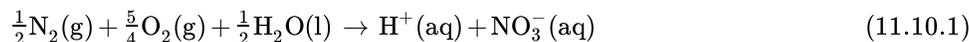


## 11.10: Chapter 11 Problems

An underlined problem number or problem-part letter indicates that the numerical answer appears in Appendix I.

### 11.1

Use values of  $\Delta_f H^\circ$  and  $\Delta_f G^\circ$  in Appendix H to evaluate the standard molar reaction enthalpy and the thermodynamic equilibrium constant at 298.15 K for the oxidation of nitrogen to form aqueous nitric acid:



### 11.2

In 1982, the International Union of Pure and Applied Chemistry recommended that the value of the standard pressure  $p^\circ$  be changed from 1 atm to 1 bar. This change affects the values of some standard molar quantities of a substance calculated from experimental data.

(a) Find the changes in  $H_m^\circ$ ,  $S_m^\circ$ , and  $G_m^\circ$  for a gaseous substance when the standard pressure is changed isothermally from 1.01325 bar (1 atm) to exactly 1 bar. (Such a small pressure change has an entirely negligible effect on these quantities for a substance in a condensed phase.)

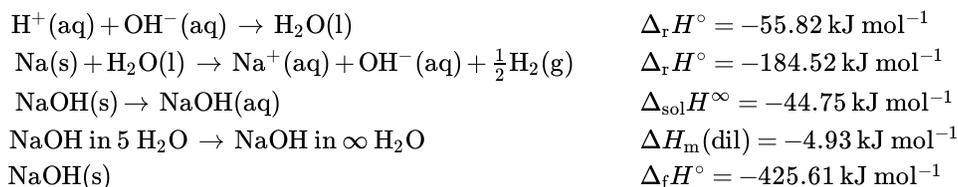
(b) What are the values of the corrections that need to be made to the standard molar enthalpy of formation, the standard molar entropy of formation, and the standard molar Gibbs energy of formation of  $\text{N}_2\text{O}_4(\text{g})$  at 298.15 K when the standard pressure is changed from 1.01325 bar to 1 bar?

### 11.3

From data for mercury listed in Appendix H, calculate the saturation vapor pressure of liquid mercury at both 298.15 K and 273.15 K. You may need to make some reasonable approximations.

### 11.4

Given the following experimental values at  $T = 298.15 \text{ K}$ ,  $p = 1 \text{ bar}$ :



Using only these values, calculate:

- (a)  $\Delta_f H^\circ$  for  $\text{Na}^+(\text{aq})$ ,  $\text{NaOH}(\text{aq})$ , and  $\text{OH}^-(\text{aq})$ ;  
 (b)  $\Delta_f H$  for  $\text{NaOH}$  in 5  $\text{H}_2\text{O}$ ;  
 (c)  $\Delta H_m(\text{sol})$  for the dissolution of 1 mol  $\text{NaOH}(\text{s})$  in 5 mol  $\text{H}_2\text{O}$ .

States 1 and 2 referred to in this problem are the initial and final states of the isothermal bomb process. The temperature is the reference temperature of 298.15 K.

(a) Parts (a)–(c) consist of simple calculations of some quantities needed in later parts of the problem. Begin by using the masses of  $\text{C}_6\text{H}_{14}$  and  $\text{H}_2\text{O}$  placed in the bomb vessel, and their molar masses, to calculate the amounts (moles) of  $\text{C}_6\text{H}_{14}$  and  $\text{H}_2\text{O}$  present initially in the bomb vessel. Then use the stoichiometry of the combustion reaction to find the amount of  $\text{O}_2$  consumed and the amounts of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  present in state 2. (There is not enough information at this stage to allow you to find the amount of  $\text{O}_2$  present, just the change.) Also find the final mass of  $\text{H}_2\text{O}$ . Assume that oxygen is present in excess and the combustion reaction goes to completion.

(b) From the molar masses and the densities of liquid  $\text{C}_6\text{H}_{14}$  and  $\text{H}_2\text{O}$ , calculate their molar volumes.

(c) From the amounts present initially in the bomb vessel and the internal volume, find the volumes of liquid  $\text{C}_6\text{H}_{14}$ , liquid  $\text{H}_2\text{O}$ , and gas in state 1 and the volumes of liquid  $\text{H}_2\text{O}$  and gas in state 2. For this calculation, you can neglect the small change in the volume of liquid  $\text{H}_2\text{O}$  due to its vaporization.

(d) When the bomb vessel is charged with oxygen and before the inlet valve is closed, the pressure at 298.15 K measured on an external gauge is found to be  $p_1 = 30.00 \text{ bar}$ . To a good approximation, the gas phase of state 1 has the equation of state of pure O

$_2$  (since the vapor pressure of water is only 0.1% of 30.00 bar). Assume that this equation of state is given by  $V_m = RT/p + B_{BB}$  (Eq. 2.2.8), where  $B_{BB}$  is the second virial coefficient of  $O_2$  listed in Table 11.3. Solve for the amount of  $O_2$  in the gas phase of state 1. The gas phase of state 2 is a mixture of  $O_2$  and  $CO_2$ , again with a negligible partial pressure of  $H_2O$ . Assume that only small fractions of the total amounts of  $O_2$  and  $CO_2$  dissolve in the liquid water, and find the amount of  $O_2$  in the gas phase of state 2 and the mole fractions of  $O_2$  and  $CO_2$  in this phase.

(e) You now have the information needed to find the pressure in state 2, which cannot be measured directly. For the mixture of  $O_2$  and  $CO_2$  in the gas phase of state 2, use Eq. 9.3.23 to calculate the second virial coefficient. Then solve the equation of state of Eq. 9.3.21 for the pressure. Also calculate the partial pressures of the  $O_2$  and  $CO_2$  in the gas mixture.

(f) Although the amounts of  $H_2O$  in the gas phases of states 1 and 2 are small, you need to know their values in order to take the energy of vaporization into account. In this part, you calculate the fugacities of the  $H_2O$  in the initial and final gas phases, in part (g) you use gas equations of state to evaluate the fugacity coefficients of the  $H_2O$  (as well as of the  $O_2$  and  $CO_2$ ), and then in part (h) you find the amounts of  $H_2O$  in the initial and final gas phases.

The pressure at which the pure liquid and gas phases of  $H_2O$  are in equilibrium at 298.15 K (the saturation vapor pressure of water) is 0.03169 bar Use Eq. 7.8.18 to estimate the fugacity of  $H_2O(g)$  in equilibrium with pure liquid water at this temperature and pressure. The effect of pressure on fugacity in a one-component liquid–gas system is discussed in Sec. 12.8.1; use Eq. 12.8.3 to find the fugacity of  $H_2O$  in gas phases equilibrated with liquid water at the pressures of states 1 and 2 of the isothermal bomb process. (The mole fraction of  $O_2$  dissolved in the liquid water is so small that you can ignore its effect on the chemical potential of the water.)

(g) Calculate the fugacity coefficients of  $H_2O$  and  $O_2$  in the gas phase of state 1 and of  $H_2O$ ,  $O_2$ , and  $CO_2$  in the gas phase of state 2.

For state 1, in which the gas phase is practically-pure  $O_2$ , you can use Eq. 7.8.18 to calculate  $\phi_{O_2}$ . The other calculations require Eq. 9.3.29, with the value of  $B'_i$  found from the formulas of Eq. 9.3.26 or Eqs. 9.3.27 and 9.3.28 ( $y_A$  is so small that you can set it equal to zero in these formulas).

Use the fugacity coefficient and partial pressure of  $O_2$  to evaluate its fugacity in states 1 and 2; likewise, find the fugacity of  $CO_2$  in state 2. [You calculated the fugacity of the  $H_2O$  in part (f).]

(h) From the values of the fugacity and fugacity coefficient of a constituent of a gas mixture, you can calculate the partial pressure with Eq. 9.3.17, then the mole fraction with  $y_i = p_i/p$ , and finally the amount with  $n_i = y_i n$ . Use this method to find the amounts of  $H_2O$  in the gas phases of states 1 and 2, and also calculate the amounts of  $H_2O$  in the liquid phases of both states.

(i) Next, consider the  $O_2$  dissolved in the water of state 1 and the  $O_2$  and  $CO_2$  dissolved in the water of state 2. Treat the solutions of these gases as ideal dilute with the molality of solute  $i$  given by  $m_i = f_i/k_{m,i}$  (Eq. 9.4.21). The values of the Henry's law constants of these gases listed in Table 11.3 are for the standard pressure of 1 bar. Use Eq. 12.8.35 to find the appropriate values of  $k_{m,i}$  at the pressures of states 1 and 2, and use these values to calculate the amounts of the dissolved gases in both states.

(j) At this point in the calculations, you know the values of all properties needed to describe the initial and final states of the isothermal bomb process. You are now able to evaluate the various Washburn corrections. These corrections are the internal energy changes, at the reference temperature of 298.15 K, of processes that connect the standard states of substances with either state 1 or state 2 of the isothermal bomb process.

First, consider the gaseous  $H_2O$ . The Washburn corrections should be based on a pure-liquid standard state for the  $H_2O$ . Section 7.9 shows that the molar internal energy of a pure gas under ideal-gas conditions (low pressure) is the same as the molar internal energy of the gas in its standard state at the same temperature. Thus, the molar internal energy change when a substance in its pure-liquid standard state changes isothermally to an ideal gas is equal to the standard molar internal energy of vaporization,  $\Delta_{vap}U^\circ$ . Using the value of  $\Delta_{vap}U^\circ$  for  $H_2O$  given in Table 11.3, calculate  $\Delta U$  for the vaporization of liquid  $H_2O$  at pressure  $p^\circ$  to ideal gas in the amount present in the gas phase of state 1. Also calculate  $\Delta U$  for the condensation of ideal gaseous  $H_2O$  in the amount present in the gas phase of state 2 to liquid at pressure  $p^\circ$ .

(k) Next, consider the dissolved  $O_2$  and  $CO_2$ , for which gas standard states are used. Assume that the solutions are sufficiently dilute to have infinite-dilution behavior; then the partial molar internal energy of either solute in the solution at the standard pressure  $p^\circ = 1$  bar is equal to the standard partial molar internal energy based on a solute standard state (Sec. 9.7.1). Values of  $\Delta_{sol}U^\circ$  are listed in Table 11.3. Find  $\Delta U$  for the dissolution of  $O_2$  from its gas standard state to ideal-dilute solution at pressure  $p^\circ$

in the amount present in the aqueous phase of state 1. Find  $\Delta U$  for the desolution (transfer from solution to gas phase) of  $O_2$  and of  $CO_2$  from ideal-dilute solution at pressure  $p^\circ$ , in the amounts present in the aqueous phase of state 2, to their gas standard states.

(l) Calculate the internal energy changes when the liquid phases of state 1 (*n*-hexane and aqueous solution) are compressed from  $p^\circ$  to  $p_1$  and the aqueous solution of state 2 is decompressed from  $p_2$  to  $p^\circ$ . Use an approximate expression from Table 7.4, and treat the cubic expansion coefficient of the aqueous solutions as being the same as that of pure water.

(m) The final Washburn corrections are internal energy changes of the gas phases of states 1 and 2.  $H_2O$  has such low mole fractions in these phases that you can ignore  $H_2O$  in these calculations; that is, treat the gas phase of state 1 as pure  $O_2$  and the gas phase of state 2 as a binary mixture of  $O_2$  and  $CO_2$ .

One of the internal energy changes is for the compression of gaseous  $O_2$ , starting at a pressure low enough for ideal-gas behavior ( $U_m = U_m^\circ$ ) and ending at pressure  $p_1$  to form the gas phase present in state 1. Use the approximate expression for  $U_m - U_m^\circ(g)$  in Table 7.5 to calculate  $\Delta U = U(p_1) - nU_m^\circ(g)$ ; a value of  $dB/dT$  for pure  $O_2$  is listed in Table 11.3.

The other internal energy change is for a process in which the gas phase of state 2 at pressure  $p_2$  is expanded until the pressure is low enough for the gas to behave ideally, and the mixture is then separated into ideal-gas phases of pure  $O_2$  and  $CO_2$ . The molar internal energies of the separated low-pressure  $O_2$  and  $CO_2$  gases are the same as the standard molar internal energies of these gases. The internal energy of unmixing ideal gases is zero (Eq. 11.1.11). The dependence of the internal energy of the gas mixture is given, to a good approximation, by  $U = \sum_i U_i^\circ(g) - npT dB/dT$ , where  $B$  is the second virial coefficient of the gas mixture; this expression is the analogy for a gas mixture of the approximate expression for  $U_m - U_m^\circ(g)$  in Table 7.5. Calculate the value of  $dB/dT$  for the mixture of  $O_2$  and  $CO_2$  in state 2 (you need Eq. 9.3.23 and the values of  $dB_{ij}/dT$  in Table 11.3) and evaluate  $\Delta U = \sum_i n_i U_i^\circ(g) - U(p_2)$  for the gas expansion.

(n) Add the internal energy changes you calculated in parts (j)–(m) to find the total internal energy change of the Washburn corrections. Note that most of the corrections occur in pairs of opposite sign and almost completely cancel one another. Which contributions are the greatest in magnitude?

(o) The internal energy change of the isothermal bomb process in the bomb vessel, corrected to the reference temperature of 298.15 K, is found to be  $\Delta U(\text{IBP}, T_{\text{ref}}) = -32.504 \text{ kJ}$ . Assume there are no side reactions or auxiliary reactions. From Eqs. 11.5.9 and 11.5.10, calculate the standard molar internal energy of combustion of *n*-hexane at 298.15 K.

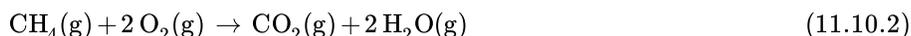
(p) From Eq. 11.5.13, calculate the standard molar enthalpy of combustion of *n*-hexane at 298.15 K.

### 11.8

By combining the results of Prob. 11.7(p) with the values of standard molar enthalpies of formation from Appendix H, calculate the standard molar enthalpy of formation of liquid *n*-hexane at 298.15 K.

### 11.9

Consider the combustion of methane:



Suppose the reaction occurs in a flowing gas mixture of methane and air. Assume that the pressure is constant at 1 bar, the reactant mixture is at a temperature of 298.15 K and has stoichiometric proportions of methane and oxygen, and the reaction goes to completion with no dissociation. For the quantity of gaseous product mixture containing 1 mol  $CO_2$ , 2 mol  $H_2O$ , and the nitrogen and other substances remaining from the air, you may use the approximate formula  $C_p(P) = a + bT$ , where the coefficients have the values  $a = 297.0 \text{ J K}^{-1}$  and  $b = 8.520 \times 10^{-2} \text{ J K}^{-2}$ . Solve Eq. 11.6.1 for  $T_2$  to estimate the flame temperature to the nearest kelvin.

### 11.10

The standard molar Gibbs energy of formation of crystalline mercury(II) oxide at 600.00 K has the value  $\Delta_f G^\circ = -26.386 \text{ kJ mol}^{-1}$ . Estimate the partial pressure of  $O_2$  in equilibrium with  $HgO$  at this temperature:  $2 \text{HgO}(\text{s}) \rightleftharpoons 2 \text{Hg}(\text{l}) + \text{O}_2(\text{g})$ .

### 11.11

The combustion of hydrogen is a reaction that is known to “go to completion.”

(a) Use data in Appendix H to evaluate the thermodynamic equilibrium constant at 298.15 K for the reaction



(b) Assume that the reaction is at equilibrium at 298.15 K in a system in which the partial pressure of  $O_2$  is 1.0 bar. Assume ideal-gas behavior and find the equilibrium partial pressure of  $H_2$  and the number of  $H_2$  molecules in  $1.0\text{ m}^3$  of the gas phase.

(c) In the preceding part, you calculated a very small value (a fraction) for the number of  $H_2$  molecules in  $1.0\text{ m}^3$ . Statistically, this fraction can be interpreted as the fraction of a given length of time during which one molecule is present in the system. Take the age of the universe as  $1.0 \times 10^{10}$  years and find the total length of time in seconds, during the age of the universe, that a  $H_2$  molecule is present in the equilibrium system. (This hypothetical value is a dramatic demonstration of the statement that the limiting reactant is essentially entirely exhausted during a reaction with a large value of  $K$ .)

### 11.12

Let G represent carbon in the form of *graphite* and D represent the *diamond* crystal form. At 298.15 K, the thermodynamic equilibrium constant for  $G \rightleftharpoons D$ , based on a standard pressure  $p^\circ = 1\text{ bar}$ , has the value  $K = 0.31$ . The molar volumes of the two crystal forms at this temperature are  $V_m(G) = 5.3 \times 10^{-6}\text{ m}^3\text{ mol}^{-1}$  and  $V_m(D) = 3.4 \times 10^{-6}\text{ m}^3\text{ mol}^{-1}$ .

(a) Write an expression for the reaction quotient  $Q_{\text{rxn}}$  as a function of pressure. Use the approximate expression of the pressure factor given in Table 9.6.

(b) Use the value of  $K$  to estimate the pressure at which the D and G crystal forms are in equilibrium with one another at 298.15 K. (This is the lowest pressure at which graphite could in principle be converted to diamond at this temperature.)

### 11.13

Consider the dissociation reaction  $N_2O_4(g) \rightarrow 2NO_2(g)$  taking place at a constant temperature of 298.15 K and a constant pressure of 0.0500 bar. Initially (at  $\xi = 0$ ) the system contains 1.000 mol of  $N_2O_4$  and no  $NO_2$ . Other needed data are found in Appendix H. Assume ideal-gas behavior.

(a) For values of the advancement  $\xi$  ranging from 0 to 1 mol, at an interval of 0.1 mol or less, calculate  $[G(\xi) - G(0)]$  to the nearest 0.01 kJ. A computer spreadsheet would be a convenient way to make the calculations.

(b) Plot your values of  $G(\xi) - G(0)$  as a function of  $\xi$ , and draw a smooth curve through the points.

(c) On your curve, indicate the estimated position of  $\xi_{\text{eq}}$ . Calculate the activities of  $N_2O_4$  and  $NO_2$  for this value of  $\xi$ , use them to estimate the thermodynamic equilibrium constant  $K$ , and compare your result with the value of  $K$  calculated from Eq. 11.8.11.

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