AP Chemistry Unit 5- Homework Problems Thermodynamics

Specific Heat Problems

1. How many J would it take to raise the temperature of 200 grams of water from 5 °C to 85 °C? Q = (200 g)(4.18)(80 °C) = 66880 J

2. How many J would problem number 1 be if it was aluminum instead of water?

 $Q = (200 \text{ g})(0.897)(80 \text{ }^{\circ}\text{C}) = 14352 \text{ J}$

3. How many grams of copper could be heated from 20 °C to 75 °C if 1200 J are applied to it? 1200 J = (x)(0.385)(55 °C) = 56.7 g

4. What is the specific heat capacity of a substance if 750 J caused 100 grams of it to go from 90 °C to 135 °C?

 $750 \text{ J} = (100 \text{ g})(\text{x})(45 \text{ }^{\circ}\text{C}) = 0.167 \text{ J/g}^{\circ}\text{C}$

5. What would the final temperature be if 500 J are applied to 150 grams of ice at -90 °C? 500 J = (150 g)(2.06)(x - (-90 °C)) = -88.4 °C

- 6. What would the temperature *change by* if a 90 gram piece of hot iron cooled by losing 200 J. -200 J = $(90 \text{ g})(0.449)(x) = -4.95 \text{ }^{\circ}\text{C}$
- 7. What was the initial temperature if 500 J were applied to 250 g of mercury and the final temperature was 50 °C?

 $500 \text{ J} = (250 \text{ g})(0.140)(50 \text{ }^{\circ}\text{C} \text{ - } \text{x}) = 35.7 \text{ }^{\circ}\text{C}$

Latent Heat Problems

1. Why can we not use the equation $Q = mc\Delta T$ for phase changes of a substance; why won't it work?

There is no temperature change at a phase change

2. What is the Latent Heat of Fusion of a substance?

Energy needed to melt or freeze

3. What is the Latent Heat of Vaporization of a substance?

Energy needed to boil or condense

4. How many J are needed to melt 30 grams of copper?

$$Q = (30 g)(209 J/g) = 6270 J$$

5. How much heat is needed to boil 63 grams of ethanol?

Q = (63 g)(838 J/g) = 52.8 kJ

6. What is the Latent Heat of Fusion of a substance if 1200 J melts 40 grams of it? 1200 J = (40 g)(x) = 30 J/g

7. What is the Latent Heat of Vaporization of a substance if 50 J boiled 3 grams of it? 50 J = (3 g)(x) = 16.7 J/g 8. How many grams of copper could be melted if 700 J are applied to it?
700 J = (x)(209 J/g) = 3.35 g
9. How many grams of water could be boiled if 8000 J are applied to it?
8000 J = (x)(2260 J/g) = 3.54 g

Combination Problems

1. How much energy is needed to heat 200 grams of diethyl ether, (C₂H₅)₂O, from 5 °C to its boiling point and boil it?

A) Heat to boiling point $Q = mc(T_f - T_i) = (200 \text{ g})(2.33)(34.6 - 5 \text{ }^{\circ}\text{C}) = 13.8 \text{ kJ}$ B) Boil $Q = mL_v = (200 \text{ g})(357 \text{ J/g}) = 71.4 \text{ kJ}$ Total = 13.8 + 71.4 = 85.2 kJ

2. How much energy is needed to turn 400 grams of liquid benzene, C₆H₆, at 20 °C to gaseous benzene at 150 °C?

A) Heat to boiling point $Q = mc(T_f - T_i) = (400 \text{ g})(1.74)(80 - 20 \text{ }^\circ\text{C}) = 41.8 \text{ kJ}$ B) Boil $Q = mL_v = (400 \text{ g})(393 \text{ J/g}) = 157.2 \text{ kJ}$ C) Heat gas from bp to 150 °C $Q = mc(T_f - T_i) = (400 \text{ g})(1.06)(150 - 80) = 29.7 \text{ kJ}$ Total = 41.8 + 157.2 + 29.7 = 228.7 kJ

3. How much energy is needed to turn a 75 g block of ice at -40 °C to steam at 250 °C?A) Heat to melting point $Q = mc(T_f T_i) = (75 g)(2.06)(0 - (-40 °C)) = 6.2 kJ$ B) Melt $Q = mL_f = (75 g)(333 J/g) = 25 kJ$ C) Heat liq from mp to bp $Q = mc(T_f T_i) = (75 g)(4.18)(100 - 0 °C) = 31.4 kJ$ B) Boil $Q = mL_v = (75 g)(2260 J/g) = 169.5 kJ$ C) Heat gas from bp to 250 °C $Q = mc(T_f T_i) = (75 g)(1.86)(250 - 100 °C) = 20.9 kJ$

Total = 6.2 + 25 + 31.4 + 169.5 + 20.9 kJ = 253 kJ

4) Which part of #3 contributes the most energy to the overall process?The boiling part (going from liquid to gas or vice versa) requires the most energy

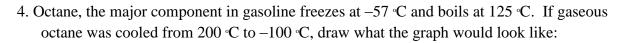
Latent Heat Graphing

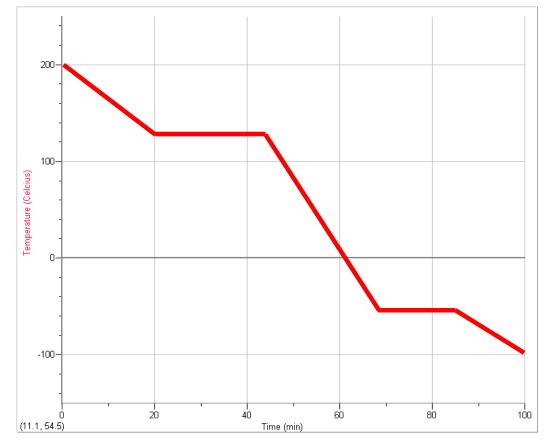
1. What do you call each of the following changes of state:

A. Solid to liquid	melt
B. Liquid to gas	boil
C. Gas to solid	deposition
D. Solid to gas	sublimation
E. Liquid to solid	freeze
F. Gas to liquid	condense

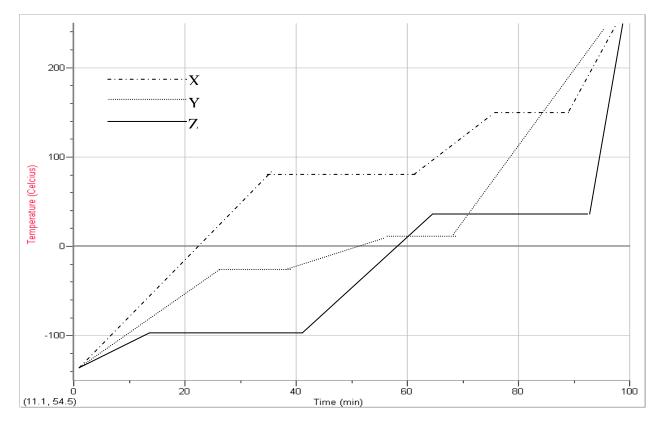
2. The melting point of a solid is the same as what other point? Freezing point

3. The condensing point of a gas is the same as what other point? Boiling point





- 5. The following graph shows three different substances and their phase changes. Answer the following questions about them:
 - A. What is the melting point of substance Y? @ $-25 \,^{\circ}C$
 - B. What is the boiling point of substance Z? @ $40 \,^{\circ}C$
 - C. Which substance is still a solid when the other two substances have turned to gases? X
 - D. Which substance has the lowest boiling point? Y
 - E. Which substance has the lowest freezing point? Z



6. Water boils at 100 °C. Why are steam burns potentially more dangerous than boiling water burns?

Under normal conditions, liquid water can only get up to 100 $^{\circ}$ C. Steam, because it is a gas, can get hotter than 100 $^{\circ}$ C and is potentially more dangerous because of it.

Calorimetry

1. What is the specific heat capacity of water? $4.18 \text{ J/g}^{\circ}\text{C}$

2. A piece of ice is placed on the sidewalk on a hot summer day. Describe what happens to energy content of the piece of ice, does it gain or lose energy? What happens to the air around the ice, does it gain or lose energy?

The ice gains energy from the surrounding air and increases its energy (endothermic).

The air loses energy to the ice and decreases its energy (exothermic)

3. 100 grams of hot water at 80 °C is combined with 100 grams of cool water at 20 °C. What is the final temperature of the combined water?

 $Q_{\text{lost}} = -Q_{\text{gain}}$ $mc(T_f - T_i) = -mc(T_f - T_i)(100 \text{ g})(4.18)(x - 80 \text{ }^{\circ}\text{C}) = -(100 \text{ g})(4.18)(x - 20 \text{ }^{\circ}\text{C})$ $T_f = 50 \text{ }^{\circ}\text{C}$ 4. 100 grams of hot water at 80 $^{\circ}\text{C}$ is combined with 50 grams of cool water at 20 $^{\circ}\text{C}$. What is the final temperature

of the combined water?

 $Q_{\text{lost}} = -Q_{\text{gain}}$ $mc(T_f - T_i) = -mc(T_f - T_i)(100 \text{ g})(4.18)(x - 80 \text{ }^{\circ}\text{C}) = -(50 \text{ g})(4.18)(x - 20 \text{ }^{\circ}\text{C})$ $T_f = 60 \text{ }^{\circ}\text{C}$

5. A 25 gram piece of hot metal at 97 °C is plunged into a 35 gram cup of cool water at 19 °C. The metal gives up its heat to the water until they are both at 22 °C. What is the specific heat capacity of the metal?

 $Q_{lost} = -Q_{gain} \qquad mc(T_f - T_i) = -mc(T_f - T_i) (25 \text{ g})(x)(22 - 97 \text{ }^{\circ}\text{C}) = -(35 \text{ g})(4.18)(22 - 19 \text{ }^{\circ}\text{C}) \qquad C = 0.234 \text{ J/g}^{\circ}\text{C}$ 6. A 75 gram piece of hot metal at 100 °C is dropped into a 50 gram cup of cool water at 22 °C. The final temperature of the system is 30 °C. What is the specific heat capacity of the metal?

 $Q_{lost} = -Q_{gain} \qquad mc(T_f - T_i) = -mc(T_f - T_i) (75 \text{ g})(x)(30 - 100 \text{ }^{\circ}\text{C}) = -(50 \text{ g})(4.18)(30 - 22 \text{ }^{\circ}\text{C}) \qquad C = 0.318 \text{ J/g}^{\circ}\text{C}$ 7. A 120 gram piece of copper at 75 °C is put into a 20 gram sample of water at 10 °C. What is the final temperature of the system after the copper releases all its extra heat?

 $Q_{\text{lost}} = -Q_{\text{gain}}$ $mc(T_f - T_i) = -mc(T_f - T_i)(120 \text{ g})(0.385)(x - 75 \text{ }^{\circ}\text{C}) = -(20 \text{ g})(4.18)(x - 10 \text{ }^{\circ}\text{C})$ $T_f = 33.1 \text{ }^{\circ}\text{C}$

8. 100 g of water at 22 °C was combined with 20 grams of ice. The final temperature of the system was 6 °C. Calculate the heat of fusion of ice based upon this data.

 $\begin{aligned} Q_{\text{lost}} &= -Q_{\text{gain}} & \text{mc}(T_{\text{f}} - T_{\text{i}}) = -\text{mL}_{\text{f}} & (100 \text{ g})(4.18)(6-22 \text{ }^{\circ}\text{C}) = -(20 \text{ g})(x) & \text{L}_{\text{f}} = 334.4 \text{ J/g} \\ \end{aligned}$ 9. 200 g of water at 22 °C was combined with 15 grams of ice. Knowing that the heat of fusion of ice is 333 J/g, calculate the final temperature of the system.

 $Q_{lost} = -Q_{gain}$ mc(T_f - T_i) = - mL_f (200 g)(4.18)(x- 22 °C) = - (15 g)(333 J/g) T_f = 16 °C

- 10. Suppose you heat a 50 g piece of silver to 99.8 °C and then drop it onto ice. When the metal's temperature has dropped to 0 °C, it is found that 3.54 g of ice has melted. What is the specific heat capacity of silver?
- $Q_{lost} = -Q_{gain} \qquad mc(T_f T_i) = -mL_f \qquad (50 \text{ g})(x)(0 99.8 \text{ }^{\circ}\text{C}) = -(3.54 \text{ g})(333 \text{ J/g}) \qquad c = 0.236 \text{ J/g}^{\circ}\text{C}$
- 11. A 9.36 g piece of Pt is heated to 98.6 °C and then dropped onto a block of ice. When the temperature of the metal has dropped to 0 °C, it is found that 0.37 g of ice melted. What is the specific heat capacity of Pt?

 $Q_{lost} = -Q_{gain} \qquad mc(T_f - T_i) = -mL_f \qquad (9.36 \text{ g})(x)(0 - 98.6 \text{ }^{o}\text{C}) = -(0.37 \text{ g})(333 \text{ J/g}) \ T_f = 0.134 \text{ J/g}^{o}\text{C}$

12. Describe each of the reactions below as either endothermic or exothermic. Some are tricky, be careful. Decide whether heat is entering or leaving the system in question:

A. Exploding fireworks	endothermic	exothermic
B. Melting snow	endothermic	exothermic
C. Lava cooling	endothermic	exothermic
D. Paper burning	endothermic	exothermic
E. An ice cube freezing	endothermic	exothermic
F. Water evaporating	endothermic	exothermic

Enthalpy Problems

- 1. For the equation: $Mg + \frac{1}{2}CO_2 \rightarrow MgO + \frac{1}{2}C$ If 16.7 kJ of heat is given off per 1.0 gram of magnesium reacted, calculate the ΔH_{rxn} $\Delta H_{rxn}^{o} = Q_{rxn}/moles$ $\Delta H_{rxn}^{o} = -16.7 \text{ kJ/0.0411 moles} = -406 \text{ kJ/mole}$
- 2. For the equation: $(NH_4)_2Cr_2O_7 \rightarrow N_2 + 4 H_2O + Cr_2O_3$ If 3 grams of $(NH_4)_2Cr_2O_7$ gives off 3.57 kJ of energy, calculate the ΔH_{rxn} $\Delta H_{rxn}^o = Q_{rxn}/moles$ $\Delta H_{rxn}^o = -3.57 \text{ kJ}/0.0119 \text{ moles} = -300 \text{ kJ/mole}$

3. For the equation: Na + H₂O \rightarrow NaOH + ¹/₂ H₂ If 5 grams of sodium is placed into 100 grams of water at 20 °C and the final temperature of the system reaches 27 °C, calculate the Δ H_{rxn} Δ H^o_{rxn} = Q_{rxn}/moles Q_{rxn} = - Q_{water} = - (100 g)(4.18 J/g°C)(7 °C) = -2926 J Δ H^o_{rxn} = -2926 J/0.217 moles = -13.5 kJ/mole

- 4. For the equation: $Ca + 2 \text{ HCl} \rightarrow CaCl_2 + H_2$ If 2 grams of calcium is placed into 75 mL of 1 M HCl at 18 °C and the final temperature of the system reaches 23 °C, calculate the ΔH_{rxn} . (Assume the density of the solution is 1 g/mL and the specific heat capacity of the HCl = 4.18 J/g°C) $\Delta H^{\circ}_{rxn} = Q_{rxn}/\text{moles}$ $Q_{rxn} = -Q_{water} = -(75 \text{ g})(4.18 \text{ J/g}^{\circ}\text{C})(5 ^{\circ}\text{C}) = -1567.5 \text{ J}$ $\Delta H^{\circ}_{rxn} = -1567.5 \text{ J}/0.0499 \text{ moles} = -31.4 \text{ kJ/mole}$
- 5. For the equation: $NaNO_3(s) \rightarrow NaNO_3(aq)$

If 20 grams of NaNO₃ were placed into 200 grams of water at 22 °C, and the temperature dropped to 12 °C, what is the ΔH_{rxn} ? $\Delta H^{o}_{rxn} = Q_{rxn}/moles$ $Q_{rxn} = -Q_{water} = -(200 \text{ g})(4.18 \text{ J/g}^{\circ}\text{C})(-10 \text{ }^{\circ}\text{C}) = +8360 \text{ J}$ $\Delta H^{o}_{rxn} = +8360 \text{ J}/0.235 \text{ moles} = +35.6 \text{ kJ/mole}$

Bond Energies

|C≡0|

1. Draw the Lewis Dot structures and determine the ΔH_{rxn} for:

$$\begin{array}{c} \text{CO} + \text{Cl}_2 \rightarrow \text{Cl}_2\text{CO} \\ |\text{O}| \\ || \\ |\overline{\text{C}} \vdash \overline{\text{CI}}| \longrightarrow |\overline{\text{C}} \vdash \overline{\text{C}} - \overline{\text{CI}}| \end{array}$$

 $\Delta H_{rxn} = \Sigma \text{ Bonds}_{react} - \Sigma \text{ Bonds}_{prod}$ $\Delta H_{rxn} = (1046 + 242) - (2*339 + 745) = -135 \text{ kJ}$

2. Draw the Lewis Dot structures for and determine the ΔH_{rxn} for:

$$\stackrel{H \longrightarrow H}{\stackrel{\square}{\longrightarrow}} \stackrel{H \longrightarrow H}{\stackrel{\square}{\longrightarrow}} \stackrel{O_2 + 2 H_2 \rightarrow 2 H_2 O}{\stackrel{H}{\xrightarrow}} \stackrel{H}{\stackrel{\square}{\longrightarrow}} \stackrel{H}{\stackrel{\square}{\longrightarrow} \stackrel{H}{\stackrel{\square}{\longrightarrow}} \stackrel{H}{\stackrel{\square}{\longrightarrow}} \stackrel{H}{\stackrel{\square}{\longrightarrow} \stackrel{H}{\stackrel{\square}{\longrightarrow}} \stackrel{H}{\stackrel{\square}{\longrightarrow} \stackrel{H}{\longrightarrow} \stackrel{H}{\stackrel{\square}{\longrightarrow} \stackrel{H}{\longrightarrow} \stackrel{H}{\stackrel{\square}{\longrightarrow} \stackrel{H}{\longrightarrow} \stackrel{H}{\stackrel{\square}{\longrightarrow} \stackrel{H}{\longrightarrow} \stackrel{H}{\longrightarrow} \stackrel{H}{\longrightarrow} \stackrel{H}{\stackrel{\square}{\longrightarrow} \stackrel{H}{\longrightarrow} \stackrel{H}{\longrightarrow}$$

 $\Delta H_{rxn} = \Sigma \text{ Bonds}_{react} - \Sigma \text{ Bonds}_{prod}$ $\Delta H_{rxn} = (498 + 2*436) - (4*463) = -482 \text{ kJ}$

3. Draw the Lewis Dot structures for and determine the energy for the O-F bond for: $OF_2 + H_2O \rightarrow O_2 + 2 HF$ $\Delta H_{rxn} = -318 kJ$

$$OF_{2} + H_{2}O \rightarrow O_{2} + 2 HF$$

$$\downarrow F \downarrow H \longrightarrow O=O \downarrow H \longrightarrow O=F \downarrow H-F$$

$$\downarrow O-F \downarrow O-H \longrightarrow O=O \downarrow H-F$$

$$\begin{split} \Delta H_{rxn} &= \Sigma \ Bonds_{react} - \Sigma \ Bonds_{prod} \\ -318 &= \ (2X + 2*463) - (498 + 2*565) \\ X &= 192 \ kJ \end{split}$$

4. For the reaction:

$$O_3 + O \rightarrow 2 O_2 \qquad \Delta H_{rxn} = -394$$

a. Draw the Lewis dot structures for all species

b. Calculate the O-O bond energy in O_3 $\Delta H_{rxn} = \Sigma \text{ Bonds}_{react} - \Sigma \text{ Bonds}_{prod}$ -394 = (2X) - (2*498)X = 301 kJ

c. What is the bond order of the O-O bond in O_3 (remember it is a resonance structure)? Bond order = 1.5

- d. Compare the answer you got in part b to the O-O bond energy and the O=O bond energy you can look up. Does your answer make sense? Why or why not?

Hess' Law Problems

1. Given the following equations: $2 H_2 + O_2 \rightarrow 2 H_2O$ $N_2O_5 + H_2O \rightarrow 2 HNO_3$ $\frac{1}{2} N_2 + \frac{3}{2} O_2 + \frac{1}{2} H_2 \rightarrow HNO_3$	ΔH_{rxn} = -74 kJ	H_2O 2 HNO ₃ $N_2 + 3O_2 + H_2$	\rightarrow N ₂ O ₅ + H ₂ O	$\Delta H_{rxn} = +74 \text{ kJ}$
Calculate ΔH_{rxn} for: N ₂ + 5/2 O ₂ \rightarrow N ₂ O ₅	ΔH_{rxn} = + 12 kJ			
2. Given the following equations: $N_2 + 3 H_2 \rightarrow 2 NH_3$ $4 NH_3 + 5 O_2 \rightarrow 4 NO + 6 H_2O$ $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	ΔH_{rxn} = -906 kJ	$\frac{1}{2}N_2 + \frac{3}{2}H_2$ NH ₃ + $\frac{5}{4}Q_2$ - $\frac{3}{2}H_2Q$	\rightarrow NO + $3/2$ H ₂ C	ΔH_{rxn} = -226 kJ
Calculate the ΔH_{rxn} for: $\frac{1}{2} N_2 + \frac{1}{2} O_2 \rightarrow NO$	ΔH_{rxn} = +91 kJ			
3. Given the following equations: $Sr + \frac{1}{2}O_2 \rightarrow SrO$ $SrO + CO_2 \rightarrow SrCO_3$ $C + O_2 \rightarrow CO_2$	ΔH_{rxn} = -234 kJ	$Sr + \frac{1}{2}O_2 \rightarrow S$ $SrO_1 + CO_2 \rightarrow C$ $C_2 + O_2 \rightarrow CO_2$	SrCO ₃	$\Delta H_{rxn} = -592 \text{ kJ}$ $\Delta H_{rxn} = -234 \text{ kJ}$ $\Delta H_{rxn} = -394$
Calculate the ΔH_{rxn} for: Sr + C + 3/2 O ₂ \rightarrow SrCO ₃	ΔH_{rxn} = -1220 kJ			
4. Given the following equations: $C + 2 H_2 \rightarrow CH_4$ $C + 2 Cl_2 \rightarrow CCl_4$ $H_2 + Cl_2 \rightarrow 2 HCl$	ΔH_{rxn} = -96 kJ	$CH_4 \rightarrow C + CH_2 \rightarrow CH_2 \rightarrow CH_2 \rightarrow CH_2 + 2 CI_2 \rightarrow CH_2 + 2 CI_2 \rightarrow CH_2 \rightarrow$	Cl_4	$\Delta H_{rxn} = +75 \text{ kJ}$ $\Delta H_{rxn} = -96 \text{ kJ}$ $\Delta H_{rxn} = 2(-92) \text{ kJ}$
Calculate the ΔH_{rxn} for: CH ₄ + 4 Cl ₂ \rightarrow CCl ₄ + 4 HCl	ΔH_{rxn} = -205 kJ			
5. Given the following equations: $C_5H_{12} + 8 O_2 \rightarrow 5 CO_2 + 6 H_2O$ $C + O_2 \rightarrow CO_2$ $2 H_2 + O_2 \rightarrow 2 H_2O$	ΔH_{rxn} = -394 kJ	$5 \text{ CO}_2 + 6 \text{ H}_2\text{Q}$ $5 \text{ C} + 5 \text{ O}_2 \rightarrow 5$ $6 \text{ H}_2 + 3 \text{ O}_2 \rightarrow 5$	CO ₂	ΔH_{rxn} = +3506 kJ ΔH_{rxn} = 5(-394) kJ ΔH_{rxn} = 3(-484) kJ
Calculate the ΔH_{rxn} for: 5 C + 6 H ₂ \rightarrow C ₅ H ₁₂	ΔH_{rxn} = +84 kJ			

$\Delta H_{f}^{\ o}$

- 1. For each of the substances below, write a balanced equation showing the formation of 1 mole of the compound from its elements in their standard states. Look up the value for ΔH_f° in the Appendix in the back of a book or online.
 - a) Al_2O_3 2 $Al(s) + 3/2 O_2(g) \rightarrow Al_2O_3(s)$ $\Delta H_f^{o} = -1676 \text{ kJ/mole}$
 - b) $Mg(OH)_2$ $Mg(s) + H_2(g) + O_2(g) \rightarrow Mg(OH)_2(s) \Delta H_f^o = -925 \text{ kJ/mole}$
 - c) $C_{12}H_{22}O_{11}$ 12 C (s) + 11 H₂ (g) + 11/2 O₂ (g) \rightarrow $C_{12}H_{22}O_{11}$ (s) $\Delta H_{f}^{o} = -2226 \text{ kJ/mole}$
 - d) NaHCO₃ Na (s) + $\frac{1}{2}$ H₂ (g) + C (s) + $\frac{3}{2}$ O₂ (g) \rightarrow NaHCO₃ (s) Δ H_f^o = -951 kJ/mole

2. For each of the reactions below, calculate ΔH^{o}_{rxn} . Look up the values for ΔH^{o}_{f} in the Appendix in the back of a book or online.

- a) $SO_2(g) + \frac{1}{2}O_2(g) \rightarrow SO_3(g) \Delta H^{o}_{rxn} = (-396) (-297) = -99 \text{ kJ}$ b) $4 \text{ NH}_3(g) + 5 O_2(g) \rightarrow 4 \text{ NO}(g) + 6 \text{ H}_2\text{O}(g) \Delta H^{o}_{rxn} = [4(91) + 6(-242)] - 4(-46) = -904 \text{ kJ}$ c) $\text{NH}_4\text{NO}_3(s) \rightarrow \text{N}_2\text{O}(g) + 2 \text{ H}_2\text{O}(g) \Delta H^{o}_{rxn} = [(82) + 2(-242)] - (-366) = -36 \text{ kJ}$
- 3. Nitroglycerin is a powerful explosive that explodes by the following equation while giving off 4200 kJ of heat. $C_3H_5(NO_3)_3 \rightarrow 3/2 N_2(g) + \frac{1}{4} O_2(g) + 3 CO_2(g) + \frac{5}{2} H_2O(g)$

Calculate the ΔH_f^{o} of nitroglycerin. -4200 kJ = [3(-394) + 5/2(-242)] - x = 2413 kJ

4. Oxygen difluoride reacts with water vapor to produce 318 kJ of heat by the following equation: $OF_2(g) + H_2O(g) \rightarrow 2 HF(g) + O_2(g)$

Calculate the ΔH_f^{o} of OF₂ -318 kJ = [2(-273)] - [x + (-242)] x = 14 kj

5. Large scale H_2 can be made by the following 3 steps:

Step 1: $SO_{2}(g) + 2H_{2}O(g) + Br_{2}(g) \rightarrow H_{2}SQ_{4}(l) + 2 HBr(g)$ $\Delta H^{o}_{rxn} = [(-814) + 2(-36)] - [(-297) + 2(-242) + 31] = -136 kJ$ Step 2: $H_{2}SQ_{4}(l) \rightarrow H_{2}O(g) + SO_{4}(g) + V_{2}O_{2}(g) \Delta H^{o}_{rxn} = [(-242) + (-297)] - [(-814)] = + 275 kJ$ <u>Step 3: 2HBr(g) $\rightarrow H_{2}(g) + Br_{2}(g) \qquad \Delta H^{o}_{rxn} = [31] - [2(-36)] = + 103 kJ$ </u> Total: $H_{2}O(g) \rightarrow H_{2}(g) + V_{2}O_{2}(g) \qquad \Delta H^{o}_{rxn} = -136 + 275 + 103 = + 242 kJ$ Calculate the ΔH^{o}_{rxn} of each step. Calculate the ΔH^{o}_{rxn} of the overall reaction. Is the overall reaction endo or exothermic?

Endothermic

Bomb Calorimetry

1. You burn 0.300 g of C in an excess of O_2 in a bomb calorimeter. The temperature of the calorimeter which contains 775 grams of water increases from 25 to 27.38 °C. The heat capacity of the bomb is 893 J/K. What is ΔH_{rxn} per mole of carbon?

$$\begin{split} Q_{rxn} &= - \left[q_{water} + q_{bomb} \right] = - \left[mc \Delta T_{water} + k \Delta T_{bomb} \right] \\ Q_{rxn} &= - \left[(775 \text{ g})(4.18 \text{ J/gC})(2.38 \text{ }^{\circ}\text{C}) + (893 \text{ J/K})(2.38 \text{ K}) \right] = -9.835 \text{ kJ} \\ 0.30 \text{ g C }^{*}(1 \text{ mole}/12 \text{ g}) = 0.025 \text{ moles C} \\ \Delta H_{rxn} &= q/\text{mole} = -9.835 \text{ kJ}/0.025 \text{ mole} = -393 \text{ kJ/mole} \end{split}$$

2. You burn 1.50 g of benzoic acid ($C_6H_5CO_2H$) in a bomb calorimeter which has a constant of 789 J/K. The calorimeter is filled with 775 g of water and the temperature increases from 22.50 to 31.69 °C. What is ΔH_{rxn} per mole of benzoic acid?

$$\begin{split} Q_{rxn} &= - \left[q_{water} + q_{bomb} \right] = - \left[mc\Delta T_{water} + k\Delta T_{bomb} \right] \\ Q_{rxn} &= - \left[(775 \text{ g})(4.18 \text{ J/gC})(9.19 \text{ }^{\text{o}}\text{C}) + (789 \text{ J/K})(9.19 \text{ K}) \right] = -37.0 \text{ kJ} \\ 1.50 \text{ g } \text{C}_6\text{H}_5\text{CO}_2\text{H} * (1 \text{ mole}/122 \text{ g}) = 0.0123 \text{ moles } \text{C}_6\text{H}_5\text{CO}_2\text{H} \\ \Delta H_{rxn} &= q/\text{mole} = -37 \text{ kJ}/0.0123 \text{ mole} = -3008 \text{ kJ/mole} \end{split}$$

Entropy Problems

1. Without doing any calculations, determine the sign of each of the entropy changes below:

a. Mg (s) + Cl ₂ (g) \rightarrow MgCl ₂ (s)	$\Delta S = negative$
b. $N_2(g) + 3 H_2(g) \rightarrow 2 NH_3(g)$	$\Delta S = negative$
c. 2 H ₂ O (l) \rightarrow 2 H ₂ (g) + O ₂ (g)	$\Delta S = positive$
d. $2 \text{ KClO}_3(s) \rightarrow 2 \text{ KCl}(s) + 3 \text{ O}_2(g)$	$\Delta S = positive$

2. Calculate the ΔS° of each of the above equations and compare the value to your predictions from #1.

a. Mg (s) + Cl ₂ (g) \rightarrow MgCl ₂ (s)	$\Delta S = (90) - [(33) + (223)] = -166 \text{ J/K}$
b. $N_2(g) + 3 H_2(g) \rightarrow 2 NH_3(g)$	$\Delta S = [2(193)] - [(153) + 3(131)] = -160 \text{ J/K}$
c. 2 H ₂ O (l) \rightarrow 2 H ₂ (g) + O ₂ (g)	$\Delta S = [2(131) + 205] - [2(70)] = +327 \text{ J/K}$
d. 2 KClO ₃ (s) \rightarrow 2 KCl (s) + 3 O ₂ (g)	$\Delta S = [2(83) + 3(205)] - [2(143)] = +495 \text{ J/K}$

3. Summarize each of the laws of Thermodynamics:

a.	1 st Law of Thermodynamics:	$\Delta \mathbf{E} = \mathbf{q} + \mathbf{w}$
b.	2 nd Law of Thermodynamics:	$\Delta S_{universe} > 0$ for a spontaneous rxn
c.	3 rd Law of Thermodynamics:	ΔS of a perfect crystal at 0 Kelvin is 0

- 4. List three things the entropy value of a substance depends upon:
 - a. Temperature
 - b. State of matter
 - c. Molecular complexity
- 5. Define entropy. A measure of the energy randomization or energy dispersal in a system (disorder)

Spontaneity and Gibb's Free Energy

- 1. Describe how the sign of ΔG determines the spontaneity of a reaction:
 - a. $\Delta G > 0$ Non-spontaneous (positive)
 - b. $\Delta G < 0$ Spontaneous (negative)
 - c. $\Delta G = 0$ At equilibrium
- 2. Given the following thermodynamic values, determine how temperature effects the spontaneity of the reaction. Is the reaction enthalpy driven, entropy driven, both, or neither.

a. $\Delta H = +327 \text{ kJ/mol}$	$\Delta S = + 127 \text{ J/molK}$	enthalpy driven	entropy driven	both	neither
b. $\Delta H = -187 \text{ kJ/mol}$	$\Delta S = -298 \text{ J/molK}$	enthalpy driven	entropy driven	both	neither
c. $\Delta H = +194 \text{ kJ/mol}$	$\Delta S = -4 \text{ J/molK}$	enthalpy driven	entropy driven	both	neither
a. $\Delta H = -397 \text{ kJ/mol}$	$\Delta S = +653 \text{ J/molK}$	enthalpy driven	entropy driven	both	neither

3. For each reaction below, determine the temperature at which the reaction will be spontaneous.

a. $\Delta H = +245 \text{ kJ/mol}$	$\Delta S = +48 \text{ J/molK}$	$T = \Delta H/\Delta S = 245/0.048$ T > 5104 K spontaneous
b. $\Delta H = +187 \text{ kJ/mol}$	$\Delta S = +365 \text{ J/molK}$	$T = \Delta H/\Delta S = 187/0.365$ T> 512 K spontaneous
c. $\Delta H = -456 \text{ kJ/mol}$	$\Delta S = -38 \text{ J/molK}$	$T = \Delta H/\Delta S = -456/-0.038 T < 12000 K$ spontaneous
d. $\Delta H = -547 \text{ kJ/mol}$	$\Delta S = -97 \text{ J/molK}$	$T = \Delta H / \Delta S = -547 / -0.097 \ T < 5639 \ K$ spontaneous

4. Define Gibb's Free Energy The energy available to do work in a thermodynamic system

5. Using the values of ΔG^{o}_{f} , calculate the ΔG^{o}_{rxn} of each of the equations below. Is each reaction spontaneous at standard conditions?

a. N_2O_4 (g) $\rightarrow 2 NO_2$ (g) b. NH_4Cl (s) $\rightarrow HCl$ (g) $+ NH_3$ (g) c. $3 H_2$ (g) $+ Fe_2O_3$ (s) $\rightarrow 2 Fe$ (s) $+ 3 H_2O$ (g) d. N_2 (g) $+ 3 H_2$ (g) $\rightarrow 2 NH_3$ (g) $\Delta G = [2(51)] - [100] = 2 \text{ kJ Non-spontaneous}$ $\Delta G = [(-95) + (-16)] - [-203] = 92 \text{ kJ Non-spontan}$ $\Delta G = [3(-229)] - [-742] = 55 \text{ kJ Non-spontaneous}$ $\Delta G = [2(-16)] - [0] = -32 \text{ kJ Spontaneous}$

Energy & Voltage

- 1. Write the equation that relates ΔG° and E° ? $\Delta G^{\circ} = -nFE^{\circ}$
- 2. What is n? the number of moles of electrons transferred
- 3. What is F? Faraday's constant, 96500 J/voltmole
- 4. For each of the following equations, what must n be?
 - a. $Cu^{+2} + Mg \rightarrow Mg^{+2} + Cu n = 2$
 - b. $2 \operatorname{Ag}^{+1} + \operatorname{Sn} \rightarrow \operatorname{Sn}^{+2} + 2 \operatorname{Ag} n = 2$
 - c. 2 Al + 3 Pb⁺² \rightarrow 3 Pb + 2 Al⁺³ n = 6
- 5. What is the ΔG° of the following batteries?

a. $Cu^{+2} + Mg \rightarrow Mg^{+2} + Cu$ $E^{\circ} = 2.71 \text{ V } \Delta G^{\circ} = -(2 \text{ moles})(96500 \text{ J/Vmol})(2.71 \text{ V}) = -523 \text{ kJ}$ b. $2 \text{ Ag}^{+1} + \text{ Sn } \rightarrow \text{ Sn}^{+2} + 2 \text{ Ag}$ $E^{\circ} = 0.94 \text{ V } \Delta G^{\circ} = -(2 \text{ moles})(96500 \text{ J/Vmol})(0.94 \text{ V}) = -181 \text{ kJ}$ c. $2 \text{ Al} + 3 \text{ Pb}^{+2} \rightarrow 3 \text{ Pb} + 2 \text{ Al}^{+3}$ $E^{\circ} = 1.53 \text{ V } \Delta G^{\circ} = -(6 \text{ moles})(96500 \text{ J/Vmol})(1.53 \text{ V}) = -886 \text{ kJ}$

- 6. What sign must each of the following be for a battery?
 - a. E^o positive
 - b. ΔG^{o} negative

Combination Thermo Problems

- 1. For the reaction: $2 \text{ NO}(g) + O_2(g) \rightarrow 2 \text{ NO}_2(g) \quad \Delta H_{rxn} = -114.1 \text{ kJ } \Delta S_{rxn} = -146.5 \text{ J/K}$ a. How much heat is released when 73.1 g of NO is converted to NO₂? 73.1 g NO *(1 mole/30 g) = 2.44 moles NO *(-114.1 kJ/2 mole NO) = -139 kJ
 - b. Indicate whether the value of ΔG_{rxn} would become more negative, less negative, or remain unchanged as the temperature is increased. Justify your answer.
 - $\Delta G = \Delta H T\Delta S$ since ΔS is negative, as T increased, it will make ΔG more positive as you subtract a negative value making it more positive
 - c. The value of $S^{\circ} = 210.8$ J/Kmol for NO. The value of $S^{\circ} = 240.1$ J/Kmol for NO₂. Calculate the value of S° for O₂

 $\Delta S = (2^*S_{NO2}) - (2^*S_{NO} + S_{O2})$

-146.5 = (2*240.1) - (2*210.8 + X)

- X = 205 J/K
- d. The bond energy of the N-O bond in NO is 607 kJ/mol. The bond energy of the O-O bond in O₂ is 495 kJ/mol. Calculate the bond energy of the N-O bond in NO₂.

 $\Delta H_{rxn} = \Sigma \text{ Bonds}_{react} - \Sigma \text{ Bonds}_{prod}$ -114.1 = (2*607 + 495) - 2(2*X)X = 456 kJ/mole

- 2. For the substance propane, C_3H_8 :
 - a. Write a balanced equation for the complete combustion of propane with oxygen to yield carbon dioxide and water.
 - $C_3H_8 + 5 O_2 \rightarrow 3 CO_2 + 4 H_2O$
 - b. Calculate the volume of air at 30 $^{\circ}$ C and 1.0 atm that is needed to burn completely 10.0 grams of propane. Assume that air is 21% O₂.

10 g C_3H_8 *(1 mole/44 g) = 0.227 moles C_3H_8 *(5 mole $O_2/1$ mole C_3H_8) = 1.136 mole O_2 V = nRT/P = (1.136 mole)(0.0821)(303 K)/(1 atm) = 28.3 L of O_2 needed Since air is only 21% O_2 you need 134.6 L air

c. The heat of combustion of propane is -2220.1 kJ/mole. Knowing that ΔH_f = -285.3 kJ/mole for H₂O and ΔH_f = -393.5 kJ/mole for CO₂, calculate the ΔH_f for propane.

 $\Delta H_{rxn} = \Sigma \Delta H_f^{o} \text{ prod} - \Sigma \Delta H_f^{o} \text{ react}$

 $\Delta H_{\rm rxn} = (3 * {\rm CO}_2 + 4 * {\rm H}_2 {\rm O}) - {\rm X}$

- -2220.1 = (3*(-393.5) + 4*(-285.3)) X
- -2220.1 = -1180.5 -1141.2 -X
- X = -101.6 kJ/mole
- d. Assuming that all of the heat evolved in burning 30.0 grams of propane is transferred to 8.00 kg of water (C_{water} = 4.18 J/gK), calculate the increase in temperature of the water.

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0.682 \text{ moles } C_3H_8 * (-2220.1 \text{ kJ/mole}) = -1514 \text{ kJ or } 1514000 \text{ J given to water}
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q_{water} = mc\Delta T 1514000 J = (8000 g)(4.18 J/gK)\Delta T \Delta T = 45.3 \ ^{\circ}C
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- 3. For the reaction: 2 Fe (s) + $3/2 O_2$ (g) \rightarrow Fe₂O₃ (s) ΔH_f = -824 kJ/mol
 - A 75.0 g sample of Fe is mixed with 11.5 L of O_2 at 2.66 atm and 298 K.
 - a. Calculate the number of moles of:
 - i) Fe 1.34 moles
 - ii) O_2 1.25 moles
 - b. Identify the limiting reagent. Justify your answer.
 - Try to use all 1.34 moles of Fe:
 - 1.34 moles Fe $*(3/2 \text{ moles } O_2/2 \text{ moles } Fe) = 1.005 \text{ moles } O_2 \text{ needed which we have enough of so Fe is limiting reagent}$
 - c. Calculate the number of moles of Fe_2O_3 produced if the reaction goes to completion.
 - 1.34 moles Fe *(1 mole $Fe_2O_3/2$ mole Fe) = 0.67 moles Fe_2O_3
 - d. If ΔG_f = -740 kJ/mole for Fe₂O₃:
 - i) Calculate the ΔS_f for Fe_2O_3
 - $\Delta \mathbf{G} = \Delta \mathbf{H} \mathbf{T} \Delta \mathbf{S}$
 - $-740,000 \text{ J} = -824000 \text{ J} (298 \text{K})\Delta \text{S}$
 - $\Delta S = -282 \text{ J/K}$
 - ii) Which is more responsible for the spontaneity of the reaction, the enthalpy or the entropy? Justify your answer.

Enthalpy (Δ H) tends to be negative for spontaneous reactions

Entropy (ΔS) tends to be positive for spontaneous reactions

Since the enthalpy is negative and the entropy is negative, the reaction is enthalpy-driven only

e. Knowing that: 2 FeO (s) + $\frac{1}{2}O_2(g) \rightarrow Fe_2O_3(s) \Delta H_{rxn}=-280 \text{ kJ}$ Calculate ΔH_f of FeO (s)

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\Delta H_{rxn} = \Sigma \Delta H_f^{o} \text{ prod} - \Sigma \Delta H_f^{o} \text{ react}
\Delta H_{rxn} = (Fe_2O_3) - 2*(FeO)
-280 = (-824) - 2X
2X = -544
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X = -272 kJ/mole

4. Consider pentane (C_5H_{12} MW = 72.15 g/mole)

a. Write the balanced equation for the combustion of pentane to yield CO₂ and H₂O C₅H₁₂ + 8 O₂ \rightarrow 5 CO₂ + 6 H₂O

b. What volume of CO₂ at 25 °C and 785 mm Hg will result from combustion of 2.5 g of pentane?

2.5 g*(1 mole/72.15 g)= 0.03465 moles C_5H_{12} *(5 mole $CO_2/1$ mole C_5H_{12}) = 0.173 mole CO_2 V = nRT/P = (0.173 mole CO_2)(0.0821)(298 K)/(1.033 atm) = 4.103 L

- c. Combustion of 5 g of pentane releases 243 kJ of heat. Calcualte $\Delta H_{combustion}$ pentane.
- $\Delta H = q/mole$
- 5 g C₅H₁₂*(1 mole/72.15 g) = 0.0693 moles
- $\Delta H = (-243 \text{ kJ}/0.0693 \text{ mole}) = -3506 \text{ kJ/mole}$
- d. Under identical conditions, an unknown gas effuses twice as fast as pentane. Calculate the molar mass of this gas.

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Rate X/Rate $C_5H_{12} = (72.15/X)^{1/2}$ 2/1 = $(72.15/X)^{1/2}$

- X = 18 g/mole
- e. Draw three structural isomers of pentane.