

1. For each of the following processes, identify the system and the surroundings. Identify those processes that are spontaneous. For each spontaneous process, identify the constraint that has been removed to enable the process to occur:
  - (a) Ammonium nitrate dissolves in water.
  - (b) Hydrogen and oxygen explode in a closed bomb.
  - (c) A rubber band is rapidly extended by a hanging weight.
  - (d) The gas in a chamber is slowly compressed by a weighted piston.
  - (e) A glass shatters on the floor.

Deciding the contents of a thermodynamical system in a problem or real-life situation is entirely up to the analyst (you). Once the system is defined, the surroundings are automatically “the rest of the universe.” A wise choice of system can greatly simplify the analysis of a thermodynamic problem. It also often pays explicitly to recognize the nature of a chosen system’s *immediate* surroundings. The following are typical useful choices of system and surroundings.

a) The system is the reaction  $\text{NH}_4\text{NO}_3(s) \rightarrow \text{NH}_4^+(aq) + \text{NO}_3^-(aq)$ . This means that the system includes solid ammonium nitrate, the water in which it dissolves and the aquated ions that dissolution generates. The inclusion of water in the system is indicated only rather subtly (by the *(aq)*’s on the formulas of the product ions). The immediate surroundings include the flask or beaker in which the system is held, the air above the system, and other neighboring materials. The dissolution of ammonium nitrate is spontaneous. Before the process can proceed, any physical barrier (such as a glass wall or an air-gap) between the water and the ammonium nitrate must be removed. The parts (sub-systems) of a system need not be physically contiguous.

b) The system is the reaction  $\text{H}_2(g) + \text{O}_2(g) \rightarrow \text{products}$ . Its immediate surroundings are the walls of the bomb and other portions of its environment that might deliver heat or work or absorb heat or work. The reaction of hydrogen with oxygen is spontaneous. Once hydrogen and oxygen are mixed in a closed bomb, no constraint exists to prevent their reaction. That is, the system just defined is thermodynamically unstable with respect to the explosion. Experimentally this system gives products quite slowly at room temperature (no immediate explosion). It explodes instantly at higher temperatures.

c) The system is the rubber band. The immediate surroundings consist of the weight (visualized as attached to the lower end of the rubber band), a hangar at the top of the rubber band, and the air in contact with the rubber band. The change is spontaneous once a constraint such as a supporting finger underneath the weight is removed.

d) The system is the gas contained in the chamber. The immediate surroundings are the walls of the chamber and the moveable piston head. The process is spontaneous if the force exerted by the weight on the piston exceeds the force exerted by the collisions of the molecules of the gas on the bottom of the piston.<sup>1</sup> Because slow compression of the gas is observed, the change is spontaneous.

9. Predict the sign of the system's entropy change in each of the following processes.
- (a) Sodium chloride melts.
  - (b) A building is demolished.
  - (c) A volume of air is divided into three separate volumes of nitrogen, oxygen, and argon, each at the same pressure and temperature as the original air.

a) When NaCl melts it goes from an ordered solid (fewer microstates) to a relatively disordered liquid state (more microstates):  $\Delta S > 0$ .

b) When a building is demolished its constituent particles go from a situation corresponding to relatively fewer microstates (the arrangements of the particles' positions and momenta that are recognizable as the building) to a situation corresponding to far many more microstates (the arrangements that are recognizable as a heap of rubble):  $\Delta S > 0$ .

c) The mixture of nitrogen, oxygen, and argon has far more microstates than the three separate volumes, each containing a different gas:  $\Delta S < 0$ .

15. If 4.00 mol hydrogen ( $c_p = 28.8 \text{ J K}^{-1} \text{ mol}^{-1}$ ) is expanded reversibly and isothermally at 400 K from an initial volume of 12.0 L to a final volume of 30.0 L, calculate  $\Delta U$ ,  $q$ ,  $w$ ,  $\Delta H$ , and  $\Delta S$  for the gas.

Assume that the 4.00 mol of hydrogen, which is a gas at 400 K, behaves ideally. The internal energy of an ideal gas depends solely on its absolute temperature  $T$ . In an isothermal process,  $T$  does not change. Hence,  $\Delta U = 0$ .

To evaluate  $\Delta H$ , use its definition

$$\Delta H = \Delta U + \Delta(PV) \quad \text{which implies} \quad \Delta H = \Delta U + nR\Delta T$$

since  $PV = nRT$  for an ideal gas. But  $\Delta T$  and  $\Delta U$  equal zero. Hence,  $\Delta H = 0$ .

The work done *on* the gas during the reversible isothermal expansion from 12.0 L to 30.0 L is

$$\begin{aligned} w &= -nRT \ln \left( \frac{V_2}{V_1} \right) = -4.00 \text{ mol} (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) (400 \text{ K}) \ln \left( \frac{30.0}{12.0} \right) \\ &= -12.2 \times 10^3 \text{ J} = \boxed{-12.2 \text{ kJ}} \end{aligned}$$

The first law requires that if  $\Delta U = 0$ , then  $q = -w$ . This means the gas absorbs 12.2 kJ of heat during its expansion, just enough to account for the 12.2 kJ of work that it performs:  $q = \boxed{+12.2 \text{ kJ}}$ . Finally,  $\Delta S = q_{\text{rev}}/T$  for an isothermal process, and  $q_{\text{rev}}$  is the  $q$  just computed

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{+12.2 \times 10^3 \text{ J}}{400 \text{ K}} = \boxed{+30.5 \text{ J K}^{-1}}$$

19. In Example 12.3, a process was considered in which 72.4 g iron initially at 100.0°C was added to 100.0 g water initially at 10.0°C, and an equilibrium temperature of 16.5°C was reached. Take  $c_p(\text{Fe})$  to be  $25.1 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $c_p(\text{H}_2\text{O})$  to be  $75.3 \text{ J K}^{-1} \text{ mol}^{-1}$ , independent of temperature. Calculate  $\Delta S$  for the iron,  $\Delta S$  for the water, and  $\Delta S_{\text{tot}}$  in this process.

The iron cools from 100.0°C to 16.5°C. This means that  $T_1 = 373.15 \text{ K}$  and  $T_2 = 289.65 \text{ K}$ . Substitute these absolute temperatures into the formula for  $\Delta S$  given in text equation 13.8

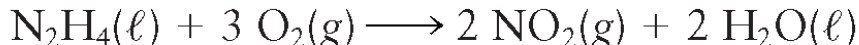
$$\Delta S_{\text{Fe}} = n c_p \ln \left( \frac{T_2}{T_1} \right) = \left( \frac{72.4 \text{ g}}{55.85 \text{ g mol}^{-1}} \right) (25.1 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \left( \frac{289.65 \text{ K}}{373.15 \text{ K}} \right) = \boxed{-8.24 \text{ J K}^{-1}}$$

The water warms from 283.15 K to 289.65 K. Use the same formula

$$\Delta S_{\text{H}_2\text{O}} = n c_p \ln \left( \frac{T_2}{T_1} \right) = \left( \frac{100.0 \text{ g}}{18.015 \text{ g mol}^{-1}} \right) (75.3 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \left( \frac{289.65 \text{ K}}{283.15 \text{ K}} \right) = \boxed{+9.49 \text{ J K}^{-1}}$$

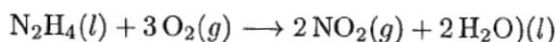
The  $\Delta S_{\text{tot}}$  in the problem refers to the whole system. It is  $-8.24 + 9.49 = \boxed{+1.25 \text{ J K}^{-1}}$ .

21. (a) Use data from Appendix D to calculate the standard entropy change at 25°C for the reaction



- (b) Suppose the hydrazine ( $\text{N}_2\text{H}_4$ ) is in the gaseous, rather than liquid, state. Will the entropy change for its reaction with oxygen be higher or lower than that calculated in part (a)? (*Hint:* Entropies of reaction can be added when chemical equations are added, in the same way that Hess's law allows enthalpies to be added.)

a) The  $\Delta S_{298}^\circ$  of the reaction as written equals the standard molar entropies of the products at 298 K, each multiplied by its coefficient in the balanced equation, minus the standard molar entropies of the reactants at 298 K, each multiplied by its coefficient in the balanced equation.<sup>2</sup> The reaction is



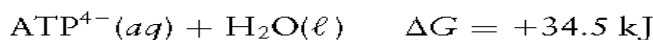
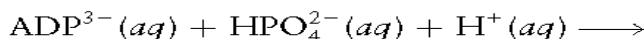
Taking data from text Appendix D, the standard entropy *change* of the reaction at 25°C is

$$\Delta S_{298}^\circ = 2 \underbrace{(239.95)}_{\text{NO}_2(g)} + 2 \underbrace{(69.91)}_{\text{H}_2\text{O}(l)} - 1 \underbrace{(121.21)}_{\text{N}_2\text{H}_4(l)} - 3 \underbrace{(205.03)}_{\text{O}_2(g)} = \boxed{-116.58 \text{ J K}^{-1}}$$

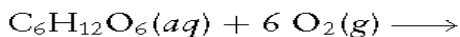
**Tip.** The symbol for a standard molar entropy at 298 K is  $S_{298}^\circ$ . These quantities are *always* positive numbers. Avoid the common error of taking the  $S_{298}^\circ$  of an element to equal zero.

b) The gaseous form of a substance always has a larger molar entropy than its liquid or solid form. This means that for the process  $\text{N}_2\text{H}_4(l) \longrightarrow \text{N}_2\text{H}_4(g)$ ,  $\Delta S > 0$ , which means that the  $S_{298}^\circ$  of  $\text{N}_2\text{H}_4(g)$  is more positive than the  $S_{298}^\circ$  of  $\text{N}_2\text{H}_4(l)$ . This causes  $\Delta S_{298}^\circ$  for the reaction of  $\text{N}_2\text{H}_4(g)$  with  $\text{O}_2(g)$  to be algebraically smaller, or more negative, than  $\Delta S_{298}^\circ$  for the reaction of  $\text{N}_2\text{H}_4(l)$  with  $\text{O}_2(g)$ .

34. The primary medium for free energy storage in living cells is adenosine triphosphate (ATP). Its formation from adenosine diphosphate (ADP) is not spontaneous:



Cells couple ATP production with the metabolism of glucose (a sugar):



The reaction of 1 molecule of glucose leads to the formation of 38 molecules of ATP from ADP. Show how the coupling makes this reaction spontaneous. What fraction of the free energy released in the oxidation of glucose is stored in the ATP?

The mode of coupling between the oxidation of glucose and the reduction of  $\text{ADP}^{-3}$  is not explained. Fortunately, it is not necessary to know it. Simply combine the free energy changes of the two reactions by adding 38 times the first to the second

$$\Delta G_{\text{tot}} = -2872 + 38(34.5) = -1561 \text{ kJ}$$

Because  $\Delta G < 0$ , the coupled process is spontaneous. The fraction of free energy stored is

$$\frac{38(34.5 \text{ kJ})}{2872 \text{ kJ}} = 0.456$$



40. In each cycle of its operation, a thermal engine absorbs 1000 J of heat from a large heat reservoir at 400 K and discharges heat to another large heat sink at 300 K. Calculate:
- (a) The thermodynamic efficiency of the heat engine, operated reversibly
  - (b) The quantity of heat discharged to the low-temperature sink each cycle
  - (c) The maximum amount of work the engine can perform each cycle

a)

$$\epsilon = \frac{T_h - T_l}{T_h} = \frac{(400 - 300) \text{ K}}{400 \text{ K}} = 0.25$$

b)

$$0.25 = \frac{q_h + q_l}{q_h} = \frac{(1000 + q_l) \text{ J}}{1000 \text{ J}} \quad \text{hence} \quad q_l = (250 - 1000) \text{ J} = -750 \text{ J}$$

c)

$$\epsilon = \frac{-w_{\text{net}}}{q_h} = \frac{-w_{\text{net}}}{1000 \text{ J}} = 0.250$$

$$-w_{\text{net}} = 250 \text{ J} = \text{maximum work performed by engine}$$

58. The strongest known chemical bond is that in carbon monoxide, CO, with bond enthalpy of  $1.05 \times 10^3 \text{ kJ mol}^{-1}$ . Furthermore, the entropy increase in a gaseous dissociation of the kind  $\text{AB} \rightleftharpoons \text{A} + \text{B}$  is about  $110 \text{ J mol}^{-1} \text{ K}^{-1}$ . These factors establish a temperature above which there is essentially no chemistry of molecules. Show why this is so, and find the temperature.

Dissociation of any substance with diatomic molecules has a positive  $\Delta H$  and a positive  $\Delta S$ . This combination of signs means that a temperature exists above which  $\Delta G$  of dissociation is negative, and the substance tends to dissociate into its constituent atoms. That temperature  $T$  is given by  $T = \Delta H / \Delta S$ . For  $\text{CO}(g)$ ,

$$T = \frac{1.05 \times 10^3 \text{ kJ}}{0.11 \text{ kJ K}^{-1}} = 9.5 \times 10^3 \text{ K}$$

If the most stable diatomic molecules tend to dissociate above 9500 K, then all molecules tend to dissociate above 9500 K: no molecules; no chemistry of molecules. Note that the  $\Delta S$  of this reaction is pressure-dependent. It increases by  $R \ln 10 = 19 \text{ J K}^{-1}$  (in accord with text equation 13.9) for each 10-fold decrease in pressure. At pressures much lower than 1 atm,  $\Delta S$  is even larger and the maximum temperature for stability is lower.