Chemistry 2e 5: Thermochemistry 5.1: Energy Basics

1. A burning match and a bonfire may have the same temperature, yet you would not sit around a burning match on a fall evening to stay warm. Why not?

Solution

The temperature of 1 gram of burning wood is approximately the same for both a match and a bonfire. This is an intensive property and depends on the material (wood). However, the overall amount of produced heat depends on the amount of material; this is an extensive property. The amount of wood in a bonfire is much greater than that in a match; the total amount of produced heat is also much greater, which is why we can sit around a bonfire to stay warm, but a match would not provide enough heat to keep us from getting cold.

3. Explain the difference between heat capacity and specific heat of a substance. Solution

Heat capacity refers to the heat required to raise the temperature of the mass of the substance 1 degree; specific heat refers to the heat required to raise the temperature of 1 gram of the substance 1 degree. Thus, heat capacity is an extensive property, and specific heat is an intensive one.

5. Calculate the heat capacity, in joules and in calories per degree, of the following:

(a) 45.8 g of nitrogen gas

(b) 1.00 pound of aluminum metal

Solution

(a)
$$45.8 \text{ g} \times 1.04 \text{ J/g}^{\circ}\text{C} = 47.6 \text{ J/}^{\circ}\text{C}; 45.8 \text{ g} \quad 1.04 \text{ J} \frac{\text{g}^{-1}}{\text{g}^{-1}} \, ^{\circ}\text{C}^{-1} \quad \frac{1 \text{ cal}}{4.184 \text{ J}} = 11.38 \text{ J} \, ^{\circ}\text{C}^{-1};$$
 (b) $454 \text{ g} \times 0.897 \text{ J/g} \, ^{\circ}\text{C} = 407 \text{ J/}^{\circ}\text{C}; 454 \text{ g} \times 0.897 \text{ J} \frac{\text{g}^{-1}}{\text{g}^{-1}} \, ^{\circ}\text{C}^{-1} \times \frac{1 \text{ cal}}{4.184 \text{ J}} = 97.3 \text{ cal} \, ^{\circ}\text{C}^{-1}$

7. How much heat, in joules and in calories, is required to heat a 28.4-g (1-oz) ice cube from -23.0 °C to -1.0 °C?

Solution

 $q = cm\Delta T$; $q = 2.093 \text{ J/g} \circ \text{C} \times 28.4 \text{ g} \times [-1 - (-23)] \circ \text{C} = 1308 \text{ J}$ (or 1310 with the correct number of significant digits); the conversion factor is 4.184 J = 1 cal; 1308 J × 1 cal / 4.184 J = 312.6 cal (313 calories with the correct number of significant digits)

9. If 14.5 kJ of heat were added to 485 g of liquid water, how much would its temperature increase?

Solution

 $q = cm\Delta T$

14,500 J = 4.184 J g⁻¹ °C ×4.85 ×10² g × ΔT

 $\Delta T = \frac{14,500 \text{ °C}}{4.184 \times 4.85 \times 10^2} = 7.15 \text{ °C}$

11. A piece of unknown solid substance weighs 437.2 g, and requires 8460 J to increase its temperature from 19.3 °C to 68.9 °C.

(a) What is the specific heat of the substance?

(b) If it is one of the substances found in Table 5.1, what is its likely identity? Solution

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(a) $q = cm\Delta T$, $c = q/(m\Delta T) = 8460 \text{ J} / [437.2 \text{ g} (68.9 - 19.3) ^{\circ}\text{C}] = 0.390 \text{ J/g }^{\circ}\text{C}$; (b) Copper is a likely candidate.

13. Most people find waterbeds uncomfortable unless the water temperature is maintained at about 85°F. Unless it is heated, a waterbed that contains 892 L of water cools from 85 °F to 72 °F in 24 hours. Estimate the amount of electrical energy required over 24 hours, in kWh, to keep the bed from cooling. Note that 1 kilowatt-hour (kWh) = 3.6×10^6 J, and assume that the density of water is 1.0 g/mL (independent of temperature). What other assumptions did you make? How did they affect your calculated result (i.e., were they likely to yield 'positive' or 'negative' errors)?

Solution

We assume that the density of water is $1.0 \text{ g/cm}^3(1 \text{ g/mL})$ and that it takes as much energy to keep the water at 85 °F as to heat it from 72 °F to 85 °F. We also assume that only the water is going to be heated. First, find the mass of water in the bed. The volume is 72 in. × 84 in. × 9 in.

= 54,432 in.³
$$\left(\frac{2.54 \text{ cm}}{1 \text{ in.}}\right)^3$$
 = 8.9 × 10⁵ cm³ \longrightarrow 8.9 × 10⁵ g;

second, convert the change of 13 °F to °C:

$$q = cm\Delta T = 4.184 \text{ J/g °C}(8.92 \times 10^5 \text{ g}) \times 7.22 \text{ °C}$$

°C = $\frac{5}{9}$ °F = $\frac{5}{9} \times 13 = 7.22 \text{ °C}$
= 2.69 × 10⁷ J
Energy required = $\frac{2.689 \times 10^7 \text{ J}}{3.6 \times 10^6 \text{ kWh}^{-1}} = 7.47 \text{ kWh}$

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Chemistry 2e 5: Thermochemistry 5.2: Calorimetry

15. Would the amount of heat measured for the reaction in Example 5.5 be greater, lesser, or remain the same if we used a calorimeter that was a poorer insulator than a coffee cup calorimeter? Explain your answer.

Solution

lesser; more heat would be lost to the coffee cup and the environment and so ΔT for the water would be lesser and the calculated *q* would be lesser

17. Would the amount of heat absorbed by the dissolution in Example 5.6 appear greater, lesser, or remain the same if the heat capacity of the calorimeter were taken into account? Explain your answer.

Solution

greater, since taking the calorimeter's heat capacity into account will compensate for the thermal energy transferred to the solution from the calorimeter; this approach includes the calorimeter itself, along with the solution, as "surroundings:" $q_{rxn} = -(q_{solution} + q_{calorimeter})$; since both $q_{solution}$ and $q_{calorimeter}$ are negative, including the latter term (q_{rxn}) will yield a greater value for the heat of the dissolution

19. How much will the temperature of a cup (180 g) of coffee at 95 °C be reduced when a 45-g silver spoon (specific heat 0.24 J/g °C) at 25 °C is placed in the coffee and the two are allowed to reach the same temperature? Assume that the coffee has the same density and specific heat as water.

Solution

Because of the law of conservation of energy, we write:

 $q_{\text{spoon}} + q_{\text{coffee}} = 0; q_{\text{spoon}} = -q_{\text{coffee}}$

 $c_{\text{spoon}} \times m_{\text{spoon}} \times \Delta T = -c_{\text{coffee}} \times m_{\text{coffee}} \times \Delta T$

 $0.24 \text{ J/g} \,^{\circ}\text{C} \times 45 \text{ g} \times (T_{\text{f}} - 25 \,^{\circ}\text{C}) = 4.184 \text{ J/g} \,^{\circ}\text{C} \times 180 \text{ g} \times (T_{\text{f}} - 95 \,^{\circ}\text{C})$

$$10.8T_{\rm f} - 270 = -753.1T_{\rm f} + 71546.4$$

763.9 $T_{\rm f} = 71816.4$

 $T_{\rm f} = 94$ °C.

The temperature of the coffee will drop 1 degree.

21. The temperature of the cooling water as it leaves the hot engine of an automobile is 240 °F. After it passes through the radiator it has a temperature of 175 °F. Calculate the amount of heat transferred from the engine to the surroundings by one gallon of water with a specific heat of 4.184 J/g °C.

Solution

First, find the change in temperature of the water in °C:

 $240 \ ^{\circ}F - 175 \ ^{\circ}F = 65 \ ^{\circ}F.$

We are concerned here only with the difference between temperatures and not the conversion from one temperature to the corresponding temperature.

$$^{\circ}C = \frac{5}{9} (^{\circ}F) = \frac{5}{9} (65) = 36.1 \ ^{\circ}C$$

Assuming 1 mL of water has a mass of 1 g, 1.0 gal of water has a mass of:

$$1.0 \text{ gal} \times \frac{4 \text{ qt}}{1 \text{ gal}} \times \frac{0.9463 \text{ L}}{1 \text{ qt}} \times 1000 \text{ g} = 3785 \text{ g}$$

 $q = cm\Delta T = 4.184 \text{ J/g} \,^{\circ}\text{C} \times 3758 \text{ g} \times 36.1 \,^{\circ}\text{C}$

$= 5.7 \times 10^2 \text{ kJ}.$

23. If a reaction produces 1.506 kJ of heat, which is trapped in 30.0 g of water initially at 26.5 °C in a calorimeter like that in Figure 5.12, what is the resulting temperature of the water? Solution

 $q = cm\Delta T = 4.184 \text{ J/g} ^{\circ}\text{C} \times 30.0 \text{ g} \times (T_{\text{f}} - 26.5 ^{\circ}\text{C}) = 1506 \text{ J}$ $T_{\text{f}} - 26.5 ^{\circ}\text{C} = 1506 \text{ J} / (4.184 \text{ J/g}^{\circ} \text{ C} \times 30.0 \text{ g}) = 12.0 ^{\circ}\text{C}$ $T_{\text{f}} = 26.5 ^{\circ}\text{C} + 12.0 ^{\circ}\text{C} = 38.5 ^{\circ}\text{C}$

25. Dissolving 3.0 g of $CaCl_2(s)$ in 150.0 g of water in a calorimeter (Figure 5.12) at 22.4 °C causes the temperature to rise to 25.8 °C. What is the approximate amount of heat involved in the dissolution, assuming the heat capacity of the resulting solution is 4.18 J/g °C? Is the reaction exothermic or endothermic?

Solution

Assume that the mass of the added CaCl₂ in solution must be added to the mass of the water: $q_{\text{reaction}} + q_{\text{solution}} = 0$

 $q_{\text{reaction}} = q_{\text{solution}}$ $q_{\text{solution}} = cm\Delta T$ $= 4.18 \text{ J/g }^{\circ}\text{C} \times 153.0 \text{ g} \times (25.8 - 22.4) \text{ }^{\circ}\text{C} = 2200 \text{ J}$ = -2.2 kJ.

The heat produced shows that the reaction is exothermic.

27. The addition of 3.15 g ofBa(OH)₂·8H₂O to a solution of 1.52 g of NH₄SCN in 100 g of water in a calorimeter caused the temperature to fall by 3.1 °C. Assuming the specific heat of the solution and products is 4.20 J/g°C, calculate the approximate amount of heat absorbed by the reaction, which can be represented by the following equation:

$$Ba(OH)_2BH_2O(s) + 2NH_4SCN(aq) \longrightarrow Ba(SCN)_2(aq) + 2NH_3(aq) + 10H_2O(l)$$

Solution

 $q = cm\Delta T$

 $= 4.20 \text{ J/g} \circ \text{C} \times (3.15 + 1.52 + 100) \text{ g} \times 3.1 \circ \text{C}$

= 1362.8 J = 1.4 kJ (two significant figures)

29. If the 3.21 g of NH₄NO₃ in Example 5.6 were dissolved in 100.0 g of water under the same conditions, how much would the temperature change? Explain your answer.

Solution

The heat of the reaction would be approximately the same as before or 1.0×10^3 J. The reaction is endothermic, and the temperature would decrease:

 $q_{\rm rxn} = -q_{\rm soln} = -(c \times m \times \Delta T)_{\rm soln}$

 $-(4.18 \text{ J/g}^{\circ} \text{ C}) \times (103.2 \text{ g}) \times (T_{\text{f}} - 24.9 \text{ }^{\circ}\text{C}) = 1000 \text{ J}$ $T_{\text{f}} - 24.9 \text{ }^{\circ}\text{C} = -2.3 \text{ }^{\circ}\text{C}$

 $T_{\rm f}$ = 22.6. Since the mass and the heat capacity of the solution is approximately equal to that of the water, the two-fold increase in the amount of water leads to a two-fold decrease of the temperature change.

31. When a 0.740-g sample of trinitrotoluene (TNT), $C_7H_5N_2O_6$, is burned in a bomb calorimeter, the temperature increases from 23.4 °C to 26.9 °C. The heat capacity of the calorimeter is 534 J/°C, and it contains 675 mL of water. How much heat was produced by the combustion of the TNT sample? Solution

The heat absorbed by the calorimeter is $q_1 = 534 \text{ J/°C} \times (26.9 \text{ °C} - 23.4 \text{ °C}) = 1869 \text{ J}$. The heat absorbed by water is $q_1 = 675 \text{ mL} \times 0.997 \text{ g/mL} \times 4.184 \text{ J/g} \text{ °C} \times (26.9 \text{ °C} - 23.4 \text{ °C}) = 9855 \text{ J}$. The overall amount of heat $q = q_1 + q_1 = 11,724 \text{ J}$ or 11.7 kJ with three significant digits. 33. The amount of fat recommended for someone with a daily diet of 2000 Calories is 65 g. What percent of the calories in this diet would be supplied by this amount of fat if the average number of Calories for fat is 9.1 Calories/g? Solution

Energy released by burning fat is: $65 \text{ g} \times 9.1 \text{ Calories/g} = 5.9 \times 10^2 \text{ Calories}$ % Calories from fat = $5.9 \times 10^2 \text{ Calories/2000 Calories} \times 100\%$ = 30% (one significant figure).

35. What is the maximum mass of carbohydrate in a 6-oz serving of diet soda that contains less than 1 Calorie per can if the average number of Calories for carbohydrates is 4.1 Calories/g? Solution

The average energy from carbohydrates is 4.1 kcal/g (4.1 Calories/g). The drink cannot contain 1 Calorie = 0.24 g

more than $\frac{1 \text{ Calorie}}{4.1 \text{ Calorie g}^{-1}} = 0.24 \text{ g}$.

37. A serving of a breakfast cereal contains 3 g of protein, 18 g of carbohydrates, and 6 g of fat. What is the Calorie content of a serving of this cereal if the average number of Calories for fat is 9.1 Calories/g, for carbohydrates is 4.1 Calories/g, and for protein is 4.1 Calories/g?

Solution

Protein: 3 g \times 4.1 Calories/g	12.3 Calories
Carbohydrates: 18 g \times 4.1 Calories/g	73.8 Calories
Fat: 6 g \times 9.1 Calories/g	54.6 Calories
	140.7 Calories

Total = 1.4×10^2 Calories

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Chemistry 2e 5: Thermochemistry 5.3: Enthalpy

39. Explain how the heat measured in Example 5.5 differs from the enthalpy change for the exothermic reaction described by the following equation:

 $\text{HCl}(aq) + \text{NaOH}(aq) \longrightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l)$

Solution

The enthalpy change of the indicated reaction is for exactly 1 mol HCL and 1 mol NaOH; the heat in the example is produced by 0.0500 mol HCl and 0.0500 mol NaOH.

41. Calculate the enthalpy of solution (ΔH for the dissolution) per mole of NH₄NO₃ under the conditions described in Example 5.6.

Solution

The molar mass of NH₄NO₃ is 80.0423 g/mol. From the example, 1000 J is required to dissolve 3.21 g of NH₄NO₃. One mole under the same conditions would require

 $\frac{80.0432 \text{ g mol}^{-1}}{3.21 \text{ g}} \times 1000 \text{ J} = 25 \text{ kJ mol}^{-1}.$

(The heat of solution is positive because the process is endothermic.)

43. Calculate the enthalpy of solution (ΔH for the dissolution) per mole of CaCl₂ (refer to Exercise 25).

Solution

The molar mass of CaCl₂ is 40.078 + 2(35.4572) = 110.992 g/mol. In Exercise 25, 3.0 g of CaCl₂ dissolved in water releases a heat of 2.2 kJ. Therefore,

$$\frac{3.0 \text{ g}}{110.992 \text{ g} \text{ mol}^{-1}} = 0.027 \text{ mol}$$
$$\frac{2.2 \text{ kJ}}{0.027 \text{ mol}} = 81 \text{ kJ mol}^{-1}$$

45. How much heat is produced by burning 4.00 moles of acetylene under standard state conditions?

Solution

The heat of combustion is -1301.1 as given in Table 5.2.

Heat released = $4.00 \text{ mol} \times (-1301.1 \text{ kJ/mol}) = 5204.4 \text{ kJ}$

47. How many moles of isooctane must be burned to produce 100 kJ of heat under standard state conditions?

Solution

The value of $\Delta H_{\text{comb}} = -5461 \text{ kJ/mol}$. To produce 100 kJ requires:

$$\frac{100 \text{ kJ}}{54511 \text{ J}} = 1.83 \times 10^{-2} \text{ mol.}$$

5461 kJ mol⁻¹

49. When 2.50 g of methane burns in oxygen, 125 kJ of heat is produced. What is the enthalpy of combustion per mole of methane under these conditions?

Solution

The molar mass of CH₄ is 16.04 g/mol.

Find the mole of CH₄ present: $\frac{2.50 \text{ g}}{16.04 \text{ g} \text{ mol}^{-1}} = 0.15586 \text{ mol}$

 $\Delta H_{\rm comb} = -\frac{125 \text{ kJ}}{0.15586 \text{ mol}} = -802 \text{ kJ mol}^{-1}.$

51. A sample of 0.562 g of carbon is burned in oxygen in a bomb calorimeter, producing carbon dioxide. Assume both the reactants and products are under standard state conditions, and that the heat released is directly proportional to the enthalpy of combustion of graphite. The temperature of the calorimeter increases from 26.74 °C to 27.93 °C. What is the heat capacity of the calorimeter and its contents?

Solution

The heat produced is found from the enthalpy of combustion:

$$\frac{0.562 \text{ g}}{-1} \approx -393.5 \text{ kJ mol}^{-1} = -18.4 \text{ kJ}.$$

12.011 g mol⁻¹ <u></u>℃

This is the heat released.

 $q = \text{heat capacity} \times \Delta T$

18.4 kJ = heat capacity \times (27.93 °C – 26.74 °C) = specific heat \times 1.19 °C specific heat = 15.5 kJ/°C

53. Homes may be heated by pumping hot water through radiators. What mass of water will provide the same amount of heat when cooled from 95.0 to 35.0 °C, as the heat provided when 100 g of steam is cooled from 110 °C to 100 °C.

Solution

$$m_{\rm water} = \frac{100 + 3}{251.04 \text{ J/g}} = 7.43 \text{ g}.$$

55. Does the standard enthalpy of formation of $H_2O(g)$ differ from ΔH° for the reaction $2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$?

Solution

Yes. The heat of this reaction is defined for 2 moles of $H_2O(g)$, thus the heat of formation is half of the heat of the reaction.

57. How many kilojoules of heat will be released when exactly 1 mole of manganese, Mn, is burned to form $Mn_3O_4(s)$ at standard state conditions?

Solution

This process requires 3 mol of Mn. For 1 mol, $\frac{1}{3}(-1378.83 \text{ kJ}) = 459.6 \text{ kJ}$.

59. The following sequence of reactions occurs in the commercial production of aqueous nitric acid:

 $4\mathrm{NH}_{3}(g) + 5\mathrm{O}_{2}(g) \longrightarrow 4\mathrm{NO}(g) + 6\mathrm{H}_{2}\mathrm{O}(l) \qquad \Delta H = -907 \text{ kJ}$ $2\mathrm{NO}(g) + \mathrm{O}_{2}(g) \longrightarrow 2\mathrm{NO}_{2}(g) \qquad \Delta H = -113 \text{ kJ}$ $3\mathrm{NO}_{2} + \mathrm{H}_{2}\mathrm{O}(l) \longrightarrow 2\mathrm{HNO}_{3}(aq) + \mathrm{NO}(g) \qquad \Delta H = -139 \text{ kJ}$

Determine the total energy change for the production of one mole of aqueous nitric acid by this process.

Solution

First, appropriately sum these three equations to yield a balanced equation for the overall reaction. Although fractional coefficients may be used in thermochemical calculations such as this, the approach shown here uses the smallest possible integer coefficients:

 $3 \times [4\mathrm{NH}_{3}(g) + 5\mathrm{O}_{2}(g) \longrightarrow 4\mathrm{NO}(g) + 6\mathrm{H}_{2}\mathrm{O}(l)] \qquad \Delta H = (3)(-907 \text{ kJ}) = -2721 \text{ kJ}$ $6 \times [2\mathrm{NO}(g) + \mathrm{O}_{2}(g) \longrightarrow 2\mathrm{NO}_{2}(g)] \qquad \Delta H = (6)(-113 \text{ kJ}) = -678 \text{ kJ}$ $4 \times [3\mathrm{NO}_{2}(g) + \mathrm{H}_{2}\mathrm{O}(l) \longrightarrow 2\mathrm{HNO}_{3}(aq) + \mathrm{NO}(g) \qquad \Delta H = (4)(-139 \text{ kJ}) = -556 \text{ kJ}$ $12\mathrm{NH}_{3}(g) + 21\mathrm{O}_{2}(g) \longrightarrow 8\mathrm{HNO}_{3}(aq) + 14\mathrm{H}_{2}\mathrm{O}(l) + 4\mathrm{NO}(g) \qquad \Delta H = -3955 \text{ kJ}$

The energy change shown is for production of 8 moles of aqueous nitric acid; therefore, production of 1 mole is

(1/8)(-3995 kJ) = -494 kJ.

61. From the molar heats of formation in Appendix G, determine how much heat is required to evaporate one mole of water: $H_2O(l) \longrightarrow H_2O(g)$

Solution

The heat of formation of $H_2O(l)$ is -285.83 kJ/mol. The heat of formation of $H_2O(g)$ is -241.82 kJ/mol. For the reaction:

 $H_2O(l) \longrightarrow H_2O(g)$,

the enthalpy of the reaction is the difference of heats of formation of the reactant and the product; thus, it is -241.82 - (-285.83) = 44.01 kJ/mol.

63. Calculate ΔH° for the process

$$\mathrm{Sb}(s) + \frac{5}{2}\mathrm{Cl}_2(g) \longrightarrow \mathrm{Sb}\mathrm{Cl}_5(g)$$

from the following information:

$$Sb(s) + \frac{3}{2}Cl_{2}(g) \longrightarrow SbCl_{3}(s) \qquad \Delta H^{\circ} = -314 \text{ kJ}$$
$$SbCl_{3}(s) + Cl_{2}(g) \longrightarrow SbCl_{5}(s) \qquad \Delta H^{\circ} = -80 \text{ kJ}$$

Solution

Add the two equations and their heat together.

$$Sb(s) + \frac{3}{2}Cl_{2}(g) \longrightarrow SbCl_{3}(g) \qquad \Delta H^{\circ} = -314 \text{ kJ}$$

$$\frac{SbCl_{3}(s) + Cl_{2}(g) \longrightarrow SbCl_{5}(s)}{Sb(s) + \frac{5}{2}Cl_{2}(g) \longrightarrow SbCl_{5}(s)} \qquad \Delta H^{\circ} = -394 \text{ kJ}$$

65. Calculate ΔH for the process Hg₂Cl₂(s) \longrightarrow 2Hg(l) + Cl₂(g)

from the following information:

$$Hg(l) + Cl_{2}(g) \longrightarrow HgCl_{2}(s) \qquad \Delta H = -224 \text{ kJ}$$

$$Hg(l) + HgCl_{2}(s) \longrightarrow Hg_{2}Cl_{2}(s) \qquad \Delta H = -41.2 \text{ kJ}$$

Solution

Reverse the direction of both equations and add the new equations and enthalpies.

$$\begin{split} & \text{HgCl}_2(s) \longrightarrow \text{Hg}(l) + \text{Cl}_2(l) & \Delta H = 224 \text{ kJ} \\ & \underline{\text{Hg}_2\text{Cl}_2(s)} \longrightarrow \text{Hg}(l) + \text{HgCl}_2(s) & \underline{\Delta H} = 41.2 \text{ kJ} \\ & \overline{\text{Hg}_2\text{Cl}_2(s)} \longrightarrow 2\text{Hg}(l) + \text{Cl}_2(g) & \Delta H = 265 \text{ kJ} \end{split}$$

67. Calculate the standard molar enthalpy of formation of NO(g) from the following data:

 $N_{2}(g) + 2O_{2}(g) \longrightarrow 2NO_{2}(g) \qquad \Delta H^{\circ} = 66.4 \text{ kJ}$ $2NO(g) + O_{2}(g) \longrightarrow 2NO_{2}(g) \qquad \Delta H^{\circ} = -114.1 \text{ kJ}$

Solution

Hess's law can be applied to the two equations by reversing the direction of the second equation. The first equation is a formation reaction and is so indicated by writing ΔH° .

$$\begin{split} N_{2}(g) &+ 2O_{2}(g) \longrightarrow 2NO_{2}(g) & \Delta H^{\circ} &= 66.4 \text{ kJ} \\ 2NO_{2}(g) \longrightarrow 2NO(g) &+ O_{2}(g) & \Delta H^{\circ} &= 114.1 \text{ kJ} \\ \text{Adding the equations yields: } N_{2}(g) &+ O_{2}(g) \longrightarrow 2NO(g) & \Delta H^{\circ} &= 180.5 \text{ kJ} \,. \end{split}$$
This is the heat of formation of 2 mol of NO. For 1 mol,

$$180.5 \text{ kJ} \,. \end{split}$$

$$\Delta H^{\circ} = \frac{180.5 \text{ kJ}}{2} = 90.3 \text{ kJ/mol of NO}.$$

69. Using the data in Appendix G, calculate the standard enthalpy change for each of the following reactions:

(a) Si(s) + 2F₂(g)
$$\longrightarrow$$
 SiF₄(g)
(b) 2C(s) + 2H₂(g) + O₂(g) \longrightarrow CH₃CO₂H(l)
(c) CH₄(g) + N₂(g) \longrightarrow HCN(g) + NH₃(g)
(d) CS₂(g) + 3Cl₂(g) \longrightarrow CCl₄(g) + S₂Cl₂(g)
Solution
(a)
Si(s) + 2F₂(g) \longrightarrow SiF₄(g)
 $\Delta H^{\circ}_{reaction} = \Delta H^{\circ}_{products} - \Delta H^{\circ}_{reactants}$
 $= \Delta H^{\circ}_{SiF_4(g)} - \Delta H^{\circ}_{Si(s)} - 2\Delta H^{\circ}_{F_2(g)}$;
 $= -1614.9 - (0) - 2(0) = -1615.0 \text{ kJ mol}^{-1}$
 $2C(s) + 2H_2(g) + O_2(g) \longrightarrow$ CH₃CO₂H(l)
 $\Delta H^{\circ}_{reaction} = \Delta H^{\circ}_{products} - \Delta H^{\circ}_{reactants}$
 $= \Delta H^{\circ}_{CH_3CO_2H(l)} - 2\Delta H^{\circ}_{C(s)} - 2\Delta H^{\circ}_{H_2(g)} - \Delta H^{\circ}_{O_2(g)}$;
 $= -484.5 - 2(0) - 2(0) - (0) = -484.3 \text{ kJ mol}^{-1}$
CH₄(g) \longrightarrow C(s) + 2H₂(g) \longrightarrow HCN(g) $\Delta H^{\circ}_2 = 135.5 \text{ kJ}$
 $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow$ HCN(g) $\Delta H^{\circ}_3 = -45.9 \text{ kJ}$
 $\Delta H^{\circ}_3 = -45.9 \text{ kJ}$

	$\operatorname{CS}_2(g) \longrightarrow \operatorname{C}(s) + 2\operatorname{S}(s)$	$\Delta H_1^{\rm o} = -(116.9 \text{ kJ})$
(4)	$\mathbf{C}(s) + 2\mathbf{Cl}_2(g) \longrightarrow \mathbf{CCl}_4(g)$	$\Delta H_2^{\rm o} = -95.7 \text{ kJ}$
(u)	$C(s) + 2Cl_2(g) \longrightarrow CCl_4(g)$ $\underline{2S(s) + Cl_2(g) \longrightarrow S_2Cl_2(g)}$	$\Delta H_3^{\rm o} = -19.50 \text{ kJ}$
	$\operatorname{CS}_2(g) + \operatorname{3Cl}_2(g) \longrightarrow \operatorname{CCl}_4(g) + \operatorname{S}_2\operatorname{Cl}_2(g)$	$\Delta H^{\circ} = -232.1 \text{ kJ}$

71. The decomposition of hydrogen peroxide, H_2O_2 , has been used to provide thrust in the control jets of various space vehicles. Using the data in Appendix G, determine how much heat is produced by the decomposition of exactly 1 mole of H_2O_2 under standard conditions.

 $2H_2O_2(l) \longrightarrow 2H_2O(g) + O_2(g)$

Solution

$$\Delta H_{\text{reaction}}^{\circ} = \Delta H_{\text{products}}^{\circ} - \Delta H_{\text{reactants}}^{\circ}$$

= $2\Delta H_{\text{H}_2\text{O}(g)}^{\circ} + \Delta H_{\text{O}_2(g)}^{\circ} - 2\Delta H_{\text{H}_2\text{O}_2(l)}^{\circ}$
= $2(-241.82) + 0 - 2(-187.78) = -108.08 \text{ k}.$

The value relates to the decomposition of 2 mol of hydrogen peroxide. For 1 mol, $\frac{-108.0}{2} = -54.04 \text{ kJ mol}^{-1}.$

73. Calculate the enthalpy of combustion of butane, $C_4H_{10}(g)$ for the formation of $H_2O(g)$ and $CO_2(g)$. The enthalpy of formation of butane is -126 kJ/mol.

Solution

Step 1:
$$4[C(s) + O_2(g) \longrightarrow CO_2(g)]$$

 $\Delta H^\circ = 4(-394 \text{ kJ mol}^{-1})$
Step 2: $5[H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)]$
 $\Delta H^\circ = 5(-242 \text{ kJ mol}^{-1})$
Step 3: $\underline{C_4H_{10}} \longrightarrow 4C(s) + 5H_2(g)$
Sum: $C_4H_{10} + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l)$
 $\Delta H^\circ = -2660 \text{ kJ mol}^{-1}$

75. The white pigment TiO₂ is prepared by the reaction of titanium tetrachloride, TiCl₄, with water vapor in the gas phase: TiCl₄(g) + 2H₂O(g) \longrightarrow TiO₂(s) + 4HCl(g).

How much heat is evolved in the production of exactly 1 mole of $TiO_2(s)$ under standard state conditions?

Solution $TiCl_{4}(g) \longrightarrow Ti(s) + 2Cl_{2}(g) \qquad \Delta H_{1}^{\circ} = -(-763.2 \text{ kJ})$ $2H_{2}O(g) \longrightarrow 2H_{2}(g) + O_{2}(s) \qquad \Delta H_{2}^{\circ} = -2(-241.82 \text{ kJ}) = 483.6 \text{ kJ}$ $Ti(s) + O_{2}(g) \longrightarrow TiO_{2}(s) \qquad \Delta H_{3}^{\circ} = -944.7 \text{ kJ}$ $\frac{2H_{2}(g) \longrightarrow 2Cl_{2}(g) + 4HCl(s)}{TiCl_{4}(g) + 2H_{2}O(g) \longrightarrow TiO_{2}(s) + 4HCl(g)} \qquad \Delta H_{4}^{\circ} = 4(-92.3 \text{ kJ}) = -369.2 \text{ kJ}$ $\Delta H^{\circ} = -67.1 \text{ kJ}$

Thus, 67.1 kJ of heat is evolved.

77. In the early days of automobiles, illumination at night was provided by burning acetylene, C_2H_2 . Though no longer used as auto headlamps, acetylene is still used as a source of light by some cave explorers. The acetylene is (was) prepared in the lamp by the reaction of water with calcium carbide, CaC_2 :

$$\operatorname{CaC}_{2}(s) + 2\operatorname{H}_{2}\operatorname{O}(l) \longrightarrow \operatorname{Ca}(\operatorname{OH})_{2}(s) + \operatorname{C}_{2}\operatorname{H}_{2}(g).$$

Calculate the standard enthalpy of the reaction. The $\Delta H_{\rm f}^{\circ}$ of CaC₂ is -15.14 kcal/mol.

Solution
convert –15.14 kcal to kJ:
–15.14 kcal × 4.184 kJ/kcal = 63.35 kJ/mol

$$DH_{reaction}^{o} = DH_{products}^{o} - DH_{reactants}^{o}$$

 $= DH_{Ca(OH)_{2}(s)}^{o} + DH_{C_{2}H_{2}(g)}^{o} - DH_{CaC_{2}(s)}^{o} - 2DH_{H_{2}O_{2}(l)}^{o}$
 $= -985.2 + 227.4 - (-63.35) - 2(-285.83) = -122.8 kJ$

79. The enthalpy of combustion of hard coal averages -35 kJ/g, that of gasoline, $-1.28 \times 10^5 \text{ kJ/gal}$. How many kilograms of hard coal provide the same amount of heat as is available from 1.0 gallon of gasoline? Assume that the density of gasoline is 0.692 g/mL (the same as the density of isooctane).

Solution

the amount of heat produced by burning of 1.0 gallon of gasoline is:

q = 1.0 gallon × (-1.28 × 10⁵ kJ/gal) = -1.28 × 10⁵ kJ

Mass × (-35 kJ/g) = $-1.28 \times 10^5 \text{ kJ}$

Mass = 3657 g or 3.7 kg

81. Among the substances that react with oxygen and that have been considered as potential rocket fuels are diborane [B₂H₆, produces B₂O₃(*s*) and H₂O(*g*)], methane [CH₄, produces CO₂(*g*) and H₂O(*g*)], and hydrazine [N₂H₄, produces N₂(*g*) and H₂O(*g*)]. On the basis of the heat released by 1.00 g of each substance in its reaction with oxygen, which of these compounds offers the best possibility as a rocket fuel? The ΔH_f° of B₂H₆(*g*), CH₄(*g*), and N₂H₄(*l*) may be

found in Appendix G.

Solution

Write the balanced equation for each reaction. $B_2H_6(g) + 3O_2(g) \longrightarrow B_2O_3(s) + 3H_2O(g)$ $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$ $N_2H_4(l) + O_2(g) \longrightarrow N_2(g) + 2H_2O(g)$ Calculate the heat released per mole; then, calculate the heat per gram. $\Delta H_{rxn}^o = \Delta H_P^o - \Delta H_R^o$ $\Delta H_{comb}^o = -1273.5 + 3(-241.82) - 36.4 = -2035.36 \text{ kJ mol}^{-1}$ $\Delta H_{comb}^o = -393.51 + 2(-241.82) - (-74.6) = -802.6 \text{ kJ mol}^{-1}$ $\Delta H_{comb}^o = 2(-241.82) - (50.63) = -534.27 \text{ kJ mol}^{-1}$ Calculate the heat per mole released per gram. For B_2H_6 : $\frac{-2035.36 \text{ kJ}}{27.610 \text{ g}} = -73.72 \text{ kJ g}^{-1}$ For CH_4 : $\frac{-802.34 \text{ kJ}}{16.043 \text{ g}} = -50.03 \text{ kJ g}^{-1}$ On the assumption that the best rocket fuel is the one that gives off the most heat, B_2H_6 is the prime candidate. Other things must be considered, however. For example, the moles of gaseous product formed are related to the specific impulse of the fuel, toxicity of products, cost, and ability to contain original fuel (stability and corrosiveness).

83. Ethylene, C₂H₄, a byproduct from the fractional distillation of petroleum, is fourth among the 50 chemical compounds produced commercially in the largest quantities. About 80% of synthetic ethanol is manufactured from ethylene by its reaction with water in the presence of a suitable catalyst. $C_2H_4(g) + H_2O(g) \longrightarrow C_2H_5OH(l)$

Using the data in the table in Appendix G, calculate ΔH° for the reaction. Solution

$$\Delta H_{\rm rxn}^{\circ} = \Delta H_{\rm C_2H_5OH(l)}^{\circ} - \Delta H_{\rm H_2O(g)}^{\circ} - \Delta H_{\rm C_2H_4(g)}^{\circ}$$

= -277.7 - (-241.82) - (52.4)
= -88.2 kJ

85. Propane, C₃H₈, is a hydrocarbon that is commonly used as a fuel.

(a) Write a balanced equation for the complete combustion of propane gas.

(b) Calculate the volume of air at 25 °C and 1.00 atmosphere that is needed to completely combust 25.0 grams of propane. Assume that air is 21.0 percent O_2 by volume. (Hint: We will see how to do this calculation in a later chapter on gases—for now use the information that 1.00 L of air at 25 °C and 1.00 atm contains 0.275 g of O_2 .)

(c) The heat of combustion of propane is -2219.2 kJ/mol. Calculate the heat of formation, $\Delta H_{\rm f}^{\circ}$,

of propane given that $\Delta H_{\rm f}^{\circ}$ of H₂O(*l*) = -285.8kJ/mol and $\Delta H_{\rm f}^{\circ}$ of CO₂(*g*) = -393.5 kJ/mol.

(d) Assuming that all of the heat released in burning 25.0 grams of propane is transferred to 4.00 kilograms of water, calculate the increase in temperature of the water. Solution

(a) $C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$

(b) Determine the number of moles of O_2 required and from that the number of grams. Then use the density to find the volume.

Mass O₂ = 25.0
$$\frac{g C_3 H_8}{g C_3 H_8} \times \frac{1 \frac{\text{mol} C_3 H_8}{44.097 \text{ g}}}{44.097 \text{ g}} \times \frac{5 \frac{\text{mol} O_2}{1 \frac{\text{mol} C_3 H_8(g)}}}{1 \frac{\text{mol} O_2}{1 \frac{\text{mol} O_2}{2}}} = 90.7 \text{ g}$$

Volume O₂ = $\frac{90.7 \text{ g}}{0.275 \text{ g} \text{ L}^{-1}} = 330 \text{ L}$
Volume air = $\frac{330 \text{ L} O_2}{\frac{21 \text{ L} O_2}{100 \frac{1}{2} \text{ air}}} = 1570 \text{ L}$ air

(c)

$$\Delta H_{\text{comb}}^{\circ}(C_{3}H_{6}(g) = -2219.2 \text{ kJ mol}^{-1} = 3\Delta H_{f}^{\circ}(CO_{2}(g)) + 4\Delta H_{f}^{\circ}(H_{2}O(l)) - \Delta H_{f}^{\circ}(C_{3}H_{6}(g))$$

$$\Delta H_{f}^{\circ}(C_{3}H_{6}(g)) = [2220.1 + 3(-393.5) + 4(-285.8)] \text{ kJ mol}^{-1} ;$$

$$= -104.5 \text{ kJ mol}^{-1}$$

$$\frac{25.0 \text{ g}}{44.097 \text{ g} \text{ mol}^{-1}} \times 2219.2 \text{ kJ mol}^{-1} = 1258 \text{ kJ} = 1.26 \times 10^{6} \text{ J}$$
(d) Heat = 1.26 × 10⁶ J = 4.18 J g⁻¹ °C⁻¹ × 4.00 × 10³ × \Delta T
$$\Delta T = 75.4 °C$$

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