

Thermal EQM Problems

T.E. Problems

- ① Converting 180. g ice at -50.0°C to steam at 120.0°C

ice at -50°C to ice at 0°C

$$q = mc\Delta T = (180. \text{g}) \left(.50 \frac{\text{cal}}{\text{g}^\circ\text{C}} \right) (50.0^\circ\text{C}) = \underline{4500 \text{ cal}}$$

ice at 0°C → liquid at 0°C

$$q = m\Delta H_{\text{fusion}} = (180. \text{g}) (79.9 \text{ cal/g}) = \underline{14382 \text{ cal}}$$

liquid at 0°C → liquid at 100°C

$$q = mc\Delta T = (180. \text{g}) (1.00 \text{ cal/g}^\circ\text{C}) (100^\circ\text{C}) = \underline{18000 \text{ cal}}$$

liquid at 100°C → gas at 100°C

$$q = m\Delta H_{\text{vaporization}} = (180. \text{g}) (540. \text{ cal/g}) = \underline{97200 \text{ cal}}$$

gas at 100°C to gas at 120.0°C

$$q = mc\Delta T = (180. \text{g}) (.48 \text{ cal/g}^\circ\text{C}) (20.0^\circ\text{C}) = \underline{1728 \text{ cal}}$$

Steam burns are nasty cause there is a lot of energy released when "steam" (vapor, really) condenses to liquid (540 cal/gram)... note in this process the largest absorbance term was the 97200 cal: $m\Delta H_{\text{vap}}$.

135810 cal

→ 135800 cal

- ② Perfect calorimeter, so assume "heat" gained by graphite = "heat" gained by H_2O .

$$|mc\Delta T|_{\text{graphite}} = |mc\Delta T|_{\text{water}}$$

$$(500.0 \text{g}) (.71 \text{ J/g}^\circ\text{C}) (T - 20.0) = (200. \text{g}) (4.184 \text{ J/g}^\circ\text{C}) (98.0^\circ\text{C} - T)$$

$$\frac{355}{^\circ\text{C}} T - 7100 = \frac{82006.4}{^\circ\text{C}} - 836.8 T$$

$$(355 + 836.8) T = \frac{89106.4}{^\circ\text{C}}$$

$$T = \frac{89106.4^\circ\text{C}}{1191.8} = 74.766^\circ\text{C} \rightarrow \boxed{74.8^\circ\text{C}}$$

- ③ Heat Lost by Al = Heat gained by H_2O

$$|mc\Delta T|_{\text{Al}} = |mc\Delta T|_{\text{H}_2\text{O}}$$

$$(150. \text{g Al}) c_{\text{Al}} (80.0^\circ\text{C} - 35.0^\circ\text{C}) = (100. \text{g H}_2\text{O}) (4.184 \frac{\text{J}}{\text{g}^\circ\text{C}}) (35.0^\circ\text{C} - 22.0^\circ\text{C})$$

$$c_{\text{Al}} = 0.806 \text{ J/g}^\circ\text{C} \quad (.80581)$$

$$\% \text{ error} = \frac{|.806 \text{ J/g}^\circ\text{C} - .89 \text{ J/g}^\circ\text{C}|}{.89 \text{ J/g}^\circ\text{C}} = \underline{\underline{9\% \text{ error}}}$$

"Thermal Equilibrium problems" cont'd

#6 $q_{H_2O} = mc\Delta T = (1000. g)(4.184 \frac{J}{g \cdot ^\circ C})(-40.0^\circ C) = -16736 \text{ J}$
 or -167.36 kJ .. 167.36 kJ are released by H_2O

$\therefore q_{gas} = +167.36 \text{ kJ}$.. the gas absorbs the heat from the water bath.

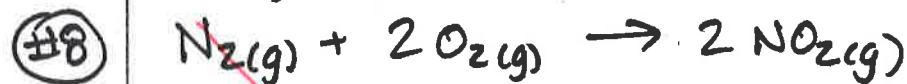
work done by gas = $p\Delta V$
 $= (1.5 \text{ atm})(18 \text{ L}) \left(\frac{8.314 \text{ J}}{.0821 \text{ L} \cdot \text{atm}} \right) = 2734 \text{ J}$
 work done by gas

\therefore work done on gas = -2734 J

$\Delta U = q + w = 167.36 \text{ kJ}$
 $\quad \quad \quad - 2.734 \text{ kJ}$
 $\quad \quad \quad \underline{\quad \quad \quad}$
 $\quad \quad \quad 164.63 \text{ kJ} \Rightarrow \boxed{\Delta U = 165 \text{ kJ}}$

#7 work done on gas = $-p\Delta V$
 $= -(2.0 \text{ atm})(-.150 \text{ L}) \left(\frac{8.314 \text{ J}}{.0821 \text{ L} \cdot \text{atm}} \right)$
 $= 30.38 \text{ J done on gas}$

$\Delta U = q + w = -5.2 \text{ J} + 30.38 \text{ J} = 25.18 \text{ J} \rightarrow \boxed{25 \text{ J}}$



a) $\Delta H_{rxn} = 2\Delta H_f(NO_2) - \Delta H_f(N_2) - 2\Delta H_f(O_2)$
 $= 2(33.84 \text{ kJ/mole}) - 0 - 0 = \boxed{67.68 \text{ kJ} = \Delta H^\circ_{rxn}}$

new #8 on next page!

b) work done by gas = $p\Delta V = \Delta nRT$
 $\Delta n = -1$ (3 moles gas \rightarrow 2 moles gas)

work done by gas = $-1(RT)$
 work done on gas = $+1(RT) = (8.314 \frac{J}{\text{mol} \cdot K})(298 \text{ K}) = 2477.6 \text{ J}$
 $\Delta U = q + w = 67.68 \text{ kJ} + 2.4776 \text{ kJ} = \boxed{70.16 \text{ kJ}} = \Delta U^\circ_{rxn}$

#9 $H \equiv$ enthalpy \equiv heat change at constant pressure

~~a bomb coffee cup calorimeter, since open to the atmosphere will measure the heat change @ const. pressure which is enthalpy.~~

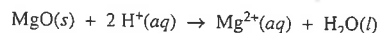
In a bomb calorimeter, volume is held constant, so no work is done by or on the gas ($w = -pdv$).

$\Delta U = q + w$.. or if $w = 0$, $\Delta U = q$.. so the heat change measured in a bomb calorimeter = ΔU .

$$(a) (1.000 \text{ L HCl}) \left(\frac{1.0 \text{ mole}}{\text{L}} \right) \left(\frac{1 \text{ mole MgO}}{2 \text{ mole HCl}} \right) \left(\frac{40.3044 \text{ g}}{\text{mole}} \right) = 2.01522 \text{ grams MgO}$$

Since the .1000 L HCl would require 2.0 grams MgO to react with, and only 0.50 g MgO (or less) is present in each trial, **MgO is the limiting reactant.**

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3. A student was assigned the task of determining the enthalpy change for the reaction between solid MgO and aqueous HCl represented by the net-ionic equation above. The student uses a polystyrene cup calorimeter and performs four trials. Data for each trial are shown in the table below.

Trial	Volume of 1.0 M HCl (mL)	Mass of MgO(s) Added (g)	Initial Temperature of Solution (°C)	Final Temperature of Solution (°C)
1	100.0	0.25	25.5	26.5
2	100.0	0.50	25.0	29.1
3	100.0	0.25	26.0	28.1
4	100.0	0.50	24.1	28.1

ΔT (°C)	ratio of $\Delta T / \text{mass MgO}$
1.0	4.0
4.1	8.2
2.1	8.4
4.0	8.0

(b) **Trial 1 is inconsistent** with the other three. Since the same volume HCl was used each time, and MgO is the limiting reactant, the ΔT value should be proportional to the mass of MgO added. Trial 1's ratio of ΔT to mass MgO is quite different from/about half as big as the ratios for the other 3 trials.

(a) Which is the limiting reactant in all four trials, HCl or MgO? Justify your answer.

(b) The data in one of the trials is inconsistent with the data in the other three trials. Identify the trial with inconsistent data and draw a line through the data from that trial in the table above. Explain how you identified the inconsistent data.

For parts (c) and (d), use the data from one of the other three trials (i.e., not from the trial you identified in part (b) above). Assume the calorimeter has a negligible heat capacity and that the specific heat of the contents of the calorimeter is $4.18 \text{ J/(g}\cdot\text{C}^\circ)$. Assume that the density of the HCl(aq) is 1.0 g/mL .

- (c) Calculate the magnitude of q , the thermal energy change, when the MgO was added to the $1.0 \text{ M HCl}(aq)$. Include units with your answer.
- (d) Determine the student's experimental value of ΔH° for the reaction between MgO and HCl in units of $\text{kJ/mol}_{\text{rxn}}$.
- (e) Enthalpies of formation for substances involved in the reaction are shown in the table below. Using the information in the table, determine the accepted value of ΔH° for the reaction between MgO(s) and HCl(aq).

Substance	ΔH_f° (kJ/mol)
MgO(s)	-602
H ₂ O(l)	-286
H ⁺ (aq)	0
Mg ²⁺ (aq)	-467

- (f) The accepted value and the experimental value do not agree. If the calorimeter leaked heat energy to the environment, would it help account for the discrepancy between the values? Explain.

yes! Heat loss would cause a low value for

ΔT , therefore a low value for q , and a low value

for the magnitude of ΔH_{rxn} . Heat loss causes a low ΔT value because some of the heat from the reaction is lost to the room, instead of transferred to/absorbed by the acid.

(c) using Trial 2:

$$q = mc\Delta T = (100.0 \text{ g} + 0.50 \text{ g})(4.18 \frac{\text{J}}{\text{g}\cdot\text{C}^\circ})(4.1 \text{ C}^\circ) = 1722.369$$

$$q = 1700 \text{ J}$$

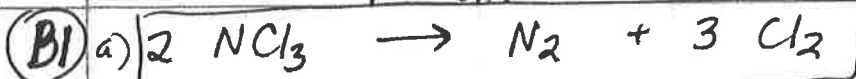
$$(d) \Delta H = \frac{-q_{\text{rxn}}}{\text{moles MgO}} = \frac{(-1722.369 \text{ J}) \left(\frac{1 \text{ kJ}}{1000 \text{ J}} \right)}{\left(\frac{.50 \text{ g}}{40.3044 \text{ g/mole}} \right)}$$

$$\Delta H = \frac{-1.722369 \text{ kJ}}{0.012406 \text{ moles}} = -140 \text{ kJ/mole}$$

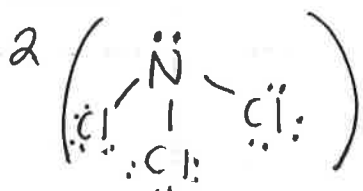
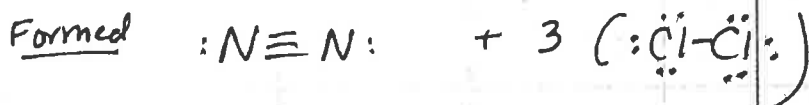
$$(e) \Delta H_{\text{rxn}} = (-467 \text{ kJ}) + (-286 \text{ kJ}) - (-602 \text{ kJ}) - 2(0)$$

$$\Delta H_{\text{rxn}} = -151 \text{ kJ/mole}$$

Problem B1



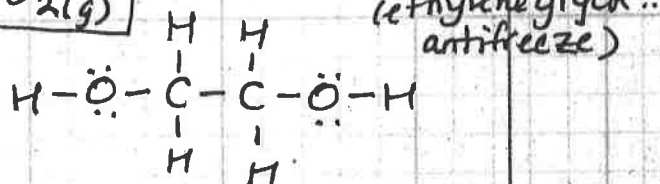
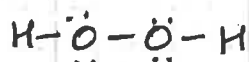
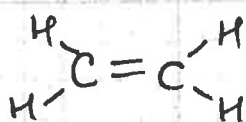
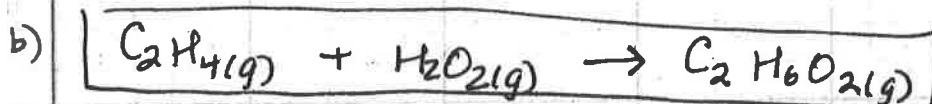
Broken



Broken: $6 (\text{N}-\text{Cl})$
 $= 6 (200 \text{ kJ/mole})$
 $= 1200 \text{ kJ/mole}$

Formed $1 (\text{N} \equiv \text{N}) + 3 (\text{Cl}-\text{Cl})$
 $1 (941) + 3 (242)$
 $= 1667 \text{ kJ/mole}$

$\Delta H_{\text{rxn}} = \sum \text{broken bonds} - \sum \text{formed bonds} = 1200 - 1667 = \boxed{-467 \text{ kJ}}$



Broken $1 \text{ C}=\text{C} = 1 (614) \text{ kJ}$
 $4 \text{ C}-\text{H} = 4 (413)$
 $2 \text{ O}-\text{H} = 2 (463)$
 $1 \text{ O}-\text{O} = 1 (146)$

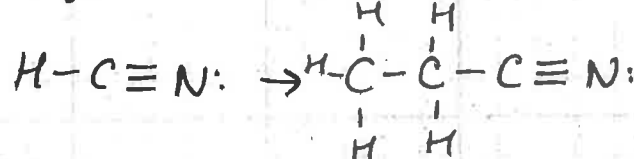
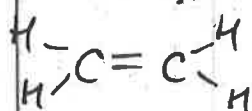
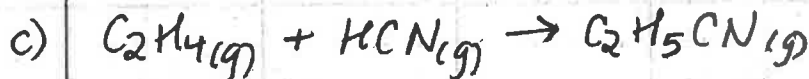
 3338 kJ

Formed $1 \text{ C}-\text{C} = 1 (348)$
 $4 \text{ C}-\text{H} = 4 (413)$
 $2 \text{ C}-\text{O} = 2 (358)$
 $2 \text{ O}-\text{H} = 2 (463)$

 3642 kJ

$\Delta H_{\text{rxn}} = 3338 - 3642 = \boxed{-304 \text{ kJ}}$

(or you could cancel some bonds out)



Broken

$4 \text{ C}-\text{H} = 4 (413)$
 $1 \text{ C}=\text{C} = 1 (614)$
 $1 \text{ C}-\text{H} = 1 (413)$
 $1 \text{ C} \equiv \text{N} = 1 (891)$

 3570 kJ absorbed

Formed

$5 \text{ C}-\text{H} = 5 (413)$
 $2 \text{ C}-\text{C} = 2 (348)$
 $1 \text{ C} \equiv \text{N} = 1 (891)$

 3652 kJ released

$\Delta H_{\text{rxn}} = 3570 \text{ kJ} - 3652 \text{ kJ} = \boxed{-82 \text{ kJ}}$

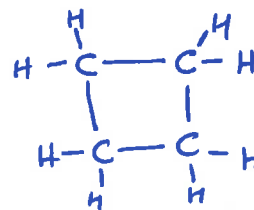
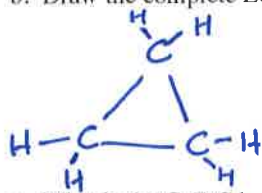
Problem B2

Problem B2. "Ring Strain."

Cyclopropane and cyclobutane have ring strain; the molecules have higher bond pair-bond pair repulsion than normal because the C-C-C bond angles are less than the normal tetrahedral bond angle. The chart on page 316 of your book shows that the typical/average C-C bond enthalpy is 348 kJ/mole. However, the bond energy will be significantly different in cyclopropane and cyclobutane due to ring strain. In this problem, you will estimate the C-C bond energy in cyclopropane and compare it to the more typical C-C value of 348 kJ!

- a. What is the normal C-C-C bond angle in non cyclic alkanes? 109.5° (tetrahedral bond \neq)

- b. Draw the complete Lewis dot structure of cyclopropane and cyclobutane.



- c. What is the C-C-C bond angle in cyclopropane? 60° in cyclobutane? 90°

- d. Write chemical equation for the complete combustion of cyclopropane. Balance with the smallest possible whole number coefficients.



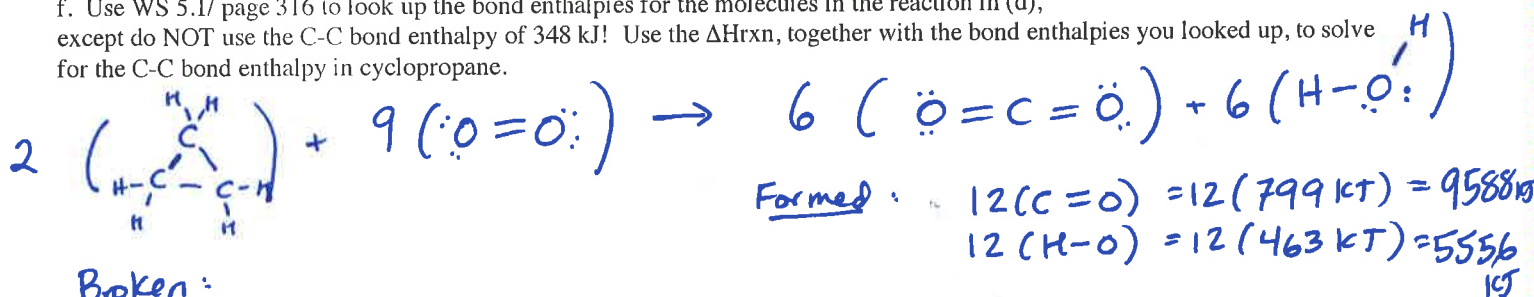
- e. Cyclopropane has an enthalpy of combustion of -2089 kJ/mole.

Based on this, determine the ΔH value for the reaction you wrote in (d). (Hint, it isn't -2089!)

$$(2089 \times 2 = 4178)$$

$$\Delta H_{\text{rxn}} = \boxed{-4178 \text{ kJ}} \quad \left(\frac{-2089 \text{ kJ}}{1 \text{ mole C}_3\text{H}_6} \right) = \left(\frac{-4178 \text{ kJ}}{2 \text{ mole C}_3\text{H}_6} \right)$$

- f. Use WS 5.1/ page 316 to look up the bond enthalpies for the molecules in the reaction in (d), except do NOT use the C-C bond enthalpy of 348 kJ! Use the ΔH_{rxn} , together with the bond enthalpies you looked up, to solve for the C-C bond enthalpy in cyclopropane.



Formed:

$$12 (\text{C}=\text{O}) = 12 (799 \text{ kJ}) = 9588 \text{ kJ}$$

$$12 (\text{H}-\text{O}) = 12 (463 \text{ kJ}) = 5556 \text{ kJ}$$

$$9588 \text{ kJ} + 5556 \text{ kJ} = 15144 \text{ kJ}$$

released when product bonds form

Broken:

$$6 (\text{C}-\text{C}) = 6x$$

$$12 (\text{C}-\text{H}) = 12 (413 \text{ kJ}) = 4956 \text{ kJ}$$

$$9 (\text{O}=\text{O}) = 9 (495 \text{ kJ}) = 4455 \text{ kJ}$$

$$6x + 4956 \text{ kJ} + 4455 \text{ kJ} = \underline{6x + 9411 \text{ kJ}}$$

energy req'd to break reactant bonds

$$\Delta H_{\text{rxn}} = \sum \Delta H_{\text{bonds broken}} - \sum \Delta H_{\text{bonds formed}}$$

$$-4178 \text{ kJ} = 6x + 9411 \text{ kJ} - 15144 \text{ kJ}$$

$$x = 259 \text{ kJ}$$

C-C bond enthalpy in cyclopropane

- g. Compare your result to the 348 kJ, does it make sense that your answer is more/less than 348? explain.

259 kJ < 348 kJ. This means that the C-C bonds in cyclopropane are weaker than typical C-C bonds (the bonds in C₃H₆ take less energy to break).

- h. If you did this same problem for cyclobutane instead of cyclopropane, would you expect the C-C bond enthalpy to be closer or further away from the value of 348 kJ? explain.
- yes - makes sense since the bond pair-bond pair repulsion in C₃H₆ is higher than normal due to the smaller than normal bond angles.
- Cyclobutane's C-C ΔH → it should be closer to 348 kJ. cyclobutane has C-C bond angles of 90°, which are closer to the normal sp³ bond angle of 109.5° (the cyclopropane's \neq of 60°).