Review ***Name*** _____
Unit 13: Spontaneity, Kinetics ***Period*** _____ ***Date*** _____

Topics:

- Enthalpy (ΔH): endothermic and exothermic reactions; Hess's Law (definition and modifying equations); Heat of formation reactions, using $\Delta H^\circ_{rxn} = \sum n \Delta H^\circ_f(\text{products}) - \sum n \Delta H^\circ_f(\text{reactants})$
  - *Is heat released or absorbed when bonds are broken?*_____ *When bonds are formed?*_____. *)*
- Definition of a state function and explanation of its relevance to Hess's Law.
- Analysis of heating and cooling curves: explain changes in temperature, why temperature plateaus, know phase changes
- Entropy (ΔS): identifying increasing or decreasing entropy changes.
- Spontaneity-- Gibbs Free Energy (ΔG), determining if spontaneous, using eq: $\Delta G = \Delta H - T\,\Delta S$
- Energy diagrams-- activation energy, ΔH, lowering E_a using a catalyst
- Conditions that effect rates (temp, concentration, surface area, catalyst), rates in terms of collisions
- Determining rate law from initial rate and initial concentration data
- Relationship between rate determining steps and rate law equations
- Questions similar to those in the Combustion Lab and Hess's Law Lab ($q = mc\Delta T$ and ΔH)

Practice Problems:

1) Use the following reaction steps, manipulate the equations and calculate the ΔH of the overall reaction:

$Fe_2O_3\,(s) + 3\,CO \longrightarrow 2\,Fe\,(s) + 3\,CO_2\,(g)$ $\quad \Delta H = -27$ kJ

$2\,CO\,(g) \longrightarrow C\,(s) + CO_2\,(g)$ $\quad \Delta H = -172$ kJ

Overall: $2\,Fe_2O_3 + 3\,C \longrightarrow 4\,Fe + 3\,CO_2$ $\quad \Delta H_{rxn} =$

2) Write the reaction showing the formation of 1 mole of KNO_3 and look up ΔH°_f of KNO_3:

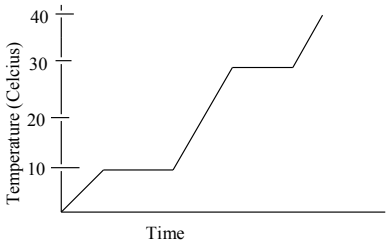
$\Delta H^\circ_f =$ _____

3) Given the ΔH°_f values shown below, calculate the ΔH_{rxn} for this reaction: *(Use "products – reactants" method)*

$4\,NH_3\,(g) + 5\,O_2\,(g) \longrightarrow 4\,NO\,(g) + 6\,H_2O\,(g)$

Substance	ΔH°_f (kJ/mole)
NH_3 (g)	–46.11
NO (g)	+ 90.3
H_2O (g)	–241.8

4) An unknown substance (initially a solid) is heated consistently and the heating curve to the right is obtained. Use the diagram to answer the questions:



   a. What is the condensation point of the unknown substance?_____
   b. At what temperature, do the solid and liquid phases exist at the same time? _____
   c. Why does the temperature stay at 30º C for some time before rising again?

5) Fill in this chart for the following three reactions.

	Endo or Exo	**$+\Delta S$ or $-\Delta S$**
a. $CaCO_3$ (s) + 176 kJ ⟶ CaO (s) + CO_2 (g)		
b. H_2O (g) ⟶ H_2O (l) + 44.02 kJ		
c. $C_6H_{12}O_6$ (s) + 6 O_2 (g) ⟶ 6 CO_2 (g) + 6 H_2O (g) + 670 kcal		

6) Given this decomposition reaction: 2 $KClO_3$ (s) ⟶ 2 KCl (s) + 3 O_2 (g)

   a. What is the free energy change (ΔG) for this reaction if the reaction is carried out at 950°C?
   $\Delta H = -90.1$ kJ/mol $\Delta S = +492.2$ J/mol·K

   b. Is this reaction spontaneous at 950°C? _____How do you know? _____
   c. Is the enthalpy change favorable?_____How do you know? _____
   d. Is the entropy change favorable? _____How do you know? _____
   e. Explain how you could answer question (d) without knowing the actual ΔS value.

7) Given this reaction: Fe_2O_3 (s) + 3 CO (g) ⟶ 2 Fe (s) + 3 CO (g)
   $\Delta H = +24.7$ kJ/mol $\Delta S = +11.4$ J/mol·K

   a. Use a calculation to verify that this reaction is not spontaneous at 25°C.

   b. However, it will become spontaneous if enough heat is applied. Why is it possible for this reaction to become spontaneous when heat is applied?

   c. At what temperature will this reaction become spontaneous?

8) C_6H_6 (l) + O_2 ⟶ 6 CO_2 (g) + 3 H_2O (g) $\Delta H = -3270$ kJ/mol of C_6H_6

a. If 15.0 g of C_6H_6 reacts with O_2, how much heat will be released?

b. If all of this heat (that you just calculated) was used to heat up 5.00 kg of water, what would be the temperature change of the water?

c. This reaction is a spontaneous reaction; however a spark is needed to get C_6H_6 to start burning (E_a = 200. kJ). Draw an energy diagram for this reaction. *Label diagram with reactants, products, numbers on axes, and arrows for E_a and ΔH.*

9) Does every molecular collision lead to a reaction? _____ Why or why not?

10) What is an activated complex? When is it formed? Why does it have high potential energy?

11) Here are four ways to increase the rate of a reaction . Use collision theory, to explain how each way increases the rate. *(more frequent collisions? harder collisions? change in activation energy?)*

a. Increase temperature

b. Increase surface area

c. Increase concentration

d. use a catalyst

12) How is it possible for a catalyst to change the rate of a reaction without being consumed?

13) Answer the following questions by using the mechanism at the right.

a. Below the steps of the mechanism, fill in the balanced equation for the overall reaction.
b. Which step is the rate-determining step?_____
c. Which step forms an activated complex with the highest amount of potential energy?_____
d. Write the rate law equation for this reaction:

e. Identify any intermediates:

f. Is there a catalyst? If so, what is it?

Mechanism for the reaction:

Step 1: $OCl^- + H_2O \longrightarrow HOCl + OH^-$ fast

Step 2: $HOCl + I^- \longrightarrow HOI + Cl^-$ slow

Step 3: $HOI + OH^- \longrightarrow H_2O + OI^-$ fast

Overall:

14) The kinetics of the reaction: 2 X + Y ⟶ Z was studied and the results are:

Run	Initial [X] (M)	Initial [Y] (M)	Initial rate (M/s)
1	0.20	0.10	7.0×10^{-4}
2	0.20	0.20	1.4×10^{-3}
3	0.40	0.20	1.4×10^{-3}
4	0.60	0.60	4.2×10^{-3}

a. Deduce the rate law

b. Determine the value of k with units.

c. What would the initial rate be if [X] = 0.35 M and [Y] = 0.55 M?

d. The following 3 mechanisms have been proposed. What is the overall reaction for each mechanism? Which mechanism is consistent with the rate law from part a?

Mechanism I
$X + Y \longrightarrow M$ slow
$X + M \longrightarrow Z$ fast

Mechanism II
$Y \longrightarrow M$ slow
$X + M \longrightarrow Z$ fast

Mechanism III
$Y \longrightarrow M$ slow
$M + X \longrightarrow N$ fast
$N + X \longrightarrow Z$ fast

15) The rate law for the reaction, OH^- (aq) + $H_2PO_2^-$ (aq) ⟶ HPO_2^- (aq) + H_2 (g), is

Rate = k $[OH^-]^2[H_2PO_2^-]$

a) If the $H_2PO_2^-$ concentration is doubled, what happens to the overall rate?_____

b) If the OH^- concentration is tripled, what happens to the rate?_____

16) How is it possible for a very spontaneous reaction to *seemingly* not occur? What must be true about the reaction? [Hint: other than being spontaneous, what does a reaction need in order to occur?]

Answers: 1) ΔH = +462 kJ; 3) ΔH = −905.2 kJ; 6a) ΔG = −692 kJ/mol; 7a) ΔG = +21.3 kJ/mol; 8a) q = −628 kJ; 8b) ΔT = 30.0°C; 14b) $k = 7.0 \times 10^{-3}$ s^{-1}; 14c) Rate = 3.9×10^{-3} M/s