

1. CKD 1.2

The units in the preceding problem were in kJ/mole, which is an example of SI units. Give values for the following quantities both in kJ/mole and in the indicated alternative units in parentheses:

(a) heat capacity of liquid water at 15 °C and 1 atm (cal mole<sup>-1</sup>K<sup>-1</sup>):

$$C_p = 7.5 \times 10^{-2} \text{ kJ mol}^{-1} \text{K}^{-1}$$

$$1 \text{ cal} = 4.186 \times 10^{-3} \text{ kJ}$$

$$C_p = 18 \text{ cal mol}^{-1} \text{K}^{-1}$$

(b) vibrational fundamental frequency of H<sup>35</sup>Cl (cm<sup>-1</sup>):

$$\nu_o = 2990 \text{ cm}^{-1}$$

$$2990 \text{ cm}^{-1} \times \left( \frac{1.986 \times 10^{-16} \text{ kJ}}{1000 \text{ cm}^{-1}} \right) \times N_a = \nu_o = 35.8 \text{ kJ mole}^{-1}$$

(c) ionization potential of H atom (eV):

$$\text{IP} = 13.6 \text{ eV}$$

$$13.6 \text{ eV} \times N_a \times \left( \frac{1.602 \times 10^{-22} \text{ kJ}}{1 \text{ eV}} \right) = 1.31 \times 10^3 \text{ kJ mole}^{-1}$$

(d) RM.S. average translational kinetic energy of Br<sub>2</sub> at 300 K (ergs molecule<sup>-1</sup>):

$$\text{KE}_{\text{RMS}} = \frac{3}{2} RT = \frac{3}{2} \times .00831451 \text{ kJ mol}^{-1} \text{K}^{-1} \times 300 \text{ K} = 3.74 \text{ kJ mole}^{-1}$$

$$3740 \text{ J mole}^{-1} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \left( \frac{100 \text{ cm}}{1 \text{ m}} \right)^2 \times \frac{1}{N_a} = 6.21 \times 10^{-14} \text{ ergs molecule}^{-1}$$

(e) energy of CO<sub>2</sub> laser photons having a wavelength of 10.59 μm (Hz):

$$\frac{h c}{10.59 \times 10^{-6} \text{ m}} \times N_a \times \frac{\text{kJ}}{1000 \text{ J}} = 11.3 \text{ kJ mole}^{-1}$$

$$\frac{c}{10.59 \times 10^{-6} \text{ m}} = 2.83 \times 10^{13} \text{ Hz}$$

2. CKD Problem 1.3

a) **Derive the integrated rate equation** for a reaction of 3/2 order in a single reactant. Derive the expression for the **half-life** of such a reaction.

Assume a reaction of the form:

$A \rightarrow B$ , with a rate expression,

$$\frac{-d[A]}{dt} = k[A]^{3/2}$$

$$\int [A]^{-3/2} d[A] = -kt$$

$$\left[ \frac{1}{[A]^{1/2}} \right]_{A_0}^{A(t)} = \frac{kt}{2}$$

$$[A(t)]^{-1/2} = [A_0]^{-1/2} + \frac{kt}{2}$$

$$\boxed{[A(t)] = \left( [A_0]^{-1/2} + kt \right)^{-2}}$$

half-life derivation:

$$\text{At } t_{1/2}, [A]_{t_{1/2}} = \frac{[A_0]}{2},$$

$$\frac{[A_0]^{-1/2}}{2} - [A_0]^{-1/2} = + \frac{kt_{1/2}}{2}$$

$$\frac{\sqrt{2} - 1}{[A_0]^{1/2}} = \frac{kt_{1/2}}{2},$$

$$\boxed{t_{1/2} = \frac{2(\sqrt{2} - 1)}{k[A_0]^{1/2}}}$$

For reaction order n:

$A \rightarrow B$ , with a rate expression,

$$\frac{-d[A]}{dt} = k[A]^n$$

$$\int [A]^{-n} d[A] = -kt$$

$$\left( \frac{[A]^{1-n}}{n-1} \right)_{A_0}^{A(t)} = kt$$

$$[A(t)]^{1-n} = \left( [A_0]^{1-n} + (n-1)kt \right)$$

$$\boxed{[A(t)] = \left( [A_0]^{1-n} + (n-1)kt \right)^{1/(1-n)}}$$

3. Show that the rate law for  $A + B \rightarrow \text{products}$  (Eq. 1-46) reduces to the rate law for  $2A \rightarrow \text{products}$  (Eq. 1-41) when the initial concentrations  $[A]_0$  and  $[B]_0$  are identical.

$$\frac{1}{[A]_o - [B]_o} \ln \left( \frac{[B]_o [A]_t}{[A]_o [B]_t} \right) = k_2 t \quad (\text{Eq. 1-46})$$

There are a number of different ways to solve this problem, **starting with Eq. 1-46**. The following is only one way:

Start with the left hand side of Eq. 1-46; let  $[B]_o \rightarrow [A]_o$  and do some re-arranging:

$$\begin{aligned} & \lim_{[B]_o \rightarrow [A]_o} \left[ \frac{\ln[B]_t - \ln[A]_t}{[B]_o - [A]_o} - \frac{\ln[B]_o - \ln[A]_o}{[B]_o - [A]_o} \right] \\ & \{ [B]_o - [A]_o = ([B]_t + x) - ([A]_t + x) = [B]_t - [A]_t \} \\ & = \lim_{[B]_t \rightarrow [A]_t} \left( \frac{\ln[B]_t - \ln[A]_t}{[B]_t - [A]_t} \right) - \lim_{[B]_o \rightarrow [A]_o} \left( \frac{\ln[B]_o - \ln[A]_o}{[B]_o - [A]_o} \right) \\ & = \frac{d(\ln[B]_t)}{d[B]_t} \Big|_{[B]_t=[A]_t} - \frac{d(\ln[B]_o)}{d[B]_o} \Big|_{[B]_o=[A]_o} \\ & = \frac{1}{[A]_t} - \frac{1}{[A]_o} = k_2 t \quad (\text{getting closer to Eq. 1-41}) \end{aligned}$$

We need to include a factor of 2, because  $[A]_o = [B]_o$ , which gets us Eq. 1-41:

$$\frac{1}{[A]_t} = \frac{1}{[A]_o} + 2k_2 t$$

#### 4. CKD Problem 1.5

The kinetics of formation of ethyl acetate from acetic acid and ethyl alcohol as homogeneously catalyzed by a constant amount of HCl has been studied by titrating 1-cc aliquots of the reaction mixture with 0.0612 N base at various times. The following data have been obtained at 25 °C.

t, min	base, cc
0	24.37
44	22.20
62	21.35
108	19.50
117	19.26
148	18.29
313	14.14
384	13.40
442	13.09
∞	12.68

Initial concentrations

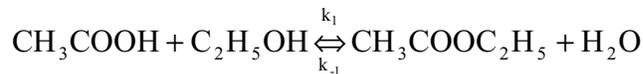
$$[\text{CH}_3\text{COOH}] = 1.000\text{M}$$

$$[\text{C}_2\text{H}_5\text{OH}] = 12.756\text{M}$$

$$[\text{H}_2\text{O}] = 12.756\text{M}$$

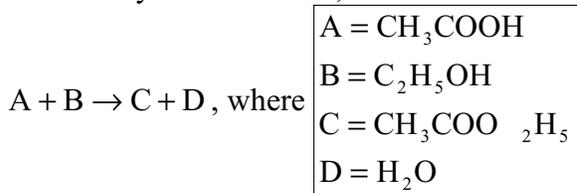
$$[\text{CH}_3\text{COOC}_2\text{H}_5] = 0$$

Overall reaction :



The reaction has been found to be first order with respect to each of the four reactants. Calculate the specific rate constants  $k_1$  and  $k_{-1}$ . What is the equilibrium constant  $K_{eq}$  at 25 °C?

To save myself some time, the reaction above will be represented as the following:



Define a progress variable, x:

Reactant/product	A	B	C	D
Initial concentration	1.00	12.756	0	12.756
Progress	- x	- x	+ x	+ x
Concentration at time, t	1.00-x	12.756-x	x	12.756+x

$$\frac{dx}{dt} = k_1(1.00 - x)(12.756 - x) - k_{-1}(12.756 + x)(x)$$

at  $t = \infty$ ,  $\frac{dx}{dt} = 0$ , or,

$$K_{eq} = \frac{k_1}{k_{-1}} = \frac{[C]_{\infty}[D]_{\infty}}{[A]_{\infty}[B]_{\infty}} = \frac{(12.756 + x_{\infty})(x_{\infty})}{(1.00 - x_{\infty})(12.756 - x_{\infty})}$$

$$x_{\infty} = [A]_0 - [A]_{\infty} = 1.000M - \left( 12.68 - \left( 24.37 - \frac{1.000}{0.0612} \right) \right) = 0.715,$$

therefore,

$$K_{eq} = 2.81$$

Make a substitution,  $k_{-1} = \frac{k_1}{2.81}$ , in the rate equation above;

$$\frac{dx}{dt} = k_1(0.644x^2 - 18.30x + 12.756)$$

Integrated to give,

$$k_1 t = 0.575 \ln \left[ \frac{1.288x - 35.68}{1.288x - 0.92} \right] - 0.210$$

Using the time values given in the table above, and plugging in x-values, where

$$x(t) = 1 - \left( \text{vol}_{\text{base}}(t) - \left( 24.37 - \frac{1.000}{0.0612} \right) \times 0.0612 \right)$$

time (min)	x	$k_1t$	volume				
0	0	0	24.37				
44	0.132796	0.011884	22.2				
62	0.184816	0.017164	21.35				
108	0.298036	0.030761	19.5				
117	0.312724	0.032796	19.26				
148	0.372088	0.04187	18.29				
313	0.626068	0.119279	14.14				
384	0.671356	0.160597	13.4				
442	0.690328	0.194094	13.09				
	0.71542		12.68				

The slope of the graph is  $k_1$  in units of  $M^{-1}min^{-1}$ :

$k_1 = 2.84 \times 10^{-4} M^{-1}min^{-1}$ , and $k_{-1} = 1.01 \times 10^{-4} M^{-1}min^{-1}$
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##### 5. CKD Problem 1.6

Nitrogen pentoxide decomposes according to the reaction  $N_2O_5 \rightarrow 2NO_2 + \frac{1}{2}O_2$

with a rate constant  $k$ . The measured rates between 273 K and 338 K are included in the chart below.

**Make an Arrhenius plot** of the data, and determine  $E_{act}$  **and**  $A$  for the first-order decomposition of nitrogen pentoxide.

The slope and y-intercept of the Arrhenius plot are related to  $E_{act}$  and  $A$  in the following manner:

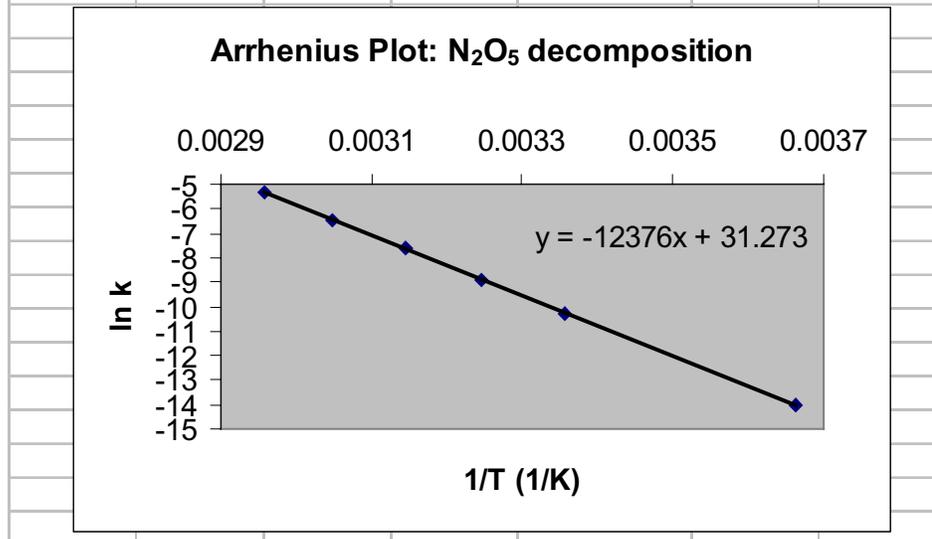
$$k(T) = A \exp\left(\frac{E_{\text{act}}}{RT}\right)$$

$$\ln k = \ln A - \frac{E_{\text{act}}}{RT}$$

$$\text{slope} = -\frac{E_{\text{act}}}{R} \text{ and}$$

$$y\text{-intercept} = \ln A$$

T / K	1/T	k (sec <sup>-1</sup> )	ln k
273	0.003663	7.87E-07	-14.055
298	0.003356	3.46E-05	-10.2717
308	0.003247	1.35E-04	-8.91024
318	0.003145	4.98E-04	-7.60491
328	0.003049	1.50E-03	-6.50229
338	0.002959	4.87E-03	-5.32466



$$-\frac{E_{\text{act}}}{R} = -12376 \text{ K}$$

$$E_{\text{act}} = 12376 \text{ K} \times 8.3144 \text{ J K}^{-1} \text{ mole}^{-1}$$

$$E_{\text{act}} = 103 \text{ kJ mole}^{-1}$$

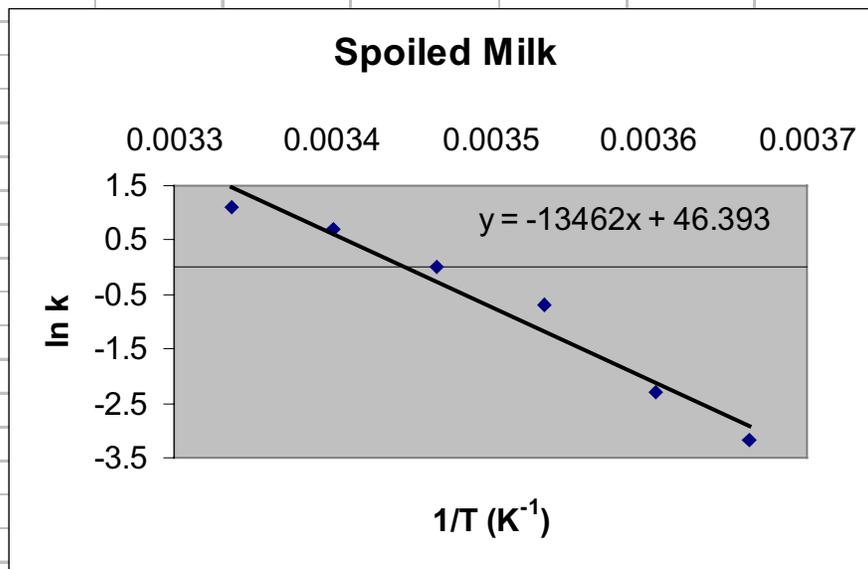
$$\ln A = 31.273$$

$$A = 3.82 \times 10^{13} \text{ s}^{-1}$$

6. According to the information provided on some milk cartons, homogenized milk will keep for 1/3 day at 80°F, for 1/2 day at 70°F, for 1 day at 60°F, for 2 days at 50°F, for 10 days at 40°F, and for 24 days at 32°F. Calculate the **activation energy** for the process that spoils milk.

We are not told how far the spoiled milk is after the given times, but it will not make a difference to the activation energy as long as we can assume the spoilage is the same at each given time (the spoilage *would* affect the Arrhenius coefficient, but nobody asked us about that). The given times are the 1/e time for spoilage, so that the rate is simply the reciprocal of the indicated time; e.g., rate at 80°F is 3 days<sup>-1</sup>. Remember to convert from °F to K.

T / F	T / K	1/T	time / days	k	ln k
80	299.6667	0.003337	0.33333333	3	1.098612
70	294.1111	0.0034	0.5	2	0.693147
60	288.5556	0.003466	1	1	0
50	283	0.003534	2	0.5	-0.69315
40	277.4444	0.003604	10	0.1	-2.30259
32	273	0.003663	24	0.041667	-3.17805



The slope of this graph will give us  $E_{act}$ .

$$E_{act} = -(R \times -13462) = \boxed{112 \text{ kJ mole}^{-1}}$$