

Hess' Law: Experimental Thermodynamics

Name	Course	Date Performed	Professor Sign-Off

Experimental Thermodynamics – Part I

Remember that for PdV work at constant pressure and volume that

$$\Delta H = q + 0 = q.$$

Remember also that

$$q = mC\Delta T,$$

where m = mass of the substance; C = heat capacity of the substance; ΔT = temperature change in Kelvins (and in degrees C, too, remember).

This is fine for solids, but what about liquids? For liquids, the mass may be calculated as follows:

$$m = V \rho,$$

where V = volume in mL; ρ = density in g/mL, so that, finally,

$$\Delta H = V\rho C\Delta T.$$

For this series of experiments, we'll be using fairly dilute solutions -- diluted in water. The density of water is approximately 1 g/mL and the heat capacity of water is roughly 4.169 J/g/K, hence,

$$\rho C = 4.169 \text{ J/mL/K} = F.$$

Hence,

$$\Delta H = VF\Delta T.$$

Since Hess' Law follows the First Law of Thermodynamics, it follows that the enthalpy changes in styrofoam "coffee-cup" calorimeters may be arithmetically expressed as follows:

$$\Delta H_T = \Delta H_c + \Delta H_{S1} + \Delta H_{S2} + \Delta H_n = 0,$$

where ΔH_T = the total enthalpic change; ΔH_c = the enthalpy change of the calorimeter (styrofoam cup and thermometer); ΔH_{S1} = the enthalpic change of solution #1; ΔH_{S2} = the enthalpic change of solution #2; ΔH_n = the enthalpic change of solution #n. This can be rewritten as:

$$(VF\Delta T)_c + (VF\Delta T)_{S1} + (VF\Delta T)_{S2} + (VF\Delta T)_n = 0,$$

where variables and subscripts are as previously defined.

In terms of the calorimeter, only a small part comes into contact with the solution. That makes it difficult to determine VF. VF must be solved for. VF is equal to the **calorimeter constant, W**:

$$(W\Delta T)_c + (VF\Delta T)_{S1} + (VF\Delta T)_{S2} + (VF\Delta T)_n = 0.$$

With only cool water and warm water, the equation looks like this:

$$(W\Delta T)_c + (VF\Delta T)_{CW} + (VF\Delta T)_{WW} = 0.$$

Rearranging, we get the following:

$$(W\Delta T)_c = -[(VF\Delta T)_{CW} + (VF\Delta T)_{WW}]$$

Isolating W_c :

$$W_c = -[(VF\Delta T)_{CW} + (VF\Delta T)_{WW}] / \Delta T_c$$

NOTE: ΔT_c and ΔT_{CW} are identical to each other. They equal the temperature increase, a positive value, of the cool water and calorimeter after absorbing heat from the warm water. ΔT_{WW} equals the temperature decrease

4. Write the balanced equation for the reaction of nitric acid with sodium hydroxide including products formed.

5. Write the reaction, balanced, for the dissociation of Nitric acid in water.

Experimental Thermodynamics -- Part II

Supplies Needed			
4-Styrofoam cups	2-Cardboard or Styrofoam Lids	2-Thermometers	Distilled Water
1 M NaOH	Concentrated HNO ₃	1 M HNO ₃	Goggles
2-Beakers	1-50 mL Graduated Cylinder	1-10 mL Graduated Cylinder	

Thermometer Temperature Correction/Calibration

Place both thermometers in the same container of tap water for 5 minutes. After 5 minutes, record the temperature on each thermometer in the following blanks.

In tap water, Thermometer #1 read: ____ and Thermometer #2 read: ____.

The difference between the two thermometers is: _____. Use degrees C. Add the difference between the 2 thermometers to the thermometer that **reads the lowest** to correct the temperature differences.

Experimental

Calorimeter Constant Determination				
Temperature of 40 mL Warm Water in Calorimeter #1		Temperature of 40 mL Cool Water in Calorimeter #2		Time (minutes)
Trial 1	Trial 2	Trial 1	Trial 2	Time
T =	T =	T =	T =	t = 1
T =	T =	T =	T =	t = 2
T =	T =	T =	T =	t = 3
T =	T =	T =	T =	t = 4
T =	T =	T =	T =	t = 5
Mix immediately after the 5 minute reading!				
T =	T =			t = 6
T =	T =			t = 7
T =	T =			t = 8
T =	T =			t = 9
T =	T =			t = 10

Do twice as per the tables, above. When recording temperatures (T), record the CORRECTED values, above.

FOR THE NEXT SECTION: CAUTION!!!!!!

Add ACID to WATER, carefully!

Heat of Neutralization and Solution – Reaction A				
Temperature of 64 mL 1 M NaOH in 12 mL Distilled Water in Calorimeter #1		Temperature of 4 mL of Concentrated Nitric Acid in 10 mL Graduated Cylinder (One Temperature Measurement Will Suffice)		Time (minutes)
Trial 1	Trial 2	Trial 1	Trial 2	Time
T =	T =	T =	T =	t = 1
T =	T =	T =	T =	t = 2
T =	T =	T =	T =	t = 3
T =	T =	T =	T =	t = 4
T =	T =	T =	T =	t = 5
Mix immediately after the 5 minute reading!				
T =	T =			t = 6
T =	T =			t = 7
T =	T =			t = 8
T =	T =			t = 9
T =	T =			t = 10

Do twice as per the tables, above.

When recording temperatures (T), record the CORRECTED values, above.

FOR THE NEXT SECTION: CAUTION!!!!!!

Add ACID to WATER, carefully!

Heat of Solution of Concentrated Nitric Acid – Reaction B				
Temperature of 60 mL Distilled Water in Calorimeter #1		Temperature of 4 mL of Concentrated Nitric Acid in 10 mL Graduated Cylinder (One Temperature Measurement Will Suffice)		Time (minutes)
Trial 1	Trial 2	Trial 1	Trial 2	Time
T =	T =	T =	T =	t = 1
T =	T =	T =	T =	t = 2
T =	T =	T =	T =	t = 3
T =	T =	T =	T =	t = 4
T =	T =	T =	T =	t = 5
Mix immediately after the 5 minute reading!				
T =	T =			t = 6
T =	T =			t = 7
T =	T =			t = 8
T =	T =			t = 9
T =	T =			t = 10

Do twice as per the tables, above.

When recording temperatures (T), record the CORRECTED values, above.

FOR THE NEXT SECTION: CAUTION!!!!!!

Add ACID to WATER, carefully!

Heat of Neutralization of 1 M HNO ₃ and 1 M NaOH – Reaction C				
Temperature of 40 mL 1 M NaOH in Calorimeter #1		Temperature of 40 mL 1 M Nitric Acid in Calorimeter #2		Time (minutes)
Trial 1	Trial 2	Trial 1	Trial 2	Time
T =	T =	T =	T =	t = 1
T =	T =	T =	T =	t = 2
T =	T =	T =	T =	t = 3
T =	T =	T =	T =	t = 4
T =	T =	T =	T =	t = 5
Mix immediately after the 5 minute reading!				
T =	T =			t = 6
T =	T =			t = 7
T =	T =			t = 8
T =	T =			t = 9
T =	T =			t = 10

Do twice as per the tables, above. When recording temperatures (T), record the CORRECTED values, above.

Using your data and a table similar in construction as above, determine the ΔH_{rxn} (in J/mol) for the following:

- A) Heat of solution and neutralization of con HNO₃ and 1 M NaOH,
 B) Heat of solution of con HNO₃ and
 C) Heat of neutralization of 1 M HNO₃ and 1 M NaOH.

Write the balanced reactions for A, B and C, above. Attach both sets of calculations and graphs to your lab for turn-in.

Complete The Table:		
Reaction	Balanced Chemical Reaction	ΔH_{rxn} (J)
Example to Get You Started:		
X	H ₂ SO ₄ (aq) + Ca(OH) ₂ (s) = CaSO ₄ (s) + 2 H ₂ O (l)	-3897 kJ
A	() ()	()
B	() ()	()
C	() ()	()

For each reaction, calculate the number of moles of nitric acid added to the calorimeter and average the answer.

Concentrated nitric acid is 15.4 M and you know the concentration of the 1 M nitric acid. Now divide each enthalpy change of each reaction by the number of mols of nitric acid for that reaction and record your results as directed below. Construct a table with the following information in it: the reaction, the enthalpy change for the reaction (J), the number of moles of nitric acid and the enthalpy change of the reaction based upon the number of moles of nitric acid added (J/mol).

Subtract the sums of the enthalpy changes for the heat of neutralization and heat of solution from the enthalpy change for the heat of solution AND neutralization -- ignore the sign on the answer.

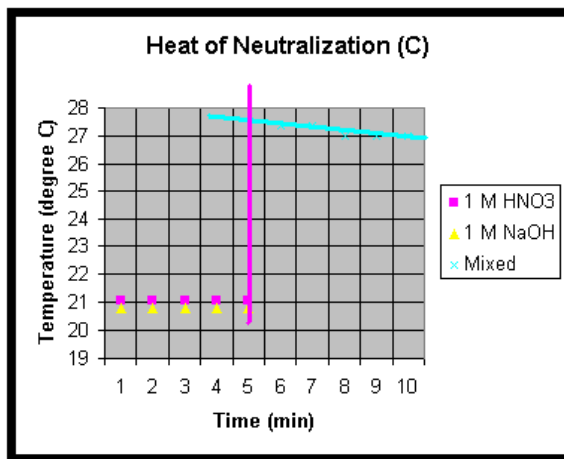
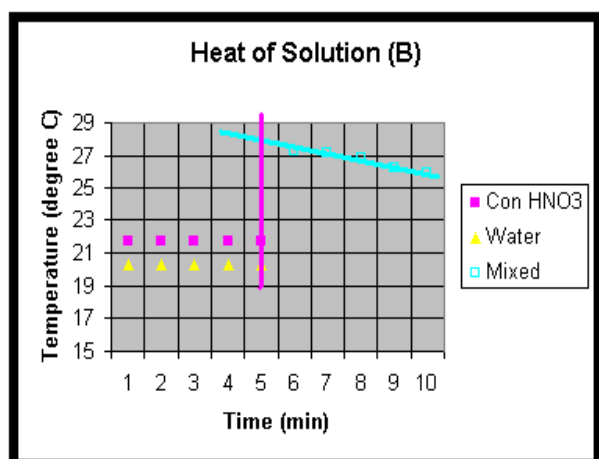
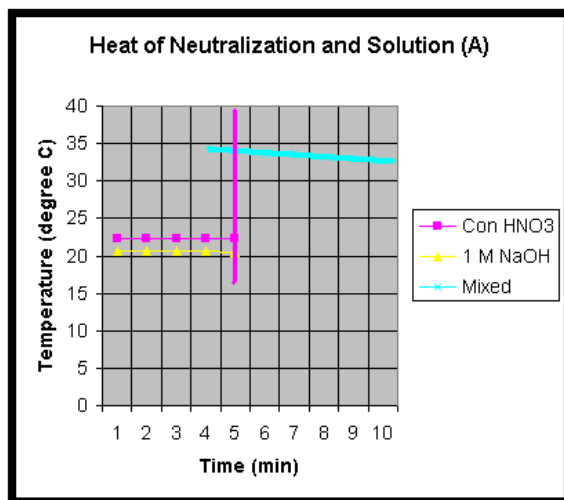
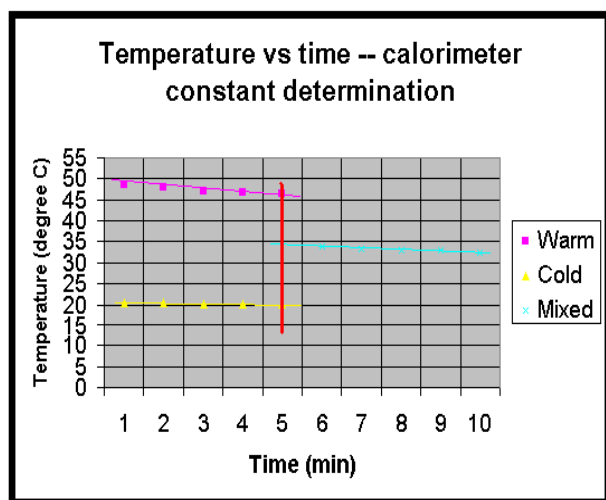
Calculate the % error of the difference from that for the overall reaction as follows:

$$\% \text{ error} = \left\{ \frac{\text{the difference between the two mathematical expressions}}{\text{the enthalpy change for the overall reaction [the first reaction after the calorimeter constant determination]}} \right\} * 100.$$

How close are your results? Remember to attach your calculations and graphs to this write-up. Sample Calculations follow to assist you in learning the process and procedure.

Sample Calculation

The first key to solving the questions to the experimental data is to plot the data systematically:



The next step is to run the straightest line through each of the three curves from the three pieces of data on each curve. BTW: These curves only have one trial per curve to simplify the explanation. Students will need to have either 2 sets of data per graph or a separate graph for every set of data. The straightest line method is illustrated in each graphic, above.

Once the straightest lines have been drawn through the data points, a line is dropped vertically between the two temperatures at 5 minutes. The line through the “after being mixed temperature data” is extrapolated BACK to that vertical line to obtain the temperature at mixing, which is where the extrapolated line intersects the vertical line. In the case of the examples, above, the approximate temperatures of mixing are summarized, below, in the table:

Calorimeter constant determination	Reaction A	Reaction B	Reaction C
34°C	33.5°C	27.7°C	27.5°C

The next step is to calculate the change in temperature from pre-mixing to that of the temperature at mixing, i.e., the ΔT ($T_{\text{final}} - T_{\text{initial}}$):

Calorimeter Constant Determination		Reaction A		Reaction B		Reaction C	
Warm Water	Cool Water	Con HNO ₃	1 M NaOH	Con HNO ₃	Cool Water	1 M HNO ₃	1 M NaOH
34 - 46.5 =	34 - 20 =	22.4 - 33.5 =	33.5 - 20.4 =	21.7 - 27.7 =	27.7 - 20.3 =	21.1 - 27.5 =	27.5 - 20.8 =
-12.5°C	14°C	-11.1°C	13.1°C	-6.0°C	7.4°C	-6.4°C	6.7°C

To calculate the calorimeter constant, use the following equation:

$$W_c = -[(VF\Delta T)_{CW} + (VF\Delta T)_{WW}]/\Delta T_c$$

ΔT_{CW} and ΔT_c are the same: 14°C; ΔT_{WW} is -12.5°C -- remember that the ΔT is the same whether in C or K and K is needed for the equation to work out right.

Each volume is identical: 40 mL

Hence the equation reduces to:

$$W_c = - \left[\frac{[(40 \text{ mL})(4.184 \text{ J})(14 \text{ K})] + [(40 \text{ mL})(4.184 \text{ J})(-12.5 \text{ K})]}{14 \text{ K} * \text{mL} * \text{K}} \right] = - \left[\frac{2343.04 - 2092}{14} \right] = -17.93 \frac{\text{J}}{\text{K}}$$

The calorimeter constant, then, is -17.93 J/K. This is the number that will be used consistently throughout the calculations for this experiment.

To calculate the enthalpy change for Reaction A, use the following equation:

$$\Delta H_{\text{rxn A}} = -\{(W\Delta T)_c + (VF\Delta T)_{\text{NaOH}} + (VF\Delta T)_{\text{HNO}_3}\}$$

This equation goes to:

$$- \left[(-17.93)(13.1) + [(76 \text{ mL})(4.184)(13.1)] + [(4 \text{ mL})(4.184)(-11.1)] \right] = -[-234.9 + 4165.6 - 185.8] = -3744.9 \text{ J}$$

To calculate the enthalpy change for Reaction B, use the following equation:

$$\Delta H_{\text{rxn B}} = -\{(W\Delta T)_c + (VF\Delta T)_{CW} + (VF\Delta T)_{\text{HNO}_3}\}$$

To calculate the enthalpy change for Reaction C, use the following equation:

$$\Delta H_{\text{rxn C}} = -\{(W\Delta T)_c + (VF\Delta T)_{\text{NaOH}} + (VF\Delta T)_{\text{HNO}_3}\}$$

$$- \left[(-17.93)(6.7) + [(40 \text{ mL})(4.184)(6.7)] + [(40 \text{ mL})(4.184)(-6.4)] \right] = -[-120.1 + 1121.3 - 1071.1] = 69.9 \text{ J}$$

Thus far we have calculated the enthalpy changes for reactions A, B and C:

Reaction	Enthalpy change	Balanced Reaction
A	-3744.9 J	$\text{HNO}_3 + \text{NaOH} \rightarrow \text{NaNO}_3 + \text{H}_2\text{O}$
B	-1624.6 J	$\text{HNO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{NO}_3^-$
C	69.9 J	$\text{HNO}_3 + \text{NaOH} \rightarrow \text{NaNO}_3 + \text{H}_2\text{O}$

To calculate the number of moles of HNO₃ in each reaction, do the following:

Reactions A & B:

$$\text{mol HNO}_3 = \frac{(4 \text{ mL})(1 \text{ L})(15.4 \text{ mol})}{1000 \text{ mL} \cdot \text{L}} = 0.0616 \text{ mol}$$

For Reaction C:

$$\text{mol HNO}_3 = \frac{(40 \text{ mL})(1 \text{ L})(1 \text{ M})}{1000 \text{ mL} \cdot \text{L}} = 0.04 \text{ mol}$$

Now combine the information you've calculated and previously tabulated:

Balanced Reaction	ΔH_{rxn}	# mol HNO ₃	J/mol
HNO ₃ + NaOH → NaNO ₃ + H ₂ O	-3744.9 J	0.0616 mol	-60793.8
HNO ₃ + H ₂ O → H ₃ O ⁺ + NO ₃ ⁻	-1624.6 J	0.0616 mol	-26373.4
HNO ₃ + NaOH → NaNO ₃ + H ₂ O	69.9 J	0.04 mol	1747.5

Subtract, now, the parts of the reaction in J/mol from the sum total:

$$-60793.8 - (-26373.4 + 1747.5) = -36167.9$$

The per cent error, then (ignore the sign from the above result), is equal to:

$$\% \text{ error} = \frac{36167.9}{-60793.8} * 100 = -59.5\% \text{ error}$$

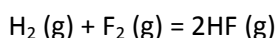
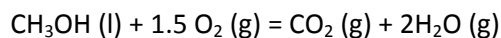
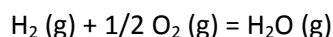
In other words, the data came up short. You do the same with your dual sets of data, remembering to determine the average heats of reactions. Attach your Excel (or Lotus or Quattro) graphs and calculations to the experiment for turn-in.

Problems

Enthalpy of Formations at STP in kcal/mol for Questions 1-4.			
H ₂ O (g)	-57.8	CH ₃ OH (l)	-57.02
CO ₂ (g)	-94.05	H ⁺ in water	0.00
Ag ⁺ in water (aq)	25.31	Cl ⁻ in water	-40.02
Br ⁻ in water	-28.90	NO ₃ ⁻ in water	-49.37
CO ₃ ²⁻ in water	-161.63	Ca ²⁺ in water	-129.77
Li ⁺ in water	-66.55	Na ⁺ in water	-57.28
K ⁺ in water	29.01	Zn ²⁺ in water	-36.43

NOTE: Something written like: HCl (g) + aq means the same as HCl in water (HCl (aq))

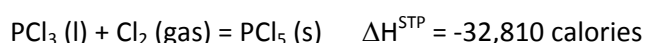
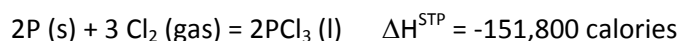
1. The following reactions might be used to power rockets:



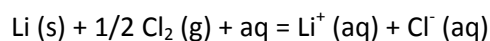
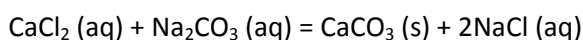
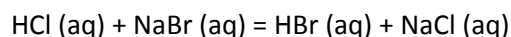
a) Calculate the enthalpy changes at STP for each of these reactions. (For HF(g), the enthalpy change at STP = -64.2 kcal/mol).

b) Since the thrust is greater when the molecular weight of the exhaust gas is lower, determine the molecular weight of the gaseous products (the average molecular weight in the case of the second reaction) and arrange the reactions in order of effectiveness of thrust.

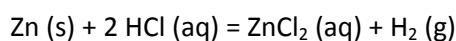
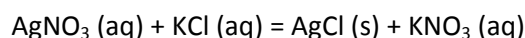
2. Calculate the enthalpy of formation of $\text{PCl}_5 (\text{s})$, given the heats of the following reactions at STP:



3. Calculate the enthalpies of reaction at STP for the following reactions in dilute aqueous solutions: (HINT: use ionic equations! (NOTE: "in water" OR "aq"))

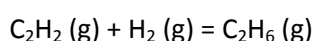
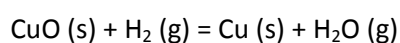
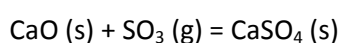
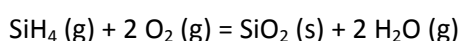
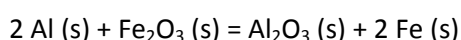


4. Calculate the enthalpies of reaction at STP for the following reactions in dilute aqueous reactions (HINT: use ionic equations! (NOTE: "in water" OR "aq"))

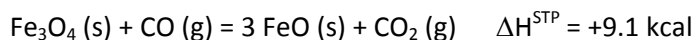
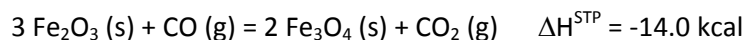
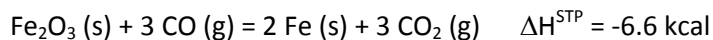


$\text{Al}_2\text{O}_3 (\text{s})$	-400.5	$\text{CO} (\text{g})$	-26.4
$\text{CO}_2 (\text{g})$	-94.1	$\text{C}_2\text{H}_6 (\text{g})$	-20.2
$\text{C}_2\text{H}_2 (\text{g})$	+54.2	$\text{CaO} (\text{s})$	-151.9
$\text{CaSO}_4 (\text{s})$	-342.4	$\text{CuO} (\text{s})$	-37.1
$\text{Fe}_2\text{O}_3 (\text{s})$	-196.5	$\text{H}_2\text{O} (\text{g})$	-57.8
$\text{SiO}_2 (\text{s})$	-217.7	$\text{SiH}_4 (\text{g})$	+8.2
$\text{SO}_3 (\text{g})$	-94.6		

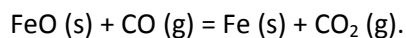
5. Use Hess' Law to calculate the heat of reaction at STP for each of the following reactions:



6. Given the following thermochemical equations:



Calculate the enthalpy of reaction at STP for the following reaction:



Answer Keys for Problems

#1) a) $\text{H}_2 (\text{g}) + \frac{1}{2} \text{O}_2 (\text{g}) \rightarrow \text{H}_2\text{O} (\text{g})$

$$\Delta H_{\text{rxn}} = \left(\sum n \Delta H_{\text{prod}} \right) - \left(\sum n \Delta H_{\text{reactants}} \right)$$

$$= (-57.8) - (0) = -57.8 \text{ kcal}$$

$\text{CH}_3\text{OH} (\text{l}) + \frac{1}{2} \text{O}_2 (\text{g}) \rightarrow \text{CO}_2 (\text{g}) + 2 \text{H}_2\text{O} (\text{g})$

$$\Delta H_{\text{rxn}} = (-94.05 + [2 \cdot -57.8]) - (-57.02 + 0)$$

$$= -209.65 + 57.02 = -152.63 \text{ kcal}$$

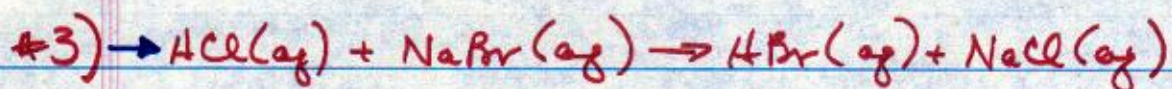
$\text{H}_2 (\text{g}) + \text{F}_2 (\text{g}) = 2 \text{HF} (\text{g})$

$$\Delta H_{\text{rxn}} = (2 \cdot -64.2) - (0) = -128.4 \text{ kcal}$$

b) $\text{MW}_{\text{H}_2\text{O}} = 18 \quad -1^{\text{st}}$
 $\text{MW}_{\text{HF}} = 20 \quad -2^{\text{d}}$
 $\text{MW}_{\text{CO}_2 + \text{H}_2\text{O}} = 31 \quad -3^{\text{d}}$

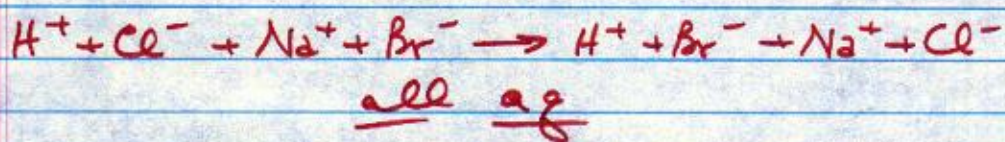
#2)

$2\text{P} (\text{s}) + 3\text{Cl}_2 (\text{g}) \rightarrow$	$2\text{PCl}_3 (\text{l})$	ΔH -151,800 cal
$2\text{PCl}_3 (\text{l}) + 2\text{Cl}_2 (\text{g}) \rightarrow$	$2\text{PCl}_5 (\text{s})$	-65,620 cal
$2\text{P} (\text{s}) + 5\text{Cl}_2 (\text{g}) \rightarrow$	$2\text{PCl}_5 (\text{s})$	-217,420 cal



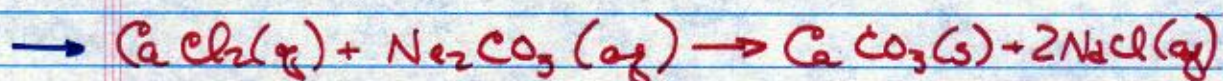
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$$\Delta H_{\text{rxn}} = (0 - 28.90 - 57.28 - 40.02) - (0 - 40.02 - 57.28 - 28.90)$$

$$= -126.2 - (-126.2) = 0 \text{ kcal}$$

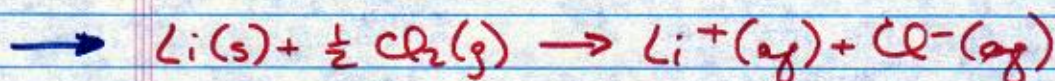


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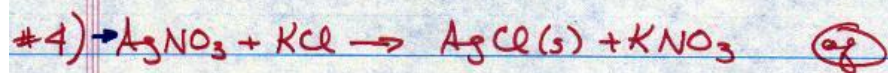


$$\Delta H_{\text{rxn}} = (-129.77 - 80.04 - 114.56 - 161.63) - (-129.77 - 161.63 - 114.56 - 80.04)$$

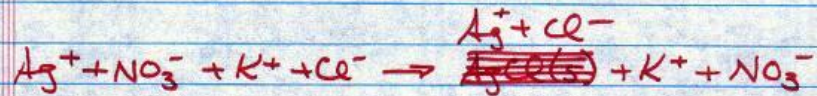
$$= 0 \text{ kcal}$$



$$\Delta H_{\text{rxn}} = (-66.55 - 40.02) - (0)$$
$$= -106.57 \text{ kcal}$$

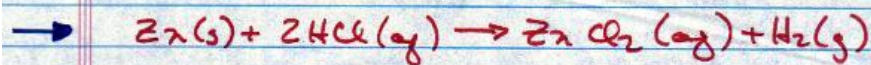


rewrite

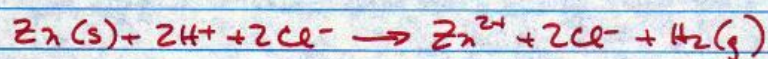


$$\Delta H_{\text{rxn}} = (25.31 - 40.02 - 60.04 - 49.37) - (25.31 - 49.37 - 60.04 - 40.02)$$

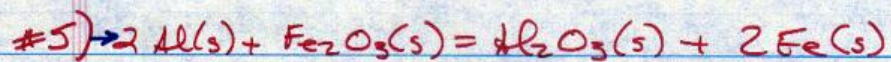
$$= 0 \text{ Kcal}$$



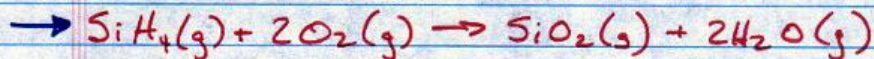
rewrite



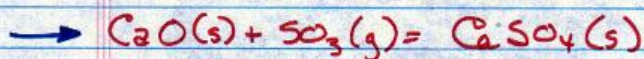
$$\Delta H_{\text{rxn}} = (-36.43 - 80.04 + 0) - (0 + 0 - 80.04) = -36.43 \text{ kcal}$$



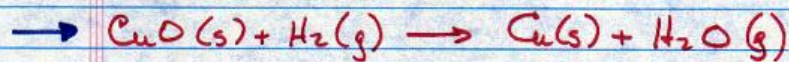
$$\Delta H_{\text{rxn}} = (-400.5) - (-196.5) = -204 \text{ kcal}$$



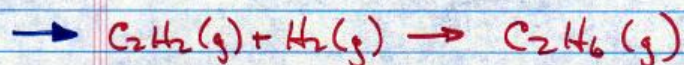
$$\Delta H_{\text{rxn}} = (-217.7 - 115.6) - (8.2 + 0) = -341.5 \text{ kcal}$$



$$\Delta H_{\text{rxn}} = (-342.4) - (-151.9 - 94.6) = -95.9 \text{ kcal}$$



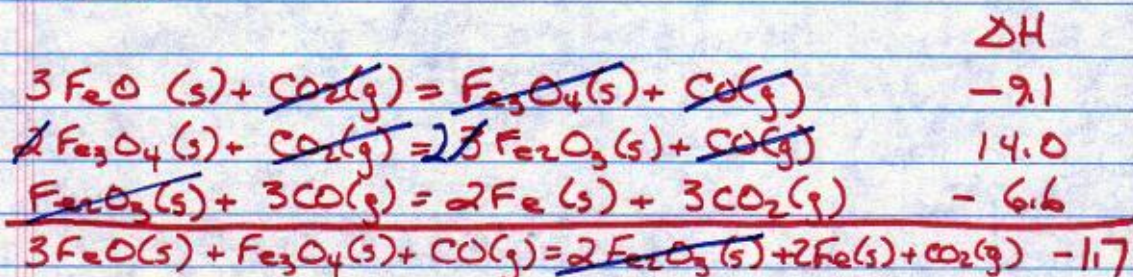
$$\Delta H_{\text{rxn}} = (-57.8) - (-37.1) = -20.7 \text{ kcal}$$



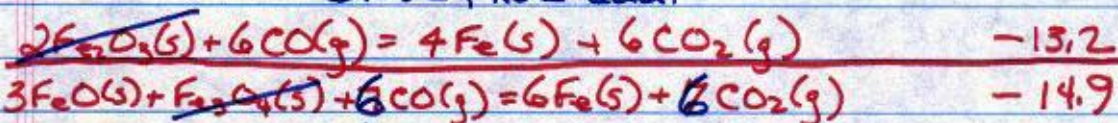
$$\Delta H_{\text{rxn}} = (-20.2) - (54.2) = -74.4 \text{ kcal}$$

#6) The easiest way in which to do this is to piece meal it:

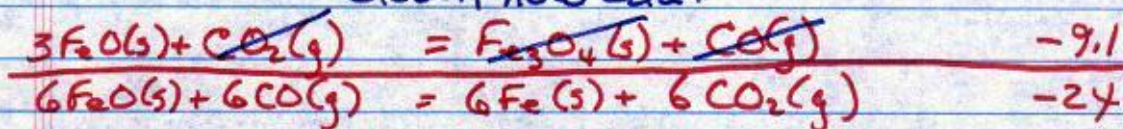
Also remember to change the sign on the ΔH of rxns when inverting them:



close, now add:



closer, now add:



$\div 6$

