

5.1 The Energy of Physical, Chemical and Nuclear Processes

Thermodynamics-

Thermochemistry –

Studying Energy Changes

-energy can be transferred or converted onto other forms.

System

Surroundings –

Universe =

ΔE universe =

$\therefore \Delta E$ system = - ΔE surroundings

Heat and Temperature:

Heat (Q) -

-

-

Temperature (T) –

-

-

Enthalpy and Enthalpy Change

Enthalpy (H) – total internal energy of a substance at a constant pressure

- we study the changes in enthalpy (ΔH) due to a particular process

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-

Enthalpy Changes in Chemical Reactions

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Endothermic reaction –

Exothermic reaction –

Reactants \longrightarrow Products
 Bonds broken \longrightarrow Bonds made

Representing Enthalpy Changes

ΔH_{rxn} –

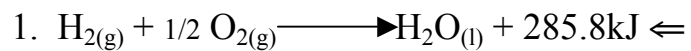
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ΔH° -

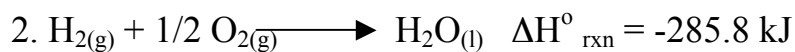
i.e. at SATP(25°C;100kPa)

Representing Exothermic Reactions

- use a thermochemical equation- balanced chemical equation that indicates the amount of heat released

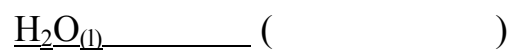
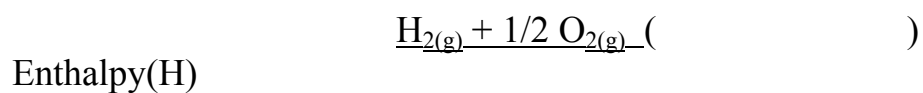
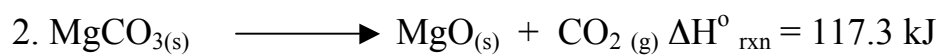
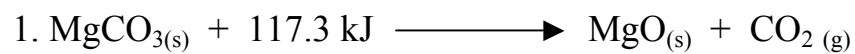


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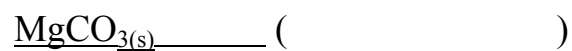
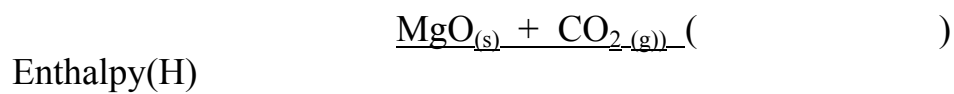
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3. enthalpy diagram

Representing Endothermic Changes

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3. enthalpy diagram



Stoichiometry and Thermochemical Equations

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e.g. Aluminum reacts readily with chlorine gas to produce aluminum chloride. The reaction is highly exothermic.



- What is the enthalpy change for 1 mole AlCl_3 ?
- What is the enthalpy change when 1.00 kg of Al reacts with excess Cl_2 ?

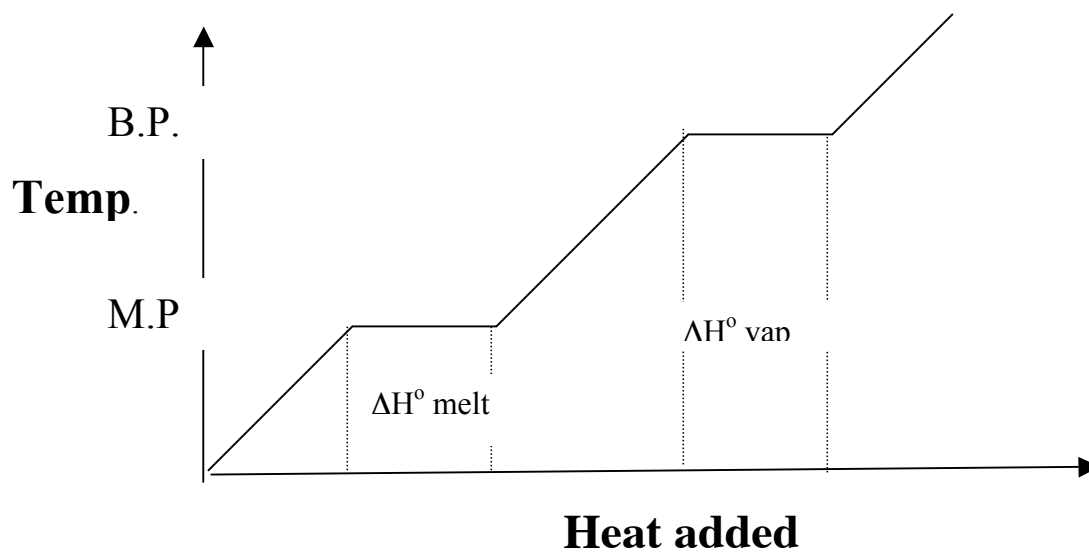
Heat Changes and Physical Changes

Boiling water

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-

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Possible to represent enthalpy change of a phase change

ΔH_{vap} –

ΔH_{cond} –

ΔH_{melt} –

$\Delta H_{\text{freezing}}$ –

$\Delta H_{\text{vap}} =$

$\Delta H_{\text{melt}} =$

Enthalpy of dissolution (ΔH_{soln}): amount of heat energy required or liberated when a solute dissolves in a solvent.

Eg.s – NaOH in water
- H_2SO_4 to water

Thermochemical Equations and Stoichiometry

1. Consider the following thermochemical equation:



- (a) How much heat is released when 3.0 mol $\text{ZnS}_{(\text{s})}$ reacts in excess oxygen?
- (b) How much heat is released when 2.3×10^{-2} mol $\text{ZnS}_{(\text{s})}$ reacts in excess oxygen?
- (c) What is the enthalpy change when 223.9 g $\text{ZnS}_{(\text{s})}$ reacts in excess oxygen?
- (d) What is the enthalpy change when 0.96 g $\text{ZnO}_{(\text{s})}$ is produced?
2. Slaked lime ($\text{Ca}(\text{OH})_{2(\text{s})}$) is produced when lime (calcium oxide, $\text{CaO}_{(\text{s})}$) reacts with liquid water. 65.2 kJ of heat is released for each mol of $\text{Ca}(\text{OH})_2$ that is produced.
- (a) Write a thermochemical equation for the reaction.
- (b) What is the enthalpy change when 523.3 kg of lime reacts with excess water?
3. The following reaction represents the complete combustion of hexane, $\text{C}_6\text{H}_{14(\text{l})}$, at SATP.
- $$\text{C}_6\text{H}_{14(\text{l})} + 19/2 \text{O}_{2(\text{g})} \rightarrow 6\text{CO}_{2(\text{g})} + 7\text{H}_2\text{O}_{(\text{l})} \quad \Delta H^\circ = -4163 \text{ kJ}$$
- (a) If 0.537 mol of carbon dioxide is produced in the reaction represented by the equation above, how much heat is released by the reaction?
- (b) If 25.0 kg of hexane is burned in sufficient oxygen, how much heat will be released?
- (c) What mass of hexane is required to produce 1.0×10^5 kJ of heat by complete combustion?

Answers:

- 1 (a) 1.3×10^3 kJ (b) 10 kJ (c) $\Delta H = -1009$ kJ (d) $\Delta H = -5.2$ kJ
2. (a) $\text{CaO}_{(\text{s})} + \text{H}_2\text{O}_{(\text{l})} \longrightarrow \text{Ca}(\text{OH})_2 \quad \Delta H = -65.2 \text{ kJ}$ (b) $\Delta H = -6.08 \times 10^5$ kJ
- 3 (a) 373 kJ (b) 1.21×10^6 kJ (c) 2.1 kg

5.2 DETERMINING ENTHALPY OF REACTION BY EXPERIMENT

SPECIFIC HEAT CAPACITY (**c**)

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i.e. High **c** means that more energy is required to raise temp. up.

eg. Al - 0.900 vs. water - 4.184

Heat capacity (**C**) -

i.e. a cup of water vs. a bathtub of water

- each has the same specific heat capacity, but 2 samples have different heat capacities (more heat for bath)

SPECIFIC HEAT CAPACITY AND HEAT TRANSFER

Possible to calculate heat change of substance

e.g. How much heat is needed to heat 1.00×10^2 g of water from 20.0°C to 45.0°C

PRACTICE PROBLEMS page 235	# 5 - 8
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Heat capacity $C = c \cdot m$

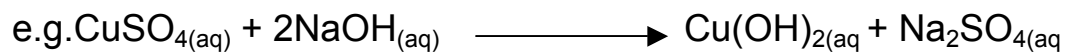
Molar Heat Capacity $C_n = c \cdot M(\text{molar mass})$

MEASURING HEAT TRANSFER IN A LAB

USING A CALORIMETER TO DETERMINE ΔH_r .

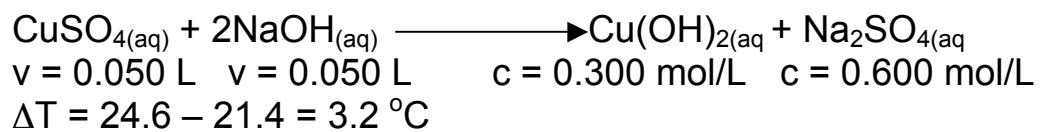
- good for dilute aqueous solutions
i.e. the water in the coffee cup either gives the heat or accepts the heat of the reaction

$$Q = m \cdot c \cdot \Delta T \quad m = \text{mass of solution}$$



If 50.0 mL of 0.300 mol/L CuSO_4 is mixed with equal volume of 0.600 mol/L NaOH , initial temp = 21.4 °C
 final temp = 24.6 °C
 $\Delta H_r?$

sol'n:



STEP # 1 -

STEP # 2 -

STEP # 3 -

STEP # 4 -

STEP # 5 -

Enthalpy of Neutralization

Read Investigation 5-A on page 240 of the student textbook before answering the question below.

1. Following a procedure similar to the one outlined in Investigation 5-A, a student mixes a 25-mL sample of a 1.0 mol/L strong common dibasic acid $\text{H}_2\text{X}_{(\text{aq})}$ with 50 mL of 1.0 mol/L $\text{NaOH}_{(\text{aq})}$ in a coffee-cup calorimeter. Both solutions are initially at 25.0 °C. The temperature stabilizes at 33.9 °C.
 - (a) Determine ΔH_{rxn} for the neutralization reaction. Write a thermochemical equation for the reaction.
 - (b) List any assumptions that you made as you carried out your calculations.
 - (c) Indicate any safety measures that you would have to take if you carried out an investigation like this one.
 - (d) Draw a diagram representing the set-up of the investigation.

Answers

- 1.(a) $\text{H}_2\text{X}_{(\text{aq})} + 2\text{NaOH}_{(\text{aq})} \rightarrow \text{Na}_2\text{X}_{(\text{aq})} + 2\text{H}_2\text{O}_{(\text{l})}$
 $\Delta H = -1.1 \times 10^2 \text{ kJ/mol}$.
- (b) No heat is lost to the surroundings, no heat is absorbed by the calorimeter. The solutions have the same density and heat capacity as water.
- (c) Wear protective clothing such as glasses, gloves, and apron; avoid contact with corrosive acids and bases; if acid or base is spilled on skin, flush with plenty of cold water; dispose of all solutions as directed by your teacher.
- (d) Diagrams should show a coffee-cup calorimeter similar to the one shown on page 240 of the student textbook. Diagrams may also include a graduated cylinder and labelled beakers containing acid and base.

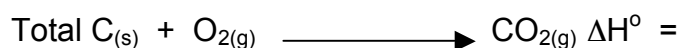
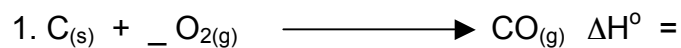
5.3 HESS'S LAW OF HEAT SUMMATION

"The enthalpy change of a physical or chemical process depends only on the beginning conditions (reactants) and the end conditions (products). The enthalpy change is independent of the pathway of the process and the number of intermediate steps in the process."

i.e.

e.g. formation of CO_2 from C and O_2 - 2 methods

Method A



Method B



- .

-

- 2 ways to determine ΔH_r

• 1

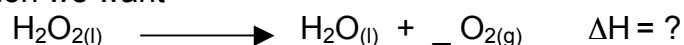
• 2.

COMBINING CHEMICAL EQUATIONS ALGEBRAICALLY:

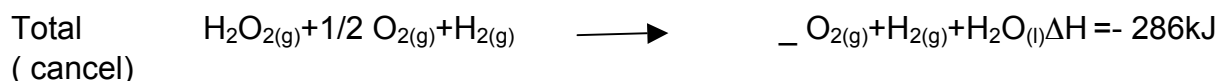
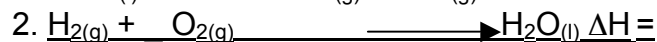
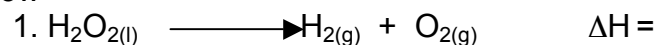
i.e.

e.g.

equation we want



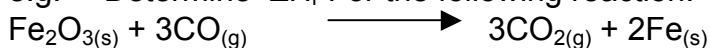
we know



-

-

e.g. Determine ΔH_r For the following reaction:



Given:



USING STANDARD MOLAR ENTHALPIES OF FORMATION

“Formation reaction” -

- Called standard molar enthalpy of formation, ΔH_f°

- “Standard state” means

- eg. O_2 or N_2 or Mg

$\Delta H_f = 0$ of graphite (according to definition)

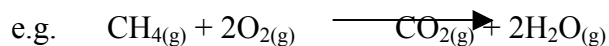
$\Delta H_f = 1.9 \text{ kJ/mol}$ for diamond



Practice p.251 #17 - 20

CALCULATING ENTHALPY CHANGES

$$\Delta H_r = \Sigma [\Delta H_f^\circ \text{ products}] - \Sigma [\Delta H_f^\circ \text{ reactants}]$$

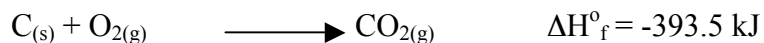


$$\Delta H_r^\circ = [\Delta H_f^\circ \text{CO}_{2(g)} + 2(\Delta H_f^\circ \text{H}_2\text{O})] - [\Delta H_f^\circ \text{CH}_{4(g)} + 2(\Delta H_f^\circ \text{O}_2)]$$

$$= [\quad \quad \quad] - [\quad \quad \quad]$$

$$= -$$

Compared with Hess's law: look at equation for formation of each compound.

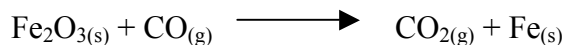


- don't worry about ΔH_f° of $\text{O}_{2(g)} = 0$

Total =

-
-
-

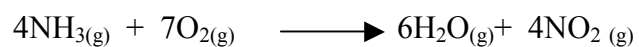
e.g. Iron (III) oxide reacts with carbon monoxide to produce elemental iron and carbon dioxide. Determine the ΔH_r° using enthalpies of formation.



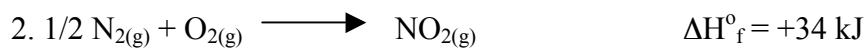
1. balance equation
2. use Appendix E for ΔH_f°
3. $\Delta H_r = \Sigma [\Delta H_f^\circ \text{ products}] - \Sigma [\Delta H_f^\circ \text{ reactants}]$
4. answer = -24.8 kJ

Practice p.254 #21-24

Determine ΔH_r for the following reaction using both methods:



Given:



Energy Assignment

1. When 1.32 g of sugar is burned in your body it produces 21.8 kJ of energy. If the formula of sucrose is $C_{12}H_{22}O_{11}$, calculate the heat of combustion $\Delta H_{\text{combustion}}$ in kJ/mol.

2. When 2.0 g of methanol is burned it raises the temperature of 250 mL of water by 8°C . Determine the heat of combustion, $\Delta H_{\text{combustion}}$ of methanol in kJ and kJ/mol.

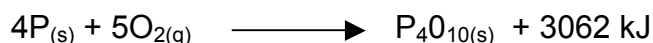
3. The heat of combustion of acetylene, C_2H_2 is $\Delta H_{\text{combustion}} = -1299 \text{ kJ/mol}$

a) What does the -ve sign tell you?

b) Write the thermal equation for the complete combustion of 2 moles of acetylene.

c) How much heat would 1 g of acetylene make?

4. Phosphorous was at one time used as chemical weapon, since it burned in the presence of air according to the following equation:



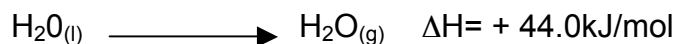
a) What sign would ΔH_{system} have for this reaction?

b) How much heat would be made by 8 moles of phosphorus?

c) How much heat would be made by 8 g of phosphorus?

d) How much phosphorus would be needed to make 1000 g of water warm up by 50°C (recall that the specific heat of water is $4.2 \text{ J/g}^{\circ}\text{C}$).

5. Maple syrup is made by evaporating the water from the sap and thereby leave the sugars behind. In fact it takes 40 litres of sap to make just 1 litre of maple syrup. The heat to evaporate the water is given by the equation.



Many modern syrup producers use propane to supply the heat needed to evaporate the unnecessary water. With the aid of the information below determine the mass of propane needed to make 1.0 litre of syrup.

density of water, $= 1.0 \text{ g/mL}$

there are 1000 mL in 1.0 litre

the heat of combustion of propane, $\Delta H_{\text{combustion}} = -2050 \text{ kJ/mol}$

1 mole of water has a mass of 18 g.

1 mole of propane has a mass of 44.0 g.

6. Late one evening in the back of room 127, Dr. Bebbly Decker has been synthesizing her new explosive for her independent study. After 3 hours she isolates 3.09 g of the precious compound. To determine its heat of reaction she places 245 mL of Varsol (she was out of water) in the coke can calorimeter. She lights the explosive and notices the temperature of the Varsol goes up by

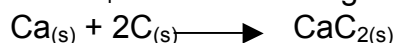
23.4 °C. Determine the ΔH , in kJ/mol, for this reaction given the following additional information:

Molar mass of the unknown = 218 g/mol

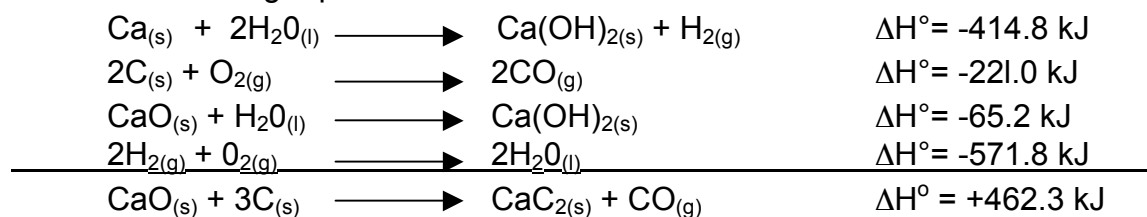
Density of Varsol = 0.872 g/mL

Specific heat of Varsol = 3.22 J/g°C

7. Determine the ΔH_f° for the following reaction:

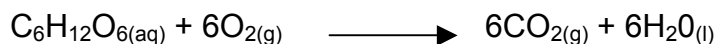


Given the following equations



8. Sugar, (glucose $\text{C}_6\text{H}_{12}\text{O}_{6(aq)}$ $\Delta H_f^\circ = -1256 \text{ kJ/mol}$), when entering our bodies has two choices. It can either be burned off in exercise or it can be stored as adipose tissue. The average 10 oz. (280 mL) can of cola contains 35 g of glucose and little else of energy value.

The reaction is:



a) Determine ΔH° for this reaction using the data in the question and the heats of formation table in your book.

b) How much energy would you get from 35 g of glucose?

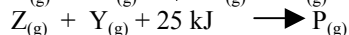
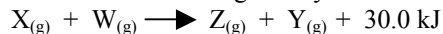
c) Watching a basketball game you burn off about 7 kJ/min, playing basketball you burn off about 110 kJ/min. How long would it take to use up the energy in one coke (Your choice of exercise)

Chapter 5 Practice Problems

1. The molar heat capacities of the elements $\text{Li}_{(s)}$ and $\text{Rb}_{(s)}$ are respectively $24.8 \text{ J/mol}\cdot^\circ\text{C}$ and $31.0 \text{ J/mol}\cdot^\circ\text{C}$.

- (a) Compare the heat absorbed by 1.00 g of each of these metals to increase the temperature by 1°C .
 (b) What mass of Rb is required to absorb the same amount of heat as 1.00 g of Li to achieve a temperature change of 1°C ?

2. Two reactions are given by the following equations:

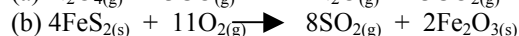
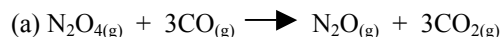


Find the ΔH° value for the reaction $\text{P}_{(g)} \longrightarrow \text{X}_{(g)} + \text{W}_{(g)}$.

3. When $\text{CO}_{2(s)}$ sublimates (changes directly from a solid to a gas) at -90°C , ΔH_{sub} is 16.20 kJ/mol . What is the mass of $\text{CO}_{2(s)}$ that must have undergone this process of sublimation if 186.0 kJ of heat is absorbed?

4. A calorimeter designed to have negligible heat loss is used to determine the specific heat capacity of metals. A piece of thallium having a mass of 111.2 g is warmed to 95.0°C and placed into the calorimeter containing 125.00 g of water at 12.5°C . The water temperature goes up to 14.9°C . Use this information to calculate the specific heat capacity of thallium. The specific heat capacity of water is $4.184 \text{ J/g}\cdot^\circ\text{C}$.

5. Use the data table of standard enthalpies of formation to help determine the enthalpy of reaction for each of the following reactions.

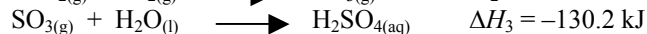
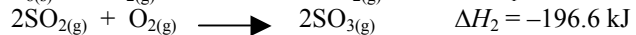
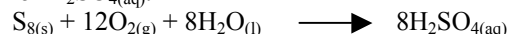


6. (a) Write the balanced equation for the complete combustion of glucose, $\text{C}_6\text{H}_{12}\text{O}_{6(s)}$, to form carbon dioxide gas and water (liquid).

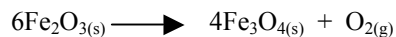
(b) When a 2.000 g sample of glucose is burned in a bomb calorimeter, the temperature of 200.00 g of water rises by 37.3°C . What is the molar enthalpy of combustion of glucose?

(c) Use the answers from (a) and (b) and the ΔH°_f values from the data table of standard enthalpies of formation to calculate the ΔH°_f value for glucose.

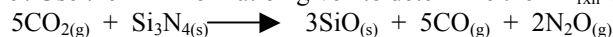
7. In the Contact process for the production of $\text{H}_2\text{SO}_{4(aq)}$, sulfur is burned to produce $\text{SO}_{2(g)}$. This gas is then converted to $\text{SO}_{3(g)}$ in the presence of a catalyst, and the resulting gas is dissolved in water to form the acid. The equations shown below summarize the process. Use this information to calculate the enthalpy of reaction, in kJ/mol , for the production of $\text{H}_2\text{SO}_{4(aq)}$.



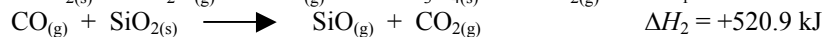
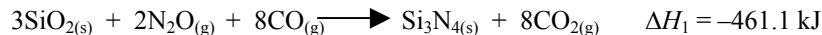
8. Determine the heat absorbed when a 5.00 g sample of $\text{Fe}_2\text{O}_{3(s)}$ undergoes the following reaction.



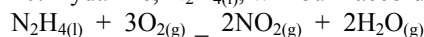
9. Use the ΔH information given to determine the ΔH_{rxn} value for the following reaction.



ΔH information:



10. Hydrazine, $\text{N}_2\text{H}_{4(l)}$, will burn according to the reaction equation below.



(a) Determine the ΔH_{comb} value for this reaction.

(b) Calculate the amount of heat that is given off when a 10.0 kg sample of 87.8% pure hydrazine is burned.

Answers

1.(a) Heat required to increase the temperature of 1.00 g of Li metal

$$= \frac{1 \text{ g}}{6.94 \text{ g/mol}} \cdot 24.8 \text{ J/mol} \cdot ^\circ\text{C} \cdot 1^\circ\text{C} = 3.57 \text{ J}$$

Heat required to increase the temperature of 1.00 g of Rb metal

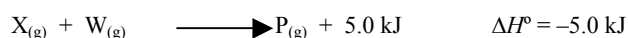
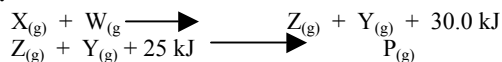
$$= \frac{1 \text{ g}}{85.478 \text{ g/mol}} \cdot 31.0 \text{ J/mol} \cdot ^\circ\text{C} \cdot 1^\circ\text{C} = 0.363 \text{ J}$$

(b) To achieve a temperature change of 1°C ,

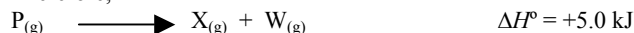
$$\frac{\text{Mass of Rb}}{1 \text{ g of Rb}} = \frac{3.57 \text{ J}}{0.363 \text{ J}}$$

$$\text{Mass of Rb} = 9.83 \text{ g of Rb}$$

2.



Therefore,



3.

$$n \text{ mol CO}_2 = \frac{\text{Mass of CO}_2}{44.01 \text{ g/mol}}$$

$$\frac{n \text{ mol CO}_2}{1 \text{ mol CO}_2} = \frac{186.0 \text{ kJ}}{16.20 \text{ kJ}}$$

$$n \text{ mol CO}_2 = 11.5 \text{ mol CO}_2$$

$$\frac{\text{Mass of CO}_2}{44.01 \text{ g/mol}} = 11.5 \text{ mol CO}_2$$

$$\text{Mass of CO}_2 = 506 \text{ g of CO}_2$$

4.

Heat lost by thallium = Heat gained by water

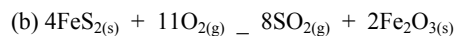
$$-m \cdot c \cdot \Delta T (\text{thallium}) = m \cdot c \cdot \Delta T (\text{water})$$

$$-(111.2 \text{ g})(c)(14.9^\circ\text{C} - 95.0^\circ\text{C}) = (125.00 \text{ g})(4.184 \text{ J/g} \cdot ^\circ\text{C})(14.9^\circ\text{C} - 12.5^\circ\text{C})$$

$$c = 0.14 \text{ J/g} \cdot ^\circ\text{C}$$

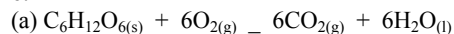
5.

$$\begin{aligned} \Delta H^\circ_{\text{rxn}} &= [\Delta H^\circ_f \text{N}_2\text{O}_{4(\text{g})} + 3\Delta H^\circ_f \text{CO}_{2(\text{g})}] - [\Delta H^\circ_f \text{N}_2\text{O}_{4(\text{g})} + 3\Delta H^\circ_f \text{CO}_{(\text{g})}] \\ &= [81.6 \text{ kJ/mol} + 3(-393.5 \text{ kJ/mol})] - [11.1 \text{ kJ/mol} + 3(-110.5 \text{ kJ/mol})] \\ &= -1441.5 \text{ kJ/mol of N}_2\text{O}_4 \end{aligned}$$



$$\begin{aligned} \Delta H^\circ_{\text{rxn}} &= [8\Delta H^\circ_f \text{SO}_{2(\text{g})} + 2\Delta H^\circ_f \text{Fe}_2\text{O}_{3(\text{s})}] - [4\Delta H^\circ_f \text{FeS}_{2(\text{s})} + 11\Delta H^\circ_f \text{O}_{2(\text{g})}] \\ &= [8(-296.8 \text{ kJ/mol}) + 2(-824.2 \text{ kJ/mol})] - [4(-178.2 \text{ kJ/mol}) + 11(0 \text{ kJ/mol})] \\ &= -3310 \text{ kJ/4 mol of FeS}_2 \\ &= -827.5 \text{ kJ/mol of FeS}_2 \end{aligned}$$

6.



(b) Heat gained by water = $m \cdot c \cdot \Delta T$ (water)

$$= (200.00 \text{ g})(4.184 \text{ J/g} \cdot ^\circ\text{C})(37.3^\circ\text{C})$$

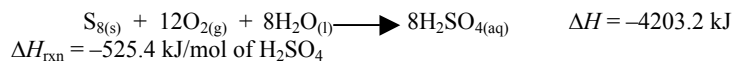
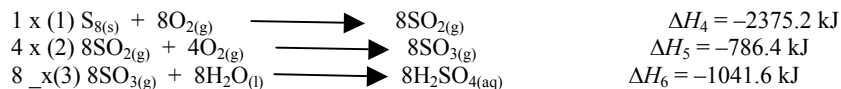
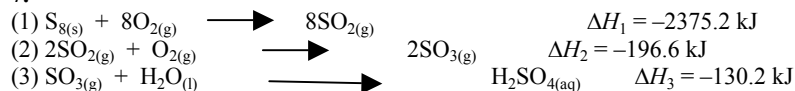
$$= 31.2 \text{ kJ}$$

$$n \text{ mol C}_6\text{H}_{12}\text{O}_6 = \frac{2.000 \text{ g}}{180.18 \text{ g/mol}} = 0.01110 \text{ mol}$$

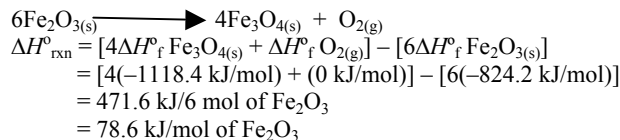
$$\Delta H^\circ_{\text{comb}} = \frac{-31.2 \text{ kJ}}{0.01110 \text{ mol}} = -2.81 \times 10^3 \text{ kJ/mol}$$

$$\begin{aligned} (c) \Delta H^\circ_{\text{comb}} &= [6\Delta H^\circ_f \text{CO}_{2(\text{g})} + 6\Delta H^\circ_f \text{H}_2\text{O}_{(\text{l})}] - [\Delta H^\circ_f \text{C}_6\text{H}_{12}\text{O}_{6(\text{s})} + 6\Delta H^\circ_f \text{O}_{2(\text{g})}] \\ -2.81 \times 10^3 \text{ kJ/mol} &= [6(-393.5 \text{ kJ/mol}) + 6(-285.8 \text{ kJ/mol})] - [\Delta H^\circ_f \text{C}_6\text{H}_{12}\text{O}_{6(\text{s})} + 6(0 \text{ kJ/mol})] \\ \Delta H^\circ_f \text{C}_6\text{H}_{12}\text{O}_{6(\text{s})} &= -1270 \text{ kJ/mol} \end{aligned}$$

7.



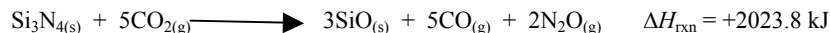
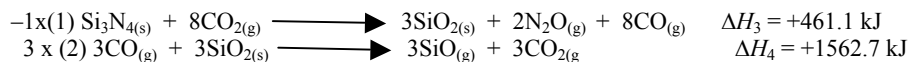
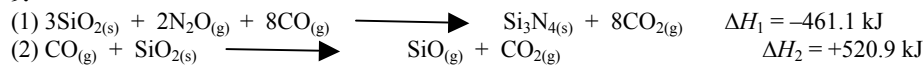
8.



$$n \text{ mol Fe}_2\text{O}_3 = \frac{5.00 \text{ g}}{159.7 \text{ g/mol}} = 0.0313 \text{ mol}$$

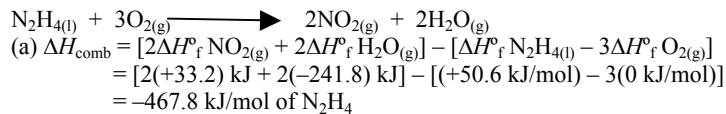
Heat absorbed by 5.00 g sample = 0.0313 mol x 78.6 kJ/mol = 2.46 kJ

9.



$$\Delta H_{\text{rxn}} = +2023.8 \text{ kJ/mol of Si}_3\text{N}_4$$

10.



(b) Mass of $\text{N}_2\text{H}_{4(l)} = 10.0 \text{ kg} \times 87.8 \% = 8.78 \text{ kg}$

$$n \text{ mol N}_2\text{H}_4 = \frac{8.78 \text{ kg}}{32.06 \text{ g/mol}} = 274 \text{ mol of N}_2\text{H}_4$$

Heat given off by the 10.0 kg sample = 274 mol x 467.8 kJ/mol = 1.28 x 10⁵ kJ