

Chapter 9

Lota_2 Dæmi A4 Varmafræði

Insight into Energy Use and the World Economy

9.2 What are the advantages of electricity as a type of energy that make it worth generating despite the sizable losses that occur during this process?

ANS Electricity is a convenient form of energy. Can you imagine a coal-fired toaster? In addition to being “ready-to-use”, the transportation aspect of electricity is appealing even though it can be blamed for a significant amount of the losses.

9.4 The total energy consumption for the United States in the year 2007, as shown in Figure 9.2, was 106.96×10^{15} Btu. (a) What percentage of that energy was obtained from imports? (b) What percentage was used to generate electricity?

ANS a) 34.6% of the energy used was imported
b) 42.1% of the energy consumed was used to generate electricity (Fig 9.3).

Defining Energy

9.6 Distinguish between kinetic and potential energy.

ANS Kinetic energy is energy due to motion; potential energy is stored energy.

9.8 How fast (in meters per second) must an iron ball with a mass of 56.6 g be traveling in order to have a kinetic energy of 15.75 J? The density of iron is 7.87 g/cm³.

ANS $KE (J) = 0.5 \times \text{mass (kg)} \times \text{velocity}^2 (m^2/s^2)$

Vel. = 23.6 m/s

9.10 The kinetic energy of molecules is often used to induce chemical reactions. The bond energy in an O₂ molecule is 8.22×10^{-19} J. Can an O₂ molecule traveling at 780 m/sec provide enough energy to break the O=O bond? What is the minimum velocity of an O₂ molecule that would give a kinetic energy capable of breaking the bond if it is converted with 100% efficiency?

ANS a) 1.62×10^{-20} J, there is insufficient energy to break the double bond in oxygen.

b) $v = 5560$ m/s

9.12 How many kilojoules are equal to 3.27 L atm of work?

ANS $kJ = 3.27 \text{ L} \cdot \text{atm} (1.013 \times 10^2 \text{ J}/(\text{L} \cdot \text{atm})) = 0.331 \text{ kJ}$

9.14 What are the products of the complete combustion of a hydrocarbon?

ANS Carbon dioxide and water

9.16 According to Figure 9.2, the total energy supply in the United States in 2007 was 106.96×10^{15} Btu. Express this value in joules and in calories.

ANS Conversion to J = 1.128×10^{20} J

Conversion to cal = 2.70×10^{19} calories

Energy Transformation and Conservation of Energy

9.18 Calculate (a) q when a system does 54 J of work and its energy decreases by 72 J and (b) ΔE for a gas that releases 38 J of heat and has 102 J of work done on it.

ANS (a) $q = -72 \text{ J} - 54 \text{ J} = -126 \text{ J}$

(b) $\Delta E = -38 \text{ J} + 102 \text{ J} = 64 \text{ J}$

9.20 State the first law of thermodynamics briefly in your own words.

ANS Energy can be transformed but it can not be created or destroyed.

9.22 PV-work occurs when volume changes and pressure remains constant. If volume is held constant, can PV-work be done? What happens to Equation 9.2 when volume is held constant?

ANS In chemical reactions we can usually only consider P Δ V work. With no change in volume, the internal energy equals the heat flow ($\Delta E = q_v$).

9.24 In which case is heat added to the system: (a) $\Delta E = -43 \text{ J}$, $w = 40 \text{ J}$; or (b) $\Delta E = 31 \text{ J}$, $w = 34 \text{ J}$?

ANS In the first case q (heat) is -73 J and in the second case $q = -3 \text{ J}$. It would appear that heat is not added to the system in either case.

9.26 Gas furnaces have achieved impressive efficiency levels largely through the addition of a second heat exchanger that condenses water vapor that would otherwise escape out the exhaust system attached to the furnace. How does this process improve efficiency?

ANS When water vapor condenses, energy is released. That permits the heat exchanger to “harvest” this energy and distribute it throughout the house rather than having that energy go out the exhaust as warm water vapor.

9.28 When an electrical appliance whose power usage is X watts is run for Y seconds, it uses $X \times Y$ joules of energy. The energy unit used by electrical utilities in their monthly bills is the *kilowatt-hour* (kWh, that is, 1 kilowatt used for 1 hour). How many joules are there in a kilowatt-hour? If electricity costs \$.09 per kilowatt-hour, how much does it cost per megajoule?

ANS $1 \text{ kWh} = 3.6 \times 10^6 \text{ J}$; $\$0.025/\text{MJ}$

Heat Capacity and Calorimetry

9.30 For the example of shallow water and sandy beaches, which material has a larger heat capacity or specific heat? How does a hot day at the beach provide evidence for your answer?

ANS The sand has a lower heat capacity because the same mass of sand will heat up much faster than the water. A barefoot stroll across a dry sand beach provides the evidence for this answer.

9.32 The material typically used to heat metal radiators is water. If a boiler generates water at 79.5°C, what mass of water was needed to provide the heat required in the previous problem? Water has a specific heat of 4.184 J/g °C.

ANS With 350,000 J required in Problem 9.31 and the assumption that the water is being raised from 25.0°C to 79.5°C, the problem is solved by solving the $mc\Delta T$ equation for mass:

$$\text{Mass} = 1.53 \text{ kg}$$

9.34 A copper nail and an iron nail of the same mass and initially at the same room temperature are both put into a vessel containing boiling water. Which one would you expect to reach 100°C first? Why?

ANS The specific heat capacity for Cu is lower than that for Fe. With this in mind, I would expect the Cu to gain temperature quicker and reach 100°C first.

9.36 Define the term *calibration*.

ANS Calibration refers to analyzing a “known” with an instrument or process. A series of “knowns” provides a range of responses by the instrument or process. From this information, an unknown signal can be traced back to the magnitude of the causal phenomenon.

9.38 The energy densities of various types of coal are listed below.

Anthracite 35 kJ/g

Sub-bituminous 31 kJ/g

Bituminous 28 kJ/g

Lignite 26 kJ/g

An unknown sample of one of these coals is burned in an apparatus with a calorimeter constant of 1.3 kJ/°C. When a 0.367-g sample is used, the temperature change is 8.75°C. Which type of coal is the sample?

ANS Sub-bituminous

9.40 How does the specific heat of water explain why cities on the coast of large bodies of water tend to be cooler in the summer than cities several miles inland?

ANS The water has a higher heat capacity than does the land. This means that the land will heat up faster and because land is a thermal conductor of sorts, the land-locked city will heat up faster.

Enthalpy

9.42 Why is enthalpy generally more useful than internal energy in the thermodynamics of real world systems?

ANS It's more useful because the majority of reactions happen at constant pressure.

9.44 List at least two phase changes that are exothermic processes.

ANS Condensation and freezing are exothermic processes.

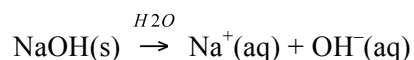
9.46 The heat of fusion of pure silicon is 43.4 kJ/mol. How much energy would be needed to melt a 5.24-g sample of silicon at its melting point of 1693 K?

ANS 8.10 kJ

9.48 Calculate the energy required to convert 1.70 g of ice originally at -12.0°C into steam at 105°C .

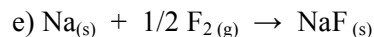
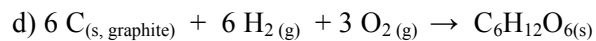
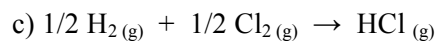
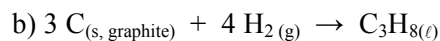
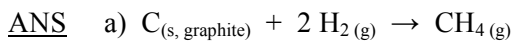
ANS 5180 J

9.50 When a 13.0-g sample of NaOH(s) dissolves in 400.0 mL water in a coffee cup calorimeter, the temperature of the water changes from 22.6°C to 30.7°C . Assuming that the specific heat capacity of the solution is the same as for water, calculate (a) the heat transfer from system to surroundings and (b) ΔH for the reaction



ANS (a) $1.4 \times 10^4 \text{ J}$ (b) -43 kJ/mol

9.52 Write the formation reaction for each of the following substances: (a) $\text{CH}_4(\text{g})$; (b) $\text{C}_3\text{H}_8(\ell)$; (c) $\text{HCl}(\text{g})$; (d) $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$; and (e) $\text{NaF}(\text{s})$.

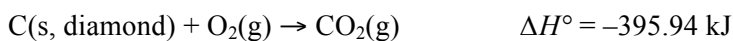
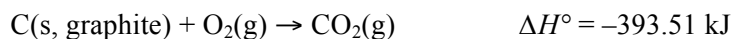


Hess's Law and Heats of Reaction

9.54 Which of the following are state functions? (a) the volume of a balloon, (b) the time it takes to drive from your home to your college or university, (c) the temperature of the water in a coffee cup, (d) the potential energy of a ball held in your hand.

ANS (a), (c), and (d) are state functions. Each of these quantities is independent of pathway.

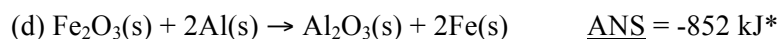
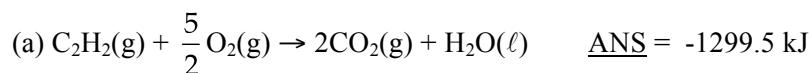
9.56 The phase change between graphite and diamond is difficult to observe directly. Both substances can be burned, however. From these equations, calculate ΔH° for the conversion of diamond into graphite.



ANS Because the transition of interest is diamond into graphite, start with the diamond reaction listed. This reaction creates CO₂, so reverse the graphite reaction (and its heat of reaction) to make CO₂ a reactant and graphite a product. Now according to Hess' Law we can add the two reactions together which will cancel out both the carbon dioxide and oxygen.

$$\Delta H = -395.94 \text{ kJ} + 393.51 \text{ kJ} = -2.43 \text{ kJ}$$

9.58 Using heats of formation tabulated in Appendix E, calculate the heats of reaction for the following:



*The aluminum oxide and iron produced in the reaction are assumed to have cooled to solid states.

9.60 When a chemical bond breaks, is energy absorbed or released?

ANS Energy is absorbed.

Energy and Stoichiometry

9.62 For the reaction $\text{C}_2\text{H}_2(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6$, $\Delta H^\circ = -136 \text{ kJ}$. What are the ratios that can be defined between moles of substances and energy?

ANS 136 kJ

9.64 Nitroglycerine, $\text{C}_3\text{H}_5(\text{NO}_3)_3(\ell)$, is an explosive most often used in mine or quarry blasting. It is a powerful explosive because four gases (N_2 , O_2 , CO_2 , and steam) are formed when nitroglycerine is detonated. In addition, 6.26 kJ of heat is given off per gram of nitroglycerine detonated. (a) Write a balanced thermochemical equation for the reaction. (b) What is ΔH when 4.65 mol of products are formed?

ANS (a) $4 \text{ C}_3\text{H}_5(\text{NO}_3)_3 (\ell) \rightarrow 6\text{N}_2 (\text{g}) + \text{O}_2 (\text{g}) + 12\text{CO}_2 (\text{g}) + 10\text{H}_2\text{O} (\ell)$

$$\Delta H = -1.42 \times 10^3 \text{ kJ}$$

(b) $-2.28 \times 10^2 \text{ kJ}$

9.66 Sulfur trioxide can be removed from the exhaust gases of power plants by reaction with lime according to the equation, $\text{CaO}(\text{s}) + \text{SO}_3(\text{g}) \rightarrow \text{CaSO}_4(\text{s})$, with $\Delta H^\circ = -886 \text{ kJ}$. If 240 kg of SO_3 is to be removed, how much heat is released?

ANS Convert 240 kg to moles of sulfur trioxide. Moles = 3000 moles $\text{SO}_3(\text{g})$

$$\text{Energy} = 3000 \text{ moles} \times -886 \text{ kJ / mol of } \text{SO}_3 = 2.7 \times 10^6 \text{ kJ}$$

9.68 In principle, ozone could be consumed in a reaction with lead and carbon with the thermochemical equation, $\text{Pb}(\text{s}) + \text{C}(\text{s}) + \text{O}_3(\text{g}) \rightarrow \text{PbCO}_3(\text{s})$, $\Delta H^\circ = -841.0$

kJ. How much energy would be released if 110 g of ozone reacts with excess lead and carbon?

ANS Same strategy is used here as in 9.66. Energy = 1920 kJ

9.70 Define the term *energy density*.

ANS The amount of energy that can be released per gram of fuel burned is energy density.

9.72 What are some features of petroleum that make it such an attractive fuel?

ANS Petroleum is a liquid which means that it's relatively easy to transport, it is relatively safe, the products of combustion are gases, and it has a high energy density.

Insight into Batteries

9.74 A small AAA battery and a much larger D battery both supply the same voltage. How does the underlying chemistry of the alkaline battery explain this? What factors would lead an engineer to specify D batteries in the design of a particular device rather than the smaller AAA cells?

ANS Each battery produces a current based on an electrochemical reaction; therefore, if the same reaction is occurring the same potential difference (voltage) exists. A "D" battery contains more reactants than a AAA and will last longer because it

takes longer for the greater concentrations of reactants to reach products.

- 9.76 Consumers face a variety of choices in selecting batteries. A typical AA alkaline battery might have a rated lifetime of about 2800 mA hours and cost around \$0.50. New high-capacity alkaline cells can last for 3100 mA hours, but typically cost about \$1.00 each. And rechargeable nickel metal hydride (NiMH) cells offer yet another option, with a lifetime of 2100 mA hours (per charge cycle) and a cost around \$3.50 each. What kinds of considerations might lead you to choose each of these options? What type of applications do you think would be best suited for each of these battery types?

ANS Usage in terms of hours per device would be one consideration. Environmental impact of disposal of primary cells (non-rechargeables would be another). Another consideration is the re-charging efficiency of the secondary cells. Very high use items should definitely be supported with rechargeable batteries whereas those that receive sporadic use are best left to primary cells.

Additional Problems

- 9.78 You make some iced tea by dropping 134 g of ice into 500.0 mL of warm tea in an insulated pitcher. If the tea is initially at 20.0°C and the ice cubes are initially at 0.0°C, how many grams of ice will still be present when the contents of the pitcher reach a final temperature? The tea is mostly water, so assume that it has the same density (1.0 g/mL), molar mass, heat capacity ($75.3 \text{ J K}^{-1} \text{ mol}^{-1}$), and heat of fusion (6.0 kJ/mol) as pure water. The heat capacity of ice is $37.7 \text{ J K}^{-1} \text{ mol}^{-1}$.

ANS The amount of ice remaining is 9 grams.

9.80 The specific heat of gold is $0.13 \text{ J g}^{-1} \text{ K}^{-1}$, and that of copper is $0.39 \text{ J g}^{-1} \text{ K}^{-1}$.

Suppose that we heat both a 25-g sample of gold and a 25-g sample of copper to 80°C and then drop each into identical beakers containing 100 mL of cold water at 10°C .

When each beaker reaches thermal equilibrium, which of the following will be true, and why? You should not need to do any calculations here.

- (i) Both beakers will be at the same temperature.
- (ii) The beaker with the copper sample in it will be at a higher temperature.
- (iii) The beaker with the gold sample in it will be at a higher temperature.

ANS The copper will have a slightly higher final temperature.

9.82 Chemical engineers often must include ways to dissipate energy in the form of heat in their designs. What does this fact say about the enthalpy change of chemical reactions that are being used?

ANS The reactions are exothermic and are releasing the energy that needs to be dissipated.

9.84 Many engineering designs must incorporate ways to dissipate energy in the form of heat. Water evaporators are common for this task. (a) What property of water makes it a good material for evaporators? (b) If an application could not use water, but instead was forced to use a material with a value for the property in (a) that was one half that of water, what changes would need to be made in the design?

ANS (a) Water has a high enthalpy of evaporation.

(b) There would need to be twice as many moles of the new material.

9.86 The curing of concrete liberates energy as heat. (a) What does this observation suggest happens in terms of chemical bonds as concrete cures? (b) What type of strategies might a civil engineer employ in designs and construction specifications to mitigate heat expansion of concrete as it cures?

ANS (a) More energy is released from the broken bonds than is stored in the newly formed bonds.

(b) Please refer to civil engineering resources.

9.88 Price spikes in gasoline in 2008 led to renewed interest in coal gasification projects, in which coal is converted to gasoline. Looking at the relative energy density of gasoline and coal in Table 9.4, which is more likely required in an engineering design for this project: the ability to input heat or the need to dissipate heat? Explain your reasoning.

ANS The energy density listed for coal is 31.4 MJ/kg while that listed for gasoline is 45.8 MJ/kg. The project requires heat and pressure on the coal to liberate the necessary components for the gasoline. It also requires cooling to finish the process. Given that the energy density is greater in the product than the reactant, it is likely that the process is endothermic with a greater requirement on the ability to input heat.

Focus on Problem Solving Exercises

9.90 Hydrogen combines with oxygen in fuel cells according to the thermochemical equation



Suppose that you are working with a firm that is using hydrogen fuel cells to power satellites. The satellite requires 4.0×10^5 kJ of energy during its useful lifetime to stabilize its orbit. Describe how you would determine the mass of hydrogen you would need in your fuel cells for this particular satellite.

ANS Divide the total energy requirement by the heat of reaction value. This should tell you how many moles of hydrogen are required. From there calculate the mass by using the molar mass of hydrogen.

9.92 Two baking sheets are made of different metals. You purchase both and bake a dozen cookies on each sheet at the same time in your oven. You observe that after nine minutes the cookies on one sheet are slightly burned on the bottom, whereas those on the other sheet are fine. (You are curious and you vary the conditions so you know the result is not caused by the oven.) (a) How can you

use this observation to infer something about the specific heat of the materials in the baking sheets? (b) What is the mathematical reasoning (equation) that you need to support your conclusion?

ANS a) If the cookie sheet with the burnt cookies has a lower specific heat, it would have heated much faster in the same conditions and resulted in the burnt cookies.

b) $\text{heat} = \text{mass} \times \text{specific heat} \times \Delta T$

9.94 A runner generates 418 kJ of energy per kilometer from the cellular oxidation of food. The runner's body must dissipate this heat or the body will overheat. Suppose that sweat evaporation is the only important cooling mechanism. If you estimate the enthalpy of evaporation of water as 44 kJ/mol and assume that sweat can be treated as water, describe how you would estimate the volume of sweat that would have to be evaporated if the runner runs a 10 km race.

ANS In a 10 km race, there is a 4180 kJ of energy to dissipate. With the enthalpy of evaporation at 44 kJ/mol, that translates into almost 100 moles of sweat (water) which would be a mass of almost 1800 g. This estimate would be something in the area of 1.75 L.

9.96 An engineer is using sodium metal as a cooling agent in a design because it has useful thermal properties. Looking up the heat capacity, the engineer finds a value of $28.2 \text{ J mol}^{-1} \text{ }^\circ\text{C}^{-1}$. Carelessly, he wrote this number down without units. As a result, it was later taken as specific heat. (a) What would be the difference between these two values? (b) Would the engineer overestimate the ability of sodium to remove heat from the system or underestimate it because of this error?

Be sure to explain your reasoning.

ANS a) 28.2 J/mol K vs. 28.2 J/g C is a rather significant difference. With a molar mass of 23 g/mol, this scenario would be potentially dangerous. A specific heat of 28.2 J/mol K underestimates the heating of this material by a factor of more than 20 times.

b) The value specific heat would appear to be 23 times too high.

9.98 A 1.0-kg sample of stainless steel is heated to 400°C. Suppose that you drop this hot sample into an insulated bucket that contains water at some known initial temperature. Assuming that there is no difficulty in transferring heat from the steel to the water, describe how you can determine the maximum mass of water that could be boiled with only the heat given off by this sample of steel. Be sure to list any quantities you would need to look up to solve this problem.

ANS The first measurement that is needed is the initial temperature of the water into which the steel will be dropped. This is required to calculate the amount of energy needed to raise the water to boiling and actually vaporize the water. From there one needs to know the specific heat of stainless steel. After this information is acquired, use $q = mc\Delta T$ to describe the heat transfer needed.

Cumulative Problems

9.100 For a car weighing 980 kg, how much work must be done to move the car 24 miles? Ignore factors such as frictional loss and assume an average acceleration of 2.3 m/sec^2 .

ANS Work = $8.7 \times 10^7 \text{ J}$

9.102 Suppose there is 2.43 mol of nitrogen gas in an insulated, sealed 31.7-L container initially at 285 K. The specific heat of nitrogen gas is $1.04 \text{ kJ kg}^{-1} \text{ K}^{-1}$ (note units). If a 5.44-kg block of iron at 755 K is placed in this container and it is sealed again (with no loss of nitrogen), what is the final pressure of the nitrogen gas?

ANS 4.8 atm

Chapter 10**Problems & Exercises*****Insight into Recycling of Plastics***

10.2 Is the recycling of most plastics primarily a chemical or a physical process? Explain and defend your choice.

ANS The recycling process is more of a physical process because the primary steps are 1) physically separating the polymer from other materials in the recycling bin, 2) crushing for shipping, and 3) grinding or chopping into flakes which are used in other applications.

10.4 Why is recycled PET rarely used to make new soft drink bottles?

ANS There are restrictions placed on the use of recycled plastics in the food and drink industry, but one of the biggest hurdles is economics. The bottles can be made much cheaper from virgin materials rather than recycled polymers.

10.6 Use the web to learn how many pounds of plastics are recycled in your area each year. How has this value changed during the past decade?

ANS This value and regional changes will vary widely by area. Some regions of the country are actually seeing decreases in plastics recycling relative to new production.

Spontaneity

10.8 In the thermodynamic definition of a spontaneous process, why is it important that the phrase “continuous intervention” be used rather than just “intervention?”

ANS Many processes will require an initial push of energy called activation energy and then proceed to happen on their own accord.

10.10 Identify each of the processes listed as spontaneous or nonspontaneous. For each nonspontaneous process, describe the corresponding spontaneous process in the opposite direction.

(a) A group of cheerleaders builds a human pyramid.

(b) Table salt dissolves in water.

(c) A cup of cold coffee in a room becomes steaming hot.

(d) Water molecules in the air are converted to hydrogen and oxygen gases.

(e) A person peels an orange, and you smell it from across the room.

ANS (a). non-spontaneous; a collapse of the pyramid would be the spontaneous process

(b). spontaneous

(c). non-spontaneous; a warm cup of coffee cooling to room temperature would be the spontaneous process.

(d). non-spontaneous; hydrogen and oxygen combining to form water is the spontaneous process.

(e). spontaneous

10.12 Athletic trainers use instant ice packs that can be cooled quickly on demand. Squeezing the pack breaks an inner container, allowing two components to mix and react. This reaction makes the pack to become cold. Describe the heat flow for this spontaneous process.

ANS This is an endothermic process, so heat is flow from the surroundings (the injured limb for example) into the system (the chemical reaction).

10.14 Enthalpy changes often help predict whether or not a process will be spontaneous. What type of reaction is more likely to be spontaneous: an exothermic or an endothermic one? Provide two examples that support your assertion and one counterexample.

ANS Intuitively we tend to think that exothermic reactions are more likely to be spontaneous and often this is the case. However, it is dangerous to base a decision on reaction spontaneity on enthalpy alone. We shall see that enthalpy AND entropy must both be considered to assess the spontaneity of a reaction or process.

10.16 Murphy's Law is a whimsical rule that says that anything that can go wrong will go wrong. But in an article in the *Journal of Chemical Education*, Frank Lambert writes, "Murphy's Law is a fraud." He also writes, "The second law of thermodynamics is time's arrow, but chemical kinetics is its clock." Read Lambert's article (*J. Chem. Ed.*, 74(8), 1997, p. 947), and write an essay explaining, in the context of the latter quotation, why Lambert claims that Murphy's Law is a fraud. (For more of Professor Lambert's unique insights into

thermodynamics, see his web site at <http://www.secondlaw.com/>)

ANS Essays will vary.

10.18 The vessel on the left contains a mixture of oxygen and nitrogen at atmospheric pressure. The vessel on the right is evacuated.

- (a) Describe what will happen when the stopcock is opened.
- (b) If you could see the individual molecules, what would you observe after a period of time has passed?
- (c) Explain your answers to (a) and (b) in terms of probabilities.
- (d) What is the probability that at any one moment all the oxygen molecules will be in one vessel and all the nitrogen molecules will be in the other? Explain.

- ANS
- (a). The gases will diffuse into the right-hand chamber until an equilibrium is reached.
 - (b). Most likely equal numbers of each type of molecule in each chamber assuming the chambers are the same size.
 - (c). The most likely situation (highest probability) to occur is that one has an even mix of the molecules in each chamber.
 - (d). The probability is very low; this scenario is simply the least likely to occur.

Entropy

10.20 Some games include dice with more than six sides. If you roll two eight-sided dice, with faces numbered one through eight, what is the probability of rolling two eights? What is the most probable roll?

ANS The chance of rolling a single eight is 1/8 (one in eight). It follows that a second eight would be a probability of 1/8 x 1/8 or 1/64. The most probable roll is a total of nine.

10.22 Define the concept of a microstate. How is this concept related to the order or disorder of a system?

ANS Microstate refers to the ways in which a group of particles can achieve a given energy. The relationship between entropy (S) and microstates (Ω) is given by:

$$S = k_B \Omega.$$

10.24 When ice melts, its volume decreases. Despite this fact, the entropy of the system increases. Explain (a) why the entropy increases and (b) why under most circumstances a decrease in volume results in an entropy decrease.

ANS (a) Entropy is about order. When a solid changes phases to a liquid, the result is that the particles are not as structured; and entropy has increased. The intriguing fact about water is that its physical chemistry makes it an anomaly in that it has less volume in its liquid state than its solid state (ice floats in water).

(b) In most cases a decrease in volume results in particles moving closer to each other which is ordering. As a substance becomes more ordered, disorder (hence entropy) is decreasing.

- 10.26 For each process, tell whether the entropy change of the system is positive or negative. (a) A glassblower heats glass (the system) to its softening temperature. (b) A teaspoon of sugar dissolves in a cup of coffee (the system consists of both sugar and coffee). (c) Calcium carbonate precipitates out of water in a cave to form stalactites and stalagmites. (Consider only the calcium carbonate to be the system.)

ANS (a) positive (b) positive (c) negative

- 10.28 For the following chemical reactions, predict the sign of ΔS for the system. (Note that this should not require any detailed calculations.)

(a). $\text{Fe(s)} + 2\text{HCl(g)} \rightarrow \text{FeCl}_2\text{(s)} + \text{H}_2\text{(g)}$ ANS ΔS is negative

(b). $3\text{NO}_2\text{(g)} + \text{H}_2\text{O(l)} \rightarrow 2\text{HNO}_3\text{(l)} + \text{NO(g)}$ ANS ΔS is negative

(c). $2\text{K(s)} + \text{Cl}_2\text{(g)} \rightarrow 2\text{KCl(s)}$ ANS ΔS is negative

(d). $\text{Cl}_2\text{(g)} + 2\text{NO(g)} \rightarrow 2\text{ClNO(g)}$ ANS ΔS is negative

(e). $\text{SiCl}_4\text{(g)} \rightarrow \text{Si(s)} + 2\text{Cl}_2\text{(g)}$ ANS ΔS is positive

- 10.30 A student opens a stack of new playing cards and shuffles them. In light of the paragraph above, have the cards increased in entropy? Explain your answer in terms of thermodynamics. Explain why the agent (the shuffler) undergoes an increase in entropy.

ANS The playing cards are now more disordered, so entropy has increased. The shuffler has exerted energy which means that glucose has been oxidized into CO₂ and H₂O. This increases the overall number of molecules, so entropy has increased as well.

10.32 Write two examples of your own that illustrate the concept in the paragraph above.

ANS (1) Cleaning a dorm room requires the room (system) to become more order which results in a decrease in the entropy of the room. The disorder in the surroundings (the cleaner of the room) increases because of the oxidation of glucose and other metabolic processes.

(2) Raking the cut grass in a yard into a pile for later disposal is an example of decreasing disorder or decreasing entropy. The raker expends energy in the process, and the metabolism of the sugar in the body results in an increase in entropy.

10.34 A researcher heats a sample of water in a closed vessel until it boils.

(a) Does the entropy of the water increase?

ANS Yes, boiling results in more gaseous molecules which is an increase in disorder.

(b) Has the randomness of the molecules increased? (In other words, are there more physical positions that the molecules can occupy?)

ANS Yes

(c) What else has increased that affects the entropy of the system?

ANS The number of microstates.

The researcher now heats the water vapor from 400 K to 500 K, keeping the volume constant. (d) Does the entropy of the system increase?

ANS Yes, the addition of heat will always increase the entropy of the system.

(e) Has the randomness of the molecules increased? (In other words, are there more physical positions the molecules can occupy?)

ANS Yes

(f) Why has an increase in temperature of the gas at constant volume caused an increase in entropy?

ANS The increase in temperature provides more ways (or combinations) to achieve the energy of the system.

The Second Law of Thermodynamics

10.36 Why do we need to consider the surroundings of a system when applying the second law of thermodynamics?

ANS The second law of thermodynamics states that the total entropy change of a spontaneous process is always positive. The universe is the sum of the system and the surroundings; therefore, the surroundings must be considered.

10.38 According to the second law of thermodynamics, how does the sign of ΔS_u relate to the concept that some energy is wasted or lost to the surroundings when we attempt to convert heat into work?

ANS Entropy changes can be defined as heat flow at constant temperature. By converting heat to work, the temperature of the system is lowered, resulting in a decrease in the entropy of the system. The entropy change of the universe must be positive, so the entropy change of the surroundings must be larger than the absolute value of the entropy change of the system and have a positive value. So heat must be lost from the system to the surroundings, $\Delta S_{\text{surr}} = q_{\text{surr}}/T$.

10.40 Some say that the job of an engineer is to fight nature and the tendencies of entropy. (a) Does this statement seem accurate in any way? (b) How can any engineering design create order without violating the second law of thermodynamics?

ANS (a) yes (b) The entropy of a system may decrease with a corresponding increase in the entropy of the surroundings.

10.42 Which reaction occurs with the greater increase in entropy? Explain your reasoning. (a) $2\text{H}_2\text{O}(\ell) \rightarrow 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$; (b) $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$

ANS Reaction (a) occurs with the greater increase in entropy because the number of moles of products is larger than reactants AND the liquid reactants have been transformed into gaseous products.

10.44 Methanol is burned as fuel in some race cars. This makes it clear that the reaction is spontaneous once methanol is ignited. Yet the entropy change for the reaction $2\text{CH}_3\text{OH}(\ell) + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\ell)$ is negative. Why doesn't this violate the second law of thermodynamics?

ANS First, the total moles have increased from five to six in the course of the reaction, but most importantly there has been a sizeable increase from two to four for the moles of liquids. This reduces the microstates and hence the negative entropy. The second law of thermodynamics states that, if the process is spontaneous, the entropy of the universe must increase. If the system is decreasing, the surroundings must increase by a larger amount. The large amount of heat given off by this reaction will certainly increase the entropy of the surroundings. We can assume this increase is larger than the decrease in the system.

The Third Law of Thermodynamics

10.46 Suppose you find out that a system has an absolute entropy of zero. What else can you conclude about that system?

ANS We can assume the substance is at absolute zero.

10.48 If you scan the values for S° in Appendix E, you will see that several aqueous ions have values that are less than zero. The third law of thermodynamics states that for a pure substance the entropy goes to zero only at 0 K. Use your understanding of the solvation of ions in water to explain how a negative value of S° can arise for aqueous species.

ANS For ions, H^+ is assigned an entropy of zero. Some have higher values, some lower (negative). Ca^{2+} and Mg^{2+} are two examples of cations with negative entropies.

10.50 Calculate the standard entropy change for the reaction $CO_2(g) + 2H_2O(\ell) \rightarrow CH_4(g) + 2O_2(g)$. What does the sign of ΔS° say about the spontaneity of this reaction?

ANS $\Delta S^\circ = \text{products} - \text{reactants} = \{[2(205) + 186.2] - [2(69.91) + 213.6]\} \text{ J mol}^{-1} \text{ K}^{-1}$
 $= 243 \text{ J K}^{-1}$

The positive ΔS° favors spontaneity under most conditions, but the enthalpy and temperature of the reaction must be known to ascertain the spontaneity of the reaction with surety.

10.52 Find websites describing two different attempts to reach the coldest temperature on record. What features do these experiments have in common?

ANS Utilize a world wide web search engine to acquire the reference.

10.54 Look up the value of the standard entropy for the following molecules: $\text{SiO}_2(\text{s})$, $\text{NH}_3(\text{g})$, $\text{C}_2\text{H}_6(\text{g})$. Rank the compounds in order of increasing entropy and then explain why this ranking makes sense.

ANS $\text{SiO}_2(\text{s}) < \text{NH}_3(\text{g}) < \text{C}_2\text{H}_6(\text{g})$

This makes sense in that the solid is the most ordered of the three and would be expected to have the lowest value. H-bonding would be present for the ammonia, so the increased intermolecular forces there should lead to a lower entropy than the hydrocarbon.

Gibbs Free Energy

10.56 Describe why it is easier to use ΔG to determine the spontaneity of a process rather than ΔS_{u} .

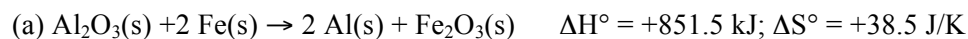
ANS Quantifying the extent of $\Delta S_{\text{surroundings}}$ may prove difficult and provide more uncertainty.

10.58 There is another free energy state function, the Helmholtz free energy (F), defined as $F = E - TS$. Comparing this to the definition of G , we see that internal energy

has replaced enthalpy in the definition. Under what conditions would this free energy tell us whether or not a process is spontaneous?

ANS The information would be conveyed if the internal energy of the system were equal to the enthalpy of the system.

10.60 Discuss the effect of temperature change on the spontaneity of the following reactions at 1 atm.



ANS $\Delta G = \Delta H - T\Delta S$ It follows that, if a process must have a negative ΔG to be spontaneous AND the process is endothermic. Therefore:

(a) is spontaneous above $2.21 \times 10^4 \text{ K}$;

(b) is always spontaneous; and

(c) is spontaneous above $1.05 \times 10^3 \text{ K}$.

10.62 Why is the free energy change of a system equal to the *maximum* work rather than just the work?

ANS Work is not a state function; therefore, maximum work can be attained only by a specific path.

10.64 For the reaction $\text{NO}(\text{g}) + \text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_3(\text{g})$, use tabulated thermodynamic data to calculate ΔH° and ΔS° . Then use those values to answer the following questions.

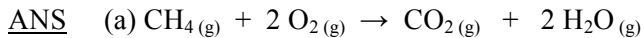
- (a) Is this reaction spontaneous at 25°C ? Explain your answer.
- (b) If the reaction is not spontaneous at 25°C , will it become spontaneous at higher temperatures or lower temperatures?
- (c) To show that your prediction is accurate, choose a temperature that corresponds to your prediction in part (b) and calculate ΔG . (Assume that both enthalpy and entropy are independent of temperature.)

ANS (a) Given that ΔH° is calculated by subtracting the values of the reactant's ΔH° from that of the product(s), ΔH° for this reaction is -39.73 kJ . Using a similar process, ΔS° for the reaction is $-129.4 \text{ J}\cdot\text{K}^{-1}$.

By using $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$ for the requested calculation, the reaction is spontaneous with a ΔG° of -1.17 kJ/mol .

- (b) See above. *The reaction will become non-spontaneous above 307 K (34°C).*
- (c) See (a) and (b).

10.66 Natural gas (methane) is being used in experimental vehicles as a clean-burning fuel. (a) Write the equation for the combustion of $\text{CH}_4(\text{g})$, assuming that all reactants and products are in the gas phase. (b) Use data from Appendix E to calculate ΔS° for this reaction. (c) Calculate ΔG° and show that the reaction is spontaneous at 25°C .



(b) $\Delta S^\circ = [2(188.7) + 213.6] - [2(205) + 186.2] = -5.2 \text{ J mol}^{-1} \text{ K}^{-1}$

(c) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -802.3 \text{ kJ/mol} - (298 \text{ K})(-5.2 \text{ J mol}^{-1} \text{ K}^{-1})$
 $= -800.8 \text{ kJ/mol}$ (neg. value indicates spontaneity)

Free Energy and Chemical Reactions

10.68 Explain why ΔG°_f of $\text{O}_2(\text{g})$ is zero.

ANS The formation reaction of any element uses the element in its standard state; therefore, the formation reaction of an element has the same chemical species as a reactant and product. There is no change in the state function.

10.70 Using tabulated thermodynamic data, calculate ΔG° for these reactions.

ANS (a). No value for ΔG° is provided for $\text{Mg}_3\text{N}_2(\text{s})$ in the text Appendix nor the CRC handbook.

(b). -4092 kJ

(c). -14 kJ

(d). insufficient thermodynamic data on P_4O_6

10.72 Phosphorus exists in multiple solid phases, including two known as red phosphorus and white phosphorus. Consider the phase transition between white and red phosphorous: $P_4(s, \text{white}) \rightarrow P_4(s, \text{red})$. Use data from Appendix E to determine which form of phosphorous is more stable at 25°C. Is this form of the solid more stable at all temperatures? If not, what temperatures are needed to make the other form more stable?

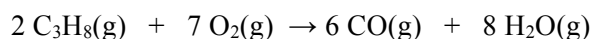
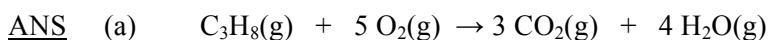
ANS At 298 K the reaction converting white to red P is spontaneous meaning that the red form is more stable. If the $\Delta G = \Delta H - T\Delta S$ approach is used to describe each substance's Gibb's Energy, the two equations can be set equal to each other to calculate the temperature at which the reaction as written is no longer spontaneous ($+\Delta G$). This temperature is 858 K. At this temperature the white form of P is favored.

10.74 Calculate ΔG° for the complete combustion of one mole of the following fossil fuels: methane (CH_4), ethane (C_2H_6), propane (C_3H_8) and n-butane (C_4H_{10}). Identify any trends that are apparent based on these calculations.

ANS Using the strategies shown in 10.70 the following ΔG° values are found for the hydrocarbons listed in the text appendix:
 $CH_4 = -800 \text{ kJ}$, $C_2H_6 = -1442 \text{ kJ}$, $C_3H_8 = -2074 \text{ kJ}$, and $C_4H_{10} = -2704 \text{ kJ}$
This appears to indicate a trend for increasingly negative ΔG° values with increase hydrocarbon size.

10.76 Recall that incomplete combustion of fossil fuels occurs when too little oxygen is present and results in the production of carbon monoxide rather than carbon dioxide. Water is the other product in each case.

- (a) Write balanced chemical equations for the complete and incomplete combustion of propane.
- (b) Using these equations, predict which will have the larger change in entropy.
- (c) Use tabulated thermodynamic data to calculate ΔG° for each reaction.
- (d) Based on these results, predict the sign and value of ΔG° for the combustion of carbon monoxide to form carbon dioxide.



- (b) The incomplete combustion would have the larger change in entropy.
- (c) ΔG° complete combustion = -2074 kJ;
 ΔG° incomplete combustion = -2605 kJ
- (d) Using a Hess' law type approach, these two reactions can be summed together for the ΔG° of this process. The first action is to turn the carbon monoxide reaction around and divide by 2. From there, the two reactions can be added together to give:



Economics of Recycling

10.78 If a particular polymerization reaction happened to be endothermic, how could it ever take place? Where would the increase in entropy of the universe have to arise?

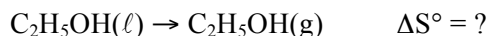
ANS It could take place as long as the temperature of the reaction is sufficiently high for $T\Delta S$ to be of a larger magnitude than ΔH .

10.80 The recycling of polymers represents only one industrial process that allows creating order in one location by creating greater disorder at some other location, often at a power plant. List three other industrial processes that must create disorder in the surroundings in order to generate the desired material.

ANS (1) the formation of paper sheets from pulp
 (2) the creation of ozone from oxygen at an industrial plant
 (3) electroplating a metal onto a surface

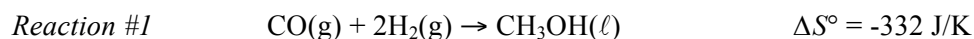
Additional Problems

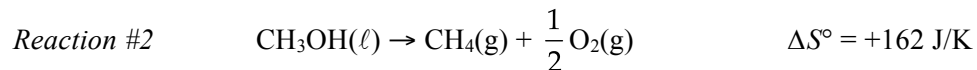
10.82 Calculate the entropy change, ΔS° , for the vaporization of ethanol, C_2H_5OH , at the boiling point of $78.3^\circ C$. The heat of vaporization of the alcohol is 39.3 kJ/mol .



ANS $112 \text{ J}\cdot\text{mol}^{-1}\text{K}^{-1}$

10.84 Methane can be produced from CO and H_2 . The process might be done in two steps, as shown below, with each step carried out in a separate reaction vessel within the production plant.





NOTE: You should be able to work this problem *without* using any additional tabulated data.

- Calculate ΔH° for reaction #1.
- Calculate ΔG_f° for $\text{CO}(\text{g})$.
- Calculate S° for $\text{O}_2(\text{g})$.
- At what temperatures is reaction #1 spontaneous?
- Suggest a reason why these two steps would need to be carried out separately.

ANS (a). $\Delta H^\circ = [-238.7 - (0 + -110.5)] \text{ kJ} = -128.2 \text{ kJ}$

(b). -137.1 kJ/mol

(c). $205 \text{ J K}^{-1} \text{ mol}^{-1}$

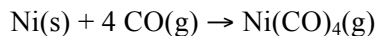
(d). The reaction is spontaneous at temperatures below 386 K.

(e). If the two steps are carried out together, the reactant H_2 in the first reaction would come into contact with the product O_2 of the second reaction. This could produce a potentially explosive situation.

- 10.86 The enthalpy of vaporization for water is $40.65 \text{ kJ mol}^{-1}$. As a design engineer for a project in a desert climate, you are exploring the option of using evaporative cooling. (a) If the air has an average volumetric heat capacity of $0.00130 \text{ J cm}^{-3} \text{ K}^{-1}$, what is the minimum mass of water that would need to evaporate in order to cool a $5 \text{ m} \times 5 \text{ m}$ room with a 3 m ceiling by 5°F using this method? (b) Is this a spontaneous or nonspontaneous process?

ANS 120 grams; it is a spontaneous process

10.88 Nickel metal reacts with carbon monoxide to form tetracarbonyl nickel, Ni(CO)₄.



This reaction is exploited in the Mond process in order to separate pure nickel from other metals. The reaction above separates nickel from impurities by dissolving it into the gas phase. Conditions are then changed so that the reaction runs in the opposite direction to recover the purified metal.

- (a). Predict the signs of ΔH° and ΔS° for the reaction as written above. (Note that bonds are formed but none are broken.)
- (b). Use tabulated thermodynamic data to calculate ΔH° , ΔS° , and ΔG° for the reaction.
- (c). Find the range of temperatures at which this reaction is spontaneous in the forward direction.

ANS (a) $\Delta H^\circ > 0$; $\Delta S^\circ < 0$

(b) $\Delta H^\circ = -160.9 \text{ kJ}$; $\Delta S^\circ = -410.1 \text{ J}\cdot\text{K}^{-1}$; $\Delta G^\circ = -38.5 \text{ kJ/mol}$

(c) The reaction is spontaneous below a temperature of 392 K.

10.90 A key component in many chemical engineering designs is the separation of mixtures of chemicals. (a). What happens to the entropy of the system when a chemical mixture is separated? (b). Are designs for chemical separation more likely to rely on spontaneous or nonspontaneous processes?

ANS (a) Separating the components of the mixture brings further order and hence decreases the entropy of the system.

(b) As mentioned in (a), separations tend to increase order and therefore require

nonspontaneous processes.

Focus on Problem Solving

10.92 Suppose that you need to know the heat of formation of 2-pentene, C₅H₁₀, but the tables you have do not provide the value. You have a sample of the chemical. What could you do to determine the heat of formation?

ANS You could use Hess' Law to determine the heat of formation.

10.94 You have a table of thermodynamic variables that includes heats of formation and standard entropies but not free energies of formation. How could you use the information you have to estimate the free energy of formation of a substance that is listed in your table?

ANS With the heat of formation and enthalpy values at hand, you can solve the $G = H - TS$ equation for 298 K for a reasonable approximation.

10.96 From a series of hydrocarbons containing only single carbon-carbon bonds how could you identify a trend for the heat of formation for successive carbon-carbon bond formation?

ANS See Problem 10.74.

10.98 Suppose you are designing a chemical reactor and you need to know the heat of vaporization for a solvent. You don't have any thermodynamic tables handy, but

you know the boiling point of the liquid and your CAD program can calculate third-law entropies. How would you determine the heat of vaporization?

ANS Use $\Delta H_{\text{vap}} = T\Delta S$ after finding the entropy using CAD.

Cumulative Problems

10.100 Ammonia can react with oxygen gas to form nitrogen dioxide and water. (a)

Write a balanced chemical equation for this reaction. (b) Use tabulated data to determine the free energy change for the reaction and comment on its spontaneity. (c) Use tabulated data to calculate the enthalpy change of the reaction (d). Determine how much heat flows and in what direction when 11.4 g of ammonia gas is burned in excess oxygen.

ANS (a) $4 \text{NH}_3(\text{g}) + 7 \text{O}_2(\text{g}) \rightarrow 4 \text{NO}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{g})$

(b) $\Delta G_f^\circ = -1100 \text{ kJ}$. The reaction is spontaneous at 298 K.

(c) $\Delta H_{\text{rxn}} = -1134 \text{ kJ}$

(d) Heat = -190 kJ (exothermic)

10.102 (a) When a chemical bond forms, what happens to the entropy of the system? (b) Thermodynamically, what allows for any bond formation to occur? (c) What do your answers to parts (a) and (b) suggest must be true about the formation of chemical bonds for the octet rule to hold?

ANS (a) When a chemical bond forms the disorder of the system drops and entropy is decreased.

(b) Bond formation occurs because the electrons are moving to a more stable state.

(c) These answers would suggest that for the octet rule to hold the entropy of the system is decreased. Therefore, for the process to be spontaneous, the entropy of the surroundings would have to increase in some fashion.