1. (5 points each) The following kinetic data were obtained for the reaction 2 ICl(g) + $H_2(g) \rightarrow I_2(g) + 2\ HCl(g)$.

	Initial concentration (mmol·L^{-1})		
Experiment	$[ICl]_0$	$[H_2]_0$	Initial rate (mol·L^{-1}·s^{-1})
1	1.5	1.5	3.7 X 10^{-7}
2	3.0	1.5	7.4 X 10^{-7}
3	3.0	4.5	2.2 X 10^{-6}
4	4.7	2.7	?

(a) Write the differential rate law for the reaction.

$$\text{Rate} = k[ICl]^x[H_2]^y$$

$$\frac{\text{rate}_1}{\text{rate}_2} = \frac{\cancel{k}[ICl]^x\cancel{[H_2]^y}}{\cancel{k}[ICl]^x\cancel{[H_2]^y}} \Rightarrow \frac{3.7\times10^{-7}}{7.4\times10^{-7}} = \frac{[1.5]^x}{[3]^x} \qquad \frac{1}{2} = \left(\frac{1}{2}\right)^x \qquad x = 1$$

$$\frac{\text{rate}_2}{\text{rate}_3} = \frac{\cancel{k}\cancel{[ICl]^x}[H_2]^y}{\cancel{k}\cancel{[ICl]^x}[H_2]^y} \Rightarrow \frac{7.4\times10^{-7}}{2.2\times10^{-6}} = \left(\frac{1.5}{4.5}\right)^y \qquad 1/3 = (1/3)^y$$

$$y = 1$$

$$R = k[ICl][H_2]$$

(b) From the data, determine the value of the rate constant (with proper units).

$$R = k[ICl][H_2]$$

$$3.7\times10^{-7} = k\,[1.5\times10^{-3}][1.5\times10^{-3}]$$

$$k = .16\ M^{-1}s^{-1}$$

units:

$$\frac{M}{s} = k\,[M][M]$$

$$k \rightarrow M^{-1}s^{-1}$$

(c) Use the data to predict the reaction rate for Experiment 4.

$$R = 1.6\ M^{-1}s^{-1}\,[4.7\times10^{-3}M][2.7\times10^{-3}M]$$

$$R = 2.0\times10^{-6}\ M/s$$

2. **(5+15 points)** The mechanism proposed for the oxidation of iodide ion by the hypochlorite ion in aqueous solution is as follows:

Step 1 $ClO^- + H_2O \underset{k_{-1}}{\overset{k_1}{\rightarrow}} HClO + OH^-$ and its reverse (both fast)

Step 2 $I^- + HClO \xrightarrow{k_2} HIO + Cl^-$ (slow)

Step 3 $HIO + OH^- \xrightarrow{k_3} IO^- + H_2O$ (fast)

(a) Write down the balanced equation for the overall reaction.

$$CLO^- + \cancel{H_2O} + I^- + \cancel{HCLO} + \cancel{HIO} + \cancel{OH^-} \rightarrow \cancel{HCLO} + \cancel{OH^-} + \cancel{HIO} + CL^- + IO^- + \cancel{H_2O}$$

$$CLO^- + I^- + \cancel{OH^-} \rightarrow CL^- + IO^- + \cancel{OH^-}$$

$$ClO^- + I^- \rightarrow Cl^- + IO^-$$

(b) Write the rate law for the formation of HIO implied by this mechanism.

$$Rate = k_2[I^-][HCLO]$$ intermediate

$$\frac{d[HCLO]}{dt} = 0 = k_1[CLO^-][H_2O] - k_{-1}[HCLO][OH^-] - k_2[I^-][HCLO]$$

$$k_1[CLO^-][H_2O] = (k_{-1}[OH^-] + k_2[I^-])[HCLO]$$

$$Rate = \frac{k_1k_2[I^-][CLO^-][H_2O]}{k_{-1}[OH^-] + k_2[I^-]}$$

3. **(15 points)** Raw milk sours in about 4 h at 28°C but in about 48 h in a refrigerator at 5°C. What is the activation energy for the souring of milk?

$28°C = 301\,K$

$5°C = 278\,K$

$Rate = k[C]^x$ so $k \propto R$ and $R = \frac{\Delta}{t}$

$R_1 = \frac{1}{4h} = .25\,hr^{-1}$ $R_2 = \frac{1}{48h} = .020\,hr^{-1}$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{-E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad \ln\left(\frac{.02}{.25}\right) = \frac{-E_a}{R}\left(\frac{1}{278} - \frac{1}{301}\right)$$

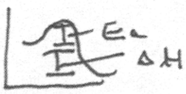
$$-2.52 = \frac{-E_a}{R}(2.67 \times 10^{-4})$$

$$E_a = 78252\ J/mol$$

4. **(5+10 points)** The activation energy for the disproportionation of hydrogen peroxide is 76 kJ/mol and the process is exothermic by 285 kJ/mol.

(a) What is the activation energy for the reverse reaction? $H_2O_2 \rightleftharpoons 2H_2O + O_2$

$E_a = 76$ kJ/mol $\Delta H = 285$ kJ/mol



total reverse = $E_a + \Delta H = 361$ kJ/mol

(b) Calculate the fraction of peroxide molecules with sufficient energy to react at 25°C.

$e^{-E_a/RT}$

$RT = 8.314$ J/mol·K $\times 298$ K $= 2477.5$ J/mol

$E_a/RT = 76{,}000/2477.5 = 30.67$

$e^{-E_a/RT} = 4.8\times10^{-14}$

5. **(4 points each)** **Short Answer**

(a) (True or False) The rates of all elementary reactions increase with increasing temperature.

True

(b) Define a "transition state" or "activated complex."

An unstable chemical species that is at the top of an energy / rc diagram. It can form either reactants or products.

(c) For a second order reaction, a plot of ___1/c___ vs. time yields a straight line with

slope ___2k___.

(d) What is the "Principle of Detailed Balance?"

at equilib rate forward rxn = rate of reverse rxn.

(e) The total world energy consumption is presently about 13-15 terra watts, 90% of which is obtained from chemical reactions.

6. (15 points) The rate of the gas-phase reaction

$$H_2 + I_2 \rightarrow 2\,HI$$

is given by

$$\text{rate} = -\frac{d[I_2]}{dt} = k[H_2][I_2]$$

With $k = 0.0242$ L mol^{-1} s^{-1} at 400°C. If the initial concentration of H_2 is 0.081 mol L^{-1} and that of I_2 is 0.036 mol L^{-1}, calculate the initial rate at which heat if absorbed or emitted during the reaction. The enthalpy of the reaction as written is -9.48 kJ/mol.

$$R = k[H_2][I_2] \rightarrow 0.0242\ \text{L/mol s}\,(0.081M)(0.036M)$$
$$= 7.06 \times 10^{-5}\ \frac{\text{mol}}{\text{L}\cdot\text{s}}$$

$$\frac{+d[HI]}{2\,dt} = \frac{-d[H_2]}{dt} = \frac{-d[I_2]}{dt}$$

$$\text{Rate} \times \text{enthalpy} = 7.06\times10^{-5}\ \frac{\text{mol}}{\text{Ls}} \times -9480\ \text{J/mol}$$
$$= -0.669\ \text{J/Ls}$$

← ~~[illegible]~~ rate of heat emitted.