Question 1

Kinetic and thermodynamic reaction control can decide what the major product of a reaction would be for a given set of conditions. The following scenario illustrates this topic. Molecule A can react under the same conditions to form two distinct products, B and C. The change in Gibbs free energies (ΔG's) and the activation energies (ΔE_a) are given below.

$$A \rightleftarrows B, \ \ \Delta G = -8 \ \frac{kcal}{mol}, \ \ E_{a,ab} = +5 \ \frac{kcal}{mol}$$

$$A \rightleftarrows C, \ \ \Delta G = -3 \ \frac{kcal}{mol}, \ \ E_{a,ac} = +2 \ \frac{kcal}{mol}$$

a. Draw both reactions on the given reaction coordinate. Clearly label all activation energies, ΔG's, transition states (TS's), reactants, and products.

- Solution: Any reasonable reaction coordinate will be accepted. Both forward and backward activation energies must be labeled. The transition state for $A \rightleftarrows B$ must be higher in energy than the transition state for $A \rightleftarrows C$, which must be higher in energy than reactant A. Product B must be lower in energy than product C, which must be lower in energy than reactant A.

b. The Arrhenius equation relates the rate constant k of a reaction to its activation energy E_a and the surrounding temperature T:

$$k = Ae^{-\frac{E_a}{RT}} .$$

i. By examining the Arrhenius equation, which product forms faster and why? This product is called the kinetic product. Assume that the constant A is identical for both reactions.

Solution: $A \rightleftarrows C$ has a faster rate, since k increases as E_a decreases.

ii. Which of the two products is more stable and why? This product is called the thermodynamic product.

Solution: Product B is more stable, since it is lower in energy on the reaction coordinate.

c. Explain the following observations:

i. Low temperatures tend to favor the formation of the kinetic product.

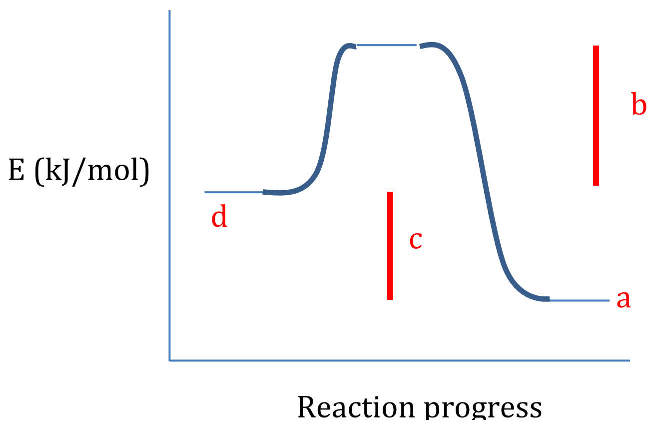
- Solution: At low temperatures, most molecules of A will only have enough energy to surpass the activation barrier of $A \rightleftarrows C$, forming product C. This reaction is essentially irreversible, since most molecules lack sufficient energy to surpass the activation barrier of the reverse reaction.

ii. High temperatures tend to favor the formation of the thermodynamic product.

- Solution: At high temperatures, most molecules have sufficient energy to surpass all activation barriers. Since molecules A, B, and C will be in equilibrium, the major product becomes the most stable one.

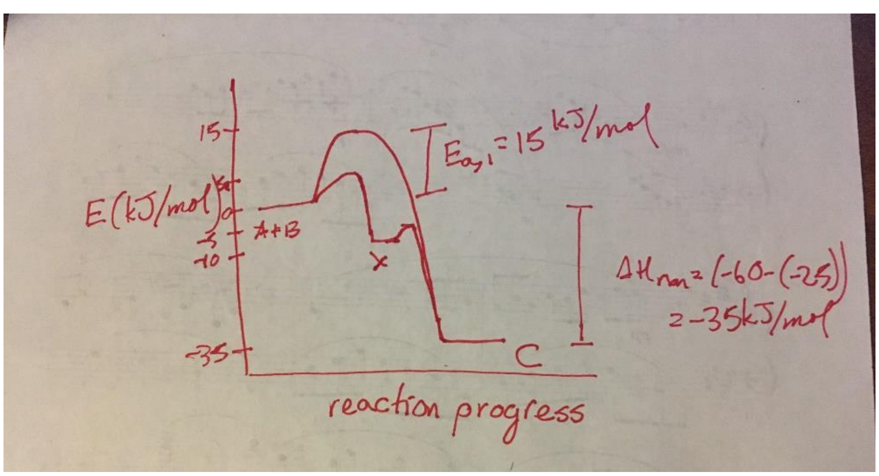
Question 2

a. Label the following components on the reaction coordinate diagram below:
   i. Products
   ii. Activation energy (E_a)
   iii. ΔH_{rxn}
   iv. Reactants



b. Below are provided two pathways to achieve the reaction $A + B \rightarrow C$

Pathway 1:
$A + B \rightarrow C$ (direct reaction)
Pathway 2 (two steps):
$A + B \rightarrow X$
$X \rightarrow C$
Given the following information, sketch on the axes below reaction coordinate diagrams for both pathways:
$\Delta H^o_{f,A} = -10\frac{kJ}{mol}$ $\Delta H^{0o}_{f,B} = -15\frac{kJ}{mol}$ $\Delta H^o_{f,C} = -60\frac{kJ}{mol}$ $\Delta H^o_{f,X} = -35\frac{kJ}{mol}$ $E_{A,1} = 15\frac{kJ}{mol}$
$E_{A,2a} = 5\frac{kJ}{mol}$ $E_{A,2b} = 5\frac{kJ}{mol}$
Where E_A represents activation energy and ΔH^o_f represents heat of formation.



c. Alex and Abhi are both trying to synthesize product C from reactants A and B. Abhi chooses to use pathway 1 under the reasoning that it requires only one step. Alex chooses to use pathway 2.

i. Suppose that both Abhi and Alex begin with 1 mol of A and 1 mol of B. Abhi runs pathway 1 and waits until 81% of A and B have been converted into C, then isolates product C. Alex runs pathway 2 and waits until 90% of A and B is converted is converted into X, then isolates X and waits until 90% of X is converted into C, then isolates C. Assuming the reactions occur at 25°C, answer the following questions:

i) Which reaction generates the greater yield and by how much?

The two reactions generate the same yield (0.81 mol C). In pathway two you first have 0.9A + 0.9 B → 0.9 X, then (0.9)(0.9)X → 0.81 C

ii) Which reaction finishes first and by how long? For simplicity, suppose that all reactions proceed at a constant rate k (units mol/s), where $k = e^{-\frac{E_a}{RT}}$, where e is the base of the natural logarithm, E_a is activation energy, R is the ideal gas constant (8.314 J/mol K), and T is the temperature.

Pathway 1: $k = e^{-\frac{10000J}{8.314\frac{J}{mol*K}*298K}} = \frac{0.0177mol}{s}, \tau = \frac{0.81\ mol}{0.0177mol/s} = 46s$

Pathway 2: $k = e^{-\frac{5000J}{8.314\frac{J}{mol*K}*298K}} = \frac{0.133mol}{s}, \tau = \frac{2*0.90\ mol}{0.133mol/s} = 14s$

Pathway 2 is faster by about 32s, (over 3x faster!)

ii. Is Abhi's reasoning justifiable? Explain briefly.

No, because Abhi considers only the number of steps but fails to recognize that different steps might take different amounts of time. Steps with higher activation energies take much longer, increasing exponentially with activation energy. Therefore, experiments might have more steps but finish more quickly, if each of those steps have a low activation energy barrier.

Question 3

The US government currently contracts all production of pennies to a single company, Penny Products. The folk here at WUCT are considering expanding from the high school tournament market into the metallurgy industry. Help the chemists at WUCT find a manufacturing procedure to outcompete Pennies Products. (Note: WUCT hooks all reactions requiring voltage to an outlet at Washington University, effectively paying no money for any electricity)

a. Modern pennies are an alloy of zinc plated with copper. The good folk at Penny Products purchase their zinc purified from an overseas mining company for about 18 cents for 100 grams. WUCT has recently obtained a large supply of zinc oxide (ZnO), priced at 10 cents for 100 grams. ZnO is insoluble in neutral water but very soluble in strongly acidic solutions.

   i. Write a balanced chemical equation showing the reaction ZnO experiences in an acidic solution.

   Ans: $ZnO_{(s)} + 2H^{+}{}_{(aq)} \leftrightarrow Zn^{2+}{}_{(aq)} + H_2O$

   ii. Explain why ZnO is insoluble in neutral water but can dissolve in an acidic solution. The following standard reduction potentials may be of use:

   Ans: If ZnO disassociated as normal compounds, it would generate an O^{2-} ion, which is very unstable, disfavoring dissolution. However, in acidic solution, trace O^{2-} is readily protonated to form water, driving dissolution.

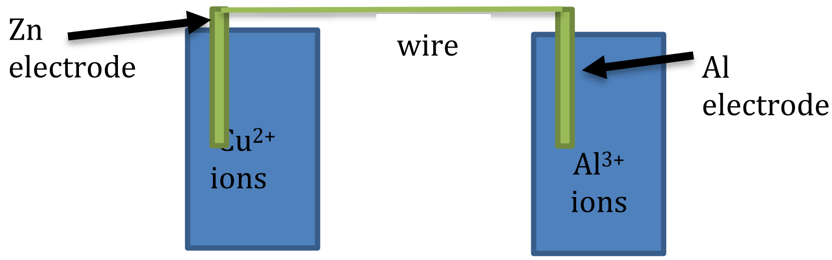
b. After dissolving zinc in a solution, the WUCT chemists attempt to obtain solid zinc by electrodeposition. Driving the electrochemical cell generates water and solid zinc, but requires water and a large external supply of voltage. What is the cell potential of this reaction? At this point, assume the concentration of Zn^{2+} and H^{+} are both 1M.

   Ans: E = -0.7618V + 1.229V = 0.4672V

c. Instead of hammering copper onto the zinc pennies, WUCT decides to electrochemically plate copper onto the zinc. Pennies Proudcts pays 60 cents for 100 grams of copper metal, while WUCT pays 55 cents for 100 grams of copper sulfate.

   i. Draw a picture of a galvanic cell using copper sulfate in one of the half cells, and an aluminum electrode with aluminum ions in the other half cell.

Sol:



ii. Write the net ionic equation occurring in the galvanic cell in part i.

Ans: $3Cu^{2+}{}_{aq} + 2Al_{(s)} \leftrightarrow 3Cu_{(s)} + 2Al^{3+}{}_{(aq)}$

iii. After some time, we notice the zinc electrode begins shrinking, although the mass of copper on the electrode keeps increasing. Furthermore, the mass of the aluminum electrode is no longer changing. Explain this observation.
Nernst potential becomes more and more unfavorable for the Al → Al^{3+} + $3e^-$ half cell due to rising concentration of Al^{3+}. Eventually, the Zn → Zn^{2+} + $2e^-$ becomes more favorable than the Al^{3+} reduction, leading to a redox reaction between the zinc and copper rather than aluminum and copper.

d. After plating the copper onto the zinc, WUCT now needs to carve out the shape of individual pennies from the copper-plated zinc sheets. Unfortunately, WUCT consists of mostly nerds, too weak to cut metal using conventional methods. However, full annealing, the processing of heating metal to 50^0C, then cooling back down to room temperature can soften metal enough to be cut by the average WUCT member.

i. WUCT members decide to use the following unbalanced reaction to heat the metal from 25^0C to 50^0C:

C_3H_8 + O_2 → H_2O + CO_2 (Enthalpy of combustion for propane is -2202.0 kJ/mol)

How many moles of the reaction are needed to heat 1kg of the metal? (assume the specific heat of the metal is 0.39 J/g^0C)
Ans: 4.43 moles of propane

ii. To cool the 1kg pennies back down, the metal is submerged in 0.5 liters of water. Assuming the metal is at 50^0C and the water is at 25^0C, what is the final temperature of water? Report your answer in Celsius.

0.5 liters of water = 0.5 kg of water = 500 grams of water

Total Thermal Energy
$(1000g)(0.39J/g^0C)(50+273K) + (500g)(4.184J/g^0C)(25+273K) =$
749386 J

Equation where temperature is equivalent for both the metal and water
$(1000g)(0.39J/g^0C)(Temp) + (500g)(4.184J/g^0C)(Temp) = 749386$ J

Solve for Temperature
Temp = 302K – 273K = 29^0C

Final Temperature of water = 29^0C