

6.1 Identify the following systems as open, closed, or isolated: (a) coffee in a very high quality thermos bottle; (b) coolant in a refrigerator coil; (c) a bomb calorimeter in which benzene is burned; (d) gasoline burning in an automobile engine; (e) mercury in a thermometer; (f) a living plant.

6.3 Air in a bicycle pump is compressed by pushing in the handle. If the inner diameter of the pump is 3.0 cm and the pump is depressed 20. cm with a pressure of 2.00 atm, (a) how much work is done in the compression? (b) Is the work positive or negative with respect to the air in the pump?

6.5 A gas sample is heated in a cylinder by supplying 524 kJ of heat. At the same time, a piston compresses the gas, doing 340. kJ of work. What is the change in internal energy of the gas during this process?

6.7 The internal energy of a system increased by 982 J when it absorbed 492 J of heat. (a) Was work done by or on the system? (b) How much work was done?

6.9 A gas in a cylinder was placed in a heater and gained 5500. kJ of heat. If the cylinder increased in volume from 345 mL to 1846 mL against an atmospheric pressure of 750. Torr during this process, what is the change in internal energy of the gas in the cylinder?

6.11 In a combustion cylinder, the total internal energy change produced from the burning of a fuel is -2573 kJ. The cooling system that surrounds the cylinder absorbs 947 kJ as heat. How much work can be done by the fuel in the cylinder?

6.13 Indicate whether each of the following statements about an adiabatic process in a closed system is always true, always false, or true in certain conditions (specify the conditions):

(a) $\Delta U = 0$; (b) $q = 0$; (c) q is negative; (d) $\Delta U = q$; (e) $\Delta U = w$.

6.15 (a) Calculate the heat that must be supplied to a 500.0 -g copper kettle containing 750.0 g of water to raise its temperature from 23.0°C to the boiling point of water, 100.0°C . (b) What percentage of the heat is used to raise the temperature of the water?

6.17 A piece of copper of mass 20.0 g at 100.0°C is placed in a vessel of negligible heat capacity but containing 50.7 g of water at 22.0°C . Calculate the final temperature of the water. Assume that there is no energy lost to the surroundings.

6.19 A calorimeter was calibrated with an electric heater, which supplied 22.5 kJ of energy to the calorimeter and increased the temperature of the calorimeter and its water bath from 22.45°C to 23.97°C . What is the heat capacity of the calorimeter?

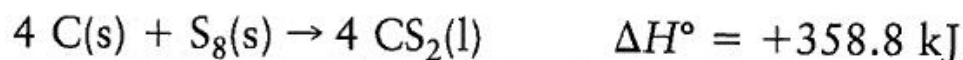
6.21 Calculate the work for each of the following processes beginning with a gas sample in a piston assembly with $T = 305 \text{ K}$, $P = 1.79 \text{ atm}$, and $V = 4.29 \text{ L}$: (a) irreversible expansion against a constant external pressure of 1.00 atm to a final volume of 6.52 L ; (b) isothermal, reversible expansion to a final volume of 6.52 L .

6.23 Which molecular substance do you expect to have the higher molar heat capacity, NO or NO_2 ? Why?

6.25 Calculate the heat released by 5.025 g of Kr(g) at 0.400 atm as it cools from 97.6°C to 25.0°C at (a) constant pressure and (b) constant volume. Assume that krypton behaves as an ideal gas.

6.33 (a) At its boiling point, the vaporization of 0.579 mol $\text{CH}_4(\text{l})$ requires 4.76 kJ of heat. What is the enthalpy of vaporization of methane? (b) An electric heater was immersed in a flask of boiling ethanol, $\text{C}_2\text{H}_5\text{OH}$, and 22.45 g of ethanol was vaporized when 21.2 kJ of energy was supplied. What is the enthalpy of vaporization of ethanol?

6.39 Carbon disulfide can be prepared from coke (an impure form of carbon) and elemental sulfur:

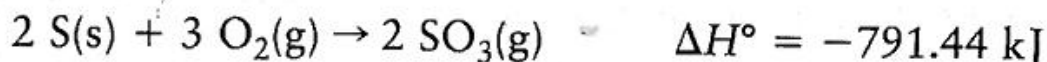


- (a) How much heat is absorbed in the reaction of 1.25 mol S_8 ?
(b) Calculate the heat absorbed in the reaction of 197 g of carbon with an excess of sulfur. (c) If the heat absorbed in the reaction was 415 kJ, how much CS_2 was produced?

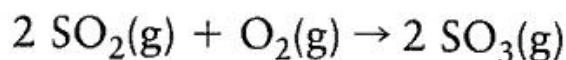
6.45 For a certain reaction at constant pressure, $\Delta H = -15 \text{ kJ}$, and 22 kJ of expansion work is done on the system. What is ΔU for this process?

6.51 The standard enthalpies of combustion of graphite and diamond are $-393.51 \text{ kJ}\cdot\text{mol}^{-1}$ and $-395.41 \text{ kJ}\cdot\text{mol}^{-1}$, respectively. Calculate the enthalpy of the graphite \rightarrow diamond transition.

6.53 Two successive stages in the industrial manufacture of sulfuric acid are the combustion of sulfur and the oxidation of sulfur dioxide to sulfur trioxide. From the standard reaction enthalpies

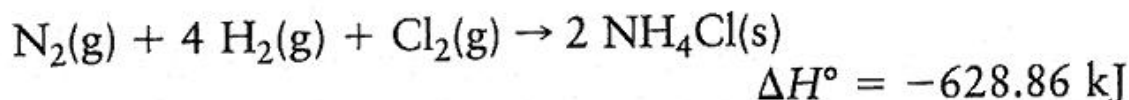
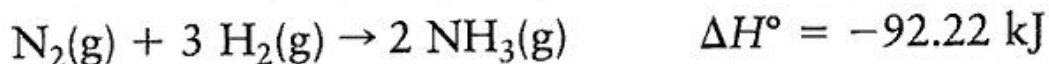
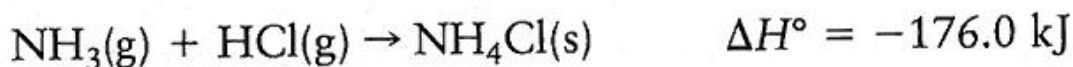


calculate the reaction enthalpy for the oxidation of sulfur dioxide to sulfur trioxide in the reaction

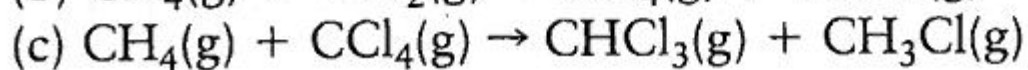
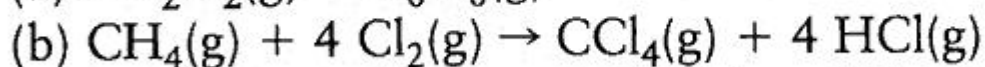
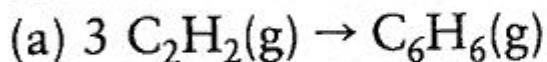


6.55 Determine the reaction enthalpy for the hydrogenation of ethyne to ethane, $\text{C}_2\text{H}_2(\text{g}) + 2 \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$, from the following data: $\Delta H_c^\circ(\text{C}_2\text{H}_2, \text{g}) = -1300. \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta H_c^\circ(\text{C}_2\text{H}_6, \text{g}) = -1560. \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta H_c^\circ(\text{H}_2, \text{g}) = -286 \text{ kJ}\cdot\text{mol}^{-1}$.

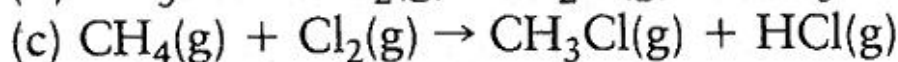
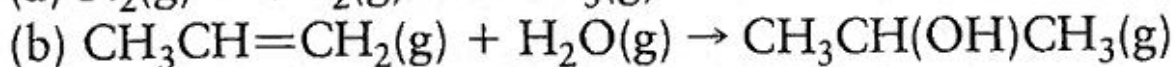
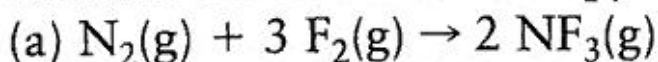
6.59 Calculate the reaction enthalpy for the synthesis of hydrogen chloride gas, $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2 \text{HCl}(\text{g})$, from the following data:



6.71 Use the bond enthalpies in Tables 6.7 and 6.8 to estimate the reaction enthalpy for



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7.3 (a) Calculate the change in entropy of a block of copper at 25°C that absorbs 65 J of energy from a heater. (b) If the block of copper is at $100.^\circ\text{C}$ and it absorbs 65 J of energy from the heater, what is its entropy change? (c) Explain any difference in entropy change.

7.5 Assuming that the heat capacity of an ideal gas is independent of temperature, calculate the entropy change associated with raising the temperature of 1.00 mol of ideal gas atoms reversibly from 37.6°C to 157.9°C at (a) constant pressure and (b) constant volume.

7.7 Calculate the entropy change associated with the isothermal expansion of 5.25 mol of ideal gas atoms from 24.252 L to 34.058 L.

7.17 The entropy of vaporization of benzene is approximately $85 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. (a) Estimate the enthalpy of vaporization of benzene at its normal boiling point of $80.^\circ\text{C}$. (b) What is the entropy change of the surroundings when 10. g of benzene, C_6H_6 , vaporizes at its normal boiling point?

7.19 Which would you expect to have a higher molar entropy at $T = 0$, single crystals of BF_3 or of COF_2 ? Why?

7.21 If SO_2F_2 adopts a disordered arrangement in its crystal form, what would its residual molar entropy be?

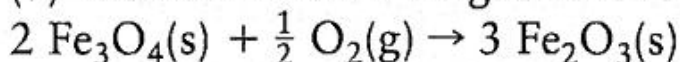
7.23 Which substance in each of the following pairs has the higher molar entropy at 298 K: (a) $\text{HBr}(\text{g})$ or $\text{HF}(\text{g})$; (b) $\text{NH}_3(\text{g})$ or $\text{Ne}(\text{g})$; (c) $\text{I}_2(\text{s})$ or $\text{I}_2(\text{l})$; (d) 1.0 mol $\text{Ar}(\text{g})$ at 1.00 atm or 1.0 mol $\text{Ar}(\text{g})$ at 2.00 atm?

7.25 List the following substances in order of increasing molar entropy at 298 K: $\text{H}_2\text{O}(\text{l})$, $\text{H}_2\text{O}(\text{g})$, $\text{H}_2\text{O}(\text{s})$, $\text{C}(\text{s}, \text{diamond})$. Explain your reasoning.

7.29 Without performing any calculations, predict whether there is an increase or a decrease in entropy for each of the following processes: (a) $\text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{HCl}(\text{aq}) + \text{HClO}(\text{aq})$; (b) $\text{Cu}_3(\text{PO}_4)_2(\text{s}) \rightarrow 3 \text{Cu}^{2+}(\text{aq}) + 2 \text{PO}_4^{3-}(\text{aq})$; (c) $\text{SO}_2(\text{g}) + \text{Br}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{SO}_4(\text{aq}) + 2 \text{HBr}(\text{aq})$.

7.47 Calculate the standard enthalpy change, entropy change, and free-energy change at 298 K for each of the following reactions by using data in Appendix 2A. For each case, confirm that the value obtained from the free energies of formation is the same as that obtained by using the relation $\Delta G_r^\circ = \Delta H_r^\circ - T\Delta S_r^\circ$.

(a) the oxidation of magnetite to hematite:

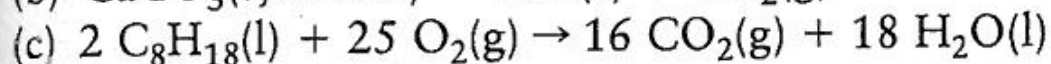
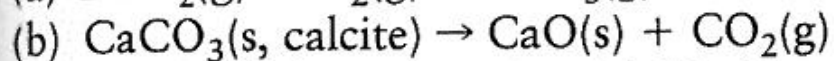
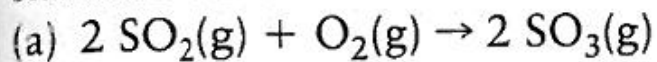


(b) the dissolution of CaF_2 in water: $\text{CaF}_2(\text{s}) \rightarrow \text{CaF}_2(\text{aq})$

(c) the dimerization of NO_2 : $2 \text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$

7.49 Write a balanced chemical equation for the formation reaction of (a) $\text{NH}_3(\text{g})$; (b) $\text{H}_2\text{O}(\text{g})$; (c) $\text{CO}(\text{g})$; (d) $\text{NO}_2(\text{g})$. For each reaction, determine ΔH_r° , ΔS_r° , and ΔG_r° from data in Appendix 2A.

7.51 Use the standard free energies of formation in Appendix 2A to calculate ΔG_r° for each of the following reactions at 25°C. Comment on the spontaneity of each reaction under standard conditions at 25°C.



7.55 Which of the following compounds become less stable with respect to the elements as the temperature is raised:

