-1}}\right)/[(8.314\,\mathrm{J\ K^{-1}\ mol^{-1}})T]}$$

$$= \frac{A_1}{A_2} e^{2.947\times10^3\ \mathrm{K}/T}$$

First use data at 320 K to calculate A_1/A_2:

$$\frac{k_1}{k_2} = 1.00 = \frac{A_1}{A_2} e^{2.947\times10^3\ \mathrm{K}/320\ \mathrm{K}}$$

$$\frac{A_1}{A_2} = 1.001 \times 10^{-4}$$

When $k_1/k_2 = 2.00$,

$$2.00 = \frac{A_1}{A_2} e^{2.947\times10^3\ \mathrm{K}/T} = \left(1.001 \times 10^{-4}\right) e^{2.947\times10^3\ \mathrm{K}/T}$$

$$\frac{1}{T} = \frac{1}{2.947 \times 10^3\ \mathrm{K}} \ln \frac{2.00}{1.001 \times 10^{-4}} = 3.360 \times 10^{-3}\ \mathrm{K^{-1}}$$

$$T = 298\ \mathrm{K}$$

9.36 The rate of the electron-exchange reaction between naphthalene ($C_{10}H_8$) and its anion radical ($C_{10}H_8^-$) is diffusion-controlled:

$$C_{10}H_8^- + C_{10}H_8 \rightleftharpoons C_{10}H_8 + C_{10}H_8^-$$

The reaction is bimolecular and second order. The rate constants are

T/K	307	299	289	273
$k/10^9 \cdot M^{-1} \cdot s^{-1}$	2.71	2.40	1.96	1.43

Calculate the values of E_a, $\Delta H^{\circ\ddagger}$, $\Delta S^{\circ\ddagger}$ and $\Delta G^{\circ\ddagger}$ at 307 K for the reaction. [*Hint*: Rearrange Equation 9.41 and plot $\ln(k/T)$ versus $1/T$.]

Equation 9.41 gives

$$k = \frac{k_B T}{h} e^{\Delta S^{\circ\ddagger}/R} e^{-\Delta H^{\circ\ddagger}/RT}$$

or

$$\ln \frac{k}{T} = \ln \frac{k_B}{h} + \frac{\Delta S^{\circ\ddagger}}{R} - \frac{\Delta H^{\circ\ddagger}}{RT}$$

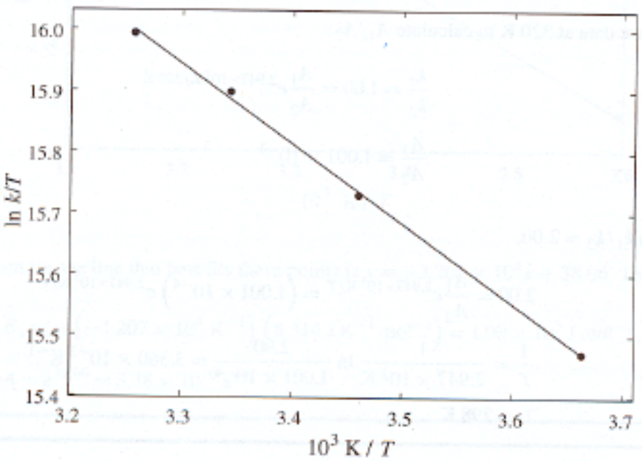
A plot of $\ln k/T$ vs $1/T$ gives a slope of $-\Delta H^{\circ\ddagger}/R$ and an intercept of $\ln k_B/h + \Delta S^{\circ\ddagger}/R$. The data used for the plot are

10^3 K/T	3.257	3.344	3.460	3.663
$\ln \frac{k}{T}$	15.9934	15.8983	15.7298	15.4715

The best fit line has a formula of $y = -1302.0x + 20.24$. Therefore,

$$\Delta H^{\circ\ddagger} = -(-1302.0\text{ K})\left(8.314\text{ J K}^{-1}\text{ mol}^{-1}\right)$$
$$= 1.082 \times 10^4\text{ J mol}^{-1}$$
$$= 1.08 \times 10^4\text{ J mol}^{-1}$$

and



$$\Delta S^{\circ\ddagger} = R\left(20.24 - \ln\frac{k_B}{h}\right)$$
$$= \left(8.314\text{ J K}^{-1}\text{ mol}^{-1}\right)\left(20.24 - \ln\frac{1.381 \times 10^{-23}}{6.626 \times 10^{-34}}\right)$$
$$= -29.3\text{ J K}^{-1}\text{ mol}^{-1}$$

From Equation 9.43 and the discussion following it, the activation energy for this reaction, which occurs in solution (condensed phase), is

$$E_a = \Delta H^{\circ\ddagger} + RT$$
$$= 1.082 \times 10^4\text{ J mol}^{-1} + \left(8.314\text{ J K}^{-1}\text{ mol}^{-1}\right)(307\text{ K})$$
$$= 1.34 \times 10^4\text{ J mol}^{-1}$$

From $\Delta H^{\circ\ddagger}$ and $\Delta S^{\circ\ddagger}$, $\Delta G^{\circ\ddagger}$ at 307 K is calculated.

$$\Delta G^{\circ\ddagger} = \Delta H^{\circ\ddagger} - T\Delta S^{\circ\ddagger}$$
$$= 1.082 \times 10^4\text{ J mol}^{-1} - (307\text{ K})\left(-29.3\text{ J K}^{-1}\text{ mol}^{-1}\right)$$
$$= 1.98 \times 10^4\text{ J mol}^{-1}$$

10.2 Measurements of a certain enzyme-catalyzed reaction give $k_1 = 8 \times 10^6\ M^{-1}\,s^{-1}$, $k_{-1} = 7 \times 10^4\ s^{-1}$, and $k_2 = 3 \times 10^3\ s^{-1}$. Does the enzyme–substrate binding follow the equilibrium or steady-state scheme?

The dissociation constant, K_S, and the Michaelis constant, K_M, must be compared.

$$K_S = \frac{k_{-1}}{k_1} = \frac{7 \times 10^4\ s^{-1}}{8 \times 10^6\ M^{-1}\,s^{-1}} = 9 \times 10^{-3}\ M$$

and

$$K_M = \frac{k_{-1} + k_2}{k_1} = \frac{7 \times 10^4\ s^{-1} + 3 \times 10^3\ s^{-1}}{8 \times 10^6\ M^{-1}\,s^{-1}} = 9 \times 10^{-3}\ M$$

Within the precision of the measurements, the two constants are equal. Thus, the binding follows the equilibrium scheme. That is, k_{-1} is sufficiently greater than k_2 so that the binding reaches equilibrium.

10.3 The hydrolysis of acetylcholine is catalyzed by the enzyme acetylcholinesterase, which has a turnover rate of $25{,}000\ s^{-1}$. Calculate how long it takes for the enzyme to cleave one acetylcholine molecule.

The time required for the enzyme to cleave one acetylcholine molecule (one turnover) is the reciprocal of the turnover rate.

$$t = \frac{1}{k_2} = \frac{1}{25000\ s^{-1}} = 4.0 \times 10^{-5}\ s = 40\ \mu s$$

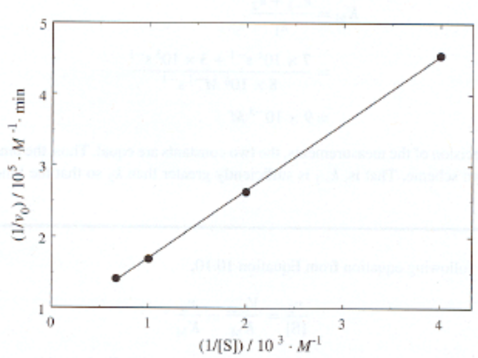
10.6 The hydrolysis of *N*-glutaryl-L-phenylalanine-*p*-nitroanilide (GPNA) to *p*-nitroaniline and *N*-glutaryl-L-phenylalanine is catalyzed by α-chymotrypsin. The following data are obtained:

$[S]/10^{-4}\ M$	2.5	5.0	10.0	15.0
$v_0/10^{-6}\ M \cdot min^{-1}$	2.2	3.8	5.9	7.1

where [S] = [GPNA]. Assuming Michaelis–Menten kinetics, calculate the values of V_{max}, K_M, and k_2 using the Lineweaver–Burk plot. Another way to treat the data is to plot v_0 versus $v_0/[S]$, which is the Eadie–Hofstee plot. Calculate the values of V_{max}, K_M, and k_2 from the Eadie–Hofstee treatment, given that $[E]_0 = 4.0 \times 10^{-6}\ M$. [*Source*: J. A. Hurlbut, T. N. Ball, H. C. Pound, and J. L. Graves, *J. Chem. Educ.* **50,** 149 (1973).]

For the Lineweaver–Burk plot, the following data are needed.

$(1/[S])/10^3 \cdot M^{-1}$	4.00	2.00	1.00	0.667
$(1/v_0)/10^5 \cdot M^{-1} \cdot min$	4.55	2.63	1.69	1.41



The best-fit line to the data has an equation of $y = 94.6x + 7.56 \times 10^4$. The intercept of a Lineweaver–Burk plot is $1/V_{max}$ giving

$$V_{max} = \frac{1}{7.56 \times 10^4\ M^{-1}\ \text{min}}$$

$$= 1.32 \times 10^{-5}\ M\ \text{min}^{-1}$$

$$= 1.3 \times 10^{-5}\ M\ \text{min}^{-1}$$

The slope is K_M/V_{max} so that

$$K_M = (94.6\ \text{min})(1.32 \times 10^{-5}\ M\ \text{min}^{-1})$$

$$= 1.2 \times 10^{-3}\ M$$

Finally,

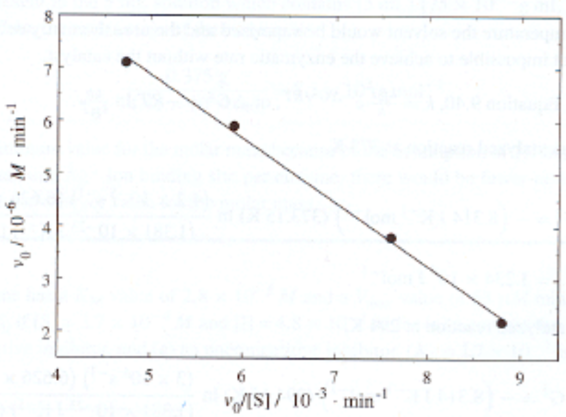
$$k_2 = \frac{V_{max}}{[E]_0}$$

$$= \frac{1.32 \times 10^{-5}\ M\ \text{min}^{-1}}{4.0 \times 10^{-6}\ M}$$

$$= 3.3\ \text{min}^{-1}$$

The Eadie–Hofstee plot uses the following data,

$(v_0/[S])/10^{-3} \cdot \text{min}^{-1}$	8.80	7.60	5.90	4.73
$v_0/10^{-6} \cdot M \cdot \text{min}^{-1}$	2.2	3.8	5.9	7.1



The best-fit line to the data has an equation of $y = -1.21 \times 10^{-3}x + 1.29 \times 10^{-5}$. In a Eadie–Hofstee plot the slope is $-K_M$ and the y-intercept is V_{max}. Thus, $V_{max} = 1.3 \times 10^{-5}\ M\ \text{min}^{-1}$ and $K_M = 1.2 \times 10^{-3}\ M$. $k_2 = 3.3\ \text{min}^{-1}$ is found as above. These are the same values as found from the Lineweaver–Burk plot, which given good data is as expected. The two plots weight the data differently, so that the values determined may be different depending on the quality of the data.