

# Chemistry 210

# Exam 2

Be sure to put your name on each page. This page can be removed from your exam so that you will have a Periodic Table handy throughout the exam, it does not need to be turned in. Show all your work for problems which require any sort of calculation, no credit will be given for answers without work shown. If you have shown a significant amount of work or multiple drawings for a problem, draw a box around what you consider your final answer.

Avogadro's Number =  $6.022 \times 10^{23}$  units/mol

$32.00^\circ\text{F} = 0.000^\circ\text{C} = 273.15\text{K}$

Density of Water =  $1.000^{\text{g}}/\text{mL}$

$R = 0.08206 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K} = 8.314 \text{ J}/\text{mol}\cdot\text{K}$

$PV = nRT$

$\Delta T_{\text{fp/bp}} = k_{\text{fp/bp}} \cdot m \cdot i$

For water:  $k_{\text{fp}} = -1.86^\circ\text{C}/m$   
 $k_{\text{bp}} = 0.512^\circ\text{C}/m$

$P_1 = X_1 P_1^\circ$

$\Pi = MRTi$

$C_1 V_1 = C_2 V_2$

Quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Integrated Rate Laws:

$$\ln[A]_t = -kt + \ln[A]_o$$

$$1/[A]_t = kt + 1/[A]_o$$

$$[A]_t = -kt + [A]_o$$

$$k = Ae^{-E_a/RT}$$

$$\ln(k) = \left( \frac{-E_a}{R} \right) \left( \frac{1}{T} \right) + \ln(A)$$

$$\ln\left( \frac{k_1}{k_2} \right) = \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\text{pH} = \text{pK}_a + \log\left( \frac{[\text{conjugate base}]}{[\text{conjugate acid}]} \right)$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln Q$$

$$E^\circ_{\text{cell}} = \frac{RT}{nF} \ln K^\circ$$

$$K^\circ = e^{(nF/RT) E^\circ_{\text{cell}}}$$

$$F = 96485 \text{ J}/\text{V}\cdot\text{mol of electrons}$$

$$\Delta G^\circ = \Delta H^\circ_{\text{system}} - T\Delta S^\circ_{\text{system}}$$

$$\Delta G^\circ = -nFE^\circ_{\text{cell}} = -RT \ln K^\circ$$

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$F = 96485 \text{ C}/\text{mol electrons}$$

$$1A = 1 \text{ C} / \text{sec}$$

|                           |                           |                           |                           |                           |                           |                           |                           |                           |                           |                           |                           |                           |                           |                           |                           |                           |                           |                          |                          |                           |                           |
|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|--------------------------|--------------------------|---------------------------|---------------------------|
| 1<br><b>H</b><br>1.0079   |                           |                           |                           |                           |                           |                           |                           |                           |                           |                           |                           |                           |                           |                           |                           |                           | 2<br><b>He</b><br>4.0026  |                          |                          |                           |                           |
| 3<br><b>Li</b><br>6.941   | 4<br><b>Be</b><br>9.0122  |                           |                           |                           |                           |                           |                           |                           |                           |                           |                           |                           |                           |                           |                           | 5<br><b>B</b><br>10.811   | 6<br><b>C</b><br>12.011   | 7<br><b>N</b><br>14.007  | 8<br><b>O</b><br>15.999  | 9<br><b>F</b><br>18.998   | 10<br><b>Ne</b><br>20.180 |
| 11<br><b>Na</b><br>22.990 | 12<br><b>Mg</b><br>24.305 |                           |                           |                           |                           |                           |                           |                           |                           |                           |                           |                           |                           |                           |                           | 13<br><b>Al</b><br>26.982 | 14<br><b>Si</b><br>28.086 | 15<br><b>P</b><br>30.974 | 16<br><b>S</b><br>32.066 | 17<br><b>Cl</b><br>35.453 | 18<br><b>Ar</b><br>39.948 |
| 19<br><b>K</b><br>39.098  | 20<br><b>Ca</b><br>40.078 | 21<br><b>Sc</b><br>44.956 | 22<br><b>Ti</b><br>47.88  | 23<br><b>V</b><br>50.942  | 24<br><b>Cr</b><br>51.996 | 25<br><b>Mn</b><br>54.938 | 26<br><b>Fe</b><br>55.847 | 27<br><b>Co</b><br>58.933 | 28<br><b>Ni</b><br>58.69  | 29<br><b>Cu</b><br>63.546 | 30<br><b>Zn</b><br>65.39  | 31<br><b>Ga</b><br>69.723 | 32<br><b>Ge</b><br>72.61  | 33<br><b>As</b><br>74.922 | 34<br><b>Se</b><br>78.96  | 35<br><b>Br</b><br>79.904 | 36<br><b>Kr</b><br>83.80  |                          |                          |                           |                           |
| 37<br><b>Rb</b><br>85.468 | 38<br><b>Sr</b><br>87.62  | 39<br><b>Y</b><br>88.906  | 40<br><b>Zr</b><br>91.224 | 41<br><b>Nb</b><br>92.906 | 42<br><b>Mo</b><br>95.94  | 43<br><b>Tc</b><br>(98)   | 44<br><b>Ru</b><br>101.07 | 45<br><b>Rh</b><br>102.91 | 46<br><b>Pd</b><br>106.42 | 47<br><b>Ag</b><br>107.87 | 48<br><b>Cd</b><br>112.41 | 49<br><b>In</b><br>114.82 | 50<br><b>Sn</b><br>118.71 | 51<br><b>Sb</b><br>121.76 | 52<br><b>Te</b><br>127.60 | 53<br><b>I</b><br>126.90  | 54<br><b>Xe</b><br>131.29 |                          |                          |                           |                           |
| 55<br><b>Cs</b><br>132.91 | 56<br><b>Ba</b><br>137.33 | 57<br><b>La</b><br>138.91 | 72<br><b>Hf</b><br>178.49 | 73<br><b>Ta</b><br>180.95 | 74<br><b>W</b><br>183.84  | 75<br><b>Re</b><br>186.21 | 76<br><b>Os</b><br>190.23 | 77<br><b>Ir</b><br>192.22 | 78<br><b>Pt</b><br>195.08 | 79<br><b>Au</b><br>196.97 | 80<br><b>Hg</b><br>200.59 | 81<br><b>Tl</b><br>204.38 | 82<br><b>Pb</b><br>207.2  | 83<br><b>Bi</b><br>208.98 | 84<br><b>Po</b><br>(209)  | 85<br><b>At</b><br>(210)  | 86<br><b>Rn</b><br>(222)  |                          |                          |                           |                           |
| 87<br><b>Fr</b><br>(223)  | 88<br><b>Ra</b><br>226.03 | 89<br><b>Ac</b><br>227.03 | 104<br><b>Rf</b><br>(261) | 105<br><b>Db</b><br>(262) | 106<br><b>Sg</b><br>(263) | 107<br><b>Bh</b><br>(262) | 108<br><b>Hs</b><br>(265) | 109<br><b>Mt</b><br>(266) | 110<br>(269)              | 111<br>(272)              | 112<br>(277)              | 114                       |                           | 116                       |                           |                           |                           |                          |                          |                           |                           |

|                           |                           |                           |                           |                           |                           |                           |                           |                           |                           |                           |                           |                           |                           |
|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| 58<br><b>Ce</b><br>140.12 | 59<br><b>Pr</b><br>140.91 | 60<br><b>Nd</b><br>144.24 | 61<br><b>Pm</b><br>(145)  | 62<br><b>Sm</b><br>150.36 | 63<br><b>Eu</b><br>151.97 | 64<br><b>Gd</b><br>157.25 | 65<br><b>Tb</b><br>158.93 | 66<br><b>Dy</b><br>162.50 | 67<br><b>Ho</b><br>164.93 | 68<br><b>Er</b><br>167.26 | 69<br><b>Tm</b><br>168.94 | 70<br><b>Yb</b><br>173.04 | 71<br><b>Lu</b><br>174.97 |
| 90<br><b>Th</b><br>232.04 | 91<br><b>Pa</b><br>231.04 | 92<br><b>U</b><br>238.03  | 93<br><b>Np</b><br>237.05 | 94<br><b>Pu</b><br>(244)  | 95<br><b>Am</b><br>(243)  | 96<br><b>Cm</b><br>(247)  | 97<br><b>Bk</b><br>(247)  | 98<br><b>Cf</b><br>(251)  | 99<br><b>Es</b><br>(252)  | 100<br><b>Fm</b><br>(258) | 101<br><b>Md</b><br>(258) | 102<br><b>No</b><br>(259) | 103<br><b>Lr</b><br>(260) |

**Multiple Choice:** Circle the letter of the most correct response. (5pts. per question)

- Which of the following does **not** affect the rate of a reaction?
  - The orientation of colliding particles
  - The coefficients of the reactants in the balanced equation**
  - The frequency of collisions between reacting particles
  - The temperature of the system
  - The energy of collisions between reacting particles
- For the generic equation
$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$
The value of the equilibrium constant,  $K_c$ :
  - Is not affected by temperature
  - Is equal to  $k[A]^a[B]^b$
  - Is equal to  $([A]^a[B]^b)/([C]^c[D]^d)$
  - Is equal to  $([C]^c[D]^d)/([A]^a[B]^b)$**
  - Must be measured, it cannot be derived from the balanced equation
- If the rate of a reaction increases by a factor of 9 when the initial concentration of reactant “A” is increased by a factor of 9, the reaction must be:
  - 2nd order overall
  - 2nd order with respect to  $[A]_o$
  - 0th order with respect to  $[A]_o$
  - 1st order with respect to  $[A]_o$**
  - The order of the reaction depends on the balanced chemical equation
- Which of the following is **true** regarding catalysts and catalyzed reactions?
  - The presence of a catalyst changes the activation energy for a reaction**
  - The presence of a catalyst does not change the mechanism of a reaction
  - The presence of a catalyst changes the equilibrium constant for a reaction
  - The concentration of a catalyst cannot appear in the rate law for a reaction
  - The presence of a catalyst changes the energy of the products and reactants in a reaction
- Which of the following is **false** regarding equilibrium?
  - Equilibrium can be shifted by changing pressure or temperature
  - The rates of the forward and reverse reactions are equal
  - The concentrations of products and reactants does not change once the reaction has reached equilibrium
  - Equilibrium concentrations do not depend upon whether you approach equilibrium from the left or the right
  - The forward and reverse reactions stop when a system reaches equilibrium**
- Which of the following is **false** regarding reaction mechanisms?
  - The observed rate law must agree with the rate law of the slowest step
  - The steps of the mechanism can contain chemical species that do not appear in the overall correctly balanced chemical equation
  - The observed rate law is equal to the sum of the rate laws from all steps**
  - Catalysts can appear in the steps of a mechanism
  - A mechanism must be composed of elementary reactions

**Problems:** Show your work.

7. A reaction is found to be first order with respect to reactant A and second order with respect to reactant B. If  $[A]_0 = 0.211M$ ,  $[B]_0 = 0.561M$  and  $k = 4.16 \times 10^{-2} M^{-2} \text{sec}^{-1}$ , what is the initial rate of the reaction? (10pts)

This is a rate law question. Given the info in the problem, the rate law expression is:

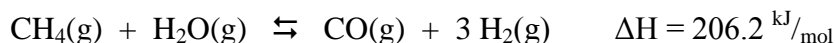
$$\text{Rate}_0 = k [A]_0^1 [B]_0^2$$

Plugging in the values given:

$$\text{Rate}_0 = (4.16 \times 10^{-2} M^{-2} \text{sec}^{-1})(0.211M)(0.561M)^2 = 2.76 \times 10^{-3} M/\text{sec}$$

Don't forget units...

8. For the reaction:



The equilibrium concentrations are observed:  $[\text{CO}]_{\text{eq}} = 1.55M$ ,  $[\text{H}_2]_{\text{eq}} = 0.488M$ ,  $[\text{CH}_4]_{\text{eq}} = 5.15 \times 10^{-4} M$ ,  $[\text{H}_2\text{O}]_{\text{eq}} = 2.64 \times 10^{-2} M$ . What is the equilibrium constant for this reaction? (10pts)

This is another “plug-n-chug” question, this time with equilibrium. Given the balanced equation, the equilibrium constant expression is shown and the values from the problem are plugged in:

$$K_c = \frac{[\text{CO}]_{\text{eq}}^1 [\text{H}_2]_{\text{eq}}^3}{[\text{CH}_4]_{\text{eq}}^1 [\text{H}_2\text{O}]_{\text{eq}}^1} = \frac{(1.55)(0.488)^3}{(5.15 \times 10^{-4})(2.64 \times 10^{-2})} = 1.32 \times 10^4$$

This equilibrium is **product-favored** based upon the value of the equilibrium constant. It's probably also obvious from the listed equilibrium concentrations.

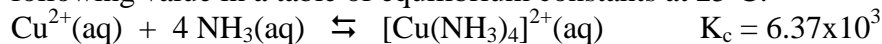
9. A reaction is found to be second order with respect to nitrate ion, a reactant. If  $[\text{NO}_3^-]_0 = 3.82M$  and  $k = 8.37 \times 10^{-5} M^{-1} \text{sec}^{-1}$ , what will the concentration be after 12 minutes have passed? (10pts)

This question is asking about how concentration changes with time, so it must be an integrated rate law question. The second-order integrated rate law expression is:

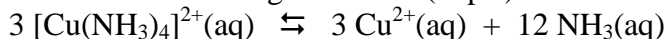
$$\frac{1}{[\text{NO}_3^-]_{12\text{min}}} = kt + \frac{1}{[\text{NO}_3^-]_0} = (8.37 \times 10^{-5} \frac{1}{M \cdot \text{sec}})(12\text{min})(\frac{60\text{sec}}{1\text{min}}) + (\frac{1}{3.82M}) = 0.3220 \frac{1}{M}$$

0.3220 is **NOT** the answer to this question! Take the inverse (that “1/x” key on your calculator...) to get the answer, 3.11M. Notice that if you keep track of units you'll have a built-in reminder.

10. You have found the following value in a table of equilibrium constants at 25°C:



What is the equilibrium constant for the following reaction? (10pts)



Determine the relationship between the two reactions to decide how to manipulate the equilibrium constant. The second reaction is the reverse of the first, so the equilibrium constant will have to be inverted, and the second reaction is 3x the first, so the equilibrium constant will have to be raised to the third power.

$$K_{\text{new}} = \left( \frac{1}{K_c} \right)^3 = \left( \frac{1}{6.37 \times 10^3} \right)^3 = 3.87 \times 10^{-12}$$

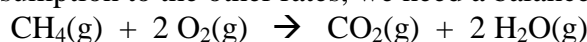
The equilibrium changes from slightly product-favored to quite reactant-favored.

11. Methane (CH<sub>4</sub>) reacts with oxygen to form carbon dioxide and water. Under some set of conditions at some point in time, you find that 6.495g of methane react every minute in a 600.0mL vessel. (15pts)
- What is the rate of methane consumption?
  - What is the rate of oxygen consumption?
  - What is the rate of carbon dioxide production?
  - What is the rate of water production?
  - What is the rate of the *reaction*?

Since this is a (relatively) long time period, this is an *average* rate. Rates are expressed as  $\frac{\Delta\text{concentration}}{\Delta\text{time}}$ , so we have to get a concentration of methane and divide by time to get rate:

$$\text{Rate}_{\text{CH}_4} = (6.495\text{g CH}_4) \left( \frac{1\text{mol CH}_4}{16.043\text{g CH}_4} \right) \left( \frac{1}{0.6000\text{L}} \right) \left( \frac{1}{1\text{min}} \right) = 0.6747\text{M}/\text{min}$$

To relate the rate of methane consumption to the other rates, we need a balanced chemical equation:



From the stoichiometry of the balanced equation:

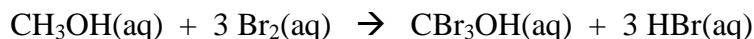
Oxygen is consumed twice as fast as methane,  $\text{Rate}_{\text{O}_2} = 1.3495\text{M}/\text{min}$ .

Carbon dioxide is produced at the same rate as methane,  $\text{Rate}_{\text{CO}_2} = 0.6747\text{M}/\text{min}$ .

Water is produced twice as fast as methane is consumed,  $\text{Rate}_{\text{H}_2\text{O}} = 1.3495\text{M}/\text{min}$ .

The rate of the reaction is equal to the rate of consumption or production of any component divided by its coefficient in the balanced equation,  $\text{Rate}_{\text{rxn}} = 0.6747\text{M}/\text{min}$ .

12. For the reaction:



You have collected the following data at 14.88°C:

| Experiment | [CH <sub>3</sub> OH] <sub>o</sub> | [Br <sub>2</sub> ] <sub>o</sub> | Rate <sub>observed</sub>    |
|------------|-----------------------------------|---------------------------------|-----------------------------|
| 1          | 3.97 M                            | 2.86 M                          | 3.49x10 <sup>-3</sup> M/sec |
| 2          | 7.94 M                            | 2.86 M                          | 6.98x10 <sup>-3</sup> M/sec |
| 3          | 3.97 M                            | 5.72 M                          | 6.98x10 <sup>-3</sup> M/sec |

What are the rate law and the value of the rate law constant, k, for this reaction?

If you redo Experiment 2 at 39.92°C, the rate is 5.73x10<sup>-2</sup> M/sec. What is the activation energy for this reaction? (20pts)

Determining the rate law expression:

Comparing Exp'ts 1 and 2, [CH<sub>3</sub>OH]<sub>o</sub> doubles and the rate doubles, so the reaction must be first order with respect to initial methanol concentration.

Comparing Exp'ts 1 and 3, [Br<sub>2</sub>]<sub>o</sub> doubles and the rate doubles, so the reaction must be first order with respect to initial bromine concentration.

$$\text{Rate}_o = k [\text{CH}_3\text{OH}]_o^1 [\text{Br}_2]_o^1$$

Plugging in and solving for k,  $k = 3.07 \times 10^{-4} \text{M}^{-1}\text{sec}^{-1}$ .

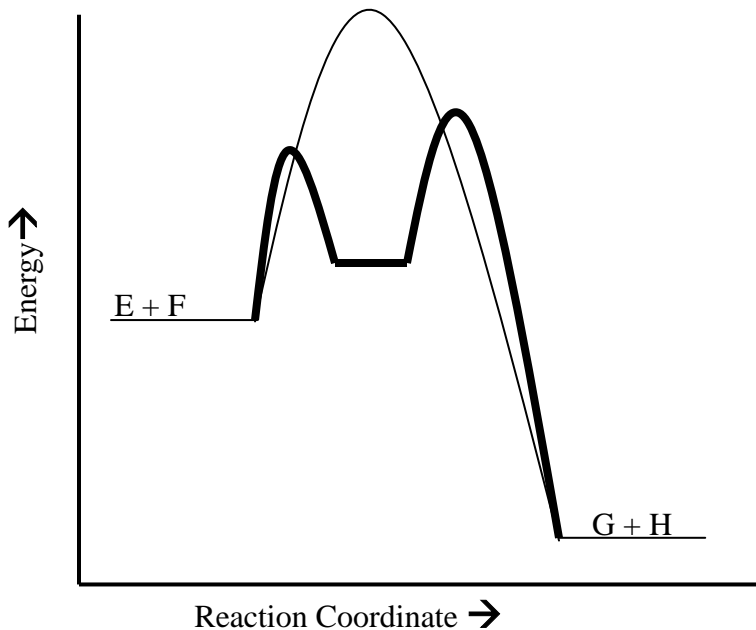
Plugging in the concentrations for Exp't 2 with the new rate observed at the increased temperature and solving for k,  $k_{39.92\text{C}} = 2.52 \times 10^{-3} \text{M}^{-1}\text{sec}^{-1}$ .

With 2 temperature conditions, we can use the comparative form of the Arrhenius equation to determine the activation energy:

$$\ln\left(\frac{k_1}{k_2}\right) = \ln\left(\frac{3.07 \times 10^{-4} \frac{1}{\text{M}\cdot\text{sec}}}{2.52 \times 10^{-3} \frac{1}{\text{M}\cdot\text{sec}}}\right) = \left(\frac{E_a}{8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}}}\right) \left(\frac{1}{313.07\text{K}} - \frac{1}{288.03\text{K}}\right) = \left(\frac{E_a}{R}\right) \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Solving,  $E_a = 6.30 \times 10^4 \text{J}/\text{mol} = 63.0 \text{kJ}/\text{mol}$

13. The graph at the right represents an uncatalyzed reaction,  $E + F \rightarrow G + H$ . Modify the graph to show what it would look like if a catalyst were used. Explain your modifications. (10pts)



A catalysts changes the mechanism (usually by adding an intermediate...) and lowers the activation energy of the reaction.

By the way, the “new” catalyzed reaction would have a slightly slower second step in the mechanism because the second activation energy hump is a little bit higher than the first. This question isn’t asking about that, but be sure to notice all the features of these graphs...

14. When 0.518mols of nitrogen dioxide  $\{NO_2(g)\}$  and 0.815mols of chlorine gas  $\{Cl_2(g)\}$  are sealed together in a 2.000L vessel, they reach equilibrium with nitrogen trichloride  $\{NCl_3(g)\}$  and oxygen  $\{O_2(g)\}$ . The equilibrium concentration of  $Cl_2(g)$  is found to be 0.316 M. (20pts)
- What are the equilibrium concentrations of all products and reactants?
  - What is the value of  $K_c$ ?
  - Is the reaction product-favored or reactant-favored?

Start with a balanced equation and start making a table:

|          |   |  |                |            |
|----------|---|--|----------------|------------|
|          | $2 NO_2(g) +$                                 | $3 Cl_2(g) \rightleftharpoons$                 | $2 NCl_3(g) +$ | $2 O_2(g)$ |
| Initial  | $\frac{0.518\text{mols}}{2.000L} =$<br>0.259M | $\frac{0.815\text{mols}}{2.000L} =$<br>0.4075M | 0M             | 0M         |
| $\Delta$ | - 2x  | - 3x   | + 2x           | + 2x       |
| @ Eq     | (0.259 - 2x)M                                 | (0.4075 - 3x)M                                 | 2x M           | 2x M       |

Since  $[Cl_2]_{eq} = 0.316M$ , we can solve for “x”:

$$0.4075 - 3x = 0.316$$

$$x = 0.0305$$

$$[NO_2]_{eq} = 0.259 - 2(0.0305) = 0.198M; [NCl_3]_{eq} = 2(0.0305) = 0.061M; [O_2]_{eq} = 2(0.0305) = 0.061M$$

Plugging in to the equilibrium constant expression:

$$K_c = \frac{[NCl_3]_{eq}^2 [O_2]_{eq}^2}{[NO_2]_{eq}^2 [Cl_2]_{eq}^3} = \frac{(0.061)^2 (0.061)^2}{(0.198)^2 (0.316)^3} = 0.011$$

The value of  $K_c$  is less than 1, so this equilibrium is reactant-favored.

NOTE: Be sure to clearly show your work, because of all the squaring and cubing (and higher powers) in equilibrium constant calculations, tiny differences in rounding can lead to significant differences in final numerical answers. If your answer doesn’t match mine and I can’t follow your calculation, it’s very hard to assign any partial credit.

15. You have been studying the reaction series:



The first step ( $A \rightarrow B$ ) is exothermic, the second step ( $B \rightarrow C$ ) is endothermic, and the overall reaction ( $A \rightarrow C$ ) is exothermic. Draw qualitatively correct Reaction Coordinate/Energy diagrams for this series of reactions if: a) the first step is slow; b) the second step is slow. Label all axes and any other features of importance on the graphs. (**Your answer will include 2 separate graphs.**) (15pts)

In the first graph, the first activation energy barrier is higher than the second, so the first step of the reaction will be slower than the second. In the second graph, the second activation energy barrier is higher than the first so the second step of the reaction is the rate determining step.

Notice a few other things:

1. Axes are labeled.
2. Exothermic and endothermic affect your graph.
3. The thermodynamics of both graphs is exactly the same, the only difference is the kinetics.

