Monday, July 14 R&R Worksheet

1) In the basement of Park you stumble upon the abandoned laboratory of the infamous Dr. Max Judish. Resting in a fume hood you find his personal notebook, which contains evidence of a newly discovered element, Judishtonium (J). Dr. Judish has performed rigorous testing on this element and notes that it is incredibly reactive, with one of the following reactions being:

$$2\ JH_3(aq) + OCl^-(aq) \rightarrow J_2H_4(aq) + Cl^-(aq) + H_2O(\ell)$$

a) You find this data table which corresponds to the reaction above. However, the research appears incomplete as there is no rate law. Using your chemical intuition, determine the experimental rate law for this reaction.

$[JH_3]$ (M)	$[OCl^-]$ (M)	Initial Rate (M/s)
0.21	0.13	0.00023
0.21	0.325	0.000575
0.84	0.13	0.00368
0.84	0.26	0.00736

$$\frac{\text{Initial Rate 1}}{\text{Initial Rate 2}} = \frac{k[JH_3]^x[OCl^-]^y}{k[JH_3]^x[OCl^-]^y}$$

$$\frac{0.00023\ M/s}{0.000575\ M/s} = \frac{k[0.21\ M]^x[0.13\ M]^y}{k[0.21\ M]^x[0.325\ M]^y}$$

$$0.4 = \left(\frac{[0.13\ M]}{[0.325\ M]}\right)^y$$

$$0.4 = 0.4^y$$

$$y = 1$$

$$\frac{0.00368\ M/s}{0.00023\ M/s} = \frac{k[0.84\ M]^x[0.13\ M]^y}{k[0.21\ M]^x[0.13\ M]^y}$$

$$16 = 4^x$$

$$4^2 = 4^x$$

$$x = 2$$

Rate = $k[JH_3]^2[OCl^-]$

b) By what factor does the rxn rate change if $[JH_3]$ is reduced to ⅔ of the initial amount and $[OCl^-]$ is tripled?

$(\frac{2}{3})^2 \times (3)^1 = 4/3$

The rxn rate will increase by a factor of 4/3

c) Since the probability of a termolecular reaction is low, Dr. Judish proposes the following reaction mechanism. Does the rate law derived from this mechanism match the experimental rate law? ***(Assume that [Cl-] is constant)***

1. $\mathrm{JH_3}(aq) + \mathrm{OCl^-}(aq) \rightleftharpoons \mathrm{JH_2Cl}(aq) + \mathrm{OH^-}(aq)$ (fast)
2. $\mathrm{JH_2Cl}(aq) + \mathrm{JH_3}(aq) \rightleftharpoons \mathrm{J_2H_5^+}(aq) + \mathrm{Cl^-}(aq)$ (fast)
3. $\mathrm{J_2H_5^+}(aq) + \mathrm{OH^-}(aq) \rightarrow \mathrm{J_2H_4}(aq) + \mathrm{H_2O}(\ell)$ (slow)

No, this rate law is not equivalent to the experimental rate law. The mechanistic rate law is Rate = ($k[JH_3]^2[OCl^-]$) / $[Cl^-]$, instead of Rate = $k[JH_3]^2[OCl^-]$.

$$R_3 = k_3 [J_2H_5^+][OH^-]$$

$$[J_2H_5^+] = K_2 \frac{[JH_2Cl][JH_3]}{[Cl^-]}$$

$$[OH^-] = K_1 \frac{[JH_3][OCl^-]}{[JH_2Cl]}$$

$$R_3 = k_3 K_1 K_2 \left(\frac{[JH_2Cl][JH_3]}{[Cl^-]}\right)\left(\frac{[JH_3][OCl^-]}{[JH_2Cl]}\right)$$

$$R_3 = k' \frac{[JH_3]^2[OCl^-]}{[Cl^-]}$$

d) What effect will increasing the concentration of the product Cl^- have on the reaction rate?

Increasing $[Cl^-]$ causes the reaction rate to decrease. This result can be explained by Le Chatelier's Principle, which states that if a dynamic equilibrium is disturbed (eg, removal of a reactant or a product), the system will shift toward the reactants or toward the products to counteract the disturbance and establish a new equilibrium. Increasing $[Cl^-]$ causes the second reaction to shift toward the reactants, thereby decreasing $[J_2H_5^+]$. Because $[J_2H_5^+]$ is a reactant for the rate-determining step, its decrease results in the reaction rate decreasing.

2) There's also a reaction involving the decomposition of Judishtonium which has the following data:

Time (s)	[J] (M)
0	2.30
2	0.64
8	0.203
15	0.113
800	0.00223

Can you determine the order and rate constant of this reaction from this graph? If not, perform the necessary analysis to determine the order and rate constant?

Time (s)	[J] (M)	1/[J] (1/M)
0	2.30	0.435
2	0.64	1.563
8	0.203	4.926
15	0.113	8.850
800	0.00223	448.430

Slope = Δ (1/[J]) / Δt

Slope from 0 s to 2 s:

- Slope = (1.563 - 0.435) / 2 = 0.564

Slope from 2 s to 8 s:

- Slope = (4.926 - 1.563) / 6 = 0.561

Slope from 15 s to 8 s:

- Slope = (8.850 - 4.926) / 7 = 0.561

Slope from 800 s to 15 s

- Slope = (448.430 - 8.850) / 785 = 0.560

Slope is roughly constant for the inverse transformation, thus this is a second order reaction with a rate constant of 0.560 $M^{-1}s^{-1}$

3) In the corner of the lab you discover a radioactive protein shake which may explain Dr. Judish's superhuman teaching ability. The shaker bottle appears half-way filled, with a radius of 5 cm and a height of 20 cm. Based on the size of the protein scooper you approximate that the bottle contains 20 grams of protein (molar mass = 4.5 g/mol). Assuming the radioactive decay of protein is a first order reaction with a half-life of 35 minutes, what is the concentration of protein after 5 hours (***in units of molarity***)?

Area of Circle = $\pi r^2 = \pi(5\ cm)^2 \approx 78.54\ cm^2$

Volume of Solution = Area * ½ (Height) = $78.54\ cm^2$ * ½ (20 cm) = $785.4\ cm^3$

$785.4\ cm^3$ * (1 mL / 1 cm^3) * (1 L / 1000 mL) = 0.7854 L

20 grams * (1 mol / 4.5 g) = 4.44 moles

Initial Molarity = Moles of Solute / Liters of Solution = 4.44 moles / 0.7854 L = 5.66 M

For first order reaction:

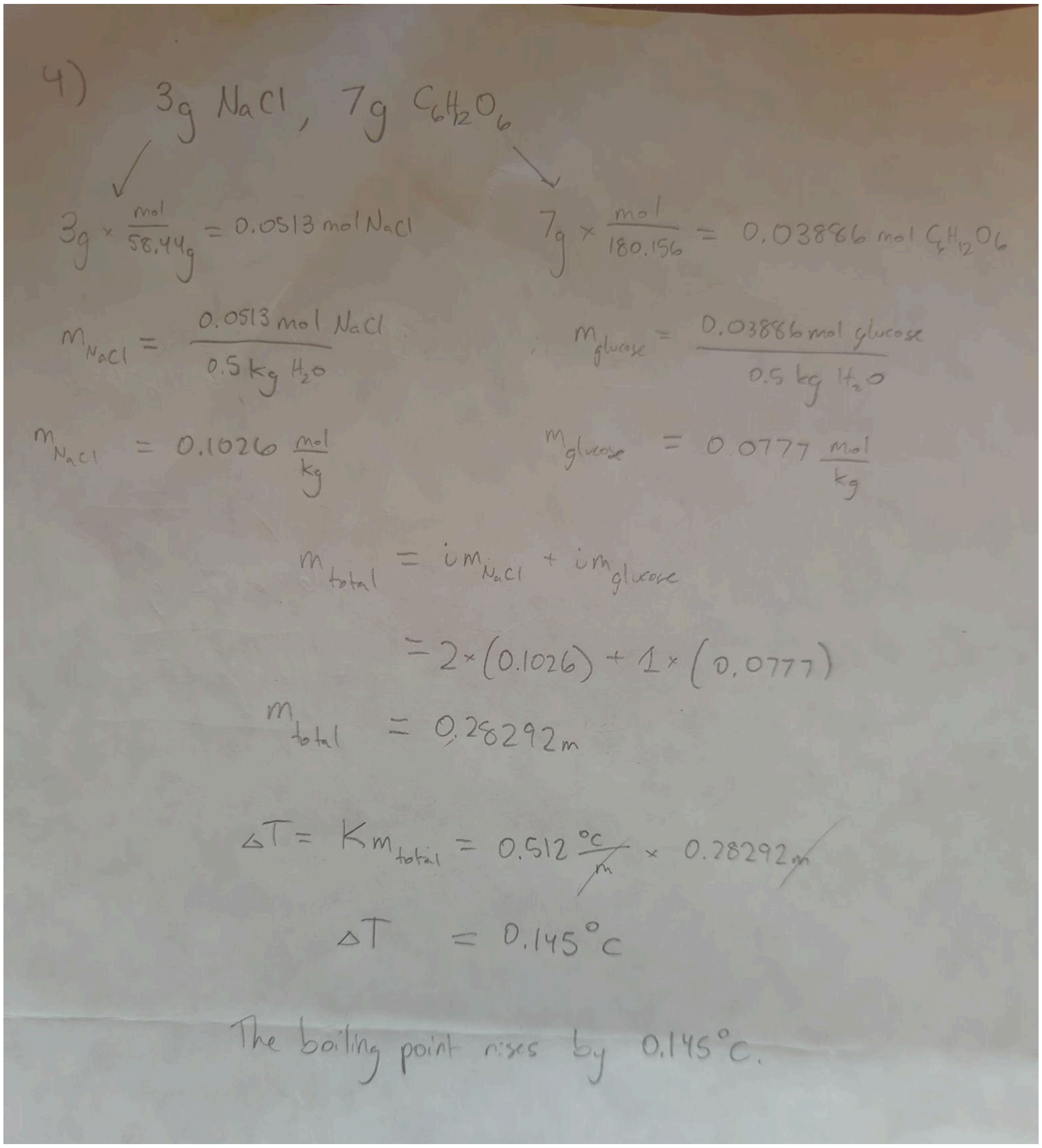
$k = \ln(2) / t_{1/2} = \ln(2) / 35\ minutes = 0.02\ min^{-1}$

First Order Reaction Integrated Rate Law Exponential Form

$[Protein] = [Protein]_o e^{-kt} = (5.66\ M)e^{-(.02\ min-1\ *\ 300\ min)} = 0.014\ M$

0.014 M protein remains after 5 hours

4) During R&R you confront Dr. Judish about his protein powder, appealing to the fact that it gives him an unfair advantage. He vehemently denies that it contains a special protein, and instead claims that it is simply a harmless mixture of 30% salt (NaCl) and 70% glucose ($C_6H_{12}O_6$). You decide to test his claim by dissolving 10.00 grams of the mixture into 500.0 g of water. What would be the change in boiling point of the "shake" if he was telling the truth? (K_b is 0.512°C/m).



4) 3g NaCl, 7g $C_6H_{12}O_6$

$3g \times \frac{mol}{58.44g} = 0.0513\ mol\ NaCl$

$7g \times \frac{mol}{180.156} = 0.03886\ mol\ C_6H_{12}O_6$

$m_{NaCl} = \frac{0.0513\ mol\ NaCl}{0.5\ kg\ H_2O}$

$m_{glucose} = \frac{0.03886\ mol\ glucose}{0.5\ kg\ H_2O}$

$m_{NaCl} = 0.1026\ \frac{mol}{kg}$

$m_{glucose} = 0.0777\ \frac{mol}{kg}$

$m_{total} = i m_{NaCl} + i m_{glucose}$

$= 2 \times (0.1026) + 1 \times (0.0777)$

$m_{total} = 0.28292 m$

$\Delta T = K m_{total} = 0.512\ \frac{°C}{m} \times 0.28292 m$

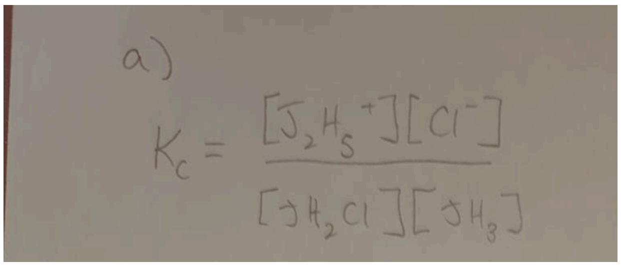
$\Delta T = 0.145°C$

The boiling point rises by 0.145°C.

5) Changing gears back to Judishtonium, recall the second step of the overall reaction $2JH_3(aq) + OCl^-(aq) \rightarrow J_2H_4(aq) + Cl^-(aq) + H_2O(\ell)$:

$$\mathrm{JH_2Cl}(aq) + \mathrm{JH_3}(aq) \rightleftharpoons \mathrm{J_2H_5^+}(aq) + \mathrm{Cl^-}(aq) \text{ (fast)}$$

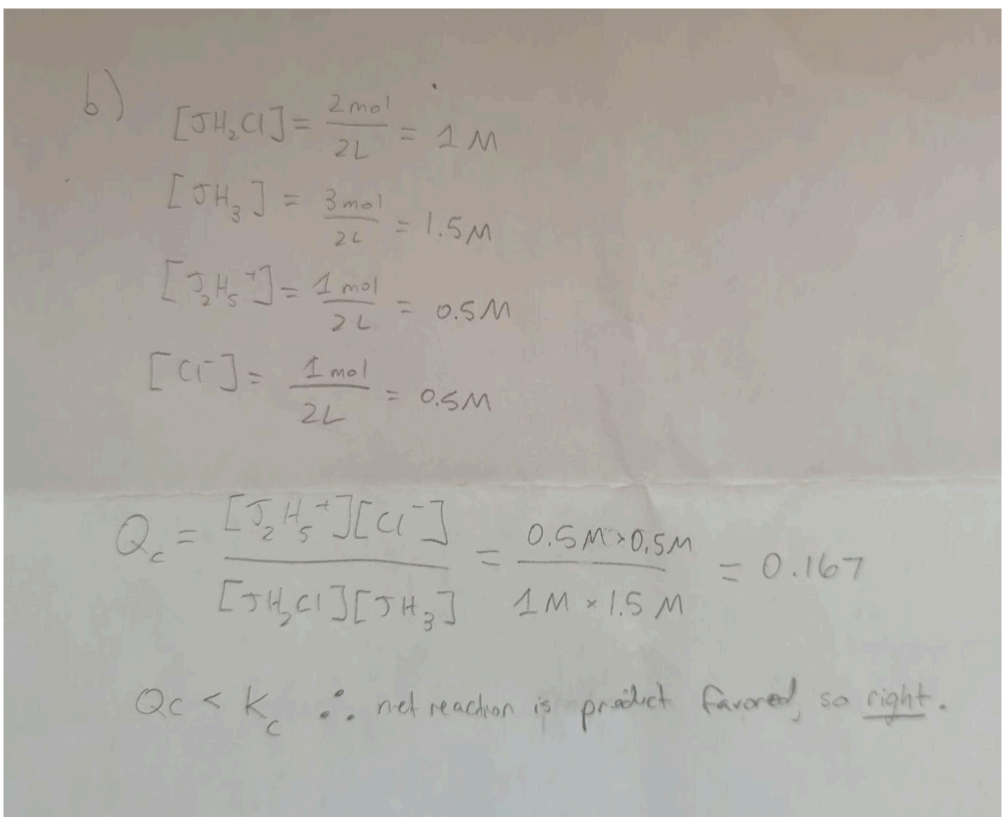
a) Write the equilibrium constant expression for the reaction. K_c = ?



a)

$$K_c = \frac{[J_2H_5^+][Cl^-]}{[JH_2Cl][JH_3]}$$

b) Suppose you dissolve 2 moles of JH_2Cl, 3 moles of JH_3, 1 mole of $J_2H_5^+$, and 1 mole of Cl^- in water so that the total volume of the solution is 2L. Given a K_c value of 0.4, predict in which direction the net reaction will proceed toward equilibrium (left, right, or no net reaction)?



b)

$$[JH_2Cl] = \frac{2\text{ mol}}{2L} = 1\text{ M}$$

$$[JH_3] = \frac{3\text{ mol}}{2L} = 1.5\text{ M}$$

$$[J_2H_5^+] = \frac{1\text{ mol}}{2L} = 0.5\text{ M}$$

$$[Cl^-] = \frac{1\text{ mol}}{2L} = 0.5\text{ M}$$

$$Q_c = \frac{[J_2H_5^+][Cl^-]}{[JH_2Cl][JH_3]} = \frac{0.5M \times 0.5M}{1M \times 1.5M} = 0.167$$

$Q_c < K_c$ ∴ net reaction is product favored, so right.