SOLUTIONS

PROBLEM SET 4

CHM 3400, Dr. Chatfield

4.2 One of the many statements of the second law of thermodynamics is: Heat cannot flow from a colder body to a warmer one without external aid. Assume two systems, 1 and 2, at T_1 and T_2 ($T_2 > T_1$). Show that if a quantity of heat q did flow spontaneously from 1 to 2, the process would result in a decrease in entropy of the universe. (You may assume that the heat flows very slowly so that the process can be regarded as reversible. Assume also that the loss of heat by system 1 and the gain of heat by system 2 do not affect T_1 and T_2.)

The universe is comprised of the two systems. Since heat flows from system 1 to 2, $q_1 = -q_{rev}$ and $q_2 = q_{rev}$.

$$\Delta S_{univ} = \Delta S_1 + \Delta S_2 = \frac{q_1}{T_1} + \frac{q_2}{T_2} = \frac{-q_{rev}}{T_1} + \frac{q_{rev}}{T_2}$$

$$= q_{rev}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) < 0 \qquad \text{since } T_1 < T_2$$

**4.8** Calculate the values of ΔU, ΔH, and ΔS for the following process:

$$\text{1 mole of liquid water at } 25°\text{ C and 1 atm} \rightarrow \text{1 mol of steam at } 100°\text{ C and 1 atm}$$

The molar heat of vaporization of water at 373 K is 40.79 kJ mol^{-1}, and the molar heat capacity of water is 75.3 J K^{-1} mol^{-1}. Assume the molar heat capacity to be temperature independent and ideal-gas behavior.

The problem can be solved readily by breaking down the process into two steps, each carried out at 1 atm: (1) H$_2$O(l) is heated from 25° C to 100° C, then (2) H$_2$O(l) at 100° C is heated to effect the phase transformation to H$_2$O(g) at 100° C.

Step 1

$$\text{H}_2\text{O}(l), \, 25°\text{ C} \rightarrow \text{H}_2\text{O}(l), \, 100°\text{ C}$$
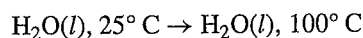
$$\Delta H = C_P \Delta T = (1 \text{ mol}) \left(75.3 \text{ J K}^{-1}\text{mol}^{-1}\right)(373.2 \text{ K} - 298.2 \text{ K}) = 5.648 \times 10^3 \text{ J}$$
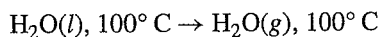
ΔU is related to ΔH by

$$\Delta U = \Delta H - P\Delta V$$

Since both reactant and product are in the liquid phase, ΔV is negligible. Therefore,

$$\Delta U = \Delta H = 5.648 \times 10^3 \text{ J}$$

$$\Delta S = C_P \ln \frac{T_2}{T_1} = (1 \text{ mol}) \left(75.3 \text{ J K}^{-1}\text{mol}^{-1}\right) \ln \frac{373.2 \text{ K}}{298.2 \text{ K}} = 16.89 \text{ J K}^{-1}$$

Step 2

$$\text{H}_2\text{O}(l), \, 100°\text{ C} \rightarrow \text{H}_2\text{O}(g), \, 100°\text{ C}$$

$$\Delta H = n\Delta_{\text{vap}}\overline{H} = (1 \text{ mol}) \left(40.79 \text{ kJ mol}^{-1}\right) = 40.79 \text{ kJ}$$

To calculate ΔU, the change in volume must first be determined. Since the volume of H$_2$O(g), V_g is much greater than that of H$_2$O(l), V_l, the latter is ignored.

$$\Delta U = \Delta H - P\Delta V = \Delta H - P\left(V_g - V_l\right) = \Delta H - PV_g$$

$$= \Delta H - P\frac{nRT}{P} = \Delta H - nRT$$

$$= 40.79 \text{ kJ} - (1 \text{ mol}) \left(8.314 \text{ J mol}^{-1}\text{K}^{-1}\right)(373.2 \text{ K}) \left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)$$

$$= 37.687 \text{ kJ}$$

$$\Delta S = \frac{\Delta_{\text{vap}}H}{T_b} = \frac{40.79 \times 10^3 \text{ J}}{373.15 \text{ K}} = 109.31 \text{ J K}^{-1}$$

The values of ΔH, ΔU, and ΔS for the entire process can be obtained by summing the corresponding quantities calculated in the two steps:

$$\Delta H = 5.648 \text{ kJ} + 40.79 \text{ kJ} = 46.44 \text{ kJ}$$

$$\Delta U = 5.648 \text{ kJ} + 37.687 \text{ kJ} = 43.34 \text{ kJ}$$

$$\Delta S = 16.89 \text{ J K}^{-1} + 109.31 \text{ J K}^{-1} = 126.2 \text{ J K}^{-1}$$

4.12 A quantity of 35.0 g of water at 25.0 °C (called A) is mixed with 160.0 g of water at ... (called B). **(a)** Calculate the final temperature of the system, assuming that the mixing is carried out adiabatically. **(b)** Calculate the entropy change of A, B, and the entire system.

(a) Let the final temperature be T_f and the specific heat of water be s. Since the process is carried out adiabatically, the energy entering A as heat, q_A, is equal in magnitude but opposite in sign to that leaving B as heat, q_B.

$$q_A = -q_B$$

$$(35.0 \text{ g}) \, s \, (T_f - 25.0° \text{ C}) = - (160.0 \text{ g}) \, s \, (T_f - 86.0° \text{ C})$$

$$T_f - 25.0° \text{ C} = -4.571 \, (T_f - 86.0° \text{ C})$$

$$= -4.571 T_f + 393.1° \text{ C}$$

$$5.571 T_f = 418.1° \text{ C}$$

$$T_f = 75.0° \text{ C}$$

(b) Let the entropy change of A be ΔS_A and the entropy change of B be ΔS_B.

$$\Delta S_A = C_P \ln \frac{348.2 \text{ K}}{298.2 \text{ K}} = \left(\frac{35.0 \text{ g}}{18.02 \text{ g mol}^{-1}} \right) \left(75.3 \text{ J K}^{-1} \text{mol}^{-1} \right) \ln \frac{348.2 \text{ K}}{298.2 \text{ K}} = 22.7 \text{ J K}^{-1}$$

$$\Delta S_B = C_P \ln \frac{348.2 \text{ K}}{359.2 \text{ K}} = \left(\frac{160.0 \text{ g}}{18.02 \text{ g mol}^{-1}} \right) \left(75.3 \text{ J K}^{-1} \text{mol}^{-1} \right) \ln \frac{348.2 \text{ K}}{359.2 \text{ K}} = -20.79 \text{ J K}^{-1}$$

$$\Delta S_{total} = \Delta S_A + \Delta S_B = 22.7 \text{ J K}^{-1} - 20.79 \text{ J K}^{-1} = 1.9 \text{ J K}^{-1}$$

4.16 One mole of an ideal gas at 298 K expands isothermally from 1.0 L to 2.0 L **(a)** reversibly and **(b)** against a constant external pressure of 12.2 atm. Calculate the values of ΔS_{sys}, ΔS_{surr}, and ΔS_{univ} in both cases. Are your results consist with the nature of the processes?

(a)

$$\Delta S_{sys} = nR \ln \frac{V_2}{V_1} = (1 \text{ mol}) \left(8.314 \text{ J K}^{-1} \text{mol}^{-1} \right) \ln \frac{2.0 \text{ L}}{1.0 \text{ L}} = 5.8 \text{ J K}^{-1}$$

$$\Delta S_{surr} = -5.8 \text{ J K}^{-1}$$

$$\Delta S_{univ} = 0 \text{ J K}^{-1}$$

(b) ΔS_{sys} is the same above, that is, 5.8 J K^{-1}, since S is a state function, although ΔS has to be calculated using a reversible path.

ΔS_{surr} can be calculated once q_{surr} is determined. The latter quantity is related to q_{sys}, which in turn can be calculated from the work done by the system, w, and the first law of thermodynamics.

$$w = -P_{ex} \Delta V = - (12.2 \text{ atm}) (2.0 \text{ L} - 1.0 \text{ L}) \left(\frac{101.3 \text{ J}}{1 \text{ L atm}} \right) = -1.236 \times 10^3 \text{ J}$$

According to the first law, $\Delta U = q + w$. Since $\Delta U = 0$ for an isothermal process, $q_{sys} = q = -w = 1.236 \times 10^3 \text{ J}$. The entropy change of the surroundings is

$$\Delta S_{surr} = \frac{q_{surr}}{T_{surr}} = \frac{-q_{sys}}{T_{surr}} = \frac{-1.236 \times 10^3 \text{ J}}{298 \text{ K}} = -4.15 \text{ J K}^{-1}$$

Now ΔS_{univ} can be determined: $\Delta S_{univ} = 5.8 \text{ J K}^{-1} - 4.15 \text{ J K}^{-1} = 1.7 \text{ J K}^{-1}$

The results in both parts are consistent with the nature of the processes. Specifically, for a reversible process, $\Delta S_{univ} = 0$, whereas for a spontaneous process, $\Delta S_{univ} > 0$.

4.23 The heat capacity of hydrogen may be represented by

$$\overline{C}_P = (1.554 + 0.0022T)\ \text{J K}^{-1}\ \text{mol}^{-1}$$

Calculate the entropy changes for the system, surroundings, and the universe for the **(a)** reversible heating, and **(b)** irreversible heating of 1.0 mole of hydrogen from 300 K to 600 K. [*Hint*: In **(b)**, assume the surroundings to be at 600 K.]

(a) For the reversible process,

$$\Delta S_{\text{sys}} = \int \frac{dq_{\text{rev}}}{T} = \int_{300\ \text{K}}^{600\ \text{K}} \frac{C_P dT}{T}$$

$$= \int_{300\ \text{K}}^{600\ \text{K}} (1.0\ \text{mol}) \left(\frac{1.554 + 0.0022T}{T}\ \text{J K}^{-1}\ \text{mol}^{-1} \right) dT$$

$$= \left[\int_{300\ \text{K}}^{600\ \text{K}} \left(\frac{1.554}{T} + 0.0022 \right) dT \right]\ \text{J K}^{-1}$$

$$= \left[(1.554 \ln T + 0.0022T)|_{300}^{600} \right]\ \text{J K}^{-1}$$

$$= \{[1.554 \ln 600 + 0.0022\,(600)] - [1.554 \ln 300 + 0.0022\,(300)]\}\ \text{J K}^{-1}$$

$$= 1.7\ \text{J K}^{-1}$$

$$\Delta S_{\text{surr}} = -1.7\ \text{J K}^{-1}$$

$$\Delta S_{\text{univ}} = 0\ \text{J K}^{-1}$$

(b) S is a state function, but ΔS_{sys} has to be calculated using a reversible path. Therefore, it is the same as that calculated above, that is, 1.7 J K^{-1}.

ΔS_{surr} can be calculated once q_{surr} is determined.

$$q_{\text{surr}} = -q_{\text{sys}} = -\Delta H \qquad \text{(P is constant)}$$

$$= -\int_{300\ \text{K}}^{600\ \text{K}} C_P dT$$

$$= -\int_{300\ \text{K}}^{600\ \text{K}} (1.0\ \text{mol}) \left[(1.554 + 0.0022T)\ \text{J K}^{-1}\ \text{mol}^{-1} \right] dT$$

$$= - \left(1.554T + 0.0011T^2 \right)_{300}^{600}\ \text{J}$$

$$= - \left\{ \left[1.554\,(600) + 0.0011\,(600)^2 \right] - \left[1.554\,(300) + 0.0011\,(300)^2 \right] \right\}\ \text{J}$$

$$= -7.63 \times 10^2\ \text{J}$$

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T_{\text{surr}}} = \frac{-7.63 \times 10^2\ \text{J}}{600\ \text{K}} = -1.3\ \text{J K}^{-1}$$

Therefore,

$$\Delta S_{\text{univ}} = 1.7\ \text{J K}^{-1} - 1.3\ \text{J K}^{-1} = 0.4\ \text{J K}^{-1}$$

4.28 A quantity of 0.35 mole of an ideal gas initially at 15.6° C is expanded from 1.2 L to 7.4 L. Calculate the values of w, q, ΔU, ΔS, and ΔG if the process is carried out **(a)** isothermally and reversibly, and **(b)** isothermally and irreversibly against an external pressure of 1.0 atm.

(a) For an isothermal process of an ideal gas, $\Delta U = 0$ and $\Delta H = 0$.

$$w = -nRT \ln \frac{V_2}{V_1} = - (0.35 \text{ mol}) \left(8.314 \text{ J K}^{-1} \text{mol}^{-1}\right) (288.8 \text{ K}) \ln \frac{7.4 \text{ L}}{1.2 \text{ L}}$$

$$= -1.53 \times 10^3 \text{ J} = -1.5 \times 10^3 \text{ J}$$

$$q = \Delta U - w = 1.53 \times 10^3 \text{ J} = 1.5 \times 10^3 \text{ J}$$

$$\Delta S = \frac{q_{rev}}{T} = \frac{1.53 \times 10^3 \text{ J}}{288.8 \text{ K}} = 5.30 \text{ J K}^{-1} = 5.3 \text{ J K}^{-1}$$

$$\Delta G = \Delta H - T\Delta S = 0 - (288.8 \text{ K}) \left(5.30 \text{ J K}^{-1}\right) = -1.5 \times 10^3 \text{ J}$$

(b) Since U, S, and G are state functions, ΔU, ΔS, ΔG depend only on the initial and final states and not on the path. Therefore, they are the same as above, that is

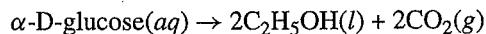$$\Delta U = 0 \text{ J}$$

$$\Delta S = 5.3 \text{ J K}^{-1}$$

$$\Delta G = -1.5 \times 10^3 \text{ J}$$

w and q, however, are path dependent.

$$w = -P_{ex}\Delta V = - (1.0 \text{ atm}) (7.4 \text{ L} - 1.2 \text{ L}) \left(\frac{101.3 \text{ J}}{1 \text{ L atm}}\right) = -6.3 \times 10^2 \text{ J}$$

$$q = \Delta U - w = 6.3 \times 10^2 \text{ J}$$

4.30 Use the values listed in Appendix 2 to calculate the value of $\Delta_r G^\circ$ for the following alcohol fermentation:

$$\alpha\text{-D-glucose}(aq) \rightarrow 2C_2H_5OH(l) + 2CO_2(g)$$

$$(\Delta_f \overline{G}^\circ[\alpha\text{-D-glucose}(aq)] = -914.5 \text{ kJ mol}^{-1})$$

$$\Delta_r G^\circ = 2\Delta_f \overline{G}^\circ \left[C_2H_5OH(l)\right] + 2\Delta_f \overline{G}^\circ \left[CO_2(g)\right] - \Delta_f \overline{G}^\circ \left[\alpha\text{-D-glucose}(aq)\right]$$

$$= 2\left(-174.2 \text{ kJ mol}^{-1}\right) + 2\left(-394.4 \text{ kJ mol}^{-1}\right) - \left(-914.5 \text{ kJ mol}^{-1}\right)$$

$$= -222.7 \text{ kJ mol}^{-1}$$

4.32 Certain bacteria in the soil obtain the necessary energy for growth by oxidizing nitrite to nitrate:

$$2NO_2^-(aq) + O_2(g) \rightarrow 2NO_3^-(aq)$$
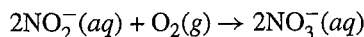
Given that the standard Gibbs energies of formation of NO_2^- and NO_3^- are $-34.6 \text{ kJ mol}^{-1}$ and $-110.5 \text{ kJ mol}^{-1}$, respectively, calculate the amount of Gibbs energy released when 1 mole of NO_2^- is oxidized to 1 mole of NO_3^-.

According to the chemical equation $2NO_2^-(aq) + O_2(g) \rightarrow 2NO_3^-(aq)$,

$$\Delta_r G^\circ = 2\Delta_f \overline{G}^\circ \left[NO_3^-(aq)\right] - 2\Delta_f \overline{G}^\circ \left[NO_2^-(aq)\right] - \Delta_f \overline{G}^\circ \left[O_2(g)\right]$$

$$= 2\left(-110.5 \text{ kJ mol}^{-1}\right) - 2\left(-34.6 \text{ kJ mol}^{-1}\right) - 0 \text{ kJ mol}^{-1}$$

$$= -151.8 \text{ kJ mol}^{-1}$$

When 1 mole of NO_2^- is oxidized to 1 mole of NO_3^-,

$$\Delta_r G^\circ = \frac{-151.8 \text{ kJ mol}^{-1}}{2} = -75.9 \text{ kJ mol}^{-1}$$