Solutions Manual for Thermodynamics and Chemistry

Second Edition

by

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Contents

Preface

This manual contains detailed solutions to the problems appearing at the end of each chapter of the text *Thermodynamics and Chemistry*.

Each problem printed in the text is reproduced in this manual, followed by a worked-out solution. If a figure or table accompanies a problem in the text, it is also reproduced here. Included within a solution may be an additional figure or table that does not appear in the text. All figures, tables, and footnotes in this manual are numbered consecutively (Figure 1, Figure 2, etc.) and so do not agree with the numbering in the text.

In most cases of a numerical calculation involving physical quantities, the setup in this manual shows the values of given individual physical quantities expressed in SI base units and SI derived units, without prefixes. The result of the calculation is then expressed in SI base units and SI derived units appropriate to the physical quantity being evaluated. Since the factors needed to convert the units of the given quantities to the units of the calculated quantity all have numerical values of unity when this procedure is followed, the conversion factors are not shown.

Of course, the solution given in this manual for any particular problem is probably not the only way the problem can be solved; other solutions may be equally valid.

Chapter 1 Introduction

1.1 Consider the following equations for the pressure of a real gas. For each equation, find the dimensions of the constants a and b and express these dimensions in SI units.

(a) The Dieterici equation:

$$p = \frac{RTe^{-(an/VRT)}}{(V/n) - b}$$

Solution:

Since an/VRT is a power, it is dimensionless and a has the same dimensions as VRT/n. These dimensions are volume · energy/amount^2, expressed in $\mathrm{m^3\,J\,mol^{-2}}$. b has the same dimensions as V/n, which are volume/amount expressed in $\mathrm{m^3\ mol^{-1}}$.

(b) The Redlich–Kwong equation:

$$p = \frac{RT}{(V/n) - b} - \frac{an^2}{T^{1/2}V(V + nb)}$$

Solution:

The term $an^2/T^{1/2}V(V + nb)$ has the same dimensions as p, so a has the same dimensions as $T^{1/2}V^2pn^{-2}$. The SI units are $\mathrm{K^{1/2}\ m^6\ Pa\,mol^{-2}}$. b has the same dimensions as V/n, which are volume/amount expressed in $\mathrm{m^3\ mol^{-1}}$.

Chapter 2 Systems and Their Properties

2.1 Let X represent the quantity V^2 with dimensions (length)^6. Give a reason that X is or is not an extensive property. Give a reason that X is or is not an intensive property.

Solution:

X is not an extensive property because it is not additive: $(V^{\alpha})^2 + (V^{\beta})^2 \neq (V^{\alpha} + V^{\beta})^2$ (e.g., $1^2 + 1^2 \neq 2^2$).
X is not an intensive property because it is dependent on volume.

2.2 Calculate the *relative uncertainty* (the uncertainty divided by the value) for each of the measurement methods listed in Table 2.2 on page 38, using the typical values shown. For each of the five physical quantities listed, which measurement method has the smallest relative uncertainty?

Solution:

Mass:
  analytical balance, $0.1 \times 10^{-3}\,\text{g}/100\,\text{g} = 1 \times 10^{-6}$
  micro balance, $0.1 \times 10^{-6}\,\text{g}/20 \times 10^{-3}\,\text{g} = 5 \times 10^{-6}$
Volume:
  pipet, $0.02\,\text{ml}/10\,\text{mL} = 2 \times 10^{-3}$
  volumetric flask, $0.3 \times 10^{-3}\,\text{L}/1\,\text{L} = 3 \times 10^{-4}$
Density:
  pycnometer, $2 \times 10^{-3}\,\text{g mL}^{-1}/1\,\text{g mL}^{-1} = 2 \times 10^{-3}$
  magnetic float densimeter, $0.1 \times 10^{-3}\,\text{g mL}^{-1}/1\,\text{g mL}^{-1} = 1 \times 10^{-4}$
Pressure:
  manometer or barometer, $0.001\,\text{Torr}/760\,\text{Torr} = 1 \times 10^{-6}$
  diaphragm gauge, $1\,\text{Torr}/100\,\text{Torr} = 1 \times 10^{-2}$
Temperature:
  gas thermometer, $0.001\,\text{K}/10\,\text{K} = 1 \times 10^{-4}$
  mercury thermometer, $0.01\,\text{K}/300\,\text{K} = 3 \times 10^{-5}$
  platinum resistance thermometer, $0.0001\,\text{K}/300\,\text{K} = 3 \times 10^{-7}$
  optical pyrometer, $0.03\,\text{K}/1300\,\text{K} = 2 \times 10^{-5}$

The measurement of temperature with a platinum resistance thermometer has the least relative uncertainty, and the measurement of pressure with a diaphragm gauge has the greatest. For each physical quantity, the measurement method with smallest relative uncertainty is underlined in the preceding list.

2.3 Table 1 on the next page lists data obtained from a constant-volume gas thermometer containing samples of varying amounts of helium maintained at a certain fixed temperature T_2 in the gas bulb.[1] The molar volume V_{m} of each sample was evaluated from its pressure in the bulb at a reference temperature of $T_1 = 7.1992\,\text{K}$, corrected for gas nonideality with the known value of the second virial coefficient at that temperature.

Use these data and Eq. 2.2.2 on page 34 to evaluate T_2 and the second virial coefficient of helium at temperature T_2. (You can assume the third and higher virial coefficients are negligible.)

Solution:

With the third and higher virial coefficients set equal to zero, Eq. 2.2.2 becomes

$$pV_{\text{m}} = RT\left(1 + \frac{B}{V_{\text{m}}}\right)$$

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[1] Ref. [13].

Table 1 Helium at a fixed temperature

$(1/V_\mathrm{m})\,/10^2\,\mathrm{mol\,m^{-3}}$	$(p_2V_\mathrm{m}/R)\,/K$
1.0225	2.7106
1.3202	2.6994
1.5829	2.6898
1.9042	2.6781
2.4572	2.6580
2.8180	2.6447
3.4160	2.6228
3.6016	2.6162
4.1375	2.5965
4.6115	2.5790
5.1717	2.5586

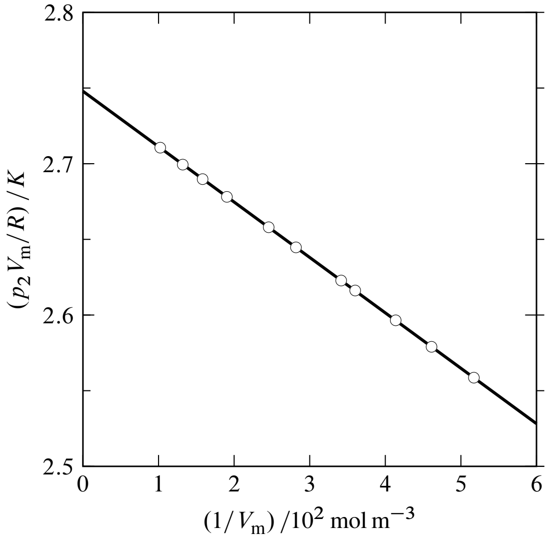

Figure 1

According to this equation, a plot of p_2V_m/R versus $1/V_\mathrm{m}$ should be linear with an intercept at $1/V_\mathrm{m}=0$ equal to T_2 and a slope equal to BT_2. The plot is shown in Fig. 1. A least-squares fit of the data to a first-order polynomial yields an intercept of 2.7478 K and a slope of $-3.659\times10^{-4}\,\mathrm{K\,m^3\,mol^{-1}}$. The temperature and second virial coefficient therefore have the values

$$T_2 = 2.7478\,\mathrm{K}$$

$$B = \frac{-3.659\times10^{-4}\,\mathrm{K\,m^3\,mol^{-1}}}{2.7478\,\mathrm{K}} = -1.332\times10^{-4}\,\mathrm{m^3\,mol^{-1}}$$

2.4 Discuss the proposition that, to a certain degree of approximation, a living organism is a steady-state system.

Solution:

The organism can be treated as being in a steady state if we assume that its mass is constant and if we neglect internal motion. Matter enters the organism in the form of food, water, and oxygen; waste matter and heat leave the system.

2.5 The value of ΔU for the formation of one mole of crystalline potassium iodide from its elements at 25 °C and 1 bar is $-327.9\,\mathrm{kJ}$. Calculate Δm for this process. Comment on the feasibility of measuring this mass change.

Solution:

$\Delta m = \Delta U/c^2 = -327.9 \times 10^3\,\mathrm{J}/(2.998 \times 10^8\,\mathrm{m\,s^{-1}})^2 = -3.648 \times 10^{-12}\,\mathrm{kg}$

This mass change is much less than the uncertainty of a microbalance (Table 2.2), which does not even have the capacity to weigh one mole of KI—so it is hopeless to try to measure this mass change.

Chapter 3 The First Law

3.1 Assume you have a metal spring that obeys Hooke's law: $F = c(l - l_0)$, where F is the force exerted on the spring of length l, l_0 is the length of the unstressed spring, and c is the spring constant. Find an expression for the work done on the spring when you reversibly compress it from length l_0 to a shorter length l'.

Solution:

$$w = \int_{l_0}^{l'} F\,\mathrm{d}l = c\int_{l_0}^{l'} (l - l_0)\,\mathrm{d}l = \tfrac{1}{2}c(l - l_0)^2\Big|_{l_0}^{l'} = \tfrac{1}{2}c(l' - l_0)^2$$

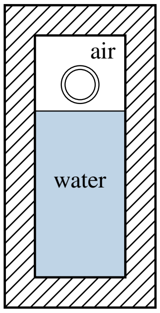

Figure 2

3.2 The apparatus shown in Fig. 2 consists of fixed amounts of water and air and an incompressible solid glass sphere (a marble), all enclosed in a rigid vessel resting on a lab bench. Assume the marble has an adiabatic outer layer so that its temperature cannot change, and that the walls of the vessel are also adiabatic.

Initially the marble is suspended above the water. When released, it falls through the air into the water and comes to rest at the bottom of the vessel, causing the water and air (but not the marble) to become slightly warmer. The process is complete when the system returns to an equilibrium state. The system energy change during this process depends on the frame of reference and on how the system is defined. ΔE_{sys} is the energy change in a lab frame, and ΔU is the energy change in a specified local frame.

For each of the following definitions of the system, give the *sign* (positive, negative, or zero) of both ΔE_{sys} and ΔU, and state your reasoning. Take the local frame for each system to be a center-of-mass frame.

Solution:

Because q is zero in each part of this problem, ΔE_{sys} is equal to w_{lab} and ΔU is equal to w. We can use Eq. 3.1.4 with $\Delta\big(v_{\mathrm{cm}}^2\big)$ set equal to zero: $\Delta U - \Delta E_{\mathrm{sys}} = w_{\mathrm{lab}} - w = -mg\Delta z_{\mathrm{cm}}$ or $\Delta E_{\mathrm{sys}} = \Delta U + mg\Delta z_{\mathrm{cm}}$.

(a) The system is the marble.

Solution:

ΔU is zero, because the state of the system is unchanged.
ΔE_{sys} is negative, because in the lab frame the marble does work on the water (page 83). This can also be deduced using $\Delta E_{\mathrm{sys}} = \Delta U + mg\Delta z_{\mathrm{cm}}$ and the fact that ΔU is zero and Δz_{cm} is negative.

(b) The system is the combination of water and air.

Solution:

ΔU is positive, because the system's temperature increases at constant volume.
ΔE_{sys} is positive, because both ΔU and Δz_{cm} are positive (the center of gravity of the water rises when the marble enters the water). This can also be deduced by considering that the net force exerted by the sinking marble on the water and the displacement of the boundary at the marble are in the same direction (downward).

(c) The system is the combination of water, air, and marble.

Solution:

ΔE_{sys} is zero, because w_{lab} is zero (there is no displacement of the system boundary in the lab frame).
ΔU is positive, because ΔE_{sys} is zero and Δz_{cm} is negative. This can also be deduced from the fact that U is an extensive property, so that ΔU for this system is equal to the sum of the internal energy change of the marble and the internal energy change of the water and air. In parts (a) and (b) these changes were found to be zero and positive, respectively.

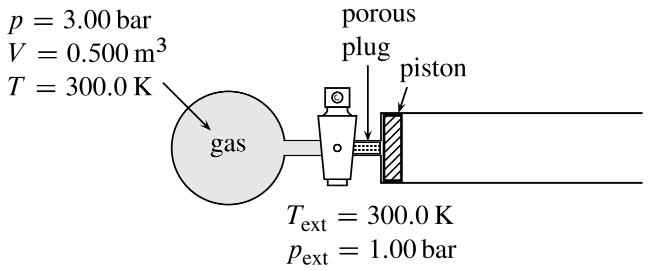

Figure 3

3.3 Figure 3 shows the initial state of an apparatus consisting of an ideal gas in a bulb, a stopcock, a porous plug, and a cylinder containing a frictionless piston. The walls are diathermal, and the surroundings are at a constant temperature of 300.0 K and a constant pressure of 1.00 bar.

When the stopcock is opened, the gas diffuses slowly through the porous plug, and the piston moves slowly to the right. The process ends when the pressures are equalized and the piston stops moving. The *system* is the gas. Assume that during the process the temperature throughout the system differs only infinitesimally from 300.0 K and the pressure on both sides of the piston differs only infinitesimally from 1.00 bar.

(a) Which of these terms correctly describes the process: isothermal, isobaric, isochoric, reversible, irreversible?

Solution:

The process is isothermal and irreversible, but not isobaric, isochoric, or reversible. Note that the pressure gradient across the porous plug prevents intermediate states of the process from being equilibrium states, and keeps the process from being reversible; there is no infinitesimal change that can reverse the motion of the piston.

(b) Calculate q and w.

Solution:

Because T is constant and the gas is ideal, the relation $p_1 V_1 = p_2 V_2$ holds, and the final volume is found from

$$V_2 = \frac{p_1 V_1}{p_2} = \frac{(3.00\,\text{bar})(0.500\,\text{m}^3)}{1.00\,\text{bar}} = 1.50\,\text{m}^3$$

The work must be calculated from the pressure at the moving portion of the boundary (the inner surface of the piston); this is a constant pressure of 1.00 bar:

$$w = -\int_{V_1}^{V_2} p\,\text{d}V = -p(V_2 - V_1) = -(1.00\times 10^5\,\text{Pa})(1.50 - 0.500)\text{m}^3$$

$$= -1.00\times 10^5\,\text{J}$$

$$q = \Delta U - w = 0 - w = 1.00\times 10^5\,\text{J}$$

3.4 Consider a horizontal cylinder-and-piston device similar to the one shown in Fig. 3.5 on page 72. The piston has mass m. The cylinder wall is diathermal and is in thermal contact with a heat reservoir of temperature T_ext. The *system* is an amount n of an ideal gas confined in the cylinder by the piston.

The initial state of the system is an equilibrium state described by p_1 and $T = T_\text{ext}$. There is a constant external pressure p_ext, equal to twice p_1, that supplies a constant external force on the piston. When the piston is released, it begins to move to the left to compress the gas. Make the idealized assumptions that (1) the piston moves with negligible friction; and (2) the gas remains practically uniform (because the piston is massive and its motion is slow) and has a practically constant temperature $T = T_\text{ext}$ (because temperature equilibration is rapid).

(a) Describe the resulting process.

Solution:

The piston will oscillate; the gas volume will change back and forth between the initial value V_1 and a minimum value V_2.

(b) Describe how you could calculate w and q during the period needed for the piston velocity to become zero again.

Solution:

The relation between V_1 and V_2 is found by equating the work done on the gas by the piston, $-nRT\ln(V_2/V_1)$, to the work done on the piston by the external pressure, $-p_\text{ext}(V_2 - V_1)$, where p_ext is given by $p_\text{ext} = 2p_1 = 2nRT/V_1$. The result is $V_2 = 0.2032V_1$, $w = 1.5936nRT$, $q = -w = -1.5936nRT$.

(c) Calculate w and q during this period for 0.500 mol gas at 300 K.

Solution:

$w = (1.5936)(0.500\,\text{mol})(8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})(300\,\text{K}) = 1.99\times 10^3\,\text{J}$,
$q = -w = -1.99\times 10^3\,\text{J}$.

3.5 This problem is designed to test the assertion on page 60 that for typical thermodynamic processes in which the elevation of the center of mass changes, it is usually a good approximation to set w equal to w_lab. The cylinder shown in Fig. 4 on the next page has a vertical orientation, so the elevation of the center of mass of the gas confined by the piston changes as the piston slides up or down. The *system* is the gas. Assume the gas is nitrogen ($M = 28.0\,\text{g}\,\text{mol}^{-1}$) at 300 K, and initially the vertical length l of the gas column is one meter. Treat the nitrogen as an ideal gas, use a center-of-mass local frame, and take the center of mass to be at the midpoint of the gas column. Find the difference between the values of w and w_lab, expressed as a percentage of w, when the gas is expanded reversibly and isothermally to twice its initial volume.

Solution:

Use Eq. 3.1.4: $w - w_\text{lab} = -\frac{1}{2}m\Delta\left(v_\text{cm}^2\right) - mg\Delta z_\text{cm}$.

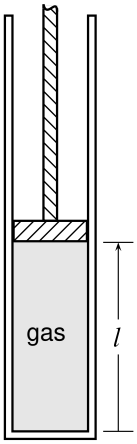

Figure 4

$\Delta(v_{\text{cm}}^2)$ is zero, and Δz_{cm} is $\frac{l_2}{2} - \frac{l_1}{2} = \frac{2l_1}{2} - \frac{l_1}{2} = \frac{1}{2}l_1$; therefore $w - w_{\text{lab}} = -\frac{1}{2}mgl_1$.

From Eq. 3.5.1, which assumes the local frame is a lab frame:
$w_{\text{lab}} = -nRT \ln \dfrac{V_2}{V_1} = -nRT \ln 2$.

Use these relations to obtain $w = w_{\text{lab}} - \frac{1}{2}mgl_1 = -nRT \ln 2 - \frac{1}{2}mgl_1$.

$$\frac{w - w_{\text{lab}}}{w} = \frac{-\frac{1}{2}mgl_1}{-nRT \ln 2 - \frac{1}{2}mgl_1} = \frac{1}{\dfrac{2nRT \ln 2}{mgl_1} + 1} = \frac{1}{\dfrac{2RT \ln 2}{Mgl_1} + 1}$$

$$= \frac{1}{\dfrac{(2)(8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})(300\,\text{K})(\ln 2)}{(28.0 \times 10^{-3}\,\text{kg}\,\text{mol}^{-1})(9.81\,\text{m}\,\text{s}^{-2})(1\,\text{m})} + 1} = 7.9 \times 10^{-5}$$

which is 0.0079%.

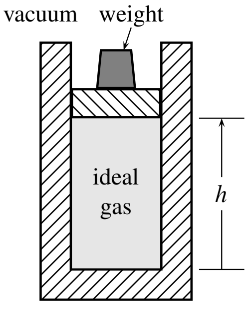

Figure 5

3.6 Figure 5 shows an ideal gas confined by a frictionless piston in a vertical cylinder. The *system* is the gas, and the boundary is adiabatic. The downward force on the piston can be varied by changing the weight on top of it.

(a) Show that when the system is in an equilibrium state, the gas pressure is given by $p = mgh/V$ where m is the combined mass of the piston and weight, g is the acceleration of free fall, and h is the elevation of the piston shown in the figure.

Solution:

The piston must be stationary in order for the system to be in an equilibrium state. Therefore the net force on the piston is zero: $pA_s - mg = 0$ (where A_s is the cross-section area of the cylinder). This gives $p = mg/A_s = mg/(V/h) = mgh/V$.

(b) Initially the combined mass of the piston and weight is m_1, the piston is at height h_1, and the system is in an equilibrium state with conditions p_1 and V_1. The initial temperature is $T_1 = p_1V_1/nR$. Suppose that an additional weight is suddenly placed on the piston, so that m increases from m_1 to m_2, causing the piston to sink and the gas to be compressed adiabatically and spontaneously. Pressure gradients in the gas, a form of friction, eventually cause the piston to come to rest at a final position h_2. Find the final volume, V_2, as a function of p_1, p_2, V_1, and C_V. (Assume that the heat capacity of the gas, C_V, is independent of temperature.) Hint: The potential energy of the surroundings changes by $m_2g\Delta h$; since the kinetic energy of the piston and weights is zero at the beginning and end of the process, and the boundary is adiabatic, the internal energy of the gas must change by $-m_2g\Delta h = -m_2g\Delta V/A_s = -p_2\Delta V$.

Solution:

There are two expressions for ΔU:

$$\Delta U = C_V(T_2 - T_1) \quad \text{and} \quad \Delta U = -p_2(V_2 - V_1)$$

Equate the two expressions and substitute $T_1 = p_1V_1/nR$ and $T_2 = p_2V_2/nR$:

$$(C_V/nR)(p_2V_2 - p_1V_1) = -p_2(V_2 - V_1)$$

Solve for V_2: $V_2 = \dfrac{C_V p_1 + nRp_2}{p_2(C_V + nR)}V_1$

(c) It might seem that by making the weight placed on the piston sufficiently large, V_2 could be made as close to zero as desired. Actually, however, this is not the case. Find expressions for V_2 and T_2 in the limit as m_2 approaches infinity, and evaluate V_2/V_1 in this limit if the heat capacity is $C_V = (3/2)nR$ (the value for an ideal monatomic gas at room temperature).

Solution:

Since p_2 is equal to m_2g/A_s, p_2 must approach ∞ as m_2 approaches ∞. In the expression for V_2, the term C_Vp_1 becomes negligible as p_2 approaches ∞; then p_2 cancels from the numerator and denominator giving

$$V_2 \to \frac{nR}{C_V + nR}V_1$$

The relation $T_2 = p_2V_2/nR$ shows that with a finite limiting value of V_2, T_2 must approach ∞ as p_2 does. If C_V equals $(3/2)nR$, then V_2/V_1 approaches $2/5 = 0.4$.

3.7 The solid curve in Fig. 3.7 on page 80 shows the path of a reversible adiabatic expansion or compression of a fixed amount of an ideal gas. Information about the gas is given in the figure caption. For compression along this path, starting at $V = 0.3000\,\mathrm{dm^3}$ and $T = 300.0\,\mathrm{K}$ and ending at $V = 0.1000\,\mathrm{dm^3}$, find the final temperature to 0.1 K and the work.

Solution:

$$C_V = nC_{V,\mathrm{m}} = n(1.500R) = (0.0120\,\mathrm{mol})(1.500)(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) = 0.1497\,\mathrm{J\,K^{-1}}$$

$$T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{nR/C_V} = (300.0\,\text{K})(3.000)^{(1/1.500)} = 624.0\,\text{K}$$

$$w = C_V(T_2 - T_1) = (0.1497\,\text{J K}^{-1})(624.0\,\text{K} - 300.0\,\text{K}) = 48.5\,\text{J}$$

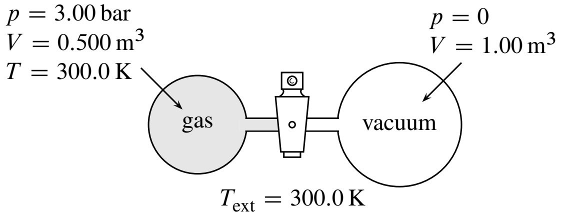

Figure 6

3.8 Figure 6 shows the initial state of an apparatus containing an ideal gas. When the stopcock is opened, gas passes into the evacuated vessel. The *system* is the gas. Find q, w, and ΔU under the following conditions.

(a) The vessels have adiabatic walls.

Solution:

$q = 0$ because the process is adiabatic; $w = 0$ because it is a free expansion; therefore, $\Delta U = q + w = 0$.

(b) The vessels have diathermal walls in thermal contact with a water bath maintained at 300. K, and the final temperature in both vessels is $T = 300.$ K.

Solution:

$\Delta U = 0$ because the gas is ideal and the final and initial temperatures are the same; $w = 0$ because it is a free expansion; therefore $q = \Delta U - w = 0$.

3.9 Consider a reversible process in which the shaft of system A in Fig. 3.11 makes one revolution in the direction of increasing ϑ. Show that the gravitational work of the weight is the same as the shaft work given by $w = mgr\Delta\vartheta$.

Solution:

The circumference of the shaft at the point where the cord is attached is $2\pi r$. When the shaft makes one revolution in the direction of increasing ϑ, a length of cord equal to $2\pi r$ becomes wrapped around the shaft, and the weight rises by a distance $\Delta z = 2\pi r$. The gravitational work, ignoring the buoyant force of the air, is $w = mg\Delta z = mgr(2\pi)$, which is the same as the shaft work $mgr\Delta\vartheta$ with $\Delta\vartheta = 2\pi$.

3.10 This problem guides you through a calculation of the mechanical equivalent of heat using data from one of James Joule's experiments with a paddle wheel apparatus (see Sec. 3.7.2). The experimental data are collected in Table 2 on the next page.

In each of his experiments, Joule allowed the weights of the apparatus to sink to the floor twenty times from a height of about 1.6 m, using a crank to raise the weights before each descent (see Fig. 3.14 on page 89). The paddle wheel was engaged to the weights through the roller and strings only while the weights descended. Each descent took about 26 seconds, and the entire experiment lasted 35 minutes. Joule measured the water temperature with a sensitive mercury-in-glass thermometer at both the start and finish of the experiment.

Table 2 Data for Problem 3.10. The values are from Joule's 1850 paper[a] and have been converted to SI units.

Properties of the paddle wheel apparatus:	
combined mass of the two lead weights	26.3182 kg
mass of water in vessel	6.04118 kg
mass of water with same heat capacity as paddle wheel, vessel, and lid[b]	0.27478 kg
Measurements during the experiment:	
number of times weights were wound up and released	20
change of elevation of weights during each descent	-1.5898 m
final downward velocity of weights during descent	$0.0615\,\mathrm{m\,s^{-1}}$
initial temperature in vessel	288.829 K
final temperature in vessel	289.148 K
mean air temperature	289.228 K

[a] Ref. [91], p. 67, experiment 5.

[b] Calculated from the masses and specific heat capacities of the materials.

For the purposes of the calculations, define the *system* to be the combination of the vessel, its contents (including the paddle wheel and water), and its lid. All energies are measured in a lab frame. Ignore the small quantity of expansion work occurring in the experiment. It helps conceptually to think of the cellar room in which Joule set up his apparatus as being effectively isolated from the rest of the universe; then the only surroundings you need to consider for the calculations are the part of the room outside the system.

(a) Calculate the change of the gravitational potential energy E_p of the lead weights during each of the descents. For the acceleration of free fall at Manchester, England (where Joule carried out the experiment) use the value $g = 9.813\,\mathrm{m\,s^{-2}}$. This energy change represents a decrease in the energy of the surroundings, and would be equal in magnitude and opposite in sign to the stirring work done on the system if there were no other changes in the surroundings.

Solution:

$$\Delta E_\mathrm{p} = mg\Delta h = (26.3182\,\mathrm{kg})(9.813\,\mathrm{m\,s^{-2}})(-1.5898\,\mathrm{m}) = -410.6\,\mathrm{J}$$

(b) Calculate the kinetic energy E_k of the descending weights just before they reached the floor. This represents an increase in the energy of the surroundings. (This energy was dissipated into thermal energy in the surroundings when the weights came to rest on the floor.)

Solution:

$$E_\mathrm{k} = (1/2)mv^2 = (1/2)(26.3182\,\mathrm{kg})(0.0615\,\mathrm{m\,sec^{-1}})^2 = 0.0498\,\mathrm{J}$$

(c) Joule found that during each descent of the weights, friction in the strings and pulleys decreased the quantity of work performed on the system by 2.87 J. This quantity represents an increase in the thermal energy of the surroundings. Joule also considered the slight stretching of the strings while the weights were suspended from them: when the weights came to rest on the floor, the tension was relieved and the potential energy of the strings changed by -1.15 J. Find the total change in the energy of the surroundings during the entire experiment from all the effects described to this point. Keep in mind that the weights descended 20 times during the experiment.

Solution:

$$\Delta E_\mathrm{sur} = (20)\,(-410.6 + 0.0498 + 2.87 - 1.15)\ \mathrm{J} = -8176.6\,\mathrm{J}$$

(d) Data in Table 2 show that change of the temperature of the system during the experiment was

$$\Delta T = (289.148 - 288.829)\,\text{K} = +0.319\,\text{K}$$

The paddle wheel vessel had no thermal insulation, and the air temperature was slighter warmer, so during the experiment there was a transfer of some heat into the system. From a correction procedure described by Joule, the temperature change that would have occurred if the vessel had been insulated is estimated to be $+0.317$ K.

Use this information together with your results from part (c) to evaluate the work needed to increase the temperature of one gram of water by one kelvin. This is the "mechanical equivalent of heat" at the average temperature of the system during the experiment. (As mentioned on p. 87, Joule obtained the value 4.165 J based on all 40 of his experiments.)

Solution:

$\Delta E_{\text{sys}} = -\Delta E_{\text{sur}} = 8176.6\,\text{J}$

$$\frac{8176.6\,\text{J}}{(6.04118\,\text{kg} + 0.27478\,\text{kg})(10^3\,\text{g kg}^{-1})(0.317\,\text{K})} = 4.08\,\text{J g}^{-1}\,\text{K}^{-1}$$

3.11 Refer to the apparatus depicted in Fig. 3.1 on page 61. Suppose the mass of the external weight is $m = 1.50\,\text{kg}$, the resistance of the electrical resistor is $R_{\text{el}} = 5.50\,\text{k}\Omega$, and the acceleration of free fall is $g = 9.81\,\text{m s}^{-2}$. For how long a period of time will the external cell need to operate, providing an electric potential difference $|\Delta\phi| = 1.30\,\text{V}$, to cause the same change in the state of the system as the change when the weight sinks 20.0 cm without electrical work? Assume both processes occur adiabatically.

Solution:

The value of ΔU is the same in both processes.
Sinking of weight:
$\Delta U = w = mg\Delta h = (1.50\,\text{kg})(9.81\,\text{m s}^{-2})(20.0 \times 10^{-2}\,\text{m}) = 2.943\,\text{J}$
Electrical work:
$\Delta U = w = I^2 R_{\text{el}} t \qquad \Delta\phi = I R_{\text{el}}$ (Ohm's law);
therefore, $\Delta U = (\Delta\phi)^2 t / R_{\text{el}}$.

$$t = \frac{R_{\text{el}}\Delta U}{(\Delta\phi)^2} = \frac{(5.50 \times 10^3\,\Omega)(2.943\,\text{J})}{(1.30\,\text{V})^2} = 9.58 \times 10^3\,\text{s}$$

Chapter 4 The Second Law

4.1 Explain why an electric refrigerator, which transfers energy by means of heat from the cold food storage compartment to the warmer air in the room, is not an impossible "Clausius device."

Solution:

In addition to heat transfer, there is consumption of electrical energy from the surroundings. The refrigerator does not fit the description of the device declared by the Clausius statement of the second law to be impossible; such a device would produce no other effect but the transfer of energy by means of heat from a cooler to a warmer body.

4.2 A system consisting of a fixed amount of an ideal gas is maintained in thermal equilibrium with a heat reservoir at temperature T. The system is subjected to the following isothermal cycle:

1. The gas, initially in an equilibrium state with volume V_0, is allowed to expand into a vacuum and reach a new equilibrium state of volume V'.
2. The gas is reversibly compressed from V' to V_0.

For this cycle, find expressions or values for w, $\oint đq/T$, and $\oint \mathrm{d}S$.

Solution:

Step 1: $w = 0$ because it is a free expansion; $\Delta U = 0$ because it is an ideal gas and isothermal; therefore $q = \Delta U - w = 0$.
Step 2: $w = -nRT \ln(V_0/V')$ (Eq. 3.5.1); $\Delta U = 0$ because it is an ideal gas and isothermal; therefore $q = \Delta U - w = nRT \ln(V_0/V')$.
Overall: $w = -nRT \ln(V_0/V')$; $\oint đq/T = q/T = nR \ln(V_0/V')$; $\oint \mathrm{d}S = 0$ because S is a state function. Note that $\oint \mathrm{d}S$ is greater than $\oint đq/T$ because of the irreversible expansion step, in agreement with the mathematical statement of the second law.

4.3 In an irreversible isothermal process of a closed system:

(a) Is it possible for ΔS to be negative?

Solution:

Yes. Provided ΔS is less negative than q/T, there is no violation of the second law.

(b) Is it possible for ΔS to be less than q/T?

Solution:

According to the second law, no.

<u>4.4</u> Suppose you have two blocks of copper, each of heat capacity $C_V = 200.0\,\mathrm{J\,K^{-1}}$. Initially one block has a uniform temperature of $300.00\,\mathrm{K}$ and the other $310.00\,\mathrm{K}$. Calculate the entropy change that occurs when you place the two blocks in thermal contact with one another and surround them with perfect thermal insulation. Is the sign of ΔS consistent with the second law? (Assume the process occurs at constant volume.)

Solution:

Since the blocks have equal heat capacities, a given quantity of heat transfer from the warmer to the cooler block causes temperature changes that are equal in magnitude and of opposite signs. The final equilibrium temperature is $305.00\,\mathrm{K}$, the average of the initial values.

When the temperature of one of the blocks changes reversibly from T_1 to T_2, the entropy change is

$$\Delta S = \int \frac{đq}{T} = \int_{T_1}^{T_2} \frac{C_V\,\mathrm{d}T}{T} = C_V \ln \frac{T_2}{T_1}$$

Cooler block: $\Delta S = 200.0\,\mathrm{J\,K^{-1}} \ln \dfrac{305.00\,\mathrm{K}}{300.00\,\mathrm{K}} = 3.306\,\mathrm{J\,K^{-1}}$

Warmer block: $\Delta S = 200.0\,\mathrm{J\,K^{-1}} \ln \dfrac{305.00\,\mathrm{K}}{310.00\,\mathrm{K}} = -3.252\,\mathrm{J\,K^{-1}}$

Total entropy change: $\Delta S = 3.306\,\mathrm{J\,K^{-1}} - 3.252\,\mathrm{J\,K^{-1}} = 0.054\,\mathrm{J\,K^{-1}}$

The sign of ΔS is positive as predicted by the second law for an irreversible process in an isolated system.

4.5 Refer to the apparatus shown in Figs. 3 on page 9 and 6 on page 13 and described in Probs. 3.3 and 3.8. For both systems, evaluate ΔS for the process that results from opening the stopcock. Also evaluate $\int đq/T_{\mathrm{ext}}$ for both processes (for the apparatus in Fig. 6, assume the vessels have adiabatic walls). Are your results consistent with the mathematical statement of the second law?

Solution:

The initial states of the ideal gas are the same in both processes, and the final states are also the same. Therefore the value of ΔS is the same for both processes. Calculate ΔS for a *reversible* isothermal expansion of the ideal gas from the initial to the final volume:

$$\begin{aligned}\Delta S &= \frac{q}{T} = \frac{-w}{T} = nR\ln\left(\frac{V_2}{V_1}\right) = \frac{p_1V_1}{T}\ln\left(\frac{V_2}{V_1}\right)\\ &= \frac{(3.00\times10^5\,\mathrm{Pa})(0.500\,\mathrm{m^3})}{300.\,\mathrm{K}}\ln\left(\frac{1.50\,\mathrm{m^3}}{0.500\,\mathrm{m^3}}\right)\\ &= 549\,\mathrm{J\,K^{-1}}\end{aligned}$$

Use the values of q found in Probs. 3.3 and 3.8 to evaluate $\int đq/T_{\mathrm{ext}}$:
For the expansion through the porous plug,
$\int đq/T_{\mathrm{ext}} = q/T = 1.00\times10^5\,\mathrm{J}/300.\,\mathrm{K} = 333\,\mathrm{J\,K^{-1}}$.
For the expansion into the evacuated vessel, $\int đq/T_{\mathrm{ext}} = q/T = 0$.
In both processes ΔS is greater than $\int đq/T_{\mathrm{ext}}$, consistent with the second law.

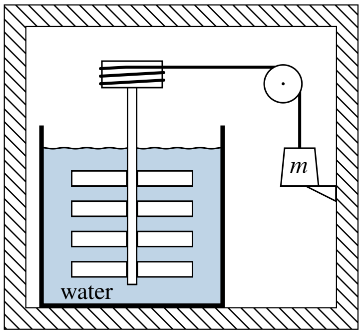

Figure 7

4.6 Figure 7 shows the walls of a rigid thermally-insulated box (cross hatching). The *system* is the contents of this box. In the box is a paddle wheel immersed in a container of water, connected by a cord and pulley to a weight of mass m. The weight rests on a stop located a distance h above the bottom of the box. Assume the heat capacity of the system, C_V, is independent of temperature. Initially the system is in an equilibrium state at temperature T_1. When the stop is removed, the weight irreversibly sinks to the bottom of the box, causing the paddle wheel to rotate in the water. Eventually the system reaches a final equilibrium state with thermal equilibrium. Describe a *reversible* process with the same entropy change as this irreversible process, and derive a formula for ΔS in terms of m, h, C_V, and T_1.

Solution:

When the stop is removed, the system is an isolated system of constant internal energy. To reversibly change the system between the same initial and final states as the irreversible process, reversibly lower the weight with gravitational work $w = -mgh$, then let reversible heat $q = C_V(T_2 - T_1)$ enter the system. Since ΔU is zero, the sum of q and w must be zero:

$$C_V(T_2 - T_1) - mgh = 0 \qquad T_2 = T_1 + \frac{mgh}{C_V}$$

The entropy change of the reversible process is

$$\Delta S = \int \frac{đq}{T_\mathrm{b}} = C_V \int_{T_1}^{T_2} \frac{\mathrm{d}T}{T} = C_V \ln \frac{T_2}{T_1} = C_V \ln\left(1 + \frac{mgh}{C_V T_1}\right)$$

This is also the entropy change of the irreversible process.

Chapter 5 Thermodynamic Potentials

5.1 Show that the enthalpy of a fixed amount of an ideal gas depends only on the temperature.

Solution:

The enthalpy H is defined by $H \overset{\text{def}}{=} U + pV$. For a fixed amount of an ideal gas, U depends only on T (Sec. 3.5.1). The product pV for an ideal gas also depends only on T since it is equal to nRT. Thus, the enthalpy of a fixed amount of an ideal gas, like the internal energy, depends only on T.

5.2 From concepts in this chapter, show that the heat capacities C_V and C_p of a fixed amount of an ideal gas are functions only of T.

Solution:

Since the internal energy and enthalpy of a fixed amount of an ideal gas depend only on T, the derivatives $\mathrm{d}U/\,\mathrm{d}T$ and $\mathrm{d}H/\,\mathrm{d}T$ must also depend only on T. These derivatives are equal to C_V and C_p in the case of an ideal gas (Eqs. 5.6.2 and 5.6.4).

5.3 During the reversible expansion of a fixed amount of an ideal gas, each increment of heat is given by the expression $đq = C_V\,\mathrm{d}T + (nRT/V)\,\mathrm{d}V$ (Eq. 4.3.4).

(a) A necessary and sufficient condition for this expression to be an exact differential is that the reciprocity relation must be satisfied for the independent variables T and V (see Appendix F). Apply this test to show that the expression is *not* an exact differential, and that heat therefore is not a state function.

Solution:

The reciprocity relation is satisfied if $(\partial C_V/\partial V)_T$ and $[\partial(nRT/V)/\partial T]_V$ are equal. For an ideal gas, C_V is a function only of T (Prob. 5.2). Thus, $(\partial C_V/\partial V)_T$ is zero. The other partial derivative is $[\partial(nRT/V)/\partial T]_V = nR/V$, which is not zero. Thus, the reciprocity relation is not satisfied, the expression is not an exact differential, and q is not a state function.

(b) By the same method, show that the entropy increment during the reversible expansion, given by the expression $\mathrm{d}S = đq/T$, is an exact differential, so that entropy is a state function.

Solution:

The expression for the entropy increment is $đq/T = (C_V/T)\,\mathrm{d}T + (nR/V)\,\mathrm{d}V$. The reciprocity relation is satisfied if $[\partial(C_V/T)/\partial V]_T$ and $[\partial(nR/V)/\partial T]_V$ are equal. Since C_V/T is a function only of T, $[\partial(C_V/T)/\partial V]_T$ is zero. $[\partial(nR/V)/\partial T]_V$ is also zero, so the reciprocity relation is satisfied, the expression is an exact differential, and S is a state function.

5.4 This problem illustrates how an expression for one of the thermodynamic potentials as a function of its natural variables contains the information needed to obtain expressions for the other thermodynamic potentials and many other state functions.

From statistical mechanical theory, a simple model for a hypothetical "hard-sphere" liquid (spherical molecules of finite size without attractive intermolecular forces) gives the following expression for the Helmholtz energy with its natural variables T, V, and n as the independent variables:

$$A = -nRT \ln\left[cT^{3/2}\left(\frac{V}{n} - b\right)\right] - nRT + na$$

Here a, b, and c are constants. Derive expressions for the following state functions of this hypothetical liquid as functions of T, V, and n.

(a) The entropy, S

Solution:

$$S = -\left(\frac{\partial A}{\partial T}\right)_{V,n} = nR\ln\left[cT^{3/2}\left(\frac{V}{n}-b\right)\right] + nR\left(\frac{3}{2}\right) + nR$$
$$= nR\ln\left[cT^{3/2}\left(\frac{V}{n}-b\right)\right] + \left(\frac{5}{2}\right)nR$$

(b) The pressure, p

Solution:

$$p = -\left(\frac{\partial A}{\partial V}\right)_{T,n} = \frac{nRT\left(\frac{1}{n}\right)}{\left(\frac{V}{n}-b\right)} = \frac{nRT}{V-nb}$$

(c) The chemical potential, μ

Solution:

$$\mu = \left(\frac{\partial A}{\partial n}\right)_{T,V} = -RT\ln\left[cT^{3/2}\left(\frac{V}{n}-b\right)\right] - \frac{nRT}{\left(\frac{V}{n}-b\right)}\left(-\frac{V}{n^2}\right) - RT + a$$
$$= -RT\ln\left[cT^{3/2}\left(\frac{V}{n}-b\right)\right] + \frac{VRT}{V-nb} - RT + a$$

(d) The internal energy, U

Solution:

$$U = A + TS = -nRT + na + \left(\frac{5}{2}\right)nRT = \left(\frac{3}{2}\right)nRT + na$$

(e) The enthalpy, H

Solution:

$$H = U + pV = \left(\frac{3}{2}\right)nRT + na + \left(\frac{nRT}{V-nb}\right)V$$

(f) The Gibbs energy, G

Solution:

$$G = U - TS + pV = H - TS$$
$$= \left(\frac{3}{2}\right)nRT + na + \left(\frac{nRT}{V-nb}\right)V - nRT\ln\left[cT^{3/2}\left(\frac{V}{n}-b\right)\right] - \left(\frac{5}{2}\right)nRT$$
$$= -nRT\ln\left[cT^{3/2}\left(\frac{V}{n}-b\right)\right] + \frac{nVRT}{V-nb} - nRT + na$$

Since μ is the molar Gibbs energy, the same result can be obtained using $G = n\mu$.

(g) The heat capacity at constant volume, C_V

Solution:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,n} = \left(\frac{3}{2}\right)nR$$

(h) The heat capacity at constant pressure, C_p (hint: use the expression for p to solve for V as a function of T, p, and n; then use $H = U + pV$)

Solution:

$$V = \frac{nRT}{p} + nb \qquad pV = nRT + nbp$$

$$C_p = \left(\frac{\partial H}{\partial T}\right)_{p,n} = \left[\frac{\partial(U + pV)}{\partial T}\right]_{p,n} = \left(\frac{3}{2}\right) nR + nR = \left(\frac{5}{2}\right) nR$$

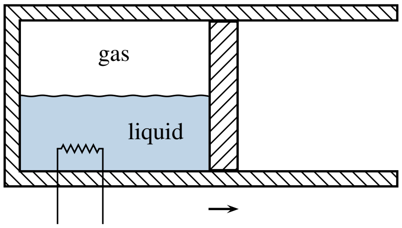

Figure 8

5.5 Figure 8 depicts a hypothetical liquid in equilibrium with its vapor. The liquid and gas are confined in a cylinder by a piston. An electrical resistor is immersed in the liquid. The *system* is the contents of the cylinder to the left of the piston (the liquid, gas, and resistor). The initial state of the system is described by

$$V_1 = 0.2200\,\text{m}^3 \qquad T_1 = 300.0\,\text{K} \qquad p_1 = 2.50\times10^5\,\text{Pa}$$

A constant current $I = 0.5000$ A is passed for 1600 s through the resistor, which has electric resistance $R_{\text{el}} = 50.00\,\Omega$. The piston moves slowly to the right against a constant external pressure equal to the vapor pressure of the liquid, 2.50×10^5 Pa, and some of the liquid vaporizes. Assume that the process is adiabatic and that T and p remain uniform and constant. The final state is described by

$$V_2 = 0.2400\,\text{m}^3 \qquad T_2 = 300.0\,\text{K} \qquad p_2 = 2.50\times10^5\,\text{Pa}$$

(a) Calculate q, w, ΔU, and ΔH.

Solution:

$q = 0$ because the process is adiabatic.

$$\begin{aligned} w &= -p\Delta V + I^2 R_{\text{el}}\Delta t \\ &= -(2.50\times10^5\,\text{Pa})(0.0200\,\text{m}^3) + (0.5000\,\text{A})^2(50.00\,\Omega)(1600\,\text{s}) \\ &= 1.50\times10^4\,\text{J} \end{aligned}$$

$$\Delta U = q + w = 1.50\times10^4\,\text{J}$$

$$\begin{aligned} \Delta H &= \Delta U + p\Delta V = 1.50\times10^4\,\text{J} + (2.50\times10^5\,\text{Pa})(0.0200\,\text{m}^3) \\ &= 2.00\times10^4\,\text{J} \end{aligned}$$

(b) Is the process reversible? Explain.

Solution:

The process is not reversible, because of the electrical work.

(c) Devise a reversible process that accomplishes the same change of state, and use it to calculate ΔS.

Solution:

The same change of state can be accomplished by omitting the electrical work and allowing energy to be reversibly transferred into the system by means of heat. The work is then equal to $-p\Delta V$. The quantity of heat must cause the same increase of internal energy as in the original process:

$$q = \Delta U - w = 1.50\times10^{4}\,\text{J} + (2.50\times10^{5}\,\text{Pa})(0.0200\,\text{m}^{3}) = 2.00\times10^{4}\,\text{J}$$

Calculate ΔS for this reversible process:

$$\Delta S = \frac{q}{T} = \frac{2.00\times10^{4}\,\text{J}}{300.0\,\text{K}} = 66.7\,\text{J}\,\text{K}^{-1}$$

(d) Compare q for the reversible process with ΔH. Does your result agree with Eq. 5.3.8?

Solution:

The heat for the isobaric process without nonexpansion work is equal to the enthalpy change, in agreement with Eq. 5.3.8.

Table 3 Surface tension of water at 1 bar[a]

$t/°\text{C}$	$\gamma/10^{-6}\,\text{J}\,\text{cm}^{-2}$
15	7.350
20	7.275
25	7.199
30	7.120
35	7.041

[a] Ref. [175].

5.6 Use the data in Table 3 to evaluate $(\partial S/\partial A_{\text{s}})_{T,p}$ at 25 °C, which is the rate at which the entropy changes with the area of the air–water interface at this temperature.

Solution:

From Eq. 5.7.4:

$$\left(\frac{\partial S}{\partial A_{\text{s}}}\right)_{T,p} = -\left(\frac{\partial \gamma}{\partial T}\right)_{p}$$

At 25 °C, $(\partial\gamma/\partial T)_p$ is about $-1.55\times10^{-8}\,\text{J}\,\text{K}^{-1}\,\text{cm}^{-2}$; thus, $(\partial S/\partial A_{\text{s}})_{T,p}$ is approximately $1.55\times10^{-8}\,\text{J}\,\text{K}^{-1}\,\text{cm}^{-2}$.

5.7 When an ordinary rubber band is hung from a clamp and stretched with constant downward force F by a weight attached to the bottom end, gentle heating is observed to cause the rubber band to contract in length. To keep the length l of the rubber band constant during heating, F must be increased. The stretching work is given by $đw' = F\,\text{d}l$. From this information, find the sign of the partial derivative $(\partial T/\partial l)_{S,p}$; then predict whether stretching of the rubber band will cause a heating or a cooling effect.

(Hint: make a Legendre transform of U whose total differential has the independent variables needed for the partial derivative, and write a reciprocity relation.)

You can check your prediction experimentally by touching a rubber band to the side of your face before and after you rapidly stretch it.

Solution:

The total differential of the internal energy is given by $\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + F\,\mathrm{d}l$.

To change the independent variables from S, V, and l to S, p, and l, subtract the conjugate pair product $(-p)(V)$ from U to make the Legendre transform H:

$$\mathrm{d}H = \mathrm{d}(U + pV) = \mathrm{d}U + p\,\mathrm{d}V + V\,\mathrm{d}p = (T\,\mathrm{d}S - p\,\mathrm{d}V + F\,\mathrm{d}l) + p\,\mathrm{d}V + V\,\mathrm{d}p$$

$$= T\,\mathrm{d}S + V\,\mathrm{d}p + F\,\mathrm{d}l$$

Reciprocity relation:

$$\left(\frac{\partial T}{\partial l}\right)_{S,p} = \left(\frac{\partial F}{\partial S}\right)_{p,l}$$

The partial derivative $(\partial F/\partial S)_{p,l}$ is positive because S increases when heat reversibly enters the rubber band and raises the temperature, and experimentally F must be increased if l is to be constant as T increases. Thus, $(\partial T/\partial l)_{S,p}$ is positive, which means that as the rubber band is stretched reversibly and adiabatically ($\mathrm{d}S = 0$), T will *increase*.

Chapter 6 The Third Law and Cryogenics

6.1 Calculate the molar entropy of carbon disulfide at 25.00 °C and 1 bar from the heat capacity data for the solid in Table 4 and the following data for $p = 1\,\text{bar}$. At the melting point, 161.11 K, the molar enthalpy of fusion is $\Delta_\text{fus}H = 4.39\times10^3\,\text{J mol}^{-1}$. The molar heat capacity of the liquid in the range 161–300 K is described by $C_{p,\text{m}} = a + bT$, where the constants have the values $a = 74.6\,\text{J K}^{-1}\,\text{mol}^{-1}$ and $b = 0.0034\,\text{J K}^{-2}\,\text{mol}^{-1}$.

Table 4 Molar heat capacity of CS_2(s) at $p = 1\,\text{bar}$[a]

T/K	$C_{p,\text{m}}/\text{J K}^{-1}\,\text{mol}^{-1}$
15.05	6.9
20.15	12.0
29.76	20.8
42.22	29.2
57.52	35.6
75.54	40.0
94.21	45.0
108.93	48.5
131.54	52.6
156.83	56.6

[a] Ref. [25].

Solution:

Debye extrapolation from 0 K to 15.05 K:

$$\Delta S_\text{m} = (6.9\,\text{J K}^{-1}\,\text{mol}^{-1})/3 = 2.3\,\text{J K}^{-1}\,\text{mol}^{-1}$$

Molar entropy of heating the solid from 15.05 K to the melting point: When the molar heat capacity of the solid is plotted versus $\ln(T/\text{K})$, a practically-linear relation is observed (Fig. 9 on the next page). The sloped line is drawn through the first and last points and extended a very short distance to the melting point at $\ln(161.11) = 5.08$. The area under this line is $75.7\,\text{J K}^{-1}\,\text{mol}^{-1}$. Numerical integration of a curve fitted to the points will yield a similar value.

Molar entropy of fusion:

$$\Delta_\text{fus}S = \frac{\Delta_\text{fus}H}{T_\text{fus}} = \frac{4.39\times10^3\,\text{J mol}^{-1}}{161.11\,\text{K}} = 27.2\,\text{J K}^{-1}\,\text{mol}^{-1}$$

Molar entropy change of heating the liquid to 298.15 K:

$$\begin{aligned}\Delta S_\text{m} &= \int_{T_1}^{T_2} \frac{C_{p,\text{m}}}{T}\,\text{d}T = \int_{T_1}^{T_2} \frac{a+bT}{T}\,\text{d}T = a\int_{T_1}^{T_2}\frac{\text{d}T}{T} + b\int_{T_1}^{T_2}\text{d}T\\ &= (74.6\,\text{J K}^{-1}\,\text{mol}^{-1})\ln\frac{298.15\,\text{K}}{161.11\,\text{K}}\\ &\quad + (0.0034\,\text{J K}^{-2}\,\text{mol}^{-1})(298.15\,\text{K} - 161.11\,\text{K})\\ &= 46.4\,\text{J K}^{-1}\,\text{mol}^{-1}\end{aligned}$$

Total molar entropy change:

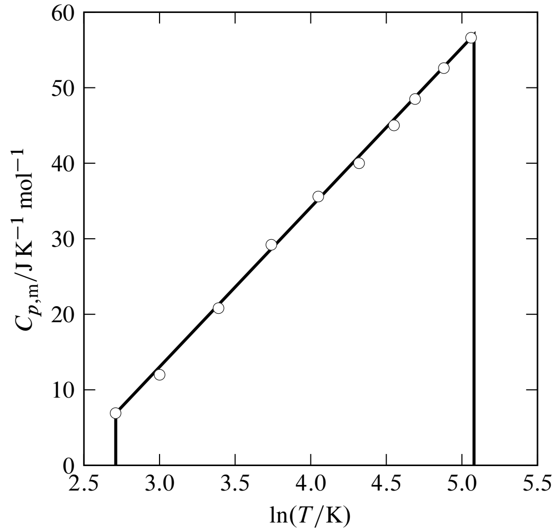

Figure 9

$\Delta S_\mathrm{m} = (2.3 + 75.7 + 27.2 + 46.4)\,\mathrm{J\,K^{-1}\,mol^{-1}} = 151.6\,\mathrm{J\,K^{-1}\,mol^{-1}}$

Thus, the molar entropy at 25.00 °C and 1 bar is close to $151.6\,\mathrm{J\,K^{-1}\,mol^{-1}}$.

Chapter 7 Pure Substances in Single Phases

7.1 Derive the following relations from the definitions of α, κ_T, and ρ:

$$\alpha = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p \qquad \kappa_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_T$$

Solution:

The definitions of α and κ_T refer to a fixed mass of a uniform phase. Let $X = 1/V = \rho/m$, where m is constant:

$$\alpha \overset{\text{def}}{=} \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = X\left[\frac{\partial(1/X)}{\partial T}\right]_p = X\left[-\frac{1}{X^2}\left(\frac{\partial X}{\partial T}\right)_p\right]$$

$$= -\frac{1}{X}\left(\frac{\partial X}{\partial T}\right)_p = -\frac{m}{\rho}\left[\frac{\partial(\rho/m)}{\partial T}\right]_p = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p$$

$$\kappa_T \overset{\text{def}}{=} -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = -X\left[\frac{\partial(1/X)}{\partial p}\right]_T = -X\left[-\frac{1}{X^2}\left(\frac{\partial X}{\partial p}\right)_T\right]$$

$$= \frac{1}{X}\left(\frac{\partial X}{\partial p}\right)_T = \frac{m}{\rho}\left[\frac{\partial(\rho/m)}{\partial p}\right]_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_T$$

7.2 Use equations in this chapter to derive the following expressions for an ideal gas:

$$\alpha = 1/T \qquad \kappa_T = 1/p$$

Solution:

In the following, n is constant:

$$\alpha \overset{\text{def}}{=} \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{V}\left[\frac{\partial(nRT/p)}{\partial T}\right]_p = \frac{1}{V}\left(\frac{nR}{p}\right)$$

$$= \frac{1}{T}$$

$$\kappa_T \overset{\text{def}}{=} -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = -\frac{1}{V}\left[\frac{\partial(nRT/p}{\partial p}\right]_T = -\frac{1}{V}\left(-\frac{nRT}{p^2}\right) = -\frac{1}{V}\left(-\frac{V}{p}\right)$$

$$= \frac{1}{p}$$

7.3 For a gas with the simple equation of state

$$V_{\text{m}} = \frac{RT}{p} + B$$

(Eq. 2.2.8), where B is the second virial coefficient (a function of T), find expressions for α, κ_T, and $(\partial U_{\text{m}}/\partial V)_T$ in terms of $\mathrm{d}B/\,\mathrm{d}T$ and other state functions.

Solution:

$$\alpha = \frac{1}{V_{\text{m}}}\left(\frac{\partial V_{\text{m}}}{\partial T}\right)_p = \frac{1}{V_{\text{m}}}\left(\frac{R}{p} + \frac{\mathrm{d}B}{\mathrm{d}T}\right)$$

$$\kappa_T = -\frac{1}{V_{\text{m}}}\left(\frac{\partial V_{\text{m}}}{\partial p}\right)_T = -\frac{1}{V_{\text{m}}}\left(-\frac{RT}{p^2}\right) = \frac{RT}{V_{\text{m}}p^2}$$

$$\left(\frac{\partial U_{\mathrm{m}}}{\partial V}\right)_T = \frac{\alpha T}{\kappa_T} - p = \frac{T}{V_{\mathrm{m}}}\left(\frac{R}{p} + \frac{\mathrm{d}B}{\mathrm{d}T}\right)\left(\frac{V_{\mathrm{m}}p^2}{RT}\right) - p$$

$$= \frac{p^2}{R}\left(\frac{\mathrm{d}B}{\mathrm{d}T}\right)$$

7.4 Show that when the virial equation $pV_{\mathrm{m}} = RT(1 + B_p p + C_p p^2 + \cdots)$ (Eq. 2.2.3) adequately represents the equation of state of a real gas, the Joule–Thomson coefficient is given by

$$\mu_{\mathrm{JT}} = \frac{RT^2[\mathrm{d}B_p/\,\mathrm{d}T + (\mathrm{d}C_p/\,\mathrm{d}T)p + \cdots]}{C_{p,\mathrm{m}}}$$

Note that the limiting value at low pressure, $RT^2(\mathrm{d}B_p/\,\mathrm{d}T)/C_{p,\mathrm{m}}$, is not necessarily equal to zero even though the equation of state approaches that of an ideal gas in this limit.

Solution:

$$\mu_{\mathrm{JT}} = \frac{(\alpha T - 1)V_{\mathrm{m}}}{C_{p,\mathrm{m}}}$$

$$\alpha V_{\mathrm{m}} = \left(\frac{\partial V_{\mathrm{m}}}{\partial T}\right)_p = \frac{R}{p}(1 + B_p p + C_p p^2 + \cdots) + \frac{RT}{p}\left[\left(\frac{\mathrm{d}B_p}{\mathrm{d}T}\right)p + \left(\frac{\mathrm{d}C_p}{\mathrm{d}T}\right)p^2 + \cdots\right]$$

Combine these expressions with the expression for V_{m} to obtain the final expression for μ_{JT}.

7.5 The quantity $(\partial T/\partial V)_U$ is called the *Joule coefficient*. James Joule attempted to evaluate this quantity by measuring the temperature change accompanying the expansion of air into a vacuum—the "Joule experiment." Write an expression for the total differential of U with T and V as independent variables, and by a procedure similar to that used in Sec. 7.5.2 show that the Joule coefficient is equal to

$$\frac{p - \alpha T/\kappa_T}{C_V}$$

Solution:

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V$$

Divide by $\mathrm{d}V$ and impose a condition of constant U:

$$0 = \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_U + \left(\frac{\partial U}{\partial V}\right)_T$$

Solve for $(\partial T/\partial V)_U$ and make appropriate substitutions:

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{(\partial U/\partial V)_T}{(\partial U/\partial T)_V} = -\frac{\alpha T/\kappa_T - p}{C_V}$$

7.6 p–V–T data for several organic liquids were measured by Gibson and Loeffler.[2] The following formulas describe the results for aniline.

Molar volume as a function of temperature at $p = 1$ bar (298–358 K):

$$V_{\mathrm{m}} = a + bT + cT^2 + dT^3$$

where the parameters have the values

$a = 69.287\,\mathrm{cm^3\,mol^{-1}}$

$c = -1.0443 \times 10^{-4}\,\mathrm{cm^3\,K^{-2}\,mol^{-1}}$

$b = 0.08852\,\mathrm{cm^3\,K^{-1}\,mol^{-1}}$

$d = 1.940 \times 10^{-7}\,\mathrm{cm^3\,K^{-3}\,mol^{-1}}$

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[2] Ref. [70].

Molar volume as a function of pressure at $T = 298.15\,\text{K}$ (1–1000 bar):

$$V_\text{m} = e - f\ln(g + p/\text{bar})$$

where the parameter values are

$$e = 156.812\,\text{cm}^3\,\text{mol}^{-1} \qquad f = 8.5834\,\text{cm}^3\,\text{mol}^{-1} \qquad g = 2006.6$$

(a) Use these formulas to evaluate α, κ_T, $(\partial p/\partial T)_V$, and $(\partial U/\partial V)_T$ (the internal pressure) for aniline at $T = 298.15\,\text{K}$ and $p = 1.000\,\text{bar}$.

Solution:

At 298.15 K and 1.000 bar, the molar volume calculated from either formula is $V_\text{m} = 91.538\,\text{cm}^3\,\text{mol}^{-1}$.

$$\alpha = \frac{1}{V_\text{m}}\left(\frac{\partial V}{\partial T}\right)_p = \frac{b + 2cT + 3dT^2}{V_\text{m}} = 8.519\times 10^{-4}\,\text{K}^{-1}$$

$$\kappa_T = -\frac{1}{V_\text{m}}\left(\frac{\partial V}{\partial p}\right)_T = \frac{1}{V_\text{m}}\left(\frac{f}{g + p/\text{bar}}\right) = 4.671\times 10^{-5}\,\text{bar}^{-1}$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa_T} = 18.24\,\text{bar}\,\text{K}^{-1}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{\alpha T}{\kappa_T} - p = 5437\,\text{bar}$$

(b) Estimate the pressure increase if the temperature of a fixed amount of aniline is increased by 0.10 K at constant volume.

Solution:

$$\Delta p \approx \left(\frac{\partial p}{\partial T}\right)_V \Delta T = (18.24\,\text{bar}\,\text{K}^{-1})(0.10\,\text{K}) = 1.8\,\text{bar}$$

7.7 (a) From the total differential of H with T and p as independent variables, derive the relation $(\partial C_{p,\text{m}}/\partial p)_T = -T(\partial^2 V_\text{m}/\partial T^2)_p$.

Solution:

$$\text{d}H = \left(\frac{\partial H}{\partial T}\right)_p \text{d}T + \left(\frac{\partial H}{\partial p}\right)_T \text{d}p = C_p\,\text{d}T + (1-\alpha T)V\,\text{d}p$$

The reciprocity relation from this total differential is

$$\left(\frac{\partial C_p}{\partial p}\right)_T = \left[\frac{\partial(1-\alpha T)V}{\partial T}\right]_p$$

or

$$\left(\frac{\partial C_p}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p - \left[\frac{\partial(\alpha T V)}{\partial T}\right]_p$$

Using the relation $\alpha V = (\partial V/\partial T)_p$, this becomes

$$\left(\frac{\partial C_p}{\partial p}\right)_T = \alpha V - \alpha V - T\left[\frac{\partial(\alpha V)}{\partial T}\right]_p = -T\left[\frac{\partial(\alpha V)}{\partial T}\right]_p = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p$$

Divide by n to obtain the final relation.

(b) Evaluate $(\partial C_{p,\text{m}}/\partial p)_T$ for liquid aniline at 300.0 K and 1 bar using data in Prob. 7.6.

Solution:

$$\left(\frac{\partial C_{p,\mathrm{m}}}{\partial p}\right)_T = -T\left(\frac{\partial^2 V_\mathrm{m}}{\partial T^2}\right)_p = -T(2c + 6dT)$$

$$= -4.210\times 10^{-2}\,\mathrm{cm^3\,K^{-1}\,mol^{-1}}$$

$$= -(4.210\times 10^{-2}\,\mathrm{cm^3\,K^{-1}\,mol^{-1}})(10^{-2}\,\mathrm{m/cm})^3$$

$$= -4.210\times 10^{-8}\,\mathrm{J\,K^{-1}\,Pa^{-1}\,mol^{-1}}$$

7.8 (a) From the total differential of V with T and p as independent variables, derive the relation $(\partial\alpha/\partial p)_T = -(\partial\kappa_T/\partial T)_p$.

Solution:

$\mathrm{d}V = \alpha V\,\mathrm{d}T - \kappa_T V\,\mathrm{d}p$ (Eq. 7.1.6)
Reciprocity relation:

$$\left[\frac{\partial(\alpha V)}{\partial p}\right]_T = -\left[\frac{\partial(\kappa_T V)}{\partial T}\right]_p$$

From the chain rule:

$$\alpha\left(\frac{\partial V}{\partial p}\right)_T + V\left(\frac{\partial\alpha}{\partial p}\right)_T = -\kappa_T\left(\frac{\partial V}{\partial T}\right)_p - V\left(\frac{\partial\kappa_T}{\partial T}\right)_p$$

or

$$\alpha(-\kappa_T V) + V\left(\frac{\partial\alpha}{\partial p}\right)_T = -\kappa_T(\alpha V) - V\left(\frac{\partial\kappa_T}{\partial T}\right)_p$$

The first term on the left equals the first term on the right, so these terms cancel, giving

$$\left(\frac{\partial\alpha}{\partial p}\right)_T = -\left(\frac{\partial\kappa_T}{\partial T}\right)_p$$

(b) Use this relation to estimate the value of α for benzene at 25 °C and 500 bar, given that the value of α is $1.2\times 10^{-3}\,\mathrm{K^{-1}}$ at 25 °C and 1 bar. (Use information from Fig. 7.2 on page 168.)

Solution:

From the curve for benzene in Fig. 7.2, the value of $(\partial\kappa_T/\partial T)_p$ at 25 °C is approximately $7.3\times 10^{-7}\,\mathrm{bar^{-1}\,K^{-1}}$.

$$\alpha(500\,\mathrm{bar}) \approx \alpha(1\,\mathrm{bar}) + \left(\frac{\partial\alpha}{\partial p}\right)_T (500-1)\mathrm{bar}$$

$$= 1.2\times 10^{-3}\,\mathrm{K^{-1}} + (-7.3\times 10^{-7}\,\mathrm{bar^{-1}\,K^{-1}})(499\,\mathrm{bar})$$

$$= 8\times 10^{-4}\,\mathrm{K^{-1}}$$

7.9 Certain equations of state supposed to be applicable to nonpolar liquids and gases are of the form $p = Tf(V_\mathrm{m}) - a/V_\mathrm{m}^2$, where $f(V_\mathrm{m})$ is a function of the molar volume only and a is a constant.

(a) Show that the van der Waals equation of state $(p + a/V_\mathrm{m}^2)(V_\mathrm{m} - b) = RT$ (where a and b are constants) is of this form.

Solution:

The van der Waals equation can be rearranged to

$$p = \frac{RT}{V_\mathrm{m} - b} - \frac{a}{V_\mathrm{m}^2}$$

The function $f(V_\mathrm{m})$ is $R/(V_\mathrm{m} - b)$.

(b) Show that any fluid with an equation of state of this form has an internal pressure equal to a/V_m^2.

Solution:

From Eq. 7.2.1, the internal pressure is equal to $T(\partial p/\partial T)_V - p$.

$$T\left(\frac{\partial p}{\partial T}\right)_{V,n} - p = Tf(V_\mathrm{m}) - \left[Tf(V_\mathrm{m}) - \frac{a}{V_\mathrm{m}^2}\right] = \frac{a}{V_\mathrm{m}^2}$$

7.10 Suppose that the molar heat capacity at constant pressure of a substance has a temperature dependence given by $C_{p,\mathrm{m}} = a + bT + cT^2$, where a, b, and c are constants. Consider the heating of an amount n of the substance from T_1 to T_2 at constant pressure. Find expressions for ΔH and ΔS for this process in terms of a, b, c, n, T_1, and T_2.

Solution:

$$\Delta H = n\int_{T_1}^{T_2} C_{p,\mathrm{m}}\,\mathrm{d}T = n\left[a(T_2 - T_1) + \left(\frac{b}{2}\right)(T_2^2 - T_1^2) + \left(\frac{c}{3}\right)(T_2^3 - T_1^3)\right]$$

$$\Delta S = n\int_{T_1}^{T_2} \frac{C_{p,\mathrm{m}}}{T}\,\mathrm{d}T = n\left[a\ln\left(\frac{T_2}{T_1}\right) + b(T_2 - T_1) + \left(\frac{c}{2}\right)(T_2^2 - T_1^2)\right]$$

<u>**7.11**</u> At $p = 1$ atm, the molar heat capacity at constant pressure of aluminum is given by

$$C_{p,\mathrm{m}} = a + bT$$

where the constants have the values

$$a = 20.67\,\mathrm{J\,K^{-1}\,mol^{-1}} \qquad b = 0.01238\,\mathrm{J\,K^{-2}\,mol^{-1}}$$

Calculate the quantity of electrical work needed to heat 2.000 mol of aluminum from 300.00 K to 400.00 K at 1 atm in an adiabatic enclosure.

Solution:

Since the process is isobaric, ΔH is equal to the heat that would be needed to cause the same change of state without electrical work:

$$\Delta H = n\int_{T_1}^{T_2} C_{p,\mathrm{m}}\,\mathrm{d}T = n\left[a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2)\right] = 5.001\times10^3\,\mathrm{J}$$

In the adiabatic enclosure, ΔH has the same value, and electrical work substitutes for heat: $w' = 5.001\times10^3$ J.

<u>**7.12**</u> The temperature dependence of the standard molar heat capacity of gaseous carbon dioxide in the temperature range 298 K–2000 K is given by

$$C_{p,\mathrm{m}}^\circ = a + bT + \frac{c}{T^2}$$

where the constants have the values

$$a = 44.2\,\mathrm{J\,K^{-1}\,mol^{-1}} \quad b = 8.8\times10^{-3}\,\mathrm{J\,K^{-2}\,mol^{-1}} \quad c = -8.6\times10^5\,\mathrm{J\,K\,mol^{-1}}$$

Calculate the enthalpy and entropy changes when one mole of CO_2 is heated at 1 bar from 300.00 K to 800.00 K. You can assume that at this pressure $C_{p,\mathrm{m}}$ is practically equal to $C^{\circ}_{p,\mathrm{m}}$.

Solution:

$$\Delta H = n\int_{T_1}^{T_2} C_{p,\mathrm{m}}\,\mathrm{d}T = n\left[a(T_2 - T_1) + \left(\frac{b}{2}\right)(T_2^2 - T_1^2) - c\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]$$

$$= 2.27\times 10^4\,\mathrm{J}$$

$$\Delta S = n\int_{T_1}^{T_2} \frac{C_{p,\mathrm{m}}}{T}\,\mathrm{d}T = n\left[a\ln\left(\frac{T_2}{T_1}\right) + b(T_2 - T_1) - \left(\frac{c}{2}\right)\left(\frac{1}{T_2^2} - \frac{1}{T_1^2}\right)\right]$$

$$= 43.6\,\mathrm{J\,K^{-1}}$$

7.13 This problem concerns gaseous carbon dioxide. At 400 K, the relation between p and V_{m} at pressures up to at least 100 bar is given to good accuracy by a virial equation of state truncated at the second virial coefficient, B. In the temperature range 300 K–800 K the dependence of B on temperature is given by

$$B = a' + b'T + c'T^2 + d'T^3$$

where the constants have the values

$$\begin{aligned} a' &= -521\,\mathrm{cm^3\,mol^{-1}} \\ b' &= 2.08\,\mathrm{cm^3\,K^{-1}\,mol^{-1}} \\ c' &= -2.89\times 10^{-3}\,\mathrm{cm^3\,K^{-2}\,mol^{-1}} \\ d' &= 1.397\times 10^{-6}\,\mathrm{cm^3\,K^{-3}\,mol^{-1}} \end{aligned}$$

(a) From information in Prob. 7.12, calculate the standard molar heat capacity at constant pressure, $C^{\circ}_{p,\mathrm{m}}$, at $T = 400.0\,\mathrm{K}$.

Solution:

$$C^{\circ}_{p,\mathrm{m}} = a + bT + c/T^2$$

$$= 44.2\,\mathrm{J\,K^{-1}\,mol^{-1}} + (8.8\times 10^{-3}\,\mathrm{J\,K^{-2}\,mol^{-1}})(400.0\,\mathrm{K}) + \frac{-8.6\times 10^5\,\mathrm{J\,K\,mol^{-1}}}{(400.0\,\mathrm{K})^2}$$

$$= (44.2 + 3.52 - 5.4)\,\mathrm{J\,K^{-1}\,mol^{-1}} = 42.3\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

(b) Estimate the value of $C_{p,\mathrm{m}}$ under the conditions $T = 400.0\,\mathrm{K}$ and $p = 100.0\,\mathrm{bar}$.

Solution:

$$B = a' + b'T + c'T^2 + d'T^3$$

$$\frac{\mathrm{d}B}{\mathrm{d}T} = b' + 2c'T + 3d'T^2$$

$$\frac{\mathrm{d}^2B}{\mathrm{d}T^2} = 2c' + 6d'T$$

$$= 2(-2.89\times 10^{-3}\,\mathrm{cm^3\,K^{-2}\,mol^{-1}})\left(\frac{10^{-2}\,\mathrm{m}}{1\,\mathrm{cm}}\right)^3$$

$$+ 6(1.397\times 10^{-6}\,\mathrm{cm^3\,K^{-3}\,mol^{-1}})\left(\frac{10^{-2}\,\mathrm{m}}{1\,\mathrm{cm}}\right)^3(400.0\,\mathrm{K})$$

$$= (-5.78\times 10^{-9} + 3.35\times 10^{-9})\,\mathrm{m^3\,K^{-2}\,mol^{-1}}$$

$$= -2.43 \times 10^{-9}\,\mathrm{m^3\,K^{-2}\,mol^{-1}}$$

$$C_{p,\mathrm{m}} - C^{\circ}_{p,\mathrm{m}} \approx -pT\frac{\mathrm{d}^2 B}{\mathrm{d}T^2}$$

$$= -(100.0\,\mathrm{bar})\left(\frac{10^5\,\mathrm{Pa}}{1\,\mathrm{bar}}\right)(400.0\,\mathrm{K})(-2.43 \times 10^{-9}\,\mathrm{m^3\,K^{-2}\,mol^{-1}})$$

$$= 9.7\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

$$C_{p,\mathrm{m}} \approx (42.3 + 9.7)\,\mathrm{J\,K^{-1}\,mol^{-1}} = 52.0\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

7.14 A chemist, needing to determine the specific heat capacity of a certain liquid but not having an electrically heated calorimeter at her disposal, used the following simple procedure known as *drop calorimetry*. She placed 500.0 g of the liquid in a thermally insulated container equipped with a lid and a thermometer. After recording the initial temperature of the liquid, 24.80 °C, she removed a 60.17-g block of aluminum metal from a boiling water bath at 100.00 °C and quickly immersed it in the liquid in the container. After the contents of the container had become thermally equilibrated, she recorded a final temperature of 27.92 °C. She calculated the specific heat capacity C_p/m of the liquid from these data, making use of the molar mass of aluminum ($M = 26.9815\,\mathrm{g\,mol^{-1}}$) and the formula for the molar heat capacity of aluminum given in Prob. 7.11.

(a) From these data, find the specific heat capacity of the liquid under the assumption that its value does not vary with temperature. Hint: Treat the temperature equilibration process as adiabatic and isobaric ($\Delta H = 0$), and equate ΔH to the sum of the enthalpy changes in the two phases.

Solution:

Enthalpy change of the aluminum block:

$$\Delta H(\mathrm{Al}) = n\int_{T_1}^{T_2} C_{p,\mathrm{m}}(\mathrm{Al})\,\mathrm{d}T = \frac{m}{M}\left[a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2)\right]$$

$$= \frac{60.17\,\mathrm{g}}{26.9815\,\mathrm{g\,mol^{-1}}}\Big\{(20.67\,\mathrm{J\,K^{-1}\,mol^{-1}})(301.07\,\mathrm{K} - 373.15\,\mathrm{K})$$

$$+ \frac{1}{2}(0.01238\,\mathrm{J\,K^{-2}\,mol^{-1}})\left[(301.07\,\mathrm{K})^2 - (373.15\,\mathrm{K})^2\right]\Big\}$$

$$= -3.993 \times 10^3\,\mathrm{J}$$

Assume that C_p for the liquid is equal to $\Delta H(\mathrm{l})/\Delta T$, and equate $\Delta H(\mathrm{l})$ to $-\Delta H(\mathrm{Al})$:

$$C_p(\mathrm{l}) = \frac{\Delta H(\mathrm{l})}{\Delta T} = \frac{3.993 \times 10^3\,\mathrm{J}}{301.07\,\mathrm{K} - 297.95\,\mathrm{K}} = 1.280 \times 10^3\,\mathrm{J\,K^{-1}}$$

Specific heat capacity:

$$\frac{C_p(\mathrm{l})}{m} = \frac{1.280 \times 10^3\,\mathrm{J\,K^{-1}}}{500.0\,\mathrm{g}} = 2.56\,\mathrm{J\,K^{-1}\,g^{-1}}$$

(b) Show that the value obtained in part (a) is actually an average value of C_p/m over the temperature range between the initial and final temperatures of the liquid given by

$$\frac{\displaystyle\int_{T_1}^{T_2}(C_p/m)\,\mathrm{d}T}{T_2 - T_1}$$

Solution:

The value in part (a) was calculated from $\Delta H(\mathrm{l})/(T_2 - T_1)m$. Make the substitution

$$\Delta H(\mathrm{l}) = \int_{T_1}^{T_2} C_p \, \mathrm{d}T$$

and rearrange.

7.15 Suppose a gas has the virial equation of state $pV_\mathrm{m} = RT(1 + B_p p + C_p p^2)$, where B_p and C_p depend only on T, and higher powers of p can be ignored.

(a) Derive an expression for the fugacity coefficient, ϕ, of this gas as a function of p.

Solution:

$$\ln \phi(p') = \int_0^{p'} \left(\frac{V_\mathrm{m}}{RT} - \frac{1}{p} \right) \mathrm{d}p = \int_0^{p'} \left(\frac{1 + B_p p + C_p p^2}{p} - \frac{1}{p} \right) \mathrm{d}p$$

$$= \int_0^{p'} (B_p + C_p p) \, \mathrm{d}p$$

$$= B_p p' + \frac{1}{2} C_p (p')^2$$

$\ln \phi = B_p p + \frac{1}{2} C_p p^2$

(b) For CO_2(g) at 0.00 °C, the virial coefficients have the values $B_p = -6.67 \times 10^{-3}\ \mathrm{bar}^{-1}$ and $C_p = -3.4 \times 10^{-5}\ \mathrm{bar}^{-2}$. Evaluate the fugacity f at 0.00 °C and $p = 20.0$ bar.

Solution:

$$\ln \phi = B_p p + \frac{1}{2} C_p p^2$$

$$= (-6.67 \times 10^{-3}\ \mathrm{bar}^{-1})(20.0\ \mathrm{bar}) + \frac{1}{2}(-3.4 \times 10^{-5}\ \mathrm{bar}^{-2})(20.0\ \mathrm{bar})^2$$

$$= -0.140$$

$f = \phi p = (0.869)(20.0\ \mathrm{bar}) = 17.4\ \mathrm{bar}$

Table 5 Molar volume of H_2O(g) at 400.00 °C[a]

$p/10^5$ Pa	$V_\mathrm{m}/10^{-3}$ m^3 mol^{-1}	$p/10^5$ Pa	$V_\mathrm{m}/10^{-3}$ m^3 mol^{-1}
1	55.896	100	0.47575
10	5.5231	120	0.37976
20	2.7237	140	0.31020
40	1.3224	160	0.25699
60	0.85374	180	0.21447
80	0.61817	200	0.17918

[a] based on data in Ref. [75]

7.16 Table 5 lists values of the molar volume of gaseous H_2O at 400.00 °C and 12 pressures.

(a) Evaluate the fugacity coefficient and fugacity of H_2O(g) at 400.00 °C and 200 bar.

Solution:

Calculate $(V_\mathrm{m}/RT - 1/p)$ at each pressure; see Table 6 on the next page. The values are

Table 6

$p/10^5$ Pa	$\left(\frac{V_m}{RT} - \frac{1}{p}\right)/10^{-8}$ Pa^{-1}	$p/10^5$ Pa	$\left(\frac{V_m}{RT} - \frac{1}{p}\right)/10^{-8}$ Pa^{-1}
1	−1.302	100	−1.4997
10	−1.318	120	−1.5481
20	−1.335	140	−1.6005
40	−1.374	160	−1.6583
60	−1.413	180	−1.7236
80	−1.455	200	−1.7986

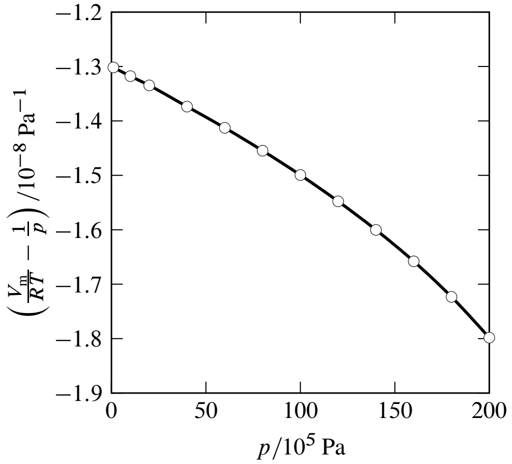

Figure 10

plotted in Fig. 10. Extrapolate these values to $p = 0$:

$$\lim_{p\to 0}\left(\frac{V_m}{RT} - \frac{1}{p}\right) = -1.300 \times 10^{-8}\ \text{Pa}^{-1}$$

Use numerical integration to find the area under the curve:

$$\ln\phi = \int_0^{200\,\text{bar}} \left(\frac{V_m}{RT} - \frac{1}{p}\right) dp = -0.3031$$

$$\phi = 0.739 \qquad f = \phi p = (0.739)(200\,\text{bar}) = 148\,\text{bar}$$

(b) Show that the second virial coefficient B in the virial equation of state, $pV_m = RT(1 + B/V_m + C/V_m^2 + \cdots)$, is given by

$$B = RT \lim_{p\to 0}\left(\frac{V_m}{RT} - \frac{1}{p}\right)$$

where the limit is taken at constant T. Then evaluate B for H_2O(g) at 400.00 °C.

Solution:

$$pV_m = RT(1 + B/V_m + C/V_m^2 + \cdots)$$

$$\frac{V_m}{RT} - \frac{1}{p} = \left(\frac{1}{p}\right)(1 + B/V_m + C/V_m^2 + \cdots) - \frac{1}{p} = \left(\frac{1}{p}\right)(B/V_m + C/V_m^2 + \cdots)$$

$$= \frac{B/V_\mathrm{m} + C/V_\mathrm{m}^2 + \cdots}{(RT/V_\mathrm{m})(1 + B/V_\mathrm{m} + C/V_\mathrm{m}^2 + \cdots)}$$

$$= \frac{1}{RT}\left(\frac{B + C/V_\mathrm{m} + \cdots}{1 + B/V_\mathrm{m} + C/V_\mathrm{m}^2 + \cdots)}\right)$$

As p approaches 0, $1/V_\mathrm{m}$ also approaches zero and the preceding expression approaches B/RT. Thus, B is the product of RT and the limiting value of the expression.

From Prob. 7.16(a), the value of B for $\mathrm{H_2O(g)}$ at 400.00 °C is

$$B = (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(673.15\,\mathrm{K})(-1.300 \times 10^{-8}\,\mathrm{Pa^{-1}})$$

$$= -7.28 \times 10^{-5}\,\mathrm{m^3\,mol^{-1}}$$

Chapter 8 Phase Transitions and Equilibria of Pure Substances

8.1 Consider the system described in Sec. 8.1.5 containing a spherical liquid droplet of radius r surrounded by pure vapor. Starting with Eq. 8.1.15, find an expression for the total differential of U. Then impose conditions of isolation and show that the equilibrium conditions are $T^{\mathrm{g}} = T^{\mathrm{l}}$, $\mu^{\mathrm{g}} = \mu^{\mathrm{l}}$, and $p^{\mathrm{l}} = p^{\mathrm{g}} + 2\gamma/r$, where γ is the surface tension.

Solution:

Internal energy change without constraints (Eq. 8.1.15):

$$\mathrm{d}U = T^{\mathrm{l}}\,\mathrm{d}S^{\mathrm{l}} - p^{\mathrm{l}}\,\mathrm{d}V^{\mathrm{l}} + \mu^{\mathrm{l}}\,\mathrm{d}n^{\mathrm{l}} + T^{\mathrm{g}}\,\mathrm{d}S^{\mathrm{g}} - p^{\mathrm{g}}\,\mathrm{d}V^{\mathrm{g}} + \mu^{\mathrm{g}}\,\mathrm{d}n^{\mathrm{g}} + \gamma\,\mathrm{d}A_{\mathrm{s}}$$

Because the system boundary contacts only the vapor phase, the constraint for no work is $-p^{\mathrm{g}}\,\mathrm{d}(V^{\mathrm{l}} + V^{\mathrm{g}}) = 0$.

$$V^{\mathrm{l}} = (4/3)\pi r^3 \qquad A_{\mathrm{s}} = 4\pi r^2$$

From the constraints $\mathrm{d}V^{\mathrm{l}} = 4\pi r^2\,\mathrm{d}r$ and $\mathrm{d}A_{\mathrm{s}} = 8\pi r\,\mathrm{d}r$, obtain $\mathrm{d}A_{\mathrm{s}} = (2/r)\,\mathrm{d}V^{\mathrm{l}}$.

Conditions for an isolated system: $\mathrm{d}U = 0$, $p^{\mathrm{g}}\,\mathrm{d}V^{\mathrm{g}} = -p^{\mathrm{g}}\,\mathrm{d}V^{\mathrm{l}}$, $\mathrm{d}n^{\mathrm{g}} = -\,\mathrm{d}n^{\mathrm{l}}$.

After substitution in the expression for $\mathrm{d}U$:

$$0 = T^{\mathrm{l}}\,\mathrm{d}S^{\mathrm{l}} + T^{\mathrm{g}}\,\mathrm{d}S^{\mathrm{g}} - (p^{\mathrm{l}} - p^{\mathrm{g}} - 2\gamma/r)\,\mathrm{d}V^{\mathrm{l}} + (\mu^{\mathrm{l}} - \mu^{\mathrm{g}})\,\mathrm{d}n^{\mathrm{l}}$$

Substitute $\mathrm{d}S^{\mathrm{l}} = \mathrm{d}S - \mathrm{d}S^{\mathrm{g}}$ and solve for $\mathrm{d}S$:

$$\mathrm{d}S = \frac{(T^{\mathrm{l}} - T^{\mathrm{g}})}{T^{\mathrm{l}}}\,\mathrm{d}S^{\mathrm{g}} + \frac{(p^{\mathrm{l}} - p^{\mathrm{g}} - 2\gamma/r)}{T^{\mathrm{l}}}\,\mathrm{d}V^{\mathrm{l}} - \frac{(\mu^{\mathrm{l}} - \mu^{\mathrm{g}})}{T^{\mathrm{l}}}\,\mathrm{d}n^{\mathrm{l}}$$

This is the total differential of S in the isolated system with S^{g}, V^{l}, and n^{l} as independent variables. In the equilibrium state, $\mathrm{d}S$ is zero for each independent change:

$$T^{\mathrm{g}} = T^{\mathrm{l}} \qquad \mu^{\mathrm{g}} = \mu^{\mathrm{l}} \qquad p^{\mathrm{l}} = p^{\mathrm{g}} + \frac{2\gamma}{r}$$

8.2 This problem concerns diethyl ether at $T = 298.15\,\mathrm{K}$. At this temperature, the standard molar entropy of the gas calculated from spectroscopic data is $S^{\circ}_{\mathrm{m}}(\mathrm{g}) = 342.2\,\mathrm{J\,K^{-1}\,mol^{-1}}$. The saturation vapor pressure of the liquid at this temperature is 0.6691 bar, and the molar enthalpy of vaporization is $\Delta_{\mathrm{vap}}H = 27.10\,\mathrm{kJ\,mol^{-1}}$. The second virial coefficient of the gas at this temperature has the value $B = -1.227\times 10^{-3}\,\mathrm{m^3\,mol^{-1}}$, and its variation with temperature is given by $\mathrm{d}B/\mathrm{d}T = 1.50\times 10^{-5}\,\mathrm{m^3\,K^{-1}\,mol^{-1}}$.

(a) Use these data to calculate the standard molar entropy of liquid diethyl ether at 298.15 K. A small pressure change has a negligible effect on the molar entropy of a liquid, so that it is a good approximation to equate $S^{\circ}_{\mathrm{m}}(\mathrm{l})$ to $S_{\mathrm{m}}(\mathrm{l})$ at the saturation vapor pressure.

Solution:

Gas at $p = 0.6691$ bar (from Table 7.5):

$$\begin{aligned} S_{\mathrm{m}}(\mathrm{g}) - S^{\circ}_{\mathrm{m}}(\mathrm{g}) &\approx -R\ln\frac{p}{p^{\circ}} - p\frac{\mathrm{d}B}{\mathrm{d}T} \\ &= 342.2\,\mathrm{J\,K^{-1}\,mol^{-1}} - (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\ln(0.6691) \\ &\quad - (0.6691\times 10^{5}\,\mathrm{Pa})(1.50\times 10^{-5}\,\mathrm{m^3\;K^{-1}\,mol^{-1}}) \\ &= 344.5\,\mathrm{J\,K^{-1}\,mol^{-1}} \end{aligned}$$

Molar entropy of reversible vaporization at $p = 0.6691$ bar:

$$\Delta_{\text{vap}}S = \frac{\Delta_{\text{vap}}H}{T} = \frac{27.10 \times 10^3\,\text{J mol}^{-1}}{298.15\,\text{K}} = 90.9\,\text{J K}^{-1}\,\text{mol}^{-1}$$

Standard molar entropy of liquid diethyl ether:

$$\begin{aligned} S^\circ_\text{m}(\text{l}) &= S_\text{m}(\text{g}) - [S_\text{m}(\text{g}) - S_\text{m}(\text{l})] + [S^\circ_\text{m}(\text{l}) - S_\text{m}(\text{l})] \\ &\approx S_\text{m}(\text{g}) - \Delta_{\text{vap}}S = (344.5 - 90.9)\,\text{J K}^{-1}\,\text{mol}^{-1} = 253.6\,\text{J K}^{-1}\,\text{mol}^{-1} \end{aligned}$$

(b) Calculate the standard molar entropy of vaporization and the standard molar enthalpy of vaporization of diethyl ether at 298.15 K. It is a good approximation to equate $H^\circ_\text{m}(\text{l})$ to $H_\text{m}(\text{l})$ at the saturation vapor pressure.

Solution:

$$\Delta_{\text{vap}}S^\circ = S^\circ_\text{m}(\text{g}) - S^\circ_\text{m}(\text{l}) = (342.2 - 253.6)\,\text{J K}^{-1}\,\text{mol}^{-1} = 88.6\,\text{J K}^{-1}\,\text{mol}^{-1}$$

Gas at $p = 0.6691$ bar (from Table 7.5):

$$\begin{aligned} H_\text{m}(\text{g}) - H^\circ_\text{m}(\text{g}) &\approx p\left(B - T\frac{\text{d}B}{\text{d}T}\right) \\ &= (0.6691 \times 10^5\,\text{Pa})[(-1.227 \times 10^{-3}\,\text{m}^3\,\text{mol}^{-1}) \\ &\quad - (298.15\,\text{K})(1.50 \times 10^{-5}\,\text{m}^3\ \text{K}^{-1}\,\text{mol}^{-1})] \\ &= -381.3\,\text{J mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta_{\text{vap}}H^\circ &= H^\circ_\text{m}(\text{g}) - H^\circ_\text{m}(\text{l}) \\ &= [H_\text{m}(\text{g}) - H_\text{m}(\text{l})] - [H_\text{m}(\text{g}) - H^\circ_\text{m}(\text{g})] + [H_\text{m}(\text{l}) - H^\circ_\text{m}(\text{l})] \\ &\approx \Delta_{\text{vap}}H - [H_\text{m}(\text{g}) - H^\circ_\text{m}(\text{g})] \\ &= (27.10 \times 10^3 + 381.3)\,\text{J mol}^{-1} = 2.748 \times 10^4\,\text{J mol}^{-1} \end{aligned}$$

8.3 Explain why the chemical potential surfaces shown in Fig. 8.12 are concave downward; that is, why $(\partial\mu/\partial T)_p$ becomes more negative with increasing T and $(\partial\mu/\partial p)_T$ becomes less positive with increasing p.

Solution:

The partial derivatives are given by Eqs. 7.8.3 and 7.8.4:

$$\left(\frac{\partial\mu}{\partial T}\right)_p = -S_\text{m} \qquad \left(\frac{\partial\mu}{\partial p}\right)_T = V_\text{m}$$

Since S_m increases with increasing T at constant p ($(\partial S/\partial T)_p = C_p/T$), and molar volume decreases with increasing p at constant T, both partial derivatives are negative.

8.4 Potassium has a standard boiling point of 773 °C and a molar enthalpy of vaporization $\Delta_{\text{vap}}H = 84.9\,\text{kJ mol}^{-1}$. Estimate the saturation vapor pressure of liquid potassium at 400. °C.

Solution:

$$\ln\frac{p_2}{p_1} \approx -\frac{\Delta_{\text{vap}}H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = -\frac{84.9 \times 10^3\,\text{J mol}^{-1}}{8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}}\left(\frac{1}{673\,\text{K}} - \frac{1}{1046\,\text{K}}\right) = -5.41$$

$$p_2/p_1 = 4.5 \times 10^{-3} \qquad p_2 = (4.5 \times 10^{-3})(1\,\text{bar}) = 4.5 \times 10^{-3}\,\text{bar}$$

8.5 Naphthalene has a melting point of 78.2 °C at 1 bar and 81.7 °C at 100 bar. The molar volume change on melting is $\Delta_{\text{fus}}V = 0.019\,\text{cm}^3\,\text{mol}^{-1}$. Calculate the molar enthalpy of fusion to two significant figures.

Solution:

Rearrange Eq. 8.4.8:

$$\begin{aligned}\Delta_{\text{fus}}H &\approx \frac{\Delta_{\text{fus}}V(p_2-p_1)}{\ln(T_2/T_1)}\\ &= \frac{(0.019\,\text{cm}^3\,\text{mol}^{-1})(10^{-2}\,\text{m/cm})^3(100-1)10^5\,\text{Pa}}{\ln(354.9\,\text{K}/351.4\,\text{K})} = 19\,\text{J}\,\text{mol}^{-1}\end{aligned}$$

8.6 The dependence of the vapor pressure of a liquid on temperature, over a limited temperature range, is often represented by the *Antoine equation*, $\log_{10}(p/\text{Torr}) = A - B/(t + C)$, where t is the Celsius temperature and A, B, and C are constants determined by experiment. A variation of this equation, using a natural logarithm and the thermodynamic temperature, is

$$\ln(p/\text{bar}) = a - \frac{b}{T+c}$$

The vapor pressure of liquid benzene at temperatures close to 298 K is adequately represented by the preceding equation with the following values of the constants:

$$a = 9.25092 \qquad b = 2771.233\,\text{K} \qquad c = -53.262\,\text{K}$$

(a) Find the standard boiling point of benzene.

Solution:

Solve the equation for T and set p equal to 1 bar:

$$T = \frac{b}{a-\ln(p/\text{bar})} - c = \frac{2771.233\,\text{K}}{9.25092-\ln(1)} - 53.262\,\text{K} = 352.82\,\text{K}$$

(b) Use the Clausius–Clapeyron equation to evaluate the molar enthalpy of vaporization of benzene at 298.15 K.

Solution:

Rearrange Eq. 8.4.13 to

$$\Delta_{\text{trs}}H \approx RT^2\frac{\mathrm{d}\ln(p/p^\circ)}{\mathrm{d}T} = RT^2\left[\frac{b}{(T+c)^2}\right] = 3.4154\times10^4\,\text{J}\,\text{mol}^{-1}$$

8.7 At a pressure of one atmosphere, water and steam are in equilibrium at 99.97 °C (the normal boiling point of water). At this pressure and temperature, the water density is $0.958\,\text{g}\,\text{cm}^{-3}$, the steam density is $5.98\times10^{-4}\,\text{g}\,\text{cm}^{-3}$, and the molar enthalpy of vaporization is $40.66\,\text{kJ}\,\text{mol}^{-1}$.

(a) Use the Clapeyron equation to calculate the slope $\mathrm{d}p/\mathrm{d}T$ of the liquid–gas coexistence curve at this point.

Solution:

$$\begin{aligned}\Delta_{\text{vap}}V &= (18.0153\,\text{g}\,\text{mol}^{-1})\left(\frac{1}{5.98\times10^{-4}\,\text{g}\,\text{cm}^{-3}} - \frac{1}{0.958\,\text{g}\,\text{cm}^{-3}}\right)\\ &= 3.011\times10^4\,\text{cm}^3\,\text{mol}^{-1}\end{aligned}$$

$$\frac{p}{T} = \frac{\Delta_{\text{vap}}H}{T\Delta_{\text{vap}}V} = \frac{40.66\times10^3\,\text{J}\,\text{mol}^{-1}}{(373.13\,\text{K})(3.011\times10^{-2}\,\text{m}^3\,\text{mol}^{-1})} = 3.62\times10^3\,\text{Pa}\,\text{K}^{-1}$$

(b) Repeat the calculation using the Clausius–Clapeyron equation.

Solution:

$$\frac{p}{T} \approx \frac{\Delta_{\text{vap}}Hp}{RT^2} = \frac{(40.66\times10^3\,\text{J}\,\text{mol}^{-1})(1.01325\times10^5\,\text{Pa})}{(8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})(373.13\,\text{K})^2} = 3.56\times10^3\,\text{Pa}\,\text{K}^{-1}$$

(c) Use your results to estimate the standard boiling point of water. (Note: The experimental value is 99.61 °C.)

Solution:

$$T_{\text{vap}}(p_2) \approx T_{\text{vap}}(p_1) + \frac{p_2 - p_1}{\mathrm{d}p/\,\mathrm{d}T}$$

Use the value of $\mathrm{d}p/\,\mathrm{d}T$ from the Clapeyron equation, which is more accurate:

$$\begin{aligned} T_{\text{vap}}(1\ \text{bar}) &\approx 373.12\,\text{K} + \frac{(1 - 1.01325) \times 10^5\,\text{Pa}}{3.62 \times 10^3\,\text{Pa}\,\text{K}^{-1}} = 373.12\,\text{K} - 0.366\,\text{K} \\ &= 372.75\,\text{K}\ (99.60\,^\circ\text{C}) \end{aligned}$$

8.8 At the standard pressure of 1 bar, liquid and gaseous H_2O coexist in equilibrium at 372.76 K, the standard boiling point of water.

(a) Do you expect the standard molar enthalpy of vaporization to have the same value as the molar enthalpy of vaporization at this temperature? Explain.

Solution:

The values of $\Delta_{\text{vap}}H^\circ$ and $\Delta_{\text{vap}}H$ are different because the standard state of a gas is the hypothetical ideal gas at the standard pressure, which is not the same as the real gas at the standard pressure.

(b) The molar enthalpy of vaporization at 372.76 K has the value $\Delta_{\text{vap}}H = 40.67\,\text{kJ}\,\text{mol}^{-1}$. Estimate the value of $\Delta_{\text{vap}}H^\circ$ at this temperature with the help of Table 7.5 and the following data for the second virial coefficient of gaseous H_2O at 372.76 K:

$$B = -4.60 \times 10^{-4}\,\text{m}^3\,\text{mol}^{-1} \qquad \mathrm{d}B/\,\mathrm{d}T = 3.4 \times 10^{-6}\,\text{m}^3\,\text{K}^{-1}\,\text{mol}^{-1}$$

Solution:

$$\begin{aligned} H_{\text{m}}(\text{g}) &\approx H^\circ_{\text{m}}(\text{g}) + p\left(B - T\frac{\mathrm{d}B}{\mathrm{d}T}\right) \\ &= H^\circ_{\text{m}}(\text{g}) + (1 \times 10^5\,\text{Pa})\big[(-4.60 \times 10^{-4}\,\text{m}^3\,\text{mol}^{-1}) \\ &\quad - (372.76\,\text{K})(3.4 \times 10^{-6}\,\text{m}^3\,\text{K}^{-1}\,\text{mol}^{-1})\big] \\ &= H^\circ_{\text{m}}(\text{g}) - 1.73 \times 10^2\,\text{J}\,\text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta_{\text{vap}}H^\circ &= \Delta_{\text{vap}}H + H^\circ_{\text{m}}(\text{g}) - H_{\text{m}}(\text{g}) = 40.67 \times 10^3\,\text{J}\,\text{mol}^{-1} + 1.73 \times 10^2\,\text{J}\,\text{mol}^{-1} \\ &= 4.084 \times 10^4\,\text{J}\,\text{mol}^{-1} \end{aligned}$$

(c) Would you expect the values of $\Delta_{\text{fus}}H$ and $\Delta_{\text{fus}}H^\circ$ to be equal at the standard freezing point of water? Explain.

Solution:

Yes, because the standard states of the solid and liquid are the same as the real coexisting phases at the standard pressure.

8.9 The standard boiling point of H_2O is 99.61 °C. The molar enthalpy of vaporization at this temperature is $\Delta_{\text{vap}}H = 40.67\,\text{kJ}\,\text{mol}^{-1}$. The molar heat capacity of the liquid at temperatures close to this value is given by

$$C_{p,\text{m}} = a + b(t - c)$$

where t is the Celsius temperature and the constants have the values

$$a = 75.94\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1} \qquad b = 0.022\,\text{J}\,\text{K}^{-2}\,\text{mol}^{-1} \qquad c = 99.61\,^\circ\text{C}$$

Suppose 100.00 mol of liquid H_2O is placed in a container maintained at a constant pressure of 1 bar, and is carefully heated to a temperature 5.00 °C above the standard boiling point, resulting in an unstable phase of superheated water. If the container is enclosed with an adiabatic boundary and the system subsequently changes spontaneously to an equilibrium state, what amount of water will vaporize? (Hint: The temperature will drop to the standard boiling point, and the enthalpy change will be zero.)

Solution:

The enthalpy change for the process is the same as the enthalpy change when the water is cooled to 99.61 °C and vaporization then takes place reversibly:

$$\Delta H = 0 = n\int_{t_1}^{t_2} C_{p,\mathrm{m}}\,\mathrm{d}t + n^{\mathrm{g}}\Delta_{\mathrm{vap}}H$$

$$n^{\mathrm{g}} = \frac{-n\displaystyle\int_{t_1}^{t_2} C_{p,\mathrm{m}}\,\mathrm{d}t}{\Delta_{\mathrm{vap}}H}$$

Write $x = t - c$, $C_{p,\mathrm{m}} = a + bx$:

$$n^{\mathrm{g}} = \frac{-n\displaystyle\int_{x_1}^{x_2}(a+bx)\,\mathrm{d}x}{\Delta_{\mathrm{vap}}H} = \frac{-n\left[a(x_2-x_1)+(b/2)(x_2^2-x_1^2)\right]}{\Delta_{\mathrm{vap}}H}$$

$$= \frac{-(100.00\,\mathrm{mol})\left[(75.94\,\mathrm{J\,K^{-1}\,mol^{-1}})(-5.00\,\mathrm{K}) + (0.022\ \mathrm{J\,K^{-2}\,mol^{-1}})(-5.00\,\mathrm{K})^2/2\right]}{4.067\times10^4\,\mathrm{J\,mol^{-1}}}$$

$$= 0.93\,\mathrm{mol}$$

Chapter 9 Mixtures

9.1 For a binary solution, find expressions for the mole fractions x_{B} and x_{A} as functions of the solute molality m_{B}.

Solution:

Equate the expressions for $n_{\text{B}}/n_{\text{A}}$ in Eqs. 9.1.9 and 9.1.12 and solve for x_{B}:

$$\frac{x_{\text{B}}}{1-x_{\text{B}}} = M_{\text{A}} m_{\text{B}} \qquad x_{\text{B}} = \frac{M_{\text{A}} m_{\text{B}}}{1+M_{\text{A}} m_{\text{B}}}$$

Find x_{A}:

$$x_{\text{A}} = 1 - x_{\text{B}} = \frac{1}{1+M_{\text{A}} m_{\text{B}}}$$

9.2 Consider a binary mixture of two liquids, A and B. The molar volume of mixing, $\Delta V(\text{mix})/n$, is given by Eq. 9.2.19.

(a) Find a formula for calculating the value of $\Delta V(\text{mix})/n$ of a binary mixture from values of x_{A}, x_{B}, M_{A}, M_{B}, ρ, ρ^*_{A}, and ρ^*_{B}.

Solution:

$$\Delta V(\text{mix})/n = V/n - x_{\text{A}} V^*_{\text{A}} - x_{\text{B}} V^*_{\text{B}}$$

Make the following substitutions:

$$V = m/\rho = (n_{\text{A}} M_{\text{A}} + n_{\text{B}} M_{\text{B}})/\rho \qquad V^*_{\text{A}} = M_{\text{A}}/\rho^*_{\text{A}} \qquad V^*_{\text{B}} = M_{\text{B}}/\rho^*_{\text{B}}$$

The result is

$$\Delta V(\text{mix})/n = \frac{n_{\text{A}} M_{\text{A}} + n_{\text{B}} M_{\text{B}}}{n\rho} - \frac{x_{\text{A}} M_{\text{A}}}{\rho^*_{\text{A}}} - \frac{x_{\text{B}} M_{\text{B}}}{\rho^*_{\text{B}}} = \frac{x_{\text{A}} M_{\text{A}} + x_{\text{B}} M_{\text{B}}}{\rho} - \frac{x_{\text{A}} M_{\text{A}}}{\rho^*_{\text{A}}} - \frac{x_{\text{B}} M_{\text{B}}}{\rho^*_{\text{B}}}$$

Table 7 Molar volumes of mixing of binary mixtures of 1-hexanol (A) and 1-octene (B) at 25 °C.[a]

x_{B}	$[\Delta V(\text{mix})/n]/\text{cm}^3\,\text{mol}^{-1}$	x_{B}	$[\Delta V(\text{mix})/n]/\text{cm}^3\,\text{mol}^{-1}$
0	0	0.555	0.005
0.049	−0.027	0.597	0.011
0.097	−0.050	0.702	0.029
0.146	−0.063	0.716	0.035
0.199	−0.077	0.751	0.048
0.235	−0.073	0.803	0.056
0.284	−0.074	0.846	0.058
0.343	−0.065	0.897	0.057
0.388	−0.053	0.944	0.049
0.448	−0.032	1	0
0.491	−0.016		

[a] Ref. [170].

(b) The molar volumes of mixing for liquid binary mixtures of 1-hexanol (A) and 1-octene (B) at 25 °C have been calculated from their measured densities. The data are in Table 7. The molar volumes of the pure constituents are $V^*_{\text{A}} = 125.31\,\text{cm}^3\,\text{mol}^{-1}$ and $V^*_{\text{B}} =$

157.85 cm^3 mol^{-1}. Use the method of intercepts to estimate the partial molar volumes of both constituents in an equimolar mixture ($x_A = x_B = 0.5$), and the partial molar volume V_B^∞ of B at infinite dilution.

Solution:

The experimental points are shown as filled circles in Fig. 11.

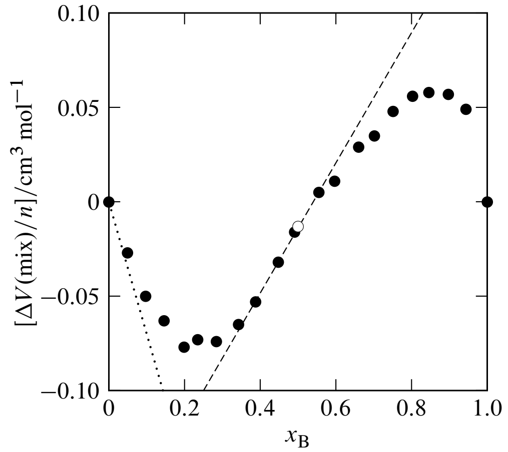

Figure 11 Molar volume of mixing as a function of x_B.

The dashed line is an estimated tangent to a curve through the experimental points at the point shown by the open circle at $x_B = 0.5$, $\Delta V(\text{mix})/n = -0.013\,\text{cm}^3\,\text{mol}^{-1}$. The slope of the line is $0.34\,\text{cm}^3\,\text{mol}^{-1}$. Represent the line by $y = ax_B + b$ and find $a = 0.34\,\text{cm}^3\,\text{mol}^{-1}$ and $b = -0.18\,\text{cm}^3\,\text{mol}^{-1}$. The intercepts are $y = -0.18\,\text{cm}^3\,\text{mol}^{-1}$ at $x_B = 0$ and $y = 0.16\,\text{cm}^3\,\text{mol}^{-1}$ at $x_B{=}1$. The partial molar volumes are therefore

$$V_A(x_B = 0.5) \approx (125.31 - 0.18)\,\text{cm}^3\,\text{mol}^{-1} = 125.13\,\text{cm}^3\,\text{mol}^{-1}$$

$$V_B(x_B = 0.5) \approx (157.85 + 0.16)\,\text{cm}^3\,\text{mol}^{-1} = 158.01\,\text{cm}^3\,\text{mol}^{-1}$$

The dotted line in Fig. 11 is an estimated tangent to a curve through the experimental points at $x_B = 0$. The slope of this line is $-0.70\,\text{cm}^3\,\text{mol}^{-1}$; this is also the value of the intercept at $x_B{=}1$. Therefore

$$V_B^\infty \approx (157.85 - 0.70)\,\text{cm}^3\,\text{mol}^{-1} = 157.15\,\text{cm}^3\,\text{mol}^{-1}$$

9.3 Extend the derivation of Prob. 8.1, concerning a liquid droplet of radius r suspended in a gas, to the case in which the liquid and gas are both mixtures. Show that the equilibrium conditions are $T^\text{g} = T^\text{l}$, $\mu_i^\text{g} = \mu_i^\text{l}$ (for each species i that can equilibrate between the two phases), and $p^\text{l} = p^\text{g} + 2\gamma/r$, where γ is the surface tension. (As in Prob. 8.1, the last relation is the Laplace equation.)

Solution:

The derivation is like that of Prob. 8.1, with the total differential of U given by

$$\text{d}U = T^\text{l}\,\text{d}S^\text{l} - p^\text{l}\,\text{d}V^\text{l} + \sum_i \mu_i^\text{l}\,\text{d}n_i^\text{l} + T^\text{g}\,\text{d}S^\text{g} - p^\text{g}\,\text{d}V^\text{g} + \sum_i \mu_i^\text{g}\,\text{d}n_i^\text{g} + \gamma\,\text{d}A_\text{s}$$

and the conditions for an isolated system given by

$$\mathrm{d}U = 0 \qquad \mathrm{d}V^{\mathrm{g}} = -\mathrm{d}V^{\mathrm{l}} \qquad \mathrm{d}n_i^{\mathrm{g}} = -\mathrm{d}n_i^{\mathrm{l}} \ \text{ for each species } i$$

The result is the total differential

$$\mathrm{d}S = \frac{(T^{\mathrm{l}} - T^{\mathrm{g}})}{T^{\mathrm{l}}}\,\mathrm{d}S^{\mathrm{g}} + \frac{(p^{\mathrm{l}} - p^{\mathrm{g}} - 2\gamma/r)}{T^{\mathrm{l}}}\,\mathrm{d}V^{\mathrm{l}} - \frac{1}{T^{\mathrm{l}}}\sum_i (\mu_i^{\mathrm{l}} - \mu_i^{\mathrm{g}})\,\mathrm{d}n_i^{\mathrm{l}}$$

The equilibrium conditions are the ones that make the coefficient of each term zero.

9.4 Consider a gaseous mixture of 4.0000×10^{-2} mol of N_2 (A) and 4.0000×10^{-2} mol of CO_2 (B) in a volume of $1.0000 \times 10^{-3}\ \mathrm{m}^3$ at a temperature of 298.15 K. The second virial coefficients at this temperature have the values[3]

$$\begin{aligned} B_{\mathrm{AA}} &= -4.8 \times 10^{-6}\ \mathrm{m^3\,mol^{-1}} \\ B_{\mathrm{BB}} &= -124.5 \times 10^{-6}\ \mathrm{m^3\,mol^{-1}} \\ B_{\mathrm{AB}} &= -47.5 \times 10^{-6}\ \mathrm{m^3\,mol^{-1}} \end{aligned}$$

Compare the pressure of the real gas mixture with that predicted by the ideal gas equation. See Eqs. 9.3.20 and 9.3.23.

Solution:

The composition is given by $y_A = 0.50000$, $y_B = 0.50000$.

Real gas:

$$V/n = \frac{1.0000 \times 10^{-3}\ \mathrm{m}^3}{8.0000 \times 10^{-2}\ \mathrm{mol}} = 1.2500 \times 10^{-2}\ \mathrm{m^3\,mol^{-1}}$$

$$B = y_{\mathrm{A}}^2 B_{\mathrm{AA}} + 2y_{\mathrm{A}}y_{\mathrm{B}}B_{\mathrm{AB}} + y_{\mathrm{B}}^2 B_{\mathrm{BB}} = -56.1 \times 10^{-6}\ \mathrm{m^3\,mol^{-1}}$$

$$p = RT\left(\frac{1}{V/n} + \frac{B}{(V/n)^2}\right) = 1.9743 \times 10^5\ \mathrm{Pa} = 1.9743\ \mathrm{bar}$$

Ideal gas: $p = nRT/V = 1.9832\ \mathrm{Pa} = 1.9832\ \mathrm{bar}$

The real gas mixture has a slightly lower pressure than the ideal gas at the same temperature and volume, due to attractive forces between the molecules.

9.5 At 25 °C and 1 bar, the Henry's law constants of nitrogen and oxygen dissolved in water are $k_{\mathrm{H,N_2}} = 8.64 \times 10^4$ bar and $k_{\mathrm{H,O_2}} = 4.41 \times 10^4$ bar.[4] The vapor pressure of water at this temperature and pressure is $p_{\mathrm{H_2O}} = 0.032$ bar. Assume that dry air contains only N_2 and O_2 at mole fractions $y_{\mathrm{N_2}} = 0.788$ and $y_{\mathrm{O_2}} = 0.212$. Consider liquid–gas systems formed by equilibrating liquid water and air at 25 °C and 1.000 bar, and assume that the gas phase behaves as an ideal gas mixture.

Hint: The sum of the partial pressures of N_2 and O_2 must be $(1.000 - 0.032)$ bar $= 0.968$ bar. If the volume of one of the phases is much larger than that of the other, then almost all of the N_2 and O_2 will be in the predominant phase and the ratio of their amounts in this phase must be practically the same as in dry air.

Determine the mole fractions of N_2 and O_2 in both phases in the following limiting cases:

(a) A large volume of air is equilibrated with just enough water to leave a small drop of liquid.

Solution:

Assume that the amounts of N_2 and O_2 in the gas phase are in the same ratio as in dry air:

$$\frac{n_{\mathrm{N_2}}}{n_{\mathrm{O_2}}} = \frac{0.788}{0.212} = 3.72$$

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[3] Refs. [3], [49], and [50]. [4] Ref. [184].

$$\frac{p_{N_2}}{p_{O_2}} = \frac{y_{N_2} p}{y_{O_2} p} = \frac{(n_{N_2}/n)p}{(n_{O_2}/n)p} = 3.72$$

Solve simultaneously with $p_{N_2} + p_{O_2} = 0.968\,\text{bar}$:

$p_{N_2} = 0.763\,\text{bar}$, $p_{O_2} = 0.205\,\text{bar}$

Calculate compositions in gas and liquid phases:

$y_{N_2} = p_{N_2}/p = 0.763$, $y_{O_2} = p_{O_2}/p = 0.205$

$x_{N_2} = p_{N_2}/k_{H,N_2} = 0.763\,\text{bar}/8.64 \times 10^4\,\text{bar} = 8.83 \times 10^{-6}$

$x_{O_2} = p_{O_2}/k_{H,O_2} = 0.205\,\text{bar}/4.41 \times 10^4\,\text{bar} = 4.65 \times 10^{-6}$

(b) A large volume of water is equilibrated with just enough air to leave a small bubble of gas.

Solution:

Assume that the amounts of N_2 and O_2 in the liquid phase are in the same ratio as in dry air:

$$\frac{x_{N_2}}{x_{O_2}} = \frac{n_{N_2}}{n_{O_2}} = \frac{0.788}{0.212} = 3.72$$

$$\frac{p_{N_2}}{p_{O_2}} = \frac{k_{H,N_2}\, x_{N_2}}{k_{H,O_2}\, x_{O_2}} = \left(\frac{8.64 \times 10^4\,\text{bar}}{4.41 \times 10^4\,\text{bar}}\right)(3.72) = 7.29$$

Solve simultaneously with $p_{N_2} + p_{O_2} = 0.968\,\text{bar}$:

$p_{N_2} = 0.851\,\text{bar}$, $p_{O_2} = 0.117\,\text{bar}$

Calculate compositions in gas and liquid phases:

$y_{N_2} = p_{N_2}/p = 0.851$, $y_{O_2} = p_{O_2}/p = 0.117$

$x_{N_2} = p_{N_2}/k_{H,N_2} = 0.851\,\text{bar}/8.64 \times 10^4\,\text{bar} = 9.85 \times 10^{-6}$

$x_{O_2} = p_{O_2}/k_{H,O_2} = 0.117\,\text{bar}/4.41 \times 10^4\,\text{bar} = 2.65 \times 10^{-6}$

9.6 Derive the expression for $\gamma_{m,B}$ given in Table 9.4, starting with Eq. 9.5.18.

Solution:

Equate the expression for $\mu_{m,B}$ from Eq. 9.5.18 and the expression for μ_B in the equilibrated gas phase:

$$\mu_{m,B}^{\text{ref}} + RT \ln\left(\gamma_{m,B} \frac{m_B}{m^\circ}\right) = \mu_B^{\text{ref}}(\text{g}) + RT \ln(f_B/p)$$

Solve for $\gamma_{m,B}$:

$$\gamma_{m,B} = \exp\left[\frac{\mu_B^{\text{ref}}(\text{g}) - \mu_{m,B}^{\text{ref}}}{RT}\right] \times \frac{m^\circ f_B}{m_B p}$$

On the right side of this expression, only f_B and m_B depend on the solution composition:

$$\gamma_{m,B} = C_{m,B} \frac{f_B}{m_B}$$

where $C_{m,B}$ is independent of m_B.

Solve for $C_{m,B}$:

$$C_{m,\mathrm{B}} = \frac{\gamma_{m,\mathrm{B}} m_{\mathrm{B}}}{f_{\mathrm{B}}}$$

In the limit as m_{B} approaches zero at constant T and p, $\gamma_{m,\mathrm{B}}$ approaches 1 and $f_{\mathrm{B}}/m_{\mathrm{B}}$ approaches $k_{m,\mathrm{B}}$. Evaluate $C_{m,\mathrm{B}}$ in this limit:

$$C_{m,\mathrm{B}} = \lim_{m_{\mathrm{B}}\to 0} \gamma_{m,\mathrm{B}} \frac{m_{\mathrm{B}}}{f_{\mathrm{B}}} = \frac{1}{k_{m,\mathrm{B}}}$$

With this value for $C_{m,\mathrm{B}}$, the activity coefficient is given by

$$\gamma_{m,\mathrm{B}} = \frac{f_{\mathrm{B}}}{k_{m,\mathrm{B}} m_{\mathrm{B}}}$$

9.7 Consider a nonideal binary gas mixture with the simple equation of state $V = nRT/p + nB$ (Eq. 9.3.21).

(a) The *rule of Lewis and Randall* states that the value of the mixed second virial coefficient B_{AB} is the average of B_{AA} and B_{BB}. Show that when this rule holds, the fugacity coefficient of A in a binary gas mixture of any composition is given by $\ln\phi_{\mathrm{A}} = B_{\mathrm{AA}}p/RT$. By comparing this expression with Eq. 7.8.18 for a pure gas, express the fugacity of A in the mixture as a function of the fugacity of pure A at the same temperature and pressure as the mixture.

Solution:

If B_{AB} is equal to $(B_{\mathrm{AA}} + B_{\mathrm{BB}})/2$, Eq. 9.3.27 gives $B'_{\mathrm{A}} = B_{\mathrm{AA}}$, and Eq. 9.3.29 becomes

$$\ln\phi_{\mathrm{A}} = \frac{B_{\mathrm{AA}}p}{RT}$$

Comparing the expression with Eq. 7.8.18 for a pure gas, $\ln\phi \approx Bp/RT$, we see that the fugacity coefficient of A in the mixture is equal to the fugacity coefficient of pure A at the same T and p:

$$\phi_{\mathrm{A}} = f_{\mathrm{A}}/p_{\mathrm{A}} = f^*_{\mathrm{A}}/p$$

Therefore, according to the rule of Lewis and Randall the fugacity of A is given by

$$f_{\mathrm{A}} = (p_{\mathrm{A}}/p)f^*_{\mathrm{A}} = y_{\mathrm{A}}f^*_{\mathrm{A}}$$

(b) The rule of Lewis and Randall is not accurately obeyed when constituents A and B are chemically dissimilar. For example, at 298.15 K, the second virial coefficients of H_2O (A) and N_2 (B) are $B_{\mathrm{AA}} = -1158\,\mathrm{cm^3\,mol^{-1}}$ and $B_{\mathrm{BB}} = -5\,\mathrm{cm^3\,mol^{-1}}$, respectively, whereas the mixed second virial coefficient is $B_{\mathrm{AB}} = -40\,\mathrm{cm^3\,mol^{-1}}$.

When liquid water is equilibrated with nitrogen at 298.15 K and 1 bar, the partial pressure of H_2O in the gas phase is $p_{\mathrm{A}} = 0.03185\,\mathrm{bar}$. Use the given values of B_{AA}, B_{BB}, and B_{AB} to calculate the fugacity of the gaseous H_2O in this binary mixture. Compare this fugacity with the fugacity calculated with the value of B_{AB} predicted by the rule of Lewis and Randall.

Solution:

The gas-phase composition is $y_{\mathrm{A}} = p_{\mathrm{A}}/p = 0.03185$, $y_{\mathrm{B}} = 1 - y_{\mathrm{A}} = 0.96815$. Using the values of B_{AA}, B_{BB}, and B_{AB} given in the problem, and Eq. 9.3.27:

$$B'_{\mathrm{A}} = -143\,\mathrm{cm^3\,mol^{-1}}$$

Then from Eq. 9.3.29:

$$\ln\phi_{\mathrm{A}} = \frac{B'_{\mathrm{A}}p}{RT} = \frac{(-143\,\mathrm{cm^3\,mol^{-1}})(10^{-2}\,\mathrm{m/cm})^3(1\times10^5\,\mathrm{Pa})}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298.15\,\mathrm{K})} = -0.00576$$

$\phi_A = 0.99425$, $f_A = \phi_A p_A = (0.99425)(0.03185\,\text{bar}) = 0.03167\,\text{bar}$

Using $B_{AB} = (B_{AA} + B_{BB})/2 = -581.5\,\text{cm}^3\,\text{mol}^{-1}$:

$B'_A = B_{AA} = -1158\,\text{cm}^3\,\text{mol}^{-1}$, $f_A = 0.03040\,\text{bar}$

Table 8 Activity coefficient of benzene (A) in mixtures of benzene and 1-octanol at 20 °C. The reference state is the pure liquid.

x_A	γ_A	x_A	γ_A
0	2.0[a]	0.7631	1.183
0.1334	1.915	0.8474	1.101
0.2381	1.809	0.9174	1.046
0.4131	1.594	0.9782	1.005
0.5805	1.370		

[a] extrapolated

9.8 Benzene and 1-octanol are two liquids that mix in all proportions. Benzene has a measurable vapor pressure, whereas 1-octanol is practically nonvolatile. The data in Table 8 were obtained by Platford[5] using the isopiestic vapor pressure method.

(a) Use numerical integration to evaluate the integral on the right side of Eq. 9.6.10 at each of the values of x_A listed in the table, and thus find γ_B at these compositions.

Solution:

Table 9 Calculations for Problem 9.8

x_A	$\ln\gamma_B = -\int_{x_A=0}^{x_A} \frac{x_A}{x_B}\,\mathrm{d}\ln\gamma_A$	γ_B	$\gamma_A x_A$	$\gamma_B x_B$
0	0	1	0	1
0.1334	0.0033	1.003	0.255	0.869
0.2381	0.0166	1.017	0.431	0.775
0.4131	0.0809	1.084	0.658	0.636
0.5805	0.2389	1.270	0.796	0.533
0.7631	0.5767	1.780	0.903	0.422
0.8474	0.8921	2.440	0.933	0.372
0.9174	1.3188	3.739	0.960	0.309
0.9782	2.438	11.45	0.983	0.250
1			1	0

The values in column 2 of Table 9 were calculated by the trapezoidal rule. The resulting values of γ_B are listed in column 3 of this table.

(b) Draw two curves on the same graph showing the effective mole fractions $\gamma_A x_A$ and $\gamma_B x_B$ as functions of x_A. Are the deviations from ideal-mixture behavior positive or negative?

Solution:

The values listed in the last two columns of Table 9 are plotted in Fig. 12 on the next page. The deviations from ideal-mixture behavior are *positive*.

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[5] Ref. [145].

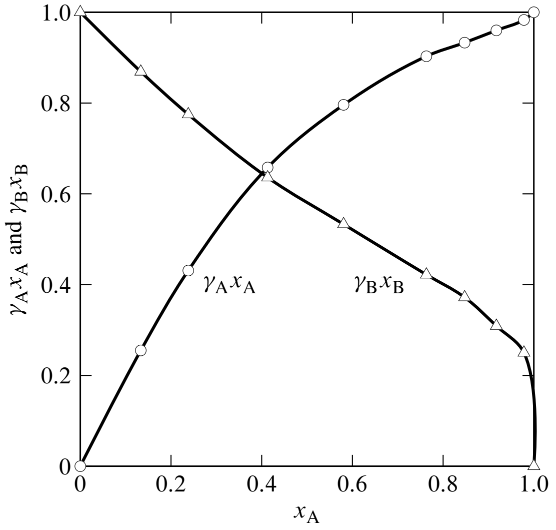

Figure 12 Results for Problem 9.8(b).

Table 10 Liquid and gas compositions in the two-phase system of methanol (A) and benzene (B) at 45 °C[a]

x_A	y_A	p/kPa	x_A	y_A	p/kPa
0	0	29.894	0.4201	0.5590	60.015
0.0207	0.2794	40.962	0.5420	0.5783	60.416
0.0314	0.3391	44.231	0.6164	0.5908	60.416
0.0431	0.3794	46.832	0.7259	0.6216	59.868
0.0613	0.4306	50.488	0.8171	0.6681	58.321
0.0854	0.4642	53.224	0.9033	0.7525	54.692
0.1811	0.5171	57.454	0.9497	0.8368	51.009
0.3217	0.5450	59.402	1	1	44.608

[a] Ref. [169].

9.9 Table 10 lists measured values of gas-phase composition and total pressure for the binary two-phase methanol–benzene system at constant temperature and varied liquid-phase composition. x_A is the mole fraction of methanol in the liquid mixture, and y_A is the mole fraction of methanol in the equilibrated gas phase.

(a) For each of the 16 different liquid-phase compositions, tabulate the partial pressures of A and B in the equilibrated gas phase.

Solution:

Calculate the partial pressures with the relations

$$p_A = y_A p$$

$$p_B = p - p_A$$

The values are tabulated in columns 2 and 3 of Table 11 on the next page.

(b) Plot p_A and p_B versus x_A on the same graph. Notice that the behavior of the mixture is far

Table 11 Calculations for Problem 9.9

x_A	p_A/kPa	p_B/kPa	γ_B	x_A	p_A/kPa	p_B/kPa	γ_B
0	0	29.894	1	0.4201	33.55	26.47	1.527
0.0207	11.44	29.52	1.008	0.5420	34.94	25.48	1.861
0.0314	15.00	29.23	1.009	0.6164	35.69	24.73	2.157
0.0431	17.77	29.06	1.016	0.7259	37.21	22.66	2.765
0.0613	21.74	28.75	1.025	0.8171	38.96	19.36	3.541
0.0854	24.71	28.51	1.043	0.9033	41.15	13.54	4.68
0.1811	29.71	27.74	1.133	0.9497	42.68	8.33	5.54
0.3217	32.37	27.03	1.333	1	44.608	0	

from that of an ideal mixture. Are the deviations from Raoult's law positive or negative?

Solution:

See Fig. 13. The deviations from Raoult's law are positive.

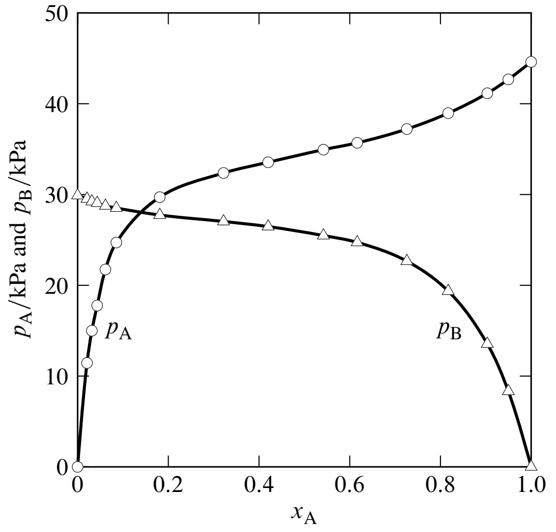

Figure 13 Results for Problem 9.9.

(c) Tabulate and plot the activity coefficient γ_B of the benzene as a function of x_A using a pure-liquid reference state. Assume that the fugacity f_B is equal to p_B, and ignore the effects of variable pressure.

Solution:

Calculate the activity coefficient with the relation

$$\gamma_B = \frac{p_B}{x_B p_B^*}$$

where the vapor pressure of pure benzene is $p_B^* = 29.894\,\text{kPa}$. The calculated values are in the last column of Table 11 and are plotted in Fig. 14 on the next page. Note how γ_B approaches 1 as x_A approaches zero.

(d) Estimate the Henry's law constant $k_{H,A}$ of methanol in the benzene environment at 45 °C by the graphical method suggested in Fig. 9.7(b). Again assume that f_A and p_A are equal,

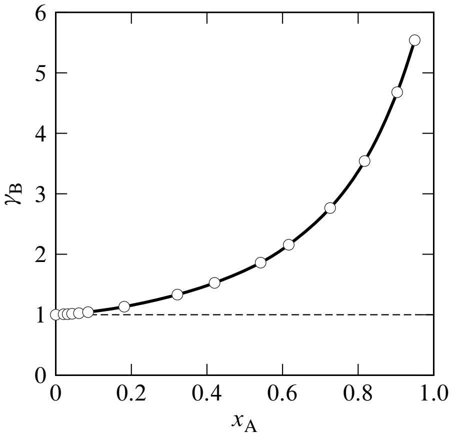

Figure 14 Activity coefficient of benzene in liquid methanol–benzene mixtures.

and ignore the effects of variable pressure.

Solution:

See Fig. 15. Based on the first three points, the extrapolation of p_A/x_A to $x_A = 0$ gives a value of $k_{H,A} \approx 680\,\text{kPa}$.

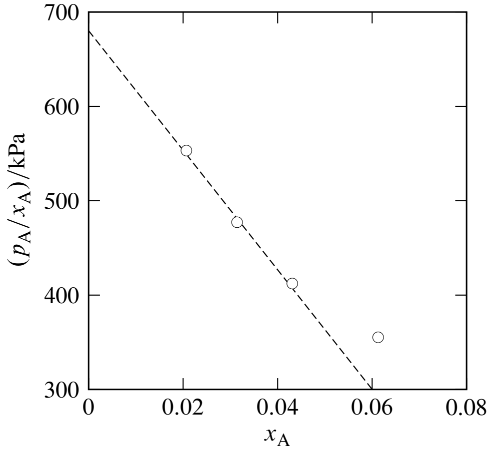

Figure 15 Estimate of the Henry's law constant of methanol in benzene.

9.10 Consider a dilute binary nonelectrolyte solution in which the dependence of the chemical potential of solute B on composition is given by

$$\mu_B = \mu^{\text{ref}}_{m,B} + RT \ln \frac{m_B}{m^\circ} + k_m m_B$$

where $\mu^{\text{ref}}_{m,B}$ and k_m are constants at a given T and p. (The derivation of this equation is sketched in Sec. 9.5.4.) Use the Gibbs–Duhem equation in the form $\mathrm{d}\mu_A = -(n_B/n_A)\,\mathrm{d}\mu_B$ to obtain an expression for $\mu_A - \mu^*_A$ as a function of m_B in this solution.

Solution:

Make the substitutions $n_B/n_A = M_A m_B$ (Eq. 9.1.12) and $d\mu_B = (RT/m_B + k_m)\,dm_B$, and integrate from pure solvent to solution of molality m_B:

$$\int_{\mu_A^*}^{\mu_A'} d\mu_A = -M_A \int_0^{m_B'} m_B \left(\frac{RT}{m_B} + k_m\right) dm_B$$

$$\mu_A' - \mu_A^* = -M_A RT m_B' - \tfrac{1}{2} M_A k_m (m_B')^2$$

$$\mu_A - \mu_A^* = -M_A RT m_B - \tfrac{1}{2} M_A k_m m_B^2$$

9.11 By means of the isopiestic vapor pressure technique, the osmotic coefficients of aqueous solutions of urea at 25 °C have been measured at molalities up to the saturation limit of about 20 mol kg^{-1}.[6] The experimental values are closely approximated by the function

$$\phi_m = 1.00 - \frac{0.050\, m_B/m^\circ}{1.00 + 0.179\, m_B/m^\circ}$$

where m° is 1 mol kg^{-1}. Calculate values of the solvent and solute activity coefficients γ_A and $\gamma_{m,B}$ at various molalities in the range 0–20 mol kg^{-1}, and plot them versus m_B/m°. Use enough points to be able to see the shapes of the curves. What are the limiting slopes of these curves as m_B approaches zero?

Solution:

Substitute the expression for μ_A given by Eq. 9.5.15 into Eq. 9.6.16 and solve for $\ln \gamma_A$:

$$\ln \gamma_A = -\ln x_A - \phi_m M_A m_B$$

Values of x_A can be found from m_B with the formula derived in Prob. 9.1:

$$x_A = \frac{1}{1 + M_A m_B}$$

$\gamma_{m,B}$ is found from Eq. 9.6.20:

$$\begin{aligned}\ln \gamma_{m,B}(m_B') &= \phi_m - 1 + \int_0^{m_B'} \frac{\phi_m - 1}{m_B}\, dm_B \\ &= -\frac{0.050 m_B'/m^\circ}{1.00 + 0.179 m_B'/m^\circ} - \int_0^{m_B'/m^\circ} \frac{0.050}{1.00 + 0.179 m_B/m^\circ}\, d(m_B/m^\circ) \\ &= -\frac{0.050 m_B'/m^\circ}{1.00 + 0.179 m_B'/m^\circ} - 0.50 \ln(1.00 + 0.179 m_B'/m^\circ)\end{aligned}$$

See Fig. 16 on the next page for the curves plotted from values calculated with these formulas. The limiting slopes are $d\gamma_A/\,d(m_B/m^\circ) = 0$ and $d\gamma_{m,B}/\,d(m_B/m^\circ) = -0.09$.

9.12 Use Eq. 9.2.49 to derive an expression for the rate at which the logarithm of the activity coefficient of component i of a liquid mixture changes with pressure at constant temperature and composition: $(\partial \ln \gamma_i/\partial p)_{T,\{n_i\}} =$?

Solution:

$$\mu_i = \mu_i^{\text{ref}} + RT \ln(\gamma_i x_i) \qquad RT \ln \gamma_i = \mu_i - \mu_i^{\text{ref}} - RT \ln x_i$$

$$\left(\frac{\partial RT \ln \gamma_i}{\partial p}\right)_{T,\{n_i\}} = \left(\frac{\partial \mu_i}{\partial p}\right)_{T,\{n_i\}} - \left(\frac{\partial \mu_i^{\text{ref}}}{\partial p}\right)_{T,\{n_i\}} = V_i - V_i^*$$

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[6] Ref. [160].

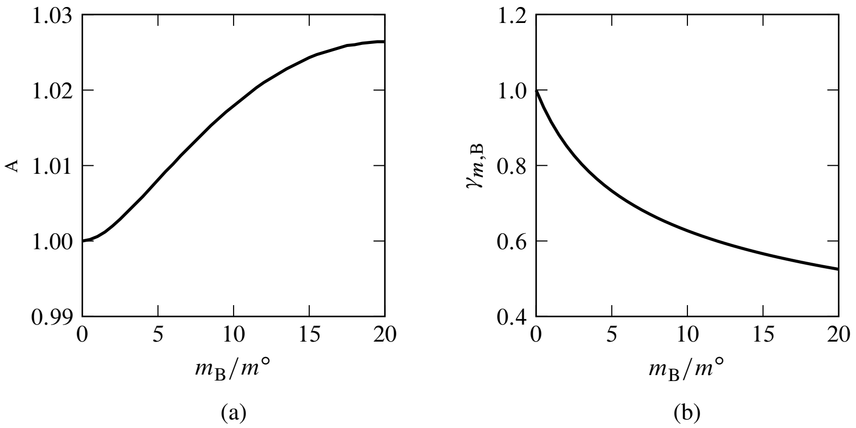

Figure 16 Activity coefficients in aqueous urea solutions at 25 °C.

$$\left(\frac{\partial \ln \gamma_i}{\partial p}\right)_{T,\{n_i\}} = \frac{V_i - V_i^*}{RT}$$

9.13 Assume that at sea level the atmosphere has a pressure of 1.00 bar and a composition given by $y_{N_2} = 0.788$ and $y_{O_2} = 0.212$. Find the partial pressures and mole fractions of N_2 and O_2, and the total pressure, at an altitude of 10.0 km, making the (drastic) approximation that the atmosphere is an ideal gas mixture in an equilibrium state at 0 °C. For g use the value of the standard acceleration of free fall listed in Appendix B.

Solution:

Partial pressures at sea level:

$$p_{N_2} = y_{N_2} p = (0.788)(1.00\,\text{bar}) = 0.788\,\text{bar}$$

$$p_{O_2} = y_{O_2} p = (0.212)(1.00\,\text{bar}) = 0.212\,\text{bar}$$

Calculate the partial pressures at elevation h with the equation $p_i(h) = p_i(0)e^{-M_i gh/RT}$ (Sec. 9.8.1):

$$p_{N_2} = (0.788\,\text{bar}) \exp\left[\frac{-(28.01\times10^{-3}\,\text{kg}\,\text{mol}^{-1})(9.806\,65\,\text{m}\,\text{s}^{-2})(10.0\times10^{3}\,\text{m})}{(8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})(273.15\,\text{K})}\right]$$

$$= 0.235\,\text{bar}$$

$$p_{O_2} = (0.212\,\text{bar}) \exp\left[\frac{-(32.00\times10^{-3}\,\text{kg}\,\text{mol}^{-1})(9.806\,65\,\text{m}\,\text{s}^{-2})(10.0\times10^{3}\,\text{m})}{(8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})(273.15\,\text{K})}\right]$$

$$= 0.0532\,\text{bar}$$

The total pressure and mole fractions are found from

$$p = p_{N_2} + p_{O_2} = 0.288\,\text{bar}$$

$$y_{N_2} = p_{N_2}/p = 0.815 \qquad y_{O_2} = p_{O_2}/p = 0.185$$

The composition of the mixture has shifted toward a higher mole fraction of N_2 at the higher elevation, because of the lower molar mass of N_2.

9.14 Consider a tall column of a dilute binary liquid solution at equilibrium in a gravitational field.

(a) Derive an expression for $\ln\left[c_{\rm B}(h)/c_{\rm B}(0)\right]$, where $c_{\rm B}(h)$ and $c_{\rm B}(0)$ are the solute concentrations at elevations h and 0. Your expression should be a function of h, $M_{\rm B}$, T, ρ, and the partial specific volume of the solute at infinite dilution, $v_{\rm B}^{\infty}$. For the dependence of pressure on elevation, you may use the hydrostatic formula $\mathrm{d}p = -\rho g\,\mathrm{d}h$ (Eq. 8.1.14 on page 200) and assume the solution density ρ is the same at all elevations. Hint: use the derivation leading to Eq. 9.8.22 as a guide.

Solution:

Only an outline of the derivation is given here. Students should be expected to provide a more complete explanation of the various steps.

Using $\mathrm{d}p = -\rho g\,\mathrm{d}h$:

$$p(h) - p(0) = -\rho g \int_0^h \mathrm{d}h = -\rho g h$$

Reversible elevation of small sample of mass m:

$$đw' = mg\,\mathrm{d}h = (n_{\rm A}M_{\rm A} + n_{\rm B}M_{\rm B})g\,\mathrm{d}h$$

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \mu_{\rm A}\,\mathrm{d}n_{\rm A} + \mu_{\rm B}\,\mathrm{d}n_{\rm B} + (n_{\rm A}M_{\rm A} + n_{\rm B}M_{\rm B})g\,\mathrm{d}h$$

$$\left(\frac{\partial \mu_{\rm B}}{\partial h}\right)_{T,p,n_{\rm A},n_{\rm B}} = \left[\frac{\partial (n_{\rm A}M_{\rm A} + n_{\rm B}M_{\rm B})g}{\partial n_{\rm B}}\right]_{T,p,n_{\rm A},h} = M_{\rm B}g$$

$$\mu_{\rm B}(h) = \mu_{\rm B}(0) + M_{\rm B}gh\ \left(a_{c,{\rm B}}(h) = a_{c,{\rm B}}(0)\right)$$

General relation:

$$\mu_{\rm B}(h) = \mu^{\circ}_{c,{\rm B}} + RT\ln a_{c,{\rm B}}(h) + M_{\rm B}gh$$

At equilibrium:

$$\mu_{\rm B}(h) = \mu_{\rm B}(0)$$

$$\mu^{\circ}_{c,{\rm B}} + RT\ln a_{c,{\rm B}}(h) + M_{\rm B}gh = \mu^{\circ}_{c,{\rm B}} + RT\ln a_{c,{\rm B}}(0)$$

$$\ln\frac{a_{c,{\rm B}}(h)}{a_{c,{\rm B}}(0)} = -\frac{M_{\rm B}gh}{RT}$$

$$a_{c,{\rm B}} = \Gamma_{c,{\rm B}}\gamma_{c,{\rm B}}c_{\rm B}/c^{\circ} \approx \exp\left[\frac{V_{\rm B}^{\infty}(p-p^{\circ})}{RT}\right]\frac{c_{\rm B}}{c^{\circ}}$$

$$\ln\frac{a_{c,{\rm B}}(h)}{a_{c,{\rm B}}(0)} = \frac{V_{\rm B}^{\infty}[p(h)-p(0)]}{RT} + \ln\frac{c_{\rm B}(h)}{c_{\rm B}(0)}$$

$$= -\frac{V_{\rm B}^{\infty}\rho gh}{RT} + \ln\frac{c_{\rm B}(h)}{c_{\rm B}(0)} = -\frac{M_{\rm B}v_{\rm B}^{\infty}\rho gh}{RT} + \ln\frac{c_{\rm B}(h)}{c_{\rm B}(0)}$$

Equate the two expressions for $\ln[a_{c,{\rm B}}(h)/a_{c,{\rm B}}(0)]$:

$$\ln\frac{c_{\rm B}(h)}{c_{\rm B}(0)} = -\frac{M_{\rm B}gh\left(1 - v_{\rm B}^{\infty}\rho\right)}{RT}$$

(b) Suppose you have a tall vessel containing a dilute solution of a macromolecule solute of molar mass $M_{\rm B} = 10.0\,\mathrm{kg\,mol^{-1}}$ and partial specific volume $v_{\rm B}^{\infty} = 0.78\,\mathrm{cm^3\,g^{-1}}$. The solution density is $\rho = 1.00\,\mathrm{g\,cm^{-3}}$ and the temperature is $T = 300\,\mathrm{K}$. Find the height h from the bottom of the vessel at which, in the equilibrium state, the concentration $c_{\rm B}$ has decreased to 99 percent of the concentration at the bottom.

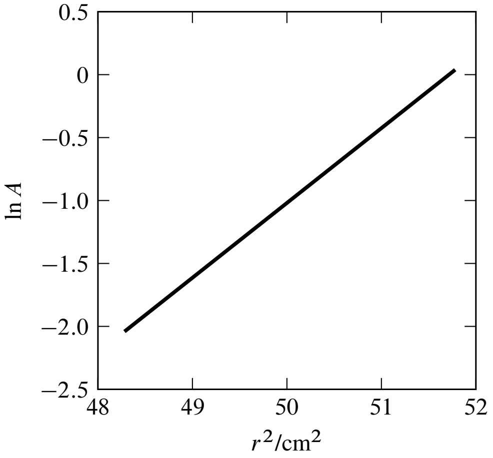

Figure 17 Sedimentation equilibrium of a dilute solution of the FhuA-dodecyl maltoside aggregate.

Solution:

$$\ln \frac{c_{\mathrm{B}}(h)}{c_{\mathrm{B}}(0)} = \ln 0.99 = -\frac{M_{\mathrm{B}} g h \left(1 - v_{\mathrm{B}}^{\infty} \rho\right)}{RT}$$

$$v_{\mathrm{B}}^{\infty} \rho = (0.78\,\mathrm{cm^3\,g^{-1}})(1.00\,\mathrm{g\,cm^{-3}}) = 0.78$$

$$h = -\frac{RT \ln 0.99}{M_{\mathrm{B}} g \left(1 - v_{\mathrm{B}}^{\infty} \rho\right)} = -\frac{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(300\,\mathrm{K})(\ln 0.99)}{(10.0\,\mathrm{kg\,mol^{-1}})(9.81\,\mathrm{m\,s^{-2}})(0.22)} = 1.2\,\mathrm{m}$$

9.15 FhuA is a protein found in the outer membrane of the *Escherichia coli* bacterium. From the known amino acid sequence, its molar mass is calculated to be $78.804\,\mathrm{kg\,mol^{-1}}$. In aqueous solution, molecules of the detergent dodecyl maltoside bind to a FhuA molecule to form an aggregate that behaves as a single solute species. Figure 17 shows data collected in a sedimentation equilibrium experiment with a dilute solution of the aggregate.[7] In the graph, A is the absorbance measured at a wavelength of 280 nm (a property that is a linear function of the aggregate concentration) and r is the radial distance from the axis of rotation of the centrifuge rotor. The experimental points fall very close to the straight line shown in the graph. The sedimentation conditions were $\omega = 838\,\mathrm{s^{-1}}$ and $T = 293\,\mathrm{K}$. The authors used the values $v_{\mathrm{B}}^{\infty} = 0.776\,\mathrm{cm^3\,g^{-1}}$ and $\rho = 1.004\,\mathrm{g\,cm^{-3}}$.

(a) The values of r at which the absorbance was measured range from 6.95 cm to 7.20 cm. Find the difference of pressure in the solution between these two positions.

Solution:

$$p'' - p' = \frac{\omega^2 \rho}{2}\left[(r'')^2 - (r')^2\right] = \frac{(838\,\mathrm{s^{-1}})^2(1.004\,\mathrm{g\,cm^{-3}})(1\,\mathrm{kg}/10^3\,\mathrm{g})}{2}$$

$$\times \left[(7.20\,\mathrm{cm})^2 - (6.95\,\mathrm{cm})^2\right](1\,\mathrm{cm}/10^{-2}\,\mathrm{m})$$

$$= 1.2 \times 10^5\,\mathrm{kg\,m^{-1}\,s^{-2}} = 1.2\,\mathrm{bar}$$

(b) Find the molar mass of the aggregate solute species, and use it to estimate the mass binding ratio (the mass of bound detergent divided by the mass of protein).

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[7] Ref. [18].

Solution:

The slope of the line is $\mathrm{d}\ln A/\,\mathrm{d}r^2 \approx 0.594\,\mathrm{cm^{-2}}$. From Eq. 9.8.22:

$$\begin{aligned} M_\mathrm{B} &= \frac{2RT\,\mathrm{d}\ln A/\,\mathrm{d}r^2}{\omega^2(1-v_\mathrm{B}^\infty\rho)} \\ &= \frac{2(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(293\,\mathrm{K})(0.594\,\mathrm{cm^{-2}})(1\,\mathrm{cm}/10^{-2}\,\mathrm{m})^2}{(838\,\mathrm{s^{-1}})^2[1-(0.776\,\mathrm{cm^3\,g^{-1}})(1.004\,\mathrm{g\,cm^{-3}})]} \\ &= 187\,\mathrm{kg\,mol^{-1}} \end{aligned}$$

Binding ratio: $\dfrac{(187-78.8)\,\mathrm{kg\,mol^{-1}}}{78.8\,\mathrm{kg\,mol^{-1}}} = 1.37$

Chapter 10 Electrolyte Solutions

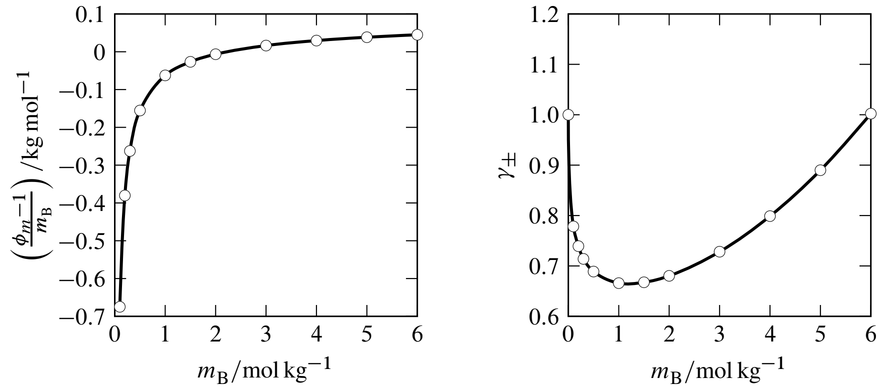
10.1 The mean ionic activity coefficient of NaCl in a 0.100 molal aqueous solution at 298.15 K has been evaluated with measurements of equilibrium cell potentials,[8] with the result $\ln \gamma_\pm = -0.2505$. Use this value in Eq. 10.6.9, together with the values of osmotic coefficients in Table 12, to evaluate $\gamma_\pm$ at each of the molalities shown in the table; then plot $\gamma_\pm$ as a function of m_B.

Table 12 Osmotic coefficients of aqueous NaCl at 298.15 K[a]

$m_\mathrm{B}/\mathrm{mol\,kg^{-1}}$	ϕ_m	$m_\mathrm{B}/\mathrm{mol\,kg^{-1}}$	ϕ_m
0.1	0.9325	2.0	0.9866
0.2	0.9239	3.0	1.0485
0.3	0.9212	4.0	1.1177
0.5	0.9222	5.0	1.1916
1.0	0.9373	6.0	1.2688
1.5	0.9598		

[a] Ref. [31].

Solution:



(a) (b)

Figure 18 Aqueous NaCl at 298.15 K.

The function $(\phi_m - 1)/m_\mathrm{B}$ is plotted versus m_B in Fig. 18(a). Values of the area under the curve from $m_\mathrm{B} = 0.1\ \mathrm{mol\,kg^{-1}}$ to higher molalities are listed in the second column of Table 13 on the next page. The last column of this table lists values of $\ln \gamma_\pm$ calculated from Eq. 10.6.9 with $m''_\mathrm{B} = 0.1\ \mathrm{mol\,kg^{-1}}$ and $\ln \gamma_\pm(m''_\mathrm{B}) = -0.2505$; Fig. 18(b) shows $\gamma_\pm$ as a function of m_B.

10.2 Rard and Miller[9] used published measurements of the freezing points of dilute aqueous solutions of $\mathrm{Na_2SO_4}$ to calculate the osmotic coefficients of these solutions at 298.15 K. Use their values listed in Table 14 on the next page to evaluate the mean ionic activity coefficient

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[8] Ref. [154], Table 9.3. [9] Ref. [151].

Table 13 Calculations for Prob. 10.1

$m'_{\mathrm{B}}/\mathrm{mol\,kg^{-1}}$	$\int_{m''_{\mathrm{B}}}^{m'_{\mathrm{B}}} \frac{\phi_m - 1}{m_{\mathrm{B}}}\,\mathrm{d}m_{\mathrm{B}}$	$\ln\gamma_{\pm}$
0.1	0	−0.2505
0.2	−0.0430	−0.3021
0.3	−0.0751	−0.3369
0.5	−0.1118	−0.3726
1.0	−0.1609	−0.4066
1.5	−0.1808	−0.4040
2.0	−0.1887	−0.3851
3.0	−0.1825	−0.3170
4.0	−0.1592	−0.2245
5.0	−0.1251	−0.1165
6.0	−0.0836	−0.0022

of $\mathrm{Na_2SO_4}$ at 298.15 K and a molality of $m_{\mathrm{B}} = 0.15\,\mathrm{mol\,kg^{-1}}$. For the parameter a in the Debye–Hückel equation (Eq. 10.4.7), use the value $a = 3.0 \times 10^{-10}\,\mathrm{m}$.

Table 14 Osmotic coefficients of aqueous $\mathrm{Na_2SO_4}$ at 298.15 K

$m_{\mathrm{B}}/\mathrm{mol\,kg^{-1}}$	ϕ_m	$m_{\mathrm{B}}/\mathrm{mol\,kg^{-1}}$	ϕ_m
0.0126	0.8893	0.0637	0.8111
0.0181	0.8716	0.0730	0.8036
0.0228	0.8607	0.0905	0.7927
0.0272	0.8529	0.0996	0.7887
0.0374	0.8356	0.1188	0.7780
0.0435	0.8294	0.1237	0.7760
0.0542	0.8178	0.1605	0.7616
0.0594	0.8141		

Solution:

Estimate $\ln\gamma_{\pm}$ at $m_{\mathrm{B}} = 0.0126\,\mathrm{mol\,kg^{-1}}$, the lowest molality for which experimental data are available, using the Debye–Hückel equation:

$$\begin{aligned}
\ln\gamma_{\pm} &= -\frac{A_{\mathrm{DH}}\,|z_+z_-|\,\sqrt{I_m}}{1 + B_{\mathrm{DH}}a\sqrt{I_m}} \\
&= -\frac{(1.1744\,\mathrm{kg^{1/2}\,mol^{-1/2}})(2)\sqrt{(3)(0.0126\,\mathrm{mol\,kg^{-1}})}}{1 + (3.285 \times 10^{9}\,\mathrm{m^{-1}\,kg^{1/2}\,mol^{-1/2}})(3.0 \times 10^{-10}\,\mathrm{m})\sqrt{(3)(0.0126\,\mathrm{mol\,kg^{-1}})}} \\
&= -0.3832
\end{aligned}$$

The experimental points are plotted in Fig. 19 on the next page (open circles). From the curve through the points, estimate $(\phi_m - 1)/m_{\mathrm{B}} = -1.58\,\mathrm{kg\,mol^{-1}}$ at $m_{\mathrm{B}} = 0.15\,\mathrm{mol\,kg^{-1}}$ (open triangle). At this point: $\phi_m = (0.15\,\mathrm{mol\,kg^{-1}})(-1.58\,\mathrm{kg\,mol^{-1}}) + 1 = 0.763$.

Let $m''_{\mathrm{B}} = 0.0126\,\mathrm{mol\,kg^{-1}}$ and $m'_{\mathrm{B}} = 0.15\,\mathrm{mol\,kg^{-1}}$. By numerical integration:

$$\int_{m''_{\mathrm{B}}}^{m'_{\mathrm{B}}} \left(\frac{\phi_m - 1}{m_{\mathrm{B}}}\right) \mathrm{d}m_{\mathrm{B}} = -0.426$$

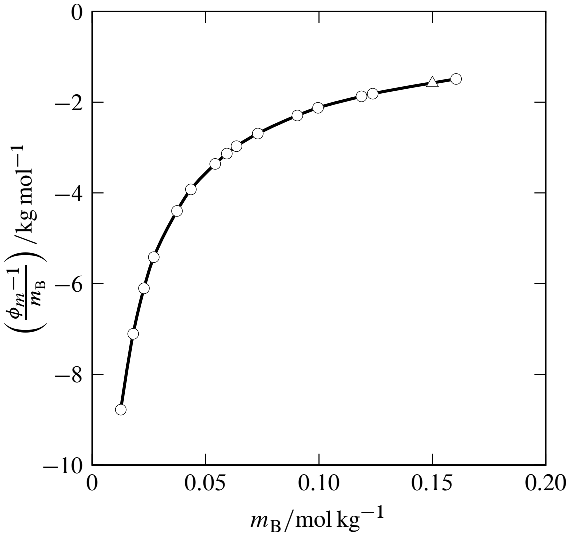

Figure 19 Aqueous Na_2SO_4 at 298.15 K.

Evaluate $\gamma_\pm$ at $m_B = m'_B$ from Eq. 10.6.9:

$$\begin{aligned}\ln\gamma_\pm(m'_B) &= \phi_m(m'_B) - \phi_m(m''_B) + \ln\gamma_\pm(m''_B) + \int_{m''_B}^{m'_B} \frac{\phi_m - 1}{m_B}\,\mathrm{d}m_B \\ &= 0.763 - 0.8893 - 0.3832 - 0.426 \\ &= -0.936\end{aligned}$$

$\gamma_\pm = 0.392$

Chapter 11 Reactions and Other Chemical Processes

11.1 Use values of $\Delta_{\text{f}}H^\circ$ and $\Delta_{\text{f}}G^\circ$ 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:

$$\tfrac{1}{2}\text{N}_2(\text{g}) + \tfrac{5}{4}\text{O}_2(\text{g}) + \tfrac{1}{2}\text{H}_2\text{O(l)} \rightarrow \text{H}^+(\text{aq}) + \text{NO}_3{}^-(\text{aq})$$

Solution:

The formation values of the elements and H^+ ion are zero.

$$\begin{aligned}\Delta_{\text{r}}H^\circ &= -\tfrac{1}{2}\Delta_{\text{f}}H^\circ(\text{H}_2\text{O}) + \Delta_{\text{f}}H^\circ(\text{NO}_3{}^-)\\ &= -\tfrac{1}{2}(-285.830\,\text{kJ mol}^{-1}) + (-206.85\,\text{kJ mol}^{-1}) = -63.94\,\text{kJ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta_{\text{r}}G^\circ &= -\tfrac{1}{2}\Delta_{\text{f}}G^\circ(\text{H}_2\text{O}) + \Delta_{\text{f}}G^\circ(\text{NO}_3{}^-)\\ &= -\tfrac{1}{2}(-237.16\,\text{kJ mol}^{-1}) + (-110.84\,\text{kJ mol}^{-1}) = 7.74\,\text{kJ mol}^{-1}\end{aligned}$$

$$K = \exp\left(-\Delta_{\text{r}}G^\circ/RT\right) = \exp\left[\frac{-7.74\times10^3\,\text{J mol}^{-1}}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(298.15\,\text{K})}\right] = 4.41\times10^{-2}$$

11.2 In 1982, the International Union of Pure and Applied Chemistry recommended that the value of the standard pressure p° 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}, S°_{m}, and G°_{m} 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.)

Solution:

The standard state of a gaseous substance is the pure gas acting ideally. From expressions in Table 7.4, which apply to isothermal changes of pressure of an ideal gas, we have

$$\Delta H_{\text{m}} = \frac{\Delta H}{n} = 0$$

$$\begin{aligned}\Delta S_{\text{m}} &= \frac{\Delta S}{n} = -R\ln\frac{p_2}{p_1} = -(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\ln\frac{1\,\text{bar}}{1.01325\,\text{bar}}\\ &= 0.109\,\text{J K}^{-1}\,\text{mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta G_{\text{m}} &= \frac{\Delta G}{n} = RT\ln\frac{p_2}{p_1} = (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})T\ln\frac{1\,\text{bar}}{1.01325\,\text{bar}}\\ &= -(0.109\,\text{J K}^{-1}\,\text{mol}^{-1})T\end{aligned}$$

(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 N_2O_4(g) at 298.15 K when the standard pressure is changed from 1.01325 bar to 1 bar?

Solution:

The formation reaction is

$$\text{N}_2(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g}) \qquad \textstyle\sum_i \nu_i = -2$$

for which the standard molar enthalpy of formation is given by

$$\Delta_f H°(N_2O_4) = -H^\circ_m(N_2) - 2H^\circ_m(O_2) + H^\circ_m(N_2O_4)$$

with analogous formulas for $\Delta_f S°$ and $\Delta_f G°$. From the formulas in part (a), no correction is needed for $\Delta_f H°$.

The correction for $\Delta_f S°$ is $(-2)(0.109\,\mathrm{J\,K^{-1}\,mol^{-1}}) = -0.219\,\mathrm{J\,K^{-1}\,mol^{-1}}$

The correction for $\Delta_f G°$ is $(-2)(-0.109\,\mathrm{J\,K^{-1}\,mol^{-1}})(298.15\,\mathrm{K}) = 65\,\mathrm{J\,mol^{-1}}$

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.

Solution:

The reference state of mercury at 298.15 K is the liquid; thus, the formation reaction of gaseous mercury is the vaporization process: Hg(l) → Hg(g). Values from Appendix H for Hg(g) at 298.15 K:

$$\Delta_f H° = 61.38\,\mathrm{kJ\,mol^{-1}} \qquad \Delta_f G° = 31.84\,\mathrm{kJ\,mol^{-1}}$$

Since the vapor pressure is low, assume that the mercury vapor is an ideal gas. Assume that the molar enthalpy and Gibbs energy of the liquid at low pressure is the same as at the standard pressure. Find the vapor pressure at 298.15 K from the equilibrium constant of the formation reaction at this temperature:

$$K = \frac{p}{p°} = \exp\left(\frac{-\Delta_r G°}{RT}\right) = \exp\left[\frac{-31.84\times10^3\,\mathrm{J\,mol^{-1}}}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298.15\,\mathrm{K})}\right] = 2.6\times10^{-6}$$

$$p = 2.6\times10^{-6}p° = 2.6\times10^{-6}\,\mathrm{bar}$$

Find the vapor pressure at 273.15 K from the Clausius–Clapeyron equation:

$$\ln\frac{p_2}{p_1} = -\frac{\Delta_{vap}H}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) = -\frac{61.38\times10^3\,\mathrm{J\,mol^{-1}}}{8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}}\left(\frac{1}{273.15\,\mathrm{K}}-\frac{1}{298.15\,\mathrm{K}}\right)$$

$$= -2.2662$$

$$p_2/p_1 = 0.1037 \qquad p_2 = (0.1037)(2.6\times10^{-6}\,\mathrm{bar}) = 2.7\times10^{-7}\,\mathrm{bar}$$

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

$$\begin{array}{ll}
\mathrm{H^+(aq) + OH^-(aq) \rightarrow H_2O(l)} & \Delta_r H° = -55.82\,\mathrm{kJ\,mol^{-1}} \\
\mathrm{Na(s) + H_2O(l) \rightarrow Na^+(aq) + OH^-(aq) + \tfrac{1}{2}H_2(g)} & \Delta_r H° = -184.52\,\mathrm{kJ\,mol^{-1}} \\
\mathrm{NaOH(s) \rightarrow NaOH(aq)} & \Delta_{sol} H^\infty = -44.75\,\mathrm{kJ\,mol^{-1}} \\
\mathrm{NaOH\ in\ 5\ H_2O \rightarrow NaOH\ in\ \infty\ H_2O} & \Delta H_m(\mathrm{dil}) = -4.93\,\mathrm{kJ\,mol^{-1}} \\
\mathrm{NaOH(s)} & \Delta_f H° = -425.61\,\mathrm{kJ\,mol^{-1}}
\end{array}$$

Using only these values, calculate:

(a) $\Delta_f H°$ for Na^+(aq), NaOH(aq), and OH^-(aq);

Solution:

Add the first two reaction equations:

$$\begin{array}{ll}
\mathrm{H^+(aq) + OH^-(aq) \rightarrow H_2O(l)} & \Delta_r H° = -55.82\,\mathrm{kJ\,mol^{-1}} \\
\mathrm{Na(s) + H_2O(l) \rightarrow Na^+(aq) + OH^-(aq) + \tfrac{1}{2}H_2(g)} & \Delta_r H° = -184.52\,\mathrm{kJ\,mol^{-1}} \\
\textit{sum:} & \\
\mathrm{Na(s) + H^+(aq) \rightarrow Na^+(aq) + \tfrac{1}{2}H_2(g)} & \Delta_r H° = -240.34\,\mathrm{kJ\,mol^{-1}}
\end{array}$$

From the relation $\Delta_{\rm r}H^\circ = \sum_i \nu_i \Delta_{\rm f}H^\circ(i)$ and because $\Delta_{\rm f}H^\circ$ is zero for each species in the reaction except $\mathrm{Na^+(aq)}$:

$$\Delta_{\rm f}H^\circ(\mathrm{Na^+, aq}) = -240.34\,\mathrm{kJ\,mol^{-1}}$$

Add the reaction equations for the dissolution of NaOH and formation of NaOH(s):

$$\begin{array}{ll} \mathrm{NaOH(s)} \rightarrow \mathrm{Na^+(aq) + OH^-(aq)} & \Delta_{\rm r}H^\circ = -44.75\,\mathrm{kJ\,mol^{-1}} \\ \mathrm{Na(s)} + \tfrac{1}{2}\mathrm{O_2(g)} + \tfrac{1}{2}\mathrm{H_2(g)} \rightarrow \mathrm{NaOH(s)} & \Delta_{\rm r}H^\circ = -425.61\,\mathrm{kJ\,mol^{-1}} \\ \textit{sum:} & \\ \mathrm{Na(s)} + \tfrac{1}{2}\mathrm{O_2(g)} + \tfrac{1}{2}\mathrm{H_2(g)} \rightarrow \mathrm{Na^+(aq) + OH^-(aq)} & \Delta_{\rm r}H^\circ = -470.36\,\mathrm{kJ\,mol^{-1}} \end{array}$$

The resulting reaction is the formation of aqueous NaOH:

$$\Delta_{\rm f}H^\circ(\mathrm{NaOH, aq}) = -470.36\,\mathrm{kJ\,mol^{-1}}$$

Apply the relation $\Delta_{\rm r}H^\circ = \sum_i \nu_i \Delta_{\rm f}H^\circ(i)$ to this reaction, setting the standard molar enthalpies of formation of the elements equal to zero:

$$\begin{aligned} -470.36\,\mathrm{kJ\,mol^{-1}} &= \Delta_{\rm f}H^\circ(\mathrm{Na^+, aq}) + \Delta_{\rm f}H^\circ(\mathrm{OH^-, aq}) \\ &= -240.34\,\mathrm{kJ\,mol^{-1}} + \Delta_{\rm f}H^\circ(\mathrm{OH^-, aq}) \end{aligned}$$

$$\Delta_{\rm f}H^\circ(\mathrm{OH^-, aq}) = -230.02\,\mathrm{kJ\,mol^{-1}}$$

(b) $\Delta_{\rm f}H$ for NaOH in 5 H_2O;

Solution:

A solute at infinite dilution has the same partial molar enthalpy as in the solute standard state. Thus, the molar enthalpy change of the process in which NaOH in 5 H_2O is formed from the elements in their reference states is the sum of the standard molar enthalpy of formation of NaOH(aq) and the molar enthalpy change of transferring NaOH from infinite dilution to NaOH in 5 H_2O:

$$\Delta_{\rm f}H(\mathrm{NaOH\ in\ 5\ H_2O}) = (-470.36 + 4.93)\,\mathrm{kJ\,mol^{-1}} = -465.43\,\mathrm{kJ\,mol^{-1}}$$

(c) $\Delta H_{\rm m}$(sol) for the dissolution of 1 mol NaOH(s) in 5 mol H_2O.

Solution:

The process can either be treated as the conversion of NaOH(s) into its elements, followed by the formation of the NaOH in the final solution:

$$\begin{aligned} \Delta_{\rm r}H &= -\Delta_{\rm f}H^\circ(\mathrm{NaOH, s}) + \Delta_{\rm f}H(\mathrm{NaOH\ in\ 5\ H_2O}) \\ &= (425.61 - 465.43)\,\mathrm{kJ\,mol^{-1}} = -39.82\,\mathrm{kJ\,mol^{-1}} \end{aligned}$$

or as the solution process to form the infinitely dilute solution, followed by a change to the final solution (the reverse of dilution):

$$\begin{aligned} \Delta_{\rm r}H &= \Delta_{\rm sol}H^\infty - \Delta H_{\rm m}(\mathrm{dil}) \\ &= (-44.75 + 4.93)\,\mathrm{kJ\,mol^{-1}} = -39.82\,\mathrm{kJ\,mol^{-1}} \end{aligned}$$

Table 15 Data for Problem 11.5[a]

Substance	$\Delta_f H/\text{kJ mol}^{-1}$	$M/\text{g mol}^{-1}$
$H_2O(l)$	−285.830	18.0153
$Na_2S_2O_3{\cdot}5H_2O(s)$	−2607.93	248.1828
$Na_2S_2O_3$ in $50\,H_2O$	−1135.914	
$Na_2S_2O_3$ in $100\,H_2O$	−1133.822	
$Na_2S_2O_3$ in $200\,H_2O$	−1132.236	
$Na_2S_2O_3$ in $300\,H_2O$	−1131.780	

[a] Ref. [177], pages 2-307 and 2-308.

11.5 Table 15 lists data for water, crystalline sodium thiosulfate pentahydrate, and several sodium thiosulfate solutions. Find ΔH to the nearest 0.01 kJ for the dissolution of 5.00 g of crystalline $Na_2S_2O_3{\cdot}5H_2O$ in 50.0 g of water at 298.15 K and 1 bar.

Solution:

The amounts in the solution are

$$n(Na_2S_2O_3) = \frac{5.00\,\text{g}}{248.1828\,\text{g mol}^{-1}} = 0.0201\,\text{mol}$$

$$n(H_2O) = \frac{50.0\,\text{g}}{18.0153\,\text{g mol}^{-1}} + 5 \times 0.0201\,\text{mol} = 2.87\,\text{mol}$$

This is $Na_2S_2O_3$ in $143\,H_2O$. From a plot of $\Delta_f H$ versus amount of H_2O, estimate

$$\Delta_f H(Na_2S_2O_3 \text{ in } 143\,H_2O) = -1132.9\,\text{kJ mol}^{-1}.$$

Write reaction equations for three reactions whose sum is the dissolution process:

$$Na_2S_2O_3{\cdot}5H_2O(s) \rightarrow 2\,Na(s) + 2\,S(s) + \tfrac{8}{2}O_2(g) + 5\,H_2(g)$$
$$2\,Na(s) + 2\,S(s) + \tfrac{3}{2}O_2(g) + 143\,H_2O(l) \rightarrow Na_2S_2O_3 \text{ in } 143\,H_2O$$
$$5\,H_2(g) + \tfrac{5}{2}O_2(g) \rightarrow 5\,H_2O(l)$$

sum:

$$Na_2S_2O_3{\cdot}5H_2O(s) + 138\,H_2O(l) \rightarrow Na_2S_2O_3 \text{ in } 143\,H_2O$$

Calculate the enthalpy change per amount of solute dissolved from the sum for the three reactions:

$$(\Delta H/n_B)/\text{kJ mol}^{-1} = 2607.93 - 1132.9 - 5 \times 285.830 = 45.9$$

Calculate the enthalpy change for $n_B = 0.0201$ mol:

$$\Delta H = (0.0201\,\text{mol})(45.9\,\text{kJ mol}^{-1}) = 0.92\,\text{kJ}$$

11.6 Use the experimental data in Table 16 on the next page to evaluate L_A and L_B at 25 °C for an aqueous HCl solution of molality $m_B = 0.0900\,\text{mol kg}^{-1}$.

Solution:

Plot $\Delta H_m(\text{dil}, m'_B{\rightarrow}m''_B)$ versus $\sqrt{m''_B}$; see Fig. 20 on the next page. Extrapolation to $\sqrt{m_B} = 0$ using the theoretical value of the limiting slope C_{Φ_L} gives $\Delta H_m(\text{dil}, m'_B{\rightarrow}0) \approx -3.836\,\text{kJ mol}^{-1}$, resulting in the scale of Φ_L shown of the right side of the figure.

Table 16 Data for Problem 11.6. Molar integral enthalpies of dilution of aqueous HCl ($m'_{\mathrm{B}} = 3.337\,\mathrm{mol\,kg^{-1}}$) at 25 °C.[a]

$m''_{\mathrm{B}}/\mathrm{mol\,kg^{-1}}$	$\Delta H_{\mathrm{m}}(\mathrm{dil}, m'_{\mathrm{B}}\!\to\! m''_{\mathrm{B}})/\mathrm{kJ\,mol^{-1}}$
0.295	−2.883
0.225	−2.999
0.199	−3.041
0.147	−3.143
0.113	−3.217
0.0716	−3.325
0.0544	−3.381
0.0497	−3.412
0.0368	−3.466
0.0179	−3.574
0.0128	−3.621

[a] Ref. [167].

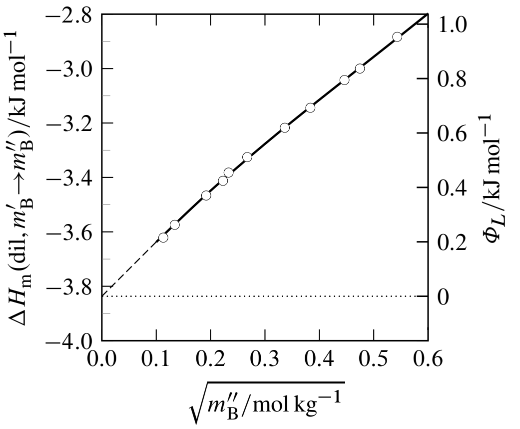

Figure 20 Plot for Problem 11.6. The dashed line has the theoretical slope $C_{\Phi_L} = 1.988\times10^{3}\,\mathrm{J\,kg^{1/2}\,mol^{-3/2}}$.

At molality $m_{\mathrm{B}} = 0.0900\,\mathrm{mol\,kg^{-1}}$ ($\sqrt{m_{\mathrm{B}}} = 0.300\,\mathrm{mol^{1/2}\,kg^{-1/2}}$), values read from the plot are $\Phi_L \approx 0.560\,\mathrm{kg\,mol^{-1}}$ and $\mathrm{d}\Phi_L/\,\mathrm{d}\sqrt{m_{\mathrm{B}}} \approx 1.670\,\mathrm{kJ\,kg^{1/2}\,mol^{-3/2}}$.

From Eq. 11.4.27:

$$\begin{aligned} L_{\mathrm{B}} &= \Phi_L + \frac{\sqrt{m_{\mathrm{B}}}}{2}\,\frac{\mathrm{d}\Phi_L}{\mathrm{d}\sqrt{m_{\mathrm{B}}}} \\ &= 0.560\,\mathrm{kg\,mol^{-1}} + \left(\frac{0.300\,\mathrm{mol^{1/2}\,kg^{-1/2}}}{2}\right)(1.670\,\mathrm{kJ\,kg^{1/2}\,mol^{-3/2}}) \\ &= 0.810\,\mathrm{kg\,mol^{-1}} \end{aligned}$$

From Eq. 11.4.24:

$$\begin{aligned} L_{\mathrm{A}} &= M_{\mathrm{A}} m_{\mathrm{B}} (\Phi_L - L_{\mathrm{B}}) \\ &= (0.018015\,\mathrm{kg\,mol^{-1}})(0.0900\,\mathrm{mol\,kg^{-1}})[(0.560 - 0.810)\,\mathrm{kJ\,mol^{-1}}] \\ &= -0.405\,\mathrm{J\,mol^{-1}} \end{aligned}$$

Table 17 Data for Problem 11.7. The values of intensive properties are for a temperature of 298.15 K and a pressure of 30 bar unless otherwise stated. Subscripts: A = H_2O, B = O_2, C = CO_2.

Properties of the bomb vessel:	
internal volume	$350.0\,\text{cm}^3$
mass of *n*-hexane placed in bomb	$0.6741\,\text{g}$
mass of water placed in bomb	$1.0016\,\text{g}$
Properties of liquid *n*-hexane:	
molar mass	$M = 86.177\,\text{g}\,\text{mol}^{-1}$
density	$\rho = 0.6548\,\text{g}\,\text{cm}^{-3}$
cubic expansion coefficient	$\alpha = 1.378 \times 10^{-3}\,\text{K}^{-1}$
Properties of liquid H_2O:	
molar mass	$M = 18.0153\,\text{g}\,\text{mol}^{-1}$
density	$\rho = 0.9970\,\text{g}\,\text{cm}^{-3}$
cubic expansion coefficient	$\alpha = 2.59 \times 10^{-4}\,\text{K}^{-1}$
standard molar energy of vaporization	$\Delta_{\text{vap}}U^\circ = 41.53\,\text{kJ}\,\text{mol}^{-1}$
Second virial coefficients, 298.15 K:	
B_{AA}	$-1158\,\text{cm}^3\,\text{mol}^{-1}$
B_{BB}	$-16\,\text{cm}^3\,\text{mol}^{-1}$
$\text{d}B_{\text{BB}}/\,\text{d}T$	$0.21\,\text{cm}^3\,\text{K}^{-1}\,\text{mol}^{-1}$
B_{CC}	$-127\,\text{cm}^3\,\text{mol}^{-1}$
$\text{d}B_{\text{CC}}/\,\text{d}T$	$0.97\,\text{cm}^3\,\text{K}^{-1}\,\text{mol}^{-1}$
B_{AB}	$-40\,\text{cm}^3\,\text{mol}^{-1}$
B_{AC}	$-214\,\text{cm}^3\,\text{mol}^{-1}$
B_{BC}	$-43.7\,\text{cm}^3\,\text{mol}^{-1}$
$\text{d}B_{\text{BC}}/\,\text{d}T$	$0.4\,\text{cm}^3\,\text{K}^{-1}\,\text{mol}^{-1}$
Henry's law constants at 1 bar (solvent = H_2O):	
O_2	$k_{m,\text{B}} = 796\,\text{bar}\,\text{kg}\,\text{mol}^{-1}$
CO_2	$k_{m,\text{C}} = 29.7\,\text{bar}\,\text{kg}\,\text{mol}^{-1}$
Partial molar volumes of solutes in water:	
O_2	$V_{\text{B}}^{\infty} = 31\,\text{cm}^3\,\text{mol}^{-1}$
CO_2	$V_{\text{C}}^{\infty} = 33\,\text{cm}^3\,\text{mol}^{-1}$
Standard molar energies of solution (solvent = H_2O):	
O_2	$\Delta_{\text{sol}}U^\circ = -9.7\,\text{kJ}\,\text{mol}^{-1}$
CO_2	$\Delta_{\text{sol}}U^\circ = -17.3\,\text{kJ}\,\text{mol}^{-1}$

11.7 This 16-part problem illustrates the use of experimental data from bomb calorimetry and other sources, combined with thermodynamic relations derived in this and earlier chapters, to evaluate the standard molar combustion enthalpy of a liquid hydrocarbon. The substance under investigation is *n*-hexane, and the combustion reaction in the bomb vessel is

$$\text{C}_6\text{H}_{14}(\text{l}) + \tfrac{19}{2}\text{O}_2(\text{g}) \rightarrow 6\,\text{CO}_2(\text{g}) + 7\,\text{H}_2\text{O}(\text{l})$$

Assume that the sample is placed in a glass ampoule that shatters at ignition. Data needed for this problem are collected in Table 17.

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 C_6H_{14} and H_2O placed in the bomb vessel, and their molar masses, to calculate the amounts (moles) of C_6H_{14} and H_2O present initially in the bomb vessel. Then use the stoichiometry of the combustion reaction to find the amount of O_2 consumed and the amounts of H_2O and CO_2 present in state 2. (There is not enough information at this stage to allow you to find the amount of O_2 present, just the change.) Also find the final mass of H_2O. Assume that oxygen is present in excess and the combustion reaction goes to completion.

Solution:

Initial amounts:

$$n_{C_6H_{14}} = \frac{0.6741\,\mathrm{g}}{86.177\,\mathrm{g\,mol^{-1}}} = 7.822\times10^{-3}\,\mathrm{mol}$$

$$n_{H_2O} = \frac{1.0016\,\mathrm{g}}{18.0153\,\mathrm{g\,mol^{-1}}} = 0.05560\,\mathrm{mol}$$

Change in amount of oxygen:

$$\Delta n_{O_2} = -(19/2)(7.822\times10^{-3}\,\mathrm{mol}) = -0.07431\,\mathrm{mol}$$

Final amounts (state 2):

$$n_{H_2O} = 0.05560\,\mathrm{mol} + (7)(7.822\times10^{-3}\,\mathrm{mol}) = 0.11035\,\mathrm{mol}$$

$$n_{CO_2} = (6)(7.822\times10^{-3}\,\mathrm{mol}) = 0.04693\,\mathrm{mol}$$

Final mass of H_2O:

$$(0.11035\,\mathrm{mol})(18.0153\,\mathrm{g\,mol^{-1}}) = 1.9880\,\mathrm{g}$$

(b) From the molar masses and the densities of liquid C_6H_{14} and H_2O, calculate their molar volumes.

Solution:

$$V_m(C_6H_{14}) = \frac{86.177\,\mathrm{g\,mol^{-1}}}{0.6548\,\mathrm{g\,cm^{-3}}} = 131.61\,\mathrm{cm^3\,mol^{-1}}$$

$$V_m(H_2O) = \frac{18.0153\,\mathrm{g\,mol^{-1}}}{0.9970\,\mathrm{g\,cm^{-3}}} = 18.070\,\mathrm{cm^3\,mol^{-1}}$$

(c) From the amounts present initially in the bomb vessel and the internal volume, find the volumes of liquid C_6H_{14}, liquid H_2O, and gas in state 1 and the volumes of liquid H_2O and gas in state 2. For this calculation, you can neglect the small change in the volume of liquid H_2O due to its vaporization.

Solution:

Initial volumes:

$$V(C_6H_{14}) = (7.822\times10^{-3}\,\mathrm{mol})(131.61\,\mathrm{cm^3 mol^{-1}}) = 1.029\,\mathrm{cm^3}$$
$$V(H_2O) = (0.05560\,\mathrm{mol})(18.070\,\mathrm{cm^3 mol^{-1}}) = 1.005\,\mathrm{cm^3}$$
$$V^g = (350.0 - 1.029 - 1.005)\,\mathrm{cm^3} = 348.0\,\mathrm{cm^3}$$

Final volumes:

$$V(H_2O) = (0.11035\,\mathrm{mol})(18.070\,\mathrm{cm^3 mol^{-1}}) = 1.994\,\mathrm{cm^3}$$
$$V^g = (350.0 - 1.994)\,\mathrm{cm^3} = 348.0\,\mathrm{cm^3}$$

(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 $p_1 = 30.00$ 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 17. 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.

Solution:

In gas phase of state 1:

$$\begin{aligned} n_{O_2} &= \frac{V^g}{\dfrac{RT}{p} + B_{BB}} = \frac{348.0 \times 10^{-6}\,\mathrm{m^3}}{\dfrac{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298.15\,\mathrm{K})}{30.00 \times 10^5\,\mathrm{Pa}} - 16 \times 10^{-6}\,\mathrm{m^3\,mol^{-1}}} \\ &= 0.429\,\mathrm{mol} \end{aligned}$$

In gas phase of state 2:

$$n_{O_2} = (0.429 - 0.07431)\,\mathrm{mol} = 0.355\,\mathrm{mol}$$

$$n^g = (0.355 + 0.04693)\,\mathrm{mol} = 0.402\,\mathrm{mol}$$

$$y_{O_2} = (0.355\,\mathrm{mol})/(0.402\,\mathrm{mol}) = 0.883$$

$$y_{CO_2} = 1 - 0.883 = 0.117$$

(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 on page 247 to calculate the second virial coefficient. Then solve the equation of state of Eq. 9.3.21 on page 246 for the pressure. Also calculate the partial pressures of the O_2 and CO_2 in the gas mixture.

Solution:

In gas phase of state 2:

$$B = y_B^2 B_{BB} + 2y_B y_C B_{BC} + y_C^2 B_{CC}$$

$$\begin{aligned} B/\mathrm{cm^3\,mol^{-1}} &= (0.883)^2(-16) + 2(0.883)(0.117)(-43.7) + (0.117)^2(-127) \\ &= -23.2\,\mathrm{cm^3\,mol^{-1}} \end{aligned}$$

$$\begin{aligned} p &= \frac{n^g RT}{V^g - n^g B} = \frac{(0.402\,\mathrm{mol})(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298.15\,\mathrm{K})}{348.0 \times 10^{-6}\,\mathrm{m^3} - (0.402\,\mathrm{mol})(-23.2 \times 10^{-6}\,\mathrm{m^3\,mol^{-1}})} \\ &= 2.79 \times 10^6\,\mathrm{Pa} = 27.9\,\mathrm{bar} \end{aligned}$$

$$p_{O_2} = y_{O_2} p = (0.883)(27.9\,\mathrm{bar}) = 24.6\,\mathrm{bar}$$

$$p_{CO_2} = y_{CO_2} p = (0.117)(27.9\,\mathrm{bar}) = 3.26\,\mathrm{bar}$$

(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 on page 187 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 on page 400 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.)

Solution:

H_2O(g) in equilibrium with H_2O(l) at 298.15 K and 0.03169 bar:

$$\ln\phi = \frac{B_{AA}p}{RT} = \frac{(-1158\times10^{-6}\,\mathrm{m^3\,mol^{-1}})(0.03169\times10^{5}\,\mathrm{Pa})}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298.15\,\mathrm{K})} = -1.48\times10^{-3}$$

$$\phi = 0.9985$$

$$f = \phi p = (0.9985)(0.03169\,\mathrm{bar}) = 0.03164\,\mathrm{bar}$$

Equation 12.8.3:

$$f_i(p_2) = f_i(p_1)\exp\left[\frac{V_i(\mathrm{l})(p_2-p_1)}{RT}\right]$$

H_2O(g) in equilibrium with H_2O(l) at 298.15 K and 30.00 bar (state 1):

$$\begin{aligned} f &= (0.03164\,\mathrm{bar})\exp\left[\frac{(18.070\times10^{-6}\,\mathrm{m^3\,mol^{-1}})(30.00-0.03169)\times10^{5}\,\mathrm{Pa}}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298.15\,\mathrm{K})}\right] \\ &= 0.03234\,\mathrm{bar} \end{aligned}$$

H_2O(g) in equilibrium with H_2O(l) at 298.15 K and 27.9 bar (state 2):

$$\begin{aligned} f &= (0.03164\,\mathrm{bar})\exp\left[\frac{(18.070\times10^{-6}\,\mathrm{m^3\,mol^{-1}})(27.9-0.03169)\times10^{5}\,\mathrm{Pa}}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298.15\,\mathrm{K})}\right] \\ &= 0.03229\,\mathrm{bar} \end{aligned}$$

(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 on page 187 to calculate ϕ_{O_2}. The other calculations require Eq. 9.3.29 on page 247, 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).]

Solution:

Gas phase of state 1:

$$\begin{aligned} B_A' &= 2B_{AB} - B_{BB} = 2(-40\times10^{-6}\,\mathrm{m^3\ mol^{-1}}) - (-16\times10^{-6}\,\mathrm{m^3\ mol^{-1}}) \\ &= -64\times10^{-6}\,\mathrm{m^3\ mol^{-1}} \end{aligned}$$

$$\ln\phi_A = \frac{B_A'p}{RT} = \frac{(-64\times10^{-6}\,\mathrm{m^3\ mol^{-1}})(30.00\times10^{5}\,\mathrm{Pa})}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298.15\,\mathrm{K})} = -0.077$$

$$\phi_A = 0.925$$

$$\ln\phi_B = \frac{B_{BB}p}{RT} = \frac{(-16\times10^{-6}\,\mathrm{m^3\ mol^{-1}})(30.00\times10^{5}\,\mathrm{Pa})}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298.15\,\mathrm{K})} = -0.019$$

$$\phi_B = 0.981$$

$$f_B = \phi_B p_B = (0.981)(30.00\,\mathrm{bar}) = 29.4\,\mathrm{bar}$$

Gas phase of state 2:

$$
\begin{aligned}
B'_{\mathrm{A}} &= 2y_{\mathrm{B}}B_{\mathrm{AB}} + 2y_{\mathrm{C}}B_{\mathrm{AC}} - 2y_{\mathrm{B}}y_{\mathrm{C}}B_{\mathrm{BC}} - y_{\mathrm{B}}^2B_{\mathrm{BB}} - y_{\mathrm{C}}^2B_{\mathrm{CC}}\\
&= [2(0.883)(-40) + 2(0.117)(-214) - 2(0.883)(0.117)(-43.7)\\
&\quad - (0.883)^2(-16) - (0.117)^2(-127)] \times 10^{-6}\,\mathrm{m^3\ mol^{-1}}\\
&= -97.5\times 10^{-6}\,\mathrm{m^3\ mol^{-1}}
\end{aligned}
$$

$$
\begin{aligned}
\ln\phi_{\mathrm{A}} &= \frac{B'_{\mathrm{A}}p}{RT} = \frac{(-97.5\times 10^{-6}\,\mathrm{m^3\ mol^{-1}})(27.9\times 10^5\,\mathrm{Pa})}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298.15\,\mathrm{K})}\\
&= -0.110
\end{aligned}
$$

$$\phi_{\mathrm{A}} = 0.896$$

$$
\begin{aligned}
B'_{\mathrm{B}} &= B_{\mathrm{BB}} - (B_{\mathrm{BB}} - 2B_{\mathrm{BC}} + B_{\mathrm{CC}})y_{\mathrm{C}}^2\\
&= [-16 - (-16 + 2\times 43.7 - 127)(0.117)^2]\times 10^{-6}\,\mathrm{m^3\ mol^{-1}}\\
&= -15\times 10^{-6}\,\mathrm{m^3\ mol^{-1}}
\end{aligned}
$$

$$
\begin{aligned}
\ln\phi_{\mathrm{B}} &= \frac{B'_{\mathrm{B}}p}{RT} = \frac{(-15\times 10^{-6}\,\mathrm{m^3\ mol^{-1}})(27.9\times 10^5\,\mathrm{Pa})}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298.15\,\mathrm{K})}\\
&= -0.017
\end{aligned}
$$

$$\phi_{\mathrm{B}} = 0.983$$

$$
\begin{aligned}
B'_{\mathrm{C}} &= B_{\mathrm{CC}} - (B_{\mathrm{BB}} - 2B_{\mathrm{BC}} + B_{\mathrm{CC}})y_{\mathrm{B}}^2\\
&= [-127 - (-16 + 2\times 43.7 - 127)(0.883)^2]\times 10^{-6}\,\mathrm{m^3\ mol^{-1}}\\
&= -84\times 10^{-6}\,\mathrm{m^3\ mol^{-1}}
\end{aligned}
$$

$$
\begin{aligned}
\ln\phi_{\mathrm{C}} &= \frac{B'_{\mathrm{C}}p}{RT} = \frac{(-84\times 10^{-6}\,\mathrm{m^3\ mol^{-1}})(27.9\times 10^5\,\mathrm{Pa})}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298.15\,\mathrm{K})}\\
&= -0.094
\end{aligned}
$$

$$\phi_{\mathrm{C}} = 0.910$$

$$f_{\mathrm{B}} = \phi_{\mathrm{B}}p_{\mathrm{B}} = (0.983)(24.6\,\mathrm{bar}) = 24.2\,\mathrm{bar}$$

$$f_{\mathrm{C}} = \phi_{\mathrm{C}}p_{\mathrm{C}} = (0.910)(3.26\,\mathrm{bar}) = 2.97\,\mathrm{bar}$$

(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 on page 245, 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.

Solution:

H_2O in gas phase of state 1:

$$p_{\mathrm{A}} = \frac{f_{\mathrm{A}}}{\phi_{\mathrm{A}}} = \frac{0.03234\,\mathrm{bar}}{0.925} = 0.0350\,\mathrm{bar}$$

$$y_{\mathrm{A}} = \frac{p_{\mathrm{A}}}{p} = \frac{0.0350\,\mathrm{bar}}{30.00\,\mathrm{bar}} = 0.00117$$

$$n_{\mathrm{A}} = y_{\mathrm{A}}n^{\mathrm{g}} = (0.00117)(0.429\,\mathrm{mol}) = 5.00\times 10^{-4}\,\mathrm{mol}$$

H_2O in gas phase of state 2:

$$p_A = \frac{f_A}{\phi_A} = \frac{0.03229\,\text{bar}}{0.896} = 0.03604\,\text{bar}$$

$$y_A = \frac{p_A}{p} = \frac{0.03604\,\text{bar}}{27.9\,\text{bar}} = 0.00129$$

$$n_A = y_A n^g = (0.00129)(0.402\,\text{mol}) = 5.19\times10^{-4}\,\text{mol}$$

H_2O in liquid phase of state 1:

$$n_A = 0.05560\,\text{mol} - 5.00\times10^{-4}\,\text{mol} = 0.05510\,\text{mol}$$

H_2O in liquid phase of state 2:

$$n_A = 0.11035\,\text{mol} - 5.19\times10^{-4}\,\text{mol} = 0.10983\,\text{mol}$$

(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 17 are for the standard pressure of 1 bar. Use Eq. 12.8.35 on page 408 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.

Solution:

Equation 12.8.35:

$$k_{m,B}(p_2) = k_{m,B}(p_1)\exp\left[\frac{V_B^\infty(p_2-p_1)}{RT}\right]$$

Dissolved O_2 in state 1:

$$\begin{aligned} k_{m,B} &= (796\,\text{bar kg mol}^{-1})\exp\left[\frac{(31\times10^{-6}\,\text{m}^3\,\text{mol}^{-1})(30.00-1)\times10^5\,\text{Pa}}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(298.15\,\text{K})}\right] \\ &= 825\,\text{bar kg mol}^{-1} \end{aligned}$$

$$m_B = \frac{f_B}{k_{m,B}} = \frac{29.4\,\text{bar}}{825\,\text{bar kg mol}^{-1}} = 0.0356\,\text{mol kg}^{-1}$$

$$n_B = (0.0356\,\text{mol kg}^{-1})(1.0016\times10^{-3}\,\text{kg}) = 3.57\times10^{-5}\,\text{mol}$$

Dissolved O_2 and CO_2 in state 2:

$$\begin{aligned} k_{m,B} &= (796\,\text{bar kg mol}^{-1})\exp\left[\frac{(31\times10^{-6}\,\text{m}^3\,\text{mol}^{-1})(27.9-1)\times10^5\,\text{Pa}}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(298.15\,\text{K})}\right] \\ &= 823\,\text{bar kg mol}^{-1} \end{aligned}$$

$$m_B = \frac{f_B}{k_{m,B}} = \frac{24.2\,\text{bar}}{823\,\text{bar kg mol}^{-1}} = 0.0294\,\text{mol kg}^{-1}$$

$$n_B = (0.0294\,\text{mol kg}^{-1})(1.9880\times10^{-3}\,\text{kg}) = 5.85\times10^{-5}\,\text{mol}$$

$$\begin{aligned} k_{m,C} &= (29.7\,\text{bar kg mol}^{-1})\exp\left[\frac{(33\times10^{-6}\,\text{m}^3\,\text{mol}^{-1})(27.9-1)\times10^5\,\text{Pa}}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(298.15\,\text{K})}\right] \\ &= 30.8\,\text{bar kg mol}^{-1} \end{aligned}$$

$$m_C = \frac{f_C}{k_{m,C}} = \frac{2.97\,\text{bar}}{30.8\,\text{bar kg mol}^{-1}} = 0.096\,\text{mol kg}^{-1}$$

$$n_C = (0.096\,\text{mol kg}^{-1})(1.9880\times10^{-3}\,\text{kg}) = 1.92\times10^{-4}\,\text{mol}$$

(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, $\Delta_{\rm vap}U^\circ$. Using the value of $\Delta_{\rm vap}U^\circ$ for H_2O given in Table 17, calculate ΔU for the vaporization of liquid H_2O at pressure p° to ideal gas in the amount present in the gas phase of state 1. Also calculate ΔU for the condensation of ideal gaseous H_2O in the amount present in the gas phase of state 2 to liquid at pressure p°.

Solution:

Vaporization:

$$\Delta U = (5.00 \times 10^{-4}\,\text{mol})(41.53 \times 10^3\,\text{J mol}^{-1}) = 20.8\,\text{J}$$

Condensation:

$$\Delta U = -(5.19 \times 10^{-4}\,\text{mol})(41.53 \times 10^3\,\text{J mol}^{-1}) = -21.6\,\text{J}$$

(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 $\Delta_{\rm sol}U^\circ$ are listed in Table 17. Find ΔU for the dissolution of O_2 from its gas standard state to ideal-dilute solution at pressure p° in the amount present in the aqueous phase of state 1. Find ΔU for the desolution (transfer from solution to gas phase) of O_2 and of CO_2 from ideal-dilute solution at pressure p°, in the amounts present in the aqueous phase of state 2, to their gas standard states.

Solution:

O_2 dissolution:

$$\Delta U = (3.57 \times 10^{-5}\,\text{mol})(-9.7 \times 10^3\,\text{J mol}^{-1}) = -0.35\,\text{J}$$

O_2 desolution:

$$\Delta U = (5.85 \times 10^{-5}\,\text{mol})(9.7 \times 10^3\,\text{J mol}^{-1}) = 0.57\,\text{J}$$

CO_2 desolution:

$$\Delta U = (1.92 \times 10^{-4}\,\text{mol})(17.3 \times 10^3\,\text{J mol}^{-1}) = 3.32\,\text{J}$$

(l) Calculate the internal energy changes when the liquid phases of state 1 (n-hexane and aqueous solution) are compressed from p° to p_1 and the aqueous solution of state 2 is decompressed from p_2 to p°. 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.

Solution:

From Table 7.4: $\Delta U \approx -\alpha T V \Delta p$

C_6H_{14}(l) compression:

$$\Delta U = -(1.378 \times 10^{-3}\,\text{K}^{-1})(298.15\,\text{K})(1.029 \times 10^{-6}\,\text{m}^3)$$

$$\times (30.00 \times 10^5\,\text{Pa} - 1 \times 10^5\,\text{Pa}) = -1.226\,\text{J}$$

Solution compression:

$$\Delta U = -(2.59 \times 10^{-4}\,\text{K}^{-1})(298.15\,\text{K})(1.005 \times 10^{-6}\,\text{m}^3)$$
$$\times (30.00 \times 10^5\,\text{Pa} - 1 \times 10^5\,\text{Pa}) = -0.225\,\text{J}$$

Solution decompression:

$$\Delta U = -(2.59 \times 10^{-4}\,\text{K}^{-1})(298.15\,\text{K})(1.994 \times 10^{-6}\,\text{m}^3)$$
$$\times (1 \times 10^5\,\text{Pa} - 27.9 \times 10^5\,\text{Pa}) = 0.414\,\text{J}$$

(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 ($U_\text{m} = U^\circ_\text{m}$) and ending at pressure p_1 to form the gas phase present in state 1. Use the approximate expression for $U_\text{m} - U^\circ_\text{m}(\text{g})$ in Table 7.5 to calculate $\Delta U = U(p_1) - nU^\circ_\text{m}(\text{g})$; a value of $\text{d}B/\text{d}T$ for pure O_2 is listed in Table 17.

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 $U = \sum_i U^\circ_i(\text{g}) - npT\,\text{d}B/\text{d}T$, 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 $U_\text{m} - U^\circ_\text{m}(\text{g})$ in Table 7.5. Calculate the value of $\text{d}B/\text{d}T$ for the mixture of O_2 and CO_2 in state 2 (you need Eq. 9.3.23 on page 247 and the values of $\text{d}B_{ij}/\text{d}T$ in Table 17) and evaluate $\Delta U = \sum_i n_i U^\circ_i(\text{g}) - U(p_2)$ for the gas expansion.

Solution:

O_2 compression:

$$\Delta U = U(p_1) - nU^\circ_\text{m}(\text{g}) = nU_\text{m}(p_1) - nU^\circ_\text{m}(\text{g}) = -np_1T\,\text{d}B_\text{BB}/\text{d}T$$
$$= -(0.429\,\text{mol})(30.00 \times 10^5\,\text{Pa})(298.15\,\text{K})(0.21 \times 10^{-6}\,\text{m}^3\,\text{K}^{-1}\,\text{mol}^{-1})$$
$$= -81\,\text{J}$$

Gas mixture:

$$\text{d}B/\text{d}T = y_\text{B}^2\,\text{d}B_\text{BB}/\text{d}T + 2y_\text{B}y_\text{C}\,\text{d}B_\text{BC}/\text{d}T + y_\text{C}^2\,\text{d}B_\text{CC}/\text{d}T$$
$$= (0.883)^2(0.21 \times 10^{-6}\,\text{m}^3\,\text{K}^{-1}\,\text{mol}^{-1})$$
$$+ 2(0.883)(0.117)(0.4 \times 10^{-6}\,\text{m}^3\,\text{K}^{-1}\,\text{mol}^{-1})$$
$$+ (0.117)^2(0.97 \times 10^{-6}\,\text{m}^3\,\text{K}^{-1}\,\text{mol}^{-1})$$
$$= 0.26 \times 10^{-6}\,\text{m}^3\text{K}^{-1}\text{mol}^{-1}$$

Gas mixture expansion:

$$\Delta U = \textstyle\sum_i n_i U^\circ_i(\text{g}) - U(p_2) = n^\text{g} p_2 T\,\text{d}B/\text{d}T$$
$$= (0.402\,\text{mol})(27.9 \times 10^5\,\text{Pa})(298.15\,\text{K})(0.26 \times 10^{-6}\,\text{m}^3\text{K}^{-1}\text{mol}^{-1})$$

$= 87\,\mathrm{J}$

(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?

Solution:

The Washburn corrections are collected in Table 18. The largest contributions are those for H_2O vaporization and condensation, for compression of the O_2, and for expansion of the product gas mixture.

Table 18 Washburn corrections

Contribution	$\Delta U/\mathrm{J}$
H_2O vaporization	20.8
H_2O condensation	−21.6
O_2 dissolution	−0.35
O_2 desolution	0.57
CO_2 desolution	3.32
C_6H_{14}(l) compression	−1.226
solution compression	−0.225
solution decompression	0.414
O_2 compression	−81.
gas mixture expansion	87.
Sum	8.

(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 $\Delta U(\mathrm{IBP}, T_{\mathrm{ref}}) = -32.504\,\mathrm{kJ}$. 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.

Solution:

$$\Delta_{\mathrm{c}} U^\circ(T_{\mathrm{ref}}) = \frac{\Delta U(\mathrm{IBP}, T_{\mathrm{ref}}) + (\text{Washburn corrections})}{n_{\mathrm{C_6H_{14}}}}$$

$$= \frac{-32.504\,\mathrm{kJ} + 8\times10^{-3}\,\mathrm{kJ}}{7.822\times10^{-3}\,\mathrm{mol}} = -4154.4\,\mathrm{kJ\,mol^{-1}}$$

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

Solution:

$$\Delta_{\mathrm{c}} H^\circ = \Delta_{\mathrm{c}} U^\circ(T_{\mathrm{ref}}) + \sum_i \nu_i^{\mathrm{g}} R T_{\mathrm{ref}}$$

$$= -4154.4\,\mathrm{kJ\,mol^{-1}} + \left(-\tfrac{19}{2} + 6\right)(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298.15\,\mathrm{K})(1\,\mathrm{kJ}/10^3\,\mathrm{J})$$

$$= -4163.1\,\mathrm{kJ\,mol^{-1}}$$

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.

Solution:

Apply the relation $\Delta_r H^\circ = \sum_i \nu_i \Delta_f H^\circ(i)$ to the combustion reaction $C_6H_{14}(l) + \frac{19}{2}O_2(g) \rightarrow 6\,CO_2(g) + 7\,H_2O(l)$:

$$\Delta_c H^\circ(C_6H_{14}) = -\Delta_f H^\circ(C_6H_{14}) + 6\,\Delta_f H^\circ(CO_2) + 7\,\Delta_f H^\circ(H_2O,l)$$

$$\begin{aligned}\Delta_f H^\circ(C_6H_{14}) &= -\Delta_c H^\circ(C_6H_{14}) + 6\,\Delta_f H^\circ(CO_2) + 7\,\Delta_f H^\circ(H_2O,l)\\ &= -(-4163.1\,\text{kJ mol}^{-1}) + 6(-393.51\,\text{kJ mol}^{-1}) + 7(-285.830\,\text{kJ mol}^{-1})\\ &= -198.8\,\text{kJ mol}^{-1}\end{aligned}$$

11.9 Consider the combustion of methane:

$$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(g)$$

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 $C_p(\text{P}) = a + bT$, 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.

Solution:

Equation 11.6.1: $\xi \Delta_r H^\circ(T_1) + \int_{T_1}^{T_2} C_p(\text{P})\,dT = 0$

Calculate $\Delta_c H^\circ(T_1)$ from values in Appendix H for $T_1 = 298.15\,\text{K}$:

$$\Delta_c H^\circ = -\Delta_f H^\circ(CH_4) + \Delta_f H^\circ(CO_2) + 2\,\Delta_f H^\circ(H_2O,g) = -802.29\,\text{kJ mol}^{-1}$$

$$\begin{aligned}\int_{T_1}^{T_2} C_p(\text{P})\,dT &= \int_{T_1}^{T_2}(a + bT)\,dT = a(T_2 - T_1) + \tfrac{b}{2}(T_2^2 - T_1^2)\\ &= aT_2^2 + \tfrac{b}{2}T_2^2 - aT_1 - \tfrac{b}{2}T_1^2\end{aligned}$$

Write Eq. 11.6.1 in the form $Ax^2 + Bx + C = 0$, where

$$x = T_2$$

$$A = b/2 = 4.260 \times 10^{-2}\,\text{J K}^{-2}$$

$$B = a = 297.0\,\text{J K}^{-1}$$

$$\begin{aligned}C &= \xi \Delta_c H^\circ(T_1) - aT_1 - \tfrac{b}{2}T_1^2\\ &= (1\,\text{mol})(-802.29 \times 10^3\,\text{J mol}^{-1}) - (297.0\,\text{J K}^{-1})(298.15\,\text{K})\\ &\quad - (4.260 \times 10^{-2}\,\text{J K}^{-2})(298.15\,\text{K})^2\\ &= -8.9463 \times 10^5\,\text{J}\end{aligned}$$

Solve with the quadratic formula:

$$T_2 = x = \frac{-B \pm \sqrt{B^2 - 4AC}}{2A} = 2272\,\text{K or } -9244\,\text{K}$$

Only the positive value is physically possible.

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: $2\,HgO(s) \rightleftharpoons 2\,Hg(l) + O_2(g)$.

Solution:

$$\Delta_r G^\circ = -2\,\Delta_f G^\circ(\text{HgO}) = 52.772\,\text{kJ mol}^{-1}$$

$$\ln K = \frac{-\Delta_r G^\circ}{RT} = \frac{-52.772\times 10^3\,\text{J mol}^{-1}}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(600.00\,\text{K})} = -10.578$$

$$K = 2.55\times 10^{-5}$$

$$K = \frac{a^2_{\text{Hg(l)}} f_{\text{O}_2}/p^\circ}{a^2_{\text{HgO(s)}}} \approx p_{\text{O}_2}/p^\circ$$

$$p_{\text{O}_2} = Kp^\circ = 2.55\times 10^{-5}\,\text{bar}$$

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

$$\text{H}_2(\text{g}) + \tfrac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O(l)}$$

Solution:

$$\Delta_r G^\circ = \Delta_f G^\circ(\text{H}_2\text{O, l}) = -237.16\,\text{kJ mol}^{-1}$$

$$K = \exp(-\Delta_r G^\circ/RT) = \exp\frac{237.16\times 10^3\,\text{J mol}^{-1}}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(298.15\,\text{K})} = 3.5\times 10^{41}$$

(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 m^3 of the gas phase.

Solution:

$$K = \frac{a_{\text{H}_2\text{O(l)}}}{(f_{\text{H}_2}/p^\circ)(f_{\text{O}_2}/p^\circ)^{1/2}}$$

For ideal gas mixture, $p_{\text{O}_2} = 1.0\,\text{bar}$:

$$K = \frac{1}{(p_{\text{H}_2}/p^\circ)(1.0)^{1/2}}$$

$$p_{\text{H}_2} = \frac{p^\circ}{K} = \frac{1\,\text{bar}}{3.5\times 10^{41}} = 2.8\times 10^{-42}\,\text{bar}$$

$$N_{\text{H}_2} = \frac{N_A p_{\text{H}_2} V}{RT}$$

$$= \frac{(6.022\times 10^{23}\,\text{mol}^{-1})(2.8\times 10^{-42}\,\text{bar})(10^5\,\text{Pa/1 bar})(1.0\,\text{m}^3)}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(298.15\,\text{K})} = 6.9\times 10^{-17}$$

(c) In the preceding part, you calculated a very small value (a fraction) for the number of H_2 molecules in 1.0 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 1.0×10^{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.)

Solution:

$$t = (6.9\times 10^{-17})(1.0\times 10^{10}\,\text{years})(365\,\text{d year}^{-1})(24\,\text{h d}^{-1})(60\,\text{min h}^{-1})(60\,\text{s min}^{-1})$$

$$= 22\,\text{s}$$

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 $\text{G}\rightleftharpoons\text{D}$, 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 $V_\text{m}(\text{G}) = 5.3\times10^{-6}\,\text{m}^3\,\text{mol}^{-1}$ and $V_\text{m}(\text{D}) = 3.4\times10^{-6}\,\text{m}^3\,\text{mol}^{-1}$.

(a) Write an expression for the reaction quotient Q_rxn as a function of pressure. Use the approximate expression of the pressure factor given in Table 9.6.

Solution:

$$Q_\text{rxn} = a(\text{D})/a(\text{G}) = \Gamma(\text{D})/\Gamma(\text{G})$$

$$\approx \frac{\exp\left[V_\text{m}(\text{D})(p-p^\circ)/RT\right]}{\exp\left[V_\text{m}(\text{G})(p-p^\circ)/RT\right]} = \exp\frac{[V_\text{m}(\text{D})-V_\text{m}(\text{G})](p-p^\circ)}{RT}$$

(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.)

Solution:

Find the pressure at which Q_rxn is equal to K:

$$\ln Q_\text{rxn} \approx \frac{[V_\text{m}(\text{D})-V_\text{m}(\text{G})](p-p^\circ)}{RT}$$

$$= \frac{(3.4-5.3)\times10^{-6}\,\text{m}^3\,\text{mol}^{-1}(p-p^\circ)}{(8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})(298.15\,\text{K})} = -7.7\times10^{-10}\,\text{m}^3\,\text{J}^{-1}(p-p^\circ)$$

At equilibrium, $\ln Q_\text{rxn} = \ln K = \ln(0.31) = -1.17$

$$p \approx \frac{-1.17}{-7.7\times10^{-10}\,\text{m}^3\,\text{J}^{-1}} = 1.5\times10^{9}\,\text{Pa} = 1.5\times10^{4}\,\text{bar}$$

11.13 Consider the dissociation reaction $\text{N}_2\text{O}_4(\text{g}) \rightarrow 2\,\text{NO}_2(\text{g})$ 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 ξ 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.

Solution:

To simplify the nomenclature, write the reaction as $\text{A}\rightarrow2\,\text{B}$. Use Eq. 11.7.19 on page 348, with $p = 0.0500p^\circ$, $y_{\text{A},0} = 1$, $n_{\text{B},0} = 0$, $\nu_\text{A} = -1$, and $\nu_\text{B} = 2$:

$$G(\xi)-G(0) = \xi\Delta_\text{r}G^\circ + n_\text{A}RT\ln y_\text{A} + n_\text{B}RT\ln y_\text{B} + RT\xi\ln(0.0500)$$

where

$$\Delta_\text{r}G^\circ = -\Delta_\text{f}G^\circ(\text{N}_2\text{O}_4) + 2\,\Delta_\text{f}G^\circ(\text{NO}_2) = -(97.72\,\text{kJ}\,\text{mol}^{-1}) + 2(51.22\,\text{kJ}\,\text{mol}^{-1})$$

$$= 4.72\,\text{kJ}\,\text{mol}^{-1}$$

$$y_\text{A} = \frac{n_\text{A}}{n_\text{A}+n_\text{B}} \qquad y_\text{B} = 1-y_\text{A}$$

$$n_\text{A} = 1.000\,\text{mol}-\xi \qquad n_\text{B} = 2\xi$$

$$RT = (8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})(298.15\,\text{K}) = 2.4790\,\text{kJ}\,\text{mol}^{-1}$$

See Table 19 for calculated values.

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

Table 19 Problem 11.13(a)

ξ/mol	n_A/mol	n_B/mol	y_A	y_B	$[G(\xi) - G(0)]/\text{kJ mol}^{-1}$
0	1.000	0	1	0	0
0.1	0.900	0.200	0.818	0.182	−1.56
0.2	0.800	0.400	0.667	0.333	−2.43
0.3	0.700	0.600	0.538	0.462	−3.04
0.4	0.600	0.800	0.429	0.571	−3.45
0.5	0.500	1.000	0.333	0.667	−3.72
0.6	0.400	1.200	0.250	0.750	−3.85
0.65	0.350	1.300	0.212	0.788	−3.87
0.7	0.300	1.400	0.176	0.824	−3.86
0.8	0.200	1.600	0.111	0.889	−3.72
0.9	0.100	1.800	0.053	0.947	−3.41
1	0	2.000	0	1	−2.71

Solution:

See Fig. 21.

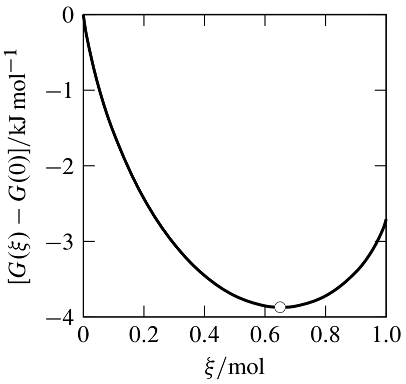

Figure 21 Problem 11.13(b). The open circle at $\xi = 0.65$ mol indicates the estimated position of ξ_{eq}.

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

Solution:

The curve minimum is at $\xi_{eq} = 0.65$ mol. The activities here are $a_A = y_A p/p^\circ = 0.0106$ and $a_B = y_B p/p^\circ = 0.0394$. The thermodynamic equilibrium constant has the value

$$K = \frac{a_B^2}{a_A} = \frac{(0.0394)^2}{0.0106} = 0.146$$

From Eq. 11.8.11:

$$K = \exp\left(-\frac{\Delta_r G^\circ}{RT}\right) = \exp\left[-\frac{4.72 \times 10^3\ \text{J mol}^{-1}}{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(298.15\ \text{K})}\right] = 0.15$$

Chapter 12 Equilibrium Conditions in Multicomponent Systems

12.1 Consider the heterogeneous equilibrium $\mathrm{CaCO_3(s)} \rightleftharpoons \mathrm{CaO(s)} + \mathrm{CO_2(g)}$. Table 20 lists pressures measured over a range of temperatures for this system.

Table 20 Pressure of an equilibrium system containing $\mathrm{CaCO_3(s)}$, CaO(s), and $\mathrm{CO_2(g)}$[a]

$t/°\mathrm{C}$	p/Torr	$t/°\mathrm{C}$	p/Torr
842.3	343.0	904.3	879.0
852.9	398.6	906.5	875.0
854.5	404.1	937.0	1350
868.9	510.9	937.0	1340

[a] Ref. [163].

(a) What is the approximate relation between p and K?
Solution:

$$K = \frac{a_{\mathrm{CaO}}a_{\mathrm{CO_2}}}{a_{\mathrm{CaCO_3}}} = \frac{\Gamma_{\mathrm{CaO}} f_{\mathrm{CO_2}}/p^\circ}{\Gamma_{\mathrm{CaCO_3}}}$$

Approximate the pressure coefficients of the solids by unity and the $\mathrm{CO_2}$ fugacity by $f_{\mathrm{CO_2}} \approx p_{\mathrm{CO_2}} = p$:

$$K \approx p/p^\circ$$

(b) Plot these data in the form ln K versus $1/T$, or fit ln K to a linear function of $1/T$. Then, evaluate the temperature at which the partial pressure of the $\mathrm{CO_2}$ is 1 bar, and the standard molar reaction enthalpy at this temperature.
Solution:

From the values of p/Torr, calculate p/p° using

$$p^\circ = (1\,\mathrm{bar})\,\frac{10^5\,\mathrm{Pa\,bar^{-1}}}{(101,325/760)\,\mathrm{Pa\,Torr^{-1}}} = 750.06\,\mathrm{Torr}$$

The values of $1/T$ and $\ln(p/p^\circ) \approx \ln K$ are listed in Table 21 and plotted in Fig. 22.

Table 21 Data for Problem 12.1(b)

$(1/T)/10^{-4}\,\mathrm{K^{-1}}$	$\ln(p/p^\circ)$	$(1/T)/10^{-4}\,\mathrm{K^{-1}}$	$\ln(p/p^\circ)$
8.965	−0.7824	8.493	0.1586
8.881	−0.6322	8.477	0.1894
8.868	−0.6185	8.263	0.5877
8.756	−0.3840	8.263	0.5803

From either the plot or the equation for the least-squares line, $p_{\mathrm{CO_2}}$ equals 1 bar and $\ln(p/p^\circ)$ is zero when $1/T$ equals $8.561 \times 10^{-4}\,\mathrm{K^{-1}}$ and T is 1168 K. Use Eq. 12.1.14 to calculate $\Delta_\mathrm{r}H^\circ$ from the slope of the least-squares line:

$$\Delta_\mathrm{r}H^\circ = -R\frac{\mathrm{d}\ln(p/p^\circ)}{\mathrm{d}(1/T)} = -(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(-1.97 \times 10^4\,\mathrm{K})$$

$$= 1.64 \times 10^5\,\mathrm{J\,mol^{-1}}$$

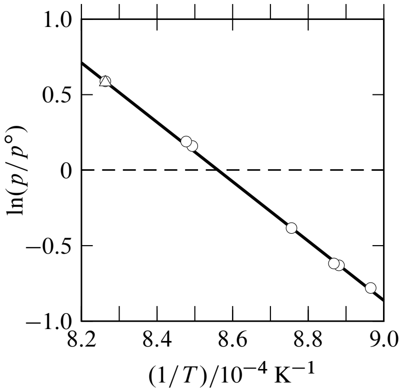

Figure 22 Graph for Problem 12.1(b). The solid line is the least-squares fit to the points: $\ln(p/p^\circ) = a + b(1/T)/10^{-4}\,\mathrm{K}^{-1}$ with $a = 16.839$, $b = -1.967$.

12.2 For a homogeneous reaction in which the reactants and products are solutes in a solution, write a rigorous relation between the standard molar reaction enthalpy and the temperature dependence of the thermodynamic equilibrium constant, with solute standard states based on concentration.

Solution:

Solve Eq. 12.1.11 for $\Delta_\mathrm{r}H^\circ$:

$$\Delta_\mathrm{r}H^\circ = RT^2\frac{\mathrm{d}\ln K}{\mathrm{d}T} + RT^2\alpha_\mathrm{A}^* \sum_{i\neq A}\nu_i$$

α_A^* is the cubic expansion coefficient of the pure solvent.

12.3 Derive an expression for the standard molar reaction entropy of a reaction that can be used to calculate its value from the thermodynamic equilibrium constant and its temperature derivative. Assume that no solute standard states are based on concentration.

Solution:

Combine the relations $\Delta_\mathrm{r}G^\circ = -RT\ln K$ (Eq. 11.8.10) and $\Delta_\mathrm{r}G^\circ = \Delta_\mathrm{r}H^\circ - T\Delta_\mathrm{r}S^\circ$ (Eq. 11.8.21):

$$\Delta_\mathrm{r}S^\circ = R\ln K + (1/T)\Delta_\mathrm{r}H^\circ$$

From Eq. 12.1.13, substitute

$$\Delta_\mathrm{r}H^\circ = RT^2\frac{\mathrm{d}\ln K}{\mathrm{d}T}$$

to obtain the relation

$$\Delta_\mathrm{r}S^\circ = R\ln K + RT\frac{\mathrm{d}\ln K}{\mathrm{d}T}$$

<u>**12.4**</u> Use the data in Table 22 on the next page to evaluate the molal freezing-point depression constant and the molal boiling-point elevation constant for H_2O at a pressure of 1 bar.

Table 22 Properties of H_2O at 1 bar

M	t_f	t_b	$\Delta_{fus}H$	$\Delta_{vap}H$
$18.0153\,g\,mol^{-1}$	$0.00\,°C$	$99.61\,°C$	$6.010\,kJ\,mol^{-1}$	$40.668\,kJ\,mol^{-1}$

Solution:

$$K_f = \frac{M_A R(T_f^*)^2}{\Delta_{fus,A}H} = \frac{(18.0153\times10^{-3}\,kg\,mol^{-1})(8.3145\,J\,K^{-1}\,mol^{-1})(273.15\,K)^2}{6.010\times10^3\,J\,mol^{-1}}$$

$$= 1.860\,K\,kg\,mol^{-1}$$

$$K_b = \frac{M_A R(T_b^*)^2}{\Delta_{vap,A}H} = \frac{(18.0153\times10^{-3}\,kg\,mol^{-1})(8.3145\,J\,K^{-1}\,mol^{-1})(372.76\,K)^2}{40.668\times10^3\,J\,mol^{-1}}$$

$$= 0.5118\,K\,kg\,mol^{-1}$$

12.5 An aqueous solution of the protein bovine serum albumin, containing 2.00×10^{-2} g of protein per cubic centimeter, has an osmotic pressure of 8.1×10^{-3} bar at 0 °C. Estimate the molar mass of this protein.

Solution:

From van't Hoff's equation for osmotic pressure:

$$c_B \approx \frac{\Pi}{\nu RT} = \frac{(8.1\times10^{-3}\,bar)(10^5\,Pa\,bar^{-1})}{(1)(8.3145\,J\,K^{-1}\,mol^{-1})(273\,K)} = 0.36\,mol\,m^{-3}$$

$$n_B \approx (0.36\,mol\,m^{-3})(1\,cm^3)(10^{-2}\,m\,cm^{-1})^3 = 3.6\times10^{-7}\,mol$$

$$M_B \approx \frac{2.00\times10^{-2}\,g}{3.6\times10^{-7}\,mol} = 5.6\times10^4\,g\,mol^{-1}$$

12.6 Figure 12.8 on page 393 shows a curve fitted to experimental points for the aqueous solubility of n-butylbenzene. The curve has the equation $\ln x_B = a(t/°C - b)^2 + c$, where the constants have the values $a = 3.34\times10^{-4}$, $b = 12.13$, and $c = -13.25$. Assume that the saturated solution behaves as an ideal-dilute solution, use a solute standard state based on mole fraction, and calculate $\Delta_{sol,B}H°$ and $\Delta_{sol,B}S°$ at 5.00 °C, 12.13 °C (the temperature of minimum solubility), and 25.00 °C.

Solution:

Rewrite the equation for the curve using thermodynamic temperature:

$$\ln x_B = A(T-B)^2 + C$$

where $A = 3.34\times10^{-4}\,K^{-2}$ $\quad B = (12.13 + 273.15)\,K = 285.28\,K \quad C = c = -13.25$

From Sec. 12.6.2, with $K = x_B$:

$$\Delta_{sol,B}H° = RT^2\frac{d\ln x_B}{dT} = [RT^2][2A(T-B)]$$

$$\Delta_{sol,B}G° = -RT\ln x_B = -RT[A(T-B)^2 + C]$$

$$\Delta_{sol,B}S° = \frac{\Delta_{sol,B}H° - \Delta_{sol,B}G°}{T}$$

The formula of Prob. 12.3 can also be used, with K replaced with x_B:

$$\Delta_{\text{sol,B}}S^{\circ} = R\ln x_{\text{B}} + RT\frac{\text{d}\ln x_{\text{B}}}{\text{d}T}$$

The values calculated at the three temperatures are listed in Table 23.

Table 23 Problem 12.6

$t/°\text{C}$	T/K	$\dfrac{\Delta_{\text{sol,B}}H^{\circ}}{\text{kJ mol}^{-1}}$	$\dfrac{\Delta_{\text{sol,B}}G^{\circ}}{\text{kJ mol}^{-1}}$	$\dfrac{\Delta_{\text{sol,B}}S^{\circ}}{\text{J K}^{-1}\,\text{mol}^{-1}}$
5.00	278.15	−3.06	30.60	−121.0
12.13	285.28	0	31.43	−110.2
25.00	298.15	6.35	32.71	−88.4

12.7 Consider a hypothetical system in which two aqueous solutions are separated by a semipermeable membrane. Solution α is prepared by dissolving 1.00×10^{-5} mol KCl in 10.0 g water. Solution β is prepared from 1.00×10^{-5} mol KCl and 1.00×10^{-6} mol of the potassium salt of a polyelectrolyte dissolved in 10.0 g water. All of solution β is used to fill a dialysis bag, which is then sealed and placed in solution α.

Each polyelectrolyte ion has a charge of −10. The membrane of the dialysis bag is permeable to the water molecules and to the K^{+} and Cl^{-} ions, but not to the polyelectrolyte. The system comes to equilibrium at 25.00 °C. Assume that the volume of the dialysis bag remains constant. Also make the drastic approximation that both solutions behave as ideal-dilute solutions.

(a) Find the equilibrium molality of each solute species in the two solution phases.

Solution:

Polyelectrolyte molality: $m_{\text{P}} = \dfrac{1.00\times10^{-6}\,\text{mol}}{10.0\times10^{-3}\,\text{kg}} = 1.00\times10^{-4}\,\text{mol kg}^{-1}$

Calculate the initial molalities of K^{+} and Cl^{-}:

$$m_{+}^{\alpha} = m_{-}^{\alpha} = m_{-}^{\beta} = \frac{1.00\times10^{-5}\,\text{mol}}{10.0\times10^{-3}\,\text{kg}} = 1.00\times10^{-3}\,\text{mol kg}^{-1}$$

$$m_{+}^{\beta} = 1.00\times10^{-3}\,\text{mol kg}^{-1} + (10)(1.00\times10^{-4}\,\text{mol kg}^{-1}) = 2.00\times10^{-3}\,\text{mol kg}^{-1}$$

Simultaneously solve the following equations for m_{-}^{α} and m_{-}^{β} in the equilibrium system:

$$m_{-}^{\alpha} + m_{-}^{\beta} = 2.00\times10^{-3}\,\text{mol kg}^{-1}$$

$$(m_{-}^{\alpha})^{2} = (m_{-}^{\beta} + zm_{\text{P}})m_{-}^{\beta} = (m_{-}^{\beta} + 1.00\times10^{-3}\,\text{mol kg}^{-1})m_{-}^{\beta}$$

The resulting equilibrium molalities are

$$m_{-}^{\alpha} = 1.20\times10^{-3}\,\text{mol kg}^{-1} \qquad m_{-}^{\beta} = 0.80\times10^{-3}\,\text{mol kg}^{-1}$$

Find the equilibrium values of m_{+}^{α} and m_{+}^{β} from the requirement of electroneutrality in each phase:

$$m_{+}^{\alpha} = m_{-}^{\alpha} = 1.20\times10^{-3}\,\text{mol kg}^{-1}$$

$$m_{+}^{\beta} = m_{-}^{\beta} + zm_{\text{P}} = 1.80\times10^{-3}\,\text{mol kg}^{-1}$$

(b) Describe the amounts and directions of any macroscopic transfers of ions across the membrane that are required to establish the equilibrium state.

Solution:

The change in the amount of KCl in phase α is

$$(1.20\times10^{-3}\,\text{mol kg}^{-1})(10.0\times10^{-3}\,\text{kg}) - 1.00\times10^{-5}\,\text{mol} = 2.0\times10^{-6}\,\text{mol}$$

Thus, 2.0×10^{-6} mol KCl has transferred from phase β to phase α.

(c) Estimate the Donnan potential, $\phi^{\alpha} - \phi^{\beta}$.

Solution:

Apply Eq. 12.7.15:

$$\phi^{\alpha} - \phi^{\beta} \approx \frac{RT}{F}\ln\frac{m_+^{\beta}}{m_+^{\alpha}} = \frac{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(298.15\,\text{K})}{(96{,}485\,\text{C mol}^{-1})}\ln\frac{1.80\times10^{-3}\,\text{mol kg}^{-1}}{1.20\times10^{-3}\,\text{mol kg}^{-1}}$$

$$= 0.0104\,\text{V}$$

(d) Estimate the pressure difference across the membrane at equilibrium. (The density of liquid H_2O at 25.00 °C is $0.997\,\text{g cm}^{-3}$.)

Solution:

From Eq. 12.7.11: $p^{\beta} - p^{\alpha} \approx \rho_A^* RT[(m_+^{\beta} + m_-^{\beta} + m_P) - (m_+^{\alpha} + m_-^{\alpha})]$

$$= (0.997\,\text{g cm}^{-3})(10^{-3}\,\text{kg g}^{-1})(10^{6}\,\text{cm}^3\,\text{m}^{-3})$$

$$\times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(298.15\,\text{K})$$

$$\times [(1.80 + 0.80 + 0.100 - 1.20 - 1.20)10^{-3}\,\text{mol kg}^{-1}]$$

$$= 7.4\times10^{2}\,\text{Pa}$$

12.8 The derivation of Prob. 9.3 on page 42 shows that the pressure in a liquid droplet of radius r is greater than the pressure of the surrounding equilibrated gas phase by a quantity $2\gamma/r$, where γ is the surface tension.

(a) Consider a droplet of water of radius 1.00×10^{-6} m at 25 °C suspended in air of the same temperature. The surface tension of water at this temperature is $0.07199\,\text{J m}^{-2}$. Find the pressure in the droplet if the pressure of the surrounding air is 1.00 bar.

Solution:

$$p^{l} = p^{g} + \frac{2\gamma}{r} = 1.00\,\text{bar} + \frac{2(0.07199\,\text{J m}^{-2})}{1.00\times10^{-6}\,\text{m}} = 2.44\times10^{5}\,\text{Pa} = 2.44\,\text{bar}$$

(b) Calculate the difference between the fugacity of H_2O in the air of pressure 1.00 bar equilibrated with this water droplet, and the fugacity in air equilibrated at the same temperature and pressure with a pool of liquid water having a flat surface. Liquid water at 25 °C and 1 bar has a vapor pressure of 0.032 bar and a molar volume of $1.807\times10^{-5}\,\text{m}^3\,\text{mol}^{-1}$.

Solution:

From Eq. 12.8.3:

$$f(p_2) = f(p_1)\exp\left[\frac{V_m(l)(p_2 - p_1)}{RT}\right]$$

$$= f(p_1)\exp\left[\frac{(1.807\times10^{-5}\,\text{m}^3\,\text{mol}^{-1})(1.44\times10^{5}\,\text{Pa})}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(298.15\,\text{K})}\right]$$

$$= 1.00105 f(p_1)$$

$$f(p_2) - f(p_1) = (1.00105 - 1)f(p_1) = (0.00105)(0.032\,\text{bar}) = 3.4\times10^{-5}\,\text{bar}$$

12.9 For a solution process in which species B is transferred from a gas phase to a liquid solution, find the relation between $\Delta_{\text{sol}}G^{\circ}$ (solute standard state based on mole fraction) and the Henry's law constant $k_{H,B}$.

Solution:

$\Delta_{\text{sol}}G^\circ = -RT \ln K$

From Eq. 12.8.30: $K = \dfrac{\Gamma_{x,\text{B}}\, p^\circ}{k_{\text{H,B}}}$

Under standard state conditions, $p = p^\circ$ and $\Gamma_{x,\text{B}} = 1$

Therefore $\Delta_{\text{sol}}G^\circ = RT \ln[k_{\text{H,B}}(p^\circ)/p^\circ]$

12.10 Crovetto[10] reviewed the published data for the solubility of gaseous CO_2 in water, and fitted the Henry's law constant $k_{\text{H,B}}$ to a function of temperature. Her recommended values of $k_{\text{H,B}}$ at five temperatures are 1233 bar at 15.00 °C, 1433 bar at 20.00 °C, 1648 bar at 25.00 °C, 1874 bar at 30.00 °C, and 2111 bar at 35 °C.

(a) The partial pressure of CO_2 in the atmosphere is typically about 3×10^{-4} bar. Assume a fugacity of 3.0×10^{-4} bar, and calculate the aqueous solubility at 25.00 °C expressed both as a mole fraction and as a molality.

Solution:

From Table 9.4: $x_\text{B} = f_\text{B}/\gamma_{x,\text{B}}\, k_{\text{H,B}}$. Assume that $\gamma_{x,\text{B}}$ is 1:

$$x_\text{B} = \frac{f_\text{B}}{k_{\text{H,B}}} = \frac{3.0 \times 10^{-4}\ \text{bar}}{1648\ \text{bar}} = 1.8 \times 10^{-7}$$

From Eq. 9.1.14, at high dilution:

$$m_\text{B} = \frac{x_\text{B}}{M_\text{A}} = \frac{1.8 \times 10^{-7}}{18.0153 \times 10^{-3}\ \text{kg mol}^{-1}} = 1.0 \times 10^{-5}\ \text{mol kg}^{-1}$$

(b) Find the standard molar enthalpy of solution at 25.00 °C.

Solution:

From Eq. 12.8.32:

$$\Delta_{\text{sol,B}}H^\circ = R\frac{\text{d} \ln(k_{\text{H,B}}/p^\circ)}{\text{d}(1/T)}$$

The values of $1/T$ and $\ln k_{\text{H,B}}/p^\circ$ are listed in Table 24.

Table 24 Data for Problem 12.10

$t/°\text{C}$	T/K	$(1/T)/10^{-3}\ \text{K}^{-1}$	$\ln(k_{\text{H,B}}/p^\circ)$
15.00	288.15	3.4704	7.117
20.00	293.15	3.4112	7.268
25.00	298.15	3.3540	7.407
30.00	303.15	3.2987	7.536
35.00	308.15	3.2452	7.655

The points are plotted in Fig. 23 on the next page. The tangent to the curve at the point for 298.15 K (dashed line) has the slope $\text{d} \ln(k_{\text{H,B}}/p^\circ)/\,\text{d}(1/T) = -2.39 \times 10^3$ K. The same value may be obtained from the slope of a line between the two end points.

$\Delta_{\text{sol,B}}H^\circ = (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(-2.39 \times 10^3\ \text{K}) = -1.99 \times 10^4\ \text{J mol}^{-1}$

(c) Dissolved carbon dioxide exists mostly in the form of CO_2 molecules, but a small fraction exists as H_2CO_3 molecules, and there is also some ionization:

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[10] Ref. [40].

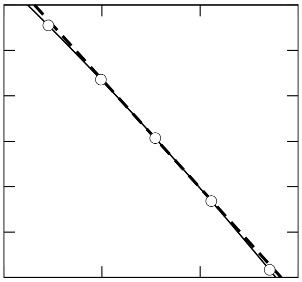

Figure 23 Plot for Problem 12.10(b).

$CO_2(aq) + H_2O(l) \rightarrow H^+(aq) + HCO_3^-(aq)$

(The equilibrium constant of this reaction is often called the first ionization constant of carbonic acid.) Combine the $k_{H,B}$ data with data in Appendix H to evaluate K and $\Delta_r H°$ for the ionization reaction at 25.00 °C. Use solute standard states based on molality, which are also the solute standard states used for the values in Appendix H.

Solution:

The ionization reaction is the difference of the reaction $CO_2(g) + H_2O(l) \rightarrow H^+(aq) + HCO_3^-(aq)$ and the solution process $CO_2(g) \rightarrow CO_2(aq)$. Calculate the standard molar reaction Gibbs energy and standard molar reaction enthalpy of the first reaction:

$$\begin{aligned}\Delta_r G°/\text{kJ mol}^{-1} &= \textstyle\sum_i \nu_i \Delta_f G°(i)/\text{kJ mol}^{-1}\\ &= -(-394.41) - (-237.16) + (0) + (-586.90) = 44.67\end{aligned}$$

$$\begin{aligned}\Delta_r H°/\text{kJ mol}^{-1} &= \textstyle\sum_i \nu_i \Delta_f H°(i)/\text{kJ mol}^{-1}\\ &= -(-393.51) - (-285.830) + (0) + (-689.93) = -10.59\end{aligned}$$

From Eq. 12.8.30, the equilibrium constant for the solution process, with standard state based on mole fraction, is related to $k_{H,B}$ by $K = \Gamma_{x,B} p°/k_{H,B}$. Approximate $\Gamma_{x,B}$ by 1 and take $k_{H,B}$ at 25.00 °C: $K = p°/k_{H,B} = 1/1648 = 6.07 \times 10^{-4}$. Since the solute standard states used in Appendix H are based on molality, convert the value using Eq. 11.8.19:

$$K(m\ \text{basis}) = \frac{K(x\ \text{basis})}{M_A m°} = \frac{6.07 \times 10^{-4}}{(18.0153 \times 10^{-3}\ \text{kg mol}^{-1})(1\ \text{mol kg}^{-1})} = 3.37 \times 10^{-2}$$

Calculate the standard molar reaction Gibbs energy of the solution process:

$$\begin{aligned}\Delta_{\text{sol,B}} G° &= -RT \ln K(m\ \text{basis}) = -(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(298.15\ \text{K}) \ln(3.37 \times 10^{-2})\\ &= 8.41 \times 10^3\ \text{J mol}^{-1}\end{aligned}$$

For the overall ionization reaction:

$$\Delta_r G°/\text{kJ mol}^{-1} = 44.67 - (8.41) = 36.26$$

$$K = \exp\left(-\frac{\Delta_r G°}{RT}\right) = \exp\left[-\frac{36.26 \times 10^3\ \text{J mol}^{-1}}{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(298.15\ \text{K})}\right] = 4.4 \times 10^{-7}$$

$$\Delta_r H°/\text{kJ mol}^{-1} = (-10.59) - (-19.9) = 9.3$$

12.11 The solubility of gaseous O_2 at a partial pressure of 1.01 bar and a temperature of 310.2 K, expressed as a concentration, is $1.07 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$ in pure water and $4.68 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}$ in a 3.0 M aqueous solution of KCl.[11] This solubility decrease is the *salting-out effect*. Calculate the activity coefficient $\gamma_{c,\mathrm{B}}$ of O_2 in the KCl solution.

Solution:

The equation for solubility expressed as a concentration analogous to Eq. 12.8.23 is

$$c_\mathrm{B} = \frac{Kc^\circ f_\mathrm{B}/p^\circ}{\Gamma_{c,\mathrm{B}}\,\gamma_{c,\mathrm{B}}}$$

Assume that $\gamma_{c,\mathrm{B}}$ is equal to 1 when no KCl is present, and that $\Gamma_{c,\mathrm{B}}$ is not affected by the presence of KCl:

$$\gamma_{c,\mathrm{B}}(3.0\text{ M KCl}) = \gamma_{c,\mathrm{B}}(0\text{ M KCl})\frac{c_\mathrm{B}(0\text{ M KCl})}{c_\mathrm{B}(3.0\text{ M KCl})} = (1)\frac{1.07 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}}{4.68 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}} = 2.29$$

12.12 At 298.15 K, the partial molar volume of $CO_2(aq)$ is $33\,\mathrm{cm^3\,mol^{-1}}$. Use Eq. 12.8.35 to estimate the percent change in the value of the Henry's law constant $k_{\mathrm{H,B}}$ for aqueous CO_2 at 298.15 K when the total pressure is changed from 1.00 bar to 10.00 bar.

Solution:

From Eq. 12.8.35:

$$k_{\mathrm{H,B}}(p_2) \approx k_{\mathrm{H,B}}(p_1)\exp\left[\frac{V_\mathrm{B}^\infty(p_2 - p_1)}{RT}\right]$$

$$k_{\mathrm{H,B}}(10.00\,\mathrm{bar}) \approx k_{\mathrm{H,B}}(1.00\,\mathrm{bar})\exp\left[\frac{(33 \times 10^{-6}\,\mathrm{m^3\,mol^{-1}})(10.00 - 1.00) \times 10^5\,\mathrm{Pa}}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298.15\,\mathrm{K})}\right]$$

$$\approx 1.012\,k_{\mathrm{H,B}}(1.00\,\mathrm{bar})$$

percent change $\approx 1.2\%$

12.13 Rettich et al[12] made high-precision measurements of the solubility of gaseous oxygen (O_2) in water. Each measurement was made by equilibrating water and oxygen in a closed vessel for a period of up to two days, at a temperature controlled within ±0.003 K. The oxygen was extracted from samples of known volume of the equilibrated liquid and gas phases, and the amount of O_2 in each sample was determined from p-V-T measurements taking gas nonideality into account. It was then possible to evaluate the mole fraction x_B of O_2 in the liquid phase and the ratio $(n_\mathrm{B}^\mathrm{g}/V^\mathrm{g})$ for the O_2 in the gas phase.

Table 25 Data for Problem 12.13 (A = H_2O, B = O_2)

$T = 298.152\,\mathrm{K}$	Second virial coefficients:
$x_\mathrm{B} = 2.02142 \times 10^{-5}$	$B_\mathrm{AA} = -1152 \times 10^{-6}\,\mathrm{m^3\,mol^{-1}}$
$(n_\mathrm{B}^\mathrm{g}/V^\mathrm{g}) = 35.9957\,\mathrm{mol\,m^{-3}}$	$B_\mathrm{BB} = -16.2 \times 10^{-6}\,\mathrm{m^3\,mol^{-1}}$
$p_\mathrm{A}^* = 3167.13\,\mathrm{Pa}$	$B_\mathrm{AB} = -27.0 \times 10^{-6}\,\mathrm{m^3\,mol^{-1}}$
$V_\mathrm{A}^* = 18.069 \times 10^{-6}\,\mathrm{m^3\,mol^{-1}}$	
$V_\mathrm{B}^\infty = 31.10 \times 10^{-6}\,\mathrm{m^3\,mol^{-1}}$	

Table 25 gives values of physical quantities at $T = 298.152\,\mathrm{K}$ needed for this problem. The values of x_B and $(n_\mathrm{B}^\mathrm{g}/V^\mathrm{g})$ were obtained by Rettich et al from samples of liquid and gas phases

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[11] Ref. [112]. [12] Ref. [152].

equilibrated at temperature T, as explained above. p_A^* is the saturation vapor pressure of pure liquid water at this temperature.

Your calculations will be similar to those used by Rettich et al to obtain values of the Henry's law constant of oxygen to six significant figures. Your own calculations should also be carried out to six significant figures. For the gas constant, use the value $R = 8.31447\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$.

The method you will use to evaluate the Henry's law constant $k_{\text{H,B}} = f_B/x_B$ at the experimental temperature and pressure is as follows. The value of x_B is known, and you need to find the fugacity f_B of the O_2 in the gas phase. f_B can be calculated from ϕ_B and p_B. These in turn can be calculated from the pressure p, the mole fraction y_B of O_2 in the gas phase, and known values of second virial coefficients. You will calculate p and y_B by an iterative procedure. Assume the gas has the virial equation of state $(V^g/n^g) = (RT/p) + B$ (Eq. 9.3.21) and use relevant relations in Sec. 9.3.4.

(a) For the equilibrated liquid-gas system, calculate initial approximate values of p and y_B by assuming that p_A is equal to p_A^* and p_B is equal to $(n_B^g/V^g)RT$.

Solution:

$$p_B = (n_B^g/V^g)RT = (35.9957\,\text{mol}\,\text{m}^{-3})(8.31447\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})(298.152\,\text{K})$$
$$= 89232.5\,\text{Pa}$$

$$p = p_A + p_B = 3167.13\,\text{Pa} + 89232.5\,\text{Pa} = 92399.6\,\text{Pa}$$

$$y_B = \frac{p_B}{p} = 0.965724$$

(b) Use your approximate values of p and y_B from part (a) to calculate ϕ_A, the fugacity coefficient of A in the gas mixture.

Solution:

From Eq. 9.3.27: $B'_A = B_{AA} + (-B_{AA} + 2B_{AB} - B_{BB})y_B^2 = -112.9 \times 10^{-6}\,\text{m}^3\,\text{mol}^{-1}$

From Eq. 9.3.29: $\phi_A = \exp(B'_A p/RT) = 0.995801$

(c) Evaluate the fugacity f_A of the H_2O in the gas phase. Assume p, y_B, and ϕ_A have the values you calculated in parts (a) and (b). Hint: start with the value of the saturation vapor pressure of pure water.

Solution:

From Eq. 9.3.27, with y_B set equal to 1: $B'_A = B_{AA} = -1152 \times 10^{-6}\,\text{m}^3\,\text{mol}^{-1}$

From Eq. 9.3.29, with p set equal to p_A^*: $\phi_A^*(p_A^*) = \exp(B'_A p_A^*/RT) = 0.998529$

$f_A^*(p_A^*) = \phi_A^*(p_A^*)p_A^* = (0.998529)(3167.13\,\text{Pa}) = 3162.47\,\text{Pa}$

From Eq. 12.8.3:

$$f_A^*(p) = f_A^*(p_A^*)\exp\left[\frac{V_A^*(p - p_A^*)}{RT}\right]$$
$$= (3162.47\,\text{Pa})\exp\left[\frac{(18.069 \times 10^{-6}\,\text{m}^3\,\text{mol}^{-1})(92399.6\,\text{Pa} - 3167.13\,\text{Pa})}{(8.31447\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})(298.152\,\text{K})}\right]$$
$$= 3164.53\,\text{Pa}$$

From Raoult's law for fugacity:

$$f_A(p) = (1 - x_B)f_A^*(p) = (0.999980)(3164.53\,\text{Pa}) = 3164.47\,\text{Pa}$$

(d) Use your most recently calculated values of p, ϕ_A, and f_A to calculate an improved value of y_B.

Solution:

$p_A = f_A/\phi_A = (3164.47\,\text{Pa})/(0.995801) = 3177.81\,\text{Pa}$

$y_B = 1 - y_A = 1 - p_A/p = 1 - (3177.81\,\text{Pa})/(92399.6\,\text{Pa}) = 0.965608$

(e) Use your current values of p and y_B to evaluate the compression factor Z of the gas mixture, taking nonideality into account.

Solution:

$y_A = 1 - y_B = 1 - 0.965608 = 0.034392$

From Eq. 9.3.23:

$$\begin{aligned} B &= y_A^2 B_{AA} + 2y_A y_B B_{AB} + y_B^2 B_{BB} \\ &= (0.034392)^2 B_{AA} + 2(0.034392)(0.965608) B_{AB} + (0.965608)^2 B_{BB} \\ &= -18.2608 \times 10^{-6}\,\text{m}^3\,\text{mol}^{-1} \end{aligned}$$

From Eq. 9.3.22:

$$Z = 1 + \frac{Bp}{RT} = 1 + \frac{(-18.2608 \times 10^{-6}\,\text{m}^3\,\text{mol}^{-1})(92399.6\,\text{Pa})}{(8.31447\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})(298.152\,\text{K})} = 0.999319$$

(f) Derive a general expression for p as a function of (n_B^g/V^g), T, y_B, and Z. Use this expression to calculate an improved value of p.

Solution:

$$Z \overset{\text{def}}{=} \frac{pV^g}{n^g RT} \qquad n^g = n_B^g/y_B$$

$$\begin{aligned} p &= \frac{n^g RTZ}{V^g} = \left(\frac{n_B^g}{V^g}\right)\frac{RTZ}{y_B} \\ &= (35.9957\,\text{mol}\,\text{m}^{-3})\frac{(8.31447\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})(298.152\,\text{K})(0.999319)}{0.965608} \\ &= 92347.7\,\text{Pa} \end{aligned}$$

(g) Finally, use the improved values of p and y_B to evaluate the Henry's law constant $k_{H,B}$ at the experimental T and p.

Solution:

From Eq. 9.3.28:

$$B'_B = B_{BB} + (-B_{AA} + 2B_{AB} - B_{BB})(1 - y_B)^2 = -14.88 \times 10^{-6}\,\text{m}^3\,\text{mol}^{-1}$$

From Eq. 9.3.29:

$$\phi_B = \exp(B'_B p/RT) = \exp\left[\frac{(-14.88 \times 10^{-6}\,\text{m}^3\,\text{mol}^{-1})(92347.7\,\text{Pa})}{(8.31447\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})(298.152\,\text{K})}\right] = 0.999446$$

$$\begin{aligned} k_{H,B} &= \frac{f_B}{x_B} = \frac{\phi_B y_B p}{x_B} = \frac{(0.999446)(0.965608)(92347.7\,\text{Pa})}{2.02142 \times 10^{-5}} \\ &= 4.40890 \times 10^9\,\text{Pa} \end{aligned}$$

12.14 The method described in Prob. 12.13 has been used to obtain high-precision values of the Henry's law constant, $k_{H,B}$, for gaseous methane dissolved in water.[13] Table 26 lists values of $\ln(k_{H,B}/p^\circ)$ at eleven temperatures in the range 275 K–328 K and at pressures close to 1 bar. Use these data to evaluate $\Delta_{\text{sol,B}}H^\circ$ and $\Delta_{\text{sol,B}}C_p^\circ$ at $T = 298.15\,\text{K}$. This can be done by a

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[13] Ref. [153].

Table 26 Data for Prob. 12.14

$1/(T/\mathrm{K})$	$\ln(k_{\mathrm{H,B}}/p^\circ)$	$1/(T/\mathrm{K})$	$\ln(k_{\mathrm{H,B}}/p^\circ)$
0.00363029	10.0569	0.00329870	10.6738
0.00359531	10.1361	0.00319326	10.8141
0.00352175	10.2895	0.00314307	10.8673
0.00347041	10.3883	0.00309444	10.9142
0.00341111	10.4951	0.00304739	10.9564
0.00335390	10.5906		

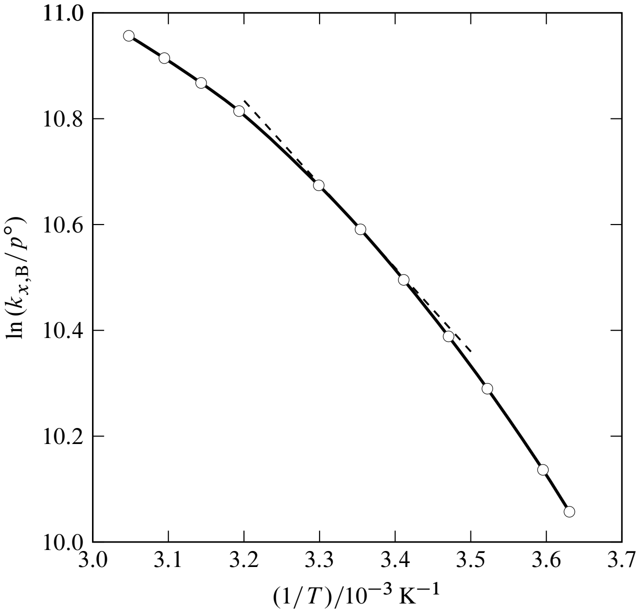

Figure 24 Plot for Prob. 12.14. Open circles: data points from Table 12.26. Dashed line: tangent to curve at $1/T = 1/298.15\,\mathrm{K}$.

graphical method. Better precision will be obtained by making a least-squares fit of the data to the three-term polynomial

$$\ln(k_{\mathrm{H,B}}/p^\circ) = a + b(1/T) + c(1/T)^2$$

and using the values of the coefficients a, b, and c for the evaluations.

Solution:

For the *graphical method*, make a plot of ln $k_{\mathrm{H,B}}$ versus $1/T$ as in Fig. 24. The tangent to the curve at $1/T = 1/298.15\,\mathrm{K}$ (dashed line) has a slope of $-1.58 \times 10^3\,\mathrm{K}$.

From Eq. 12.8.32:

$$\Delta_{\mathrm{sol,B}}H^\circ = R\,\frac{\mathrm{d}\ln(k_{\mathrm{H,B}}/p^\circ)}{\mathrm{d}(1/T)} = (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(-1.58\times10^3\,\mathrm{K}) = -13.1\,\mathrm{kJ\,mol^{-1}}$$

From Eq. 11.3.6:

$$\Delta_{\mathrm{sol,B}}C_p^\circ = \mathrm{d}\Delta_{\mathrm{sol,B}}H^\circ/\,\mathrm{d}T$$

From the slope between the first two points on the graph:

$\Delta_{\mathrm{sol,B}} H^\circ = (-897\,\mathrm{K})R$ at $T \approx 325.6\,\mathrm{K}$

From the slope between the last two points on the graph:

$\Delta_{\mathrm{sol,B}} H^\circ = (-2264\,\mathrm{K})R$ at $T \approx 276.8\,\mathrm{K}$

$$\Delta_{\mathrm{sol,B}} C_p^\circ \approx \frac{(-897\,\mathrm{K} + 2264\,\mathrm{K})(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})}{325.6\,\mathrm{K} - 276.8\,\mathrm{K}} = 233\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

Using a *least-squares fit* to $\ln(k_{\mathrm{H,B}}/p^\circ) = a + b(1/T) + c(1/T)^2$:

$a = 1.6755 \qquad b = 6896.86\,\mathrm{K} \qquad c = -1.263836 \times 10^6\,\mathrm{K}^2$

$$\Delta_{\mathrm{sol,B}} H^\circ = R\,\frac{\mathrm{d}\ln(k_{\mathrm{H,B}}/p^\circ)}{\mathrm{d}(1/T)} = R[b + 2c(1/T)] = -13.145\,\mathrm{kJ\,mol^{-1}}$$

$$\Delta_{\mathrm{sol,B}} C_p^\circ = \mathrm{d}\Delta_{\mathrm{sol,B}} H^\circ/\,\mathrm{d}T = -2Rc(1/T)^2 = 236.42\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

12.15 Liquid water and liquid benzene have very small mutual solubilities. Equilibria in the binary water–benzene system were investigated by Tucker, Lane, and Christian[14] as follows. A known amount of distilled water was admitted to an evacuated, thermostatted vessel. Part of the water vaporized to form a vapor phase. Small, precisely measured volumes of liquid benzene were then added incrementally from the sample loop of a liquid-chromatography valve. The benzene distributed itself between the liquid and gaseous phases in the vessel. After each addition, the pressure was read with a precision pressure gauge. From the known amounts of water and benzene and the total pressure, the liquid composition and the partial pressure of the benzene were calculated. The fugacity of the benzene in the vapor phase was calculated from its partial pressure and the second virial coefficient.

At a fixed temperature, for mole fractions x_{B} of benzene in the liquid phase up to about 3×10^{-4} (less than the solubility of benzene in water), the fugacity of the benzene in the equilibrated gas phase was found to have the following dependence on x_{B}:

$$\frac{f_{\mathrm{B}}}{x_{\mathrm{B}}} = k_{\mathrm{H,B}} - Ax_{\mathrm{B}}$$

Here $k_{\mathrm{H,B}}$ is the Henry's law constant and A is a constant related to deviations from Henry's law. At 30 °C, the measured values were $k_{\mathrm{H,B}} = 385.5$ bar and $A = 2.24 \times 10^4$ bar.

(a) Treat benzene (B) as the solute and find its activity coefficient on a mole fraction basis, $\gamma_{x,\mathrm{B}}$, at 30 °C in the solution of composition $x_{\mathrm{B}} = 3.00 \times 10^{-4}$.

Solution:

From Table 9.5, with the pressure factor of unity:

$$a_{x,\mathrm{B}} = \gamma_{x,\mathrm{B}}\, x_{\mathrm{B}} = \frac{f_{\mathrm{B}}}{k_{\mathrm{H,B}}}$$

$$\gamma_{x,\mathrm{B}} = \frac{f_{\mathrm{B}}}{k_{\mathrm{H,B}}\, x_{\mathrm{B}}} = 1 - \frac{Ax_{\mathrm{B}}}{k_{\mathrm{H,B}}} = 1 - \frac{(2.24 \times 10^4\,\mathrm{bar})(3.00 \times 10^{-4})}{385.5\,\mathrm{bar}} = 0.9826$$

(b) The fugacity of benzene vapor in equilibrium with pure liquid benzene at 30 °C is $f_{\mathrm{B}}^* = 0.1576$ bar. Estimate the mole fraction solubility of liquid benzene in water at this temperature.

Solution:

Assume that the fugacity of benzene vapor in equilibrium with a saturated aqueous solution of benzene is 0.1576 bar, and solve the equation $f_{\mathrm{B}}/x_{\mathrm{B}} = k_{\mathrm{H,B}} - Ax_{\mathrm{B}}$ for x_{B}:

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[14] Ref. [171].

$$Ax_B^2 - k_{H,B}x_B + f_B = 0$$

$$x_B = \frac{k_{H,B} \pm \sqrt{k_{H,B}^2 - 4Af_B}}{2A} = 1.68 \times 10^{-2} \quad \text{or} \quad 4.19 \times 10^{-4}$$

As x_B is increased in the unsaturated solution the saturation condition is reached at the lower of the two values: $x_B = 4.19 \times 10^{-4}$.

(c) The calculation of $\gamma_{x,B}$ in part (a) treated the benzene as a single solute species with deviations from infinite-dilution behavior. Tucker et al suggested a dimerization model to explain the observed negative deviations from Henry's law. (Classical thermodynamics, of course, cannot prove such a molecular interpretation of observed macroscopic behavior.) The model assumes that there are two solute species, a monomer (M) and a dimer (D), in reaction equilibrium: 2M $\rightleftharpoons$ D. Let n_B be the total amount of C_6H_6 present in solution, and define the mole fractions

$$x_B \overset{\text{def}}{=} \frac{n_B}{n_A + n_B} \approx \frac{n_B}{n_A}$$

$$x_M \overset{\text{def}}{=} \frac{n_M}{n_A + n_M + n_D} \approx \frac{n_M}{n_A} \qquad x_D \overset{\text{def}}{=} \frac{n_D}{n_A + n_M + n_D} \approx \frac{n_D}{n_A}$$

where the approximations are for dilute solution. In the model, the individual monomer and dimer particles behave as solutes in an ideal-dilute solution, with activity coefficients of unity. The monomer is in transfer equilibrium with the gas phase: $x_M = f_B/k_{H,B}$. The equilibrium constant expression (using a mole fraction basis for the solute standard states and setting pressure factors equal to 1) is $K = x_D/x_M^2$. From the relation $n_B = n_M + 2n_D$, and because the solution is very dilute, the expression becomes

$$K = \frac{x_B - x_M}{2x_M^2}$$

Make individual calculations of K from the values of f_B measured at $x_B = 1.00 \times 10^{-4}$, $x_B = 2.00 \times 10^{-4}$, and $x_B = 3.00 \times 10^{-4}$. Extrapolate the calculated values of K to x_B=0 in order to eliminate nonideal effects such as higher aggregates. Finally, find the fraction of the benzene molecules present in the dimer form at $x_B = 3.00 \times 10^{-4}$ if this model is correct.

Solution:

Use the formulas

$$x_M = \frac{f_B}{k_{H,B}} = x_B - \frac{Ax_B^2}{k_{H,B}} \quad \text{and} \quad K = \frac{x_B - x_M}{2x_M^2}$$

The results are $K = 29.4$ at $x_B = 1.00 \times 10^{-4}$, $K = 29.7$ at $x_B = 2.00 \times 10^{-4}$, and $K = 30.1$ at $x_B = 3.00 \times 10^{-4}$. The extrapolated value is $K \approx 29.1$. At $x_B = 3.00 \times 10^{-4}$, the fraction of benzene molecules in the dimer form is

$$\frac{2n_D}{n_B} = 1 - \frac{n_M}{n_B} \approx 1 - \frac{x_M}{x_B} = 1 - \frac{2.95 \times 10^{-4}}{3.00 \times 10^{-4}} = 0.017$$

12.16 Use data in Appendix H to evaluate the thermodynamic equilibrium constant at 298.15 K for the limestone reaction

$$\text{CaCO}_3(\text{cr, calcite}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O(l)} \rightarrow \text{Ca}^{2+}(\text{aq}) + 2\text{HCO}_3{}^{-}(\text{aq})$$

Solution:

$\Delta_r G^\circ/\text{kJ mol}^{-1} = \sum_i \nu_i \Delta_f G^\circ(i)/\text{kJ mol}^{-1}$

$$= -(-1128.8) - (-394.41) - (-237.16) + (-552.8) + 2(-586.90)$$

$$= 33.8$$

$$K = \exp\left(-\frac{\Delta_r G^\circ}{RT}\right) = \exp\left[-\frac{33.8\times10^3\,\mathrm{J\,mol^{-1}}}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298.15\,\mathrm{K})}\right] = 1.2\times10^{-6}$$

12.17 For the dissociation equilibrium of formic acid, $HCO_2H(aq) \rightleftharpoons H^+(aq) + HCO_2{}^-(aq)$, the acid dissociation constant at 298.15 K has the value $K_a = 1.77\times10^{-4}$.

(a) Use Eq. 12.9.7 to find the degree of dissociation and the hydrogen ion molality in a 0.01000 molal formic acid solution. You can safely set Γ_r and $\gamma_{m,\mathrm{HA}}$ equal to 1, and use the Debye–Hückel limiting law (Eq. 10.4.8) to calculate $\gamma_\pm$. You can do this calculation by iteration: Start with an initial estimate of the ionic strength (in this case 0), calculate $\gamma_\pm$ and α, and repeat these steps until the value of α no longer changes.

Solution:

Equation 12.9.7:

$$K_a = \Gamma_r \frac{\gamma_\pm^2 \alpha^2 m_B/m^\circ}{\gamma_{m,\mathrm{HA}}(1-\alpha)} \approx \frac{\gamma_\pm^2 \alpha^2 m_B/m^\circ}{1-\alpha}$$

Solve for α:

$$\alpha = \frac{-K_a + \left[K_a^2 + 4\gamma_\pm^2 (m_B/m^\circ) K_a\right]^{1/2}}{2\gamma_\pm^2 (m_B/m^\circ)}$$

Calculate $\gamma_\pm$ from Eq. 10.4.8:

$$\ln\gamma_\pm = -A\,|z_+z_-|\sqrt{I_m} = -1.1744(\alpha m_B/m^\circ)^{1/2}$$

First estimate ($I_m = 0, \gamma_\pm = 1$):

$$\alpha = \frac{-1.77\times10^{-4} + \left[(1.77\times10^{-4})^2 + 4(0.01000)(1.77\times10^{-4})\right]^{1/2}}{2(0.01000)} = 0.124$$

$$\ln\gamma_\pm = -(1.1744)(0.00124)^{1/2} = -0.0414 \qquad \gamma_\pm = 0.9594$$

Second estimate:

$$\alpha = \frac{-1.77\times10^{-4} + \left[(1.77\times10^{-4})^2 + 4(0.9594)^2(0.01000)(1.77\times10^{-4})\right]^{1/2}}{2(0.9594)^2(0.01000)}$$

$$= 0.129$$

$$\ln\gamma_\pm = -(1.1744)(0.00129)^{1/2} = -0.0422 \qquad \gamma_\pm = 0.9586$$

Third estimate:

$$\alpha = \frac{-1.77\times10^{-4} + \left[(1.77\times10^{-4})^2 + 4(0.9586)^2(0.01000)(1.77\times10^{-4})\right]^{1/2}}{2(0.9586)^2(0.01000)}$$

$$= 0.129$$

The calculated degree of dissociation has become constant at $\alpha = 0.129$; the hydrogen ion molality is $m_+ = \alpha m_B = 1.29\times10^{-3}\,\mathrm{mol\,kg^{-1}}$.

(b) Estimate the degree of dissociation of formic acid in a solution that is 0.01000 molal in both formic acid and sodium nitrate, again using the Debye–Hückel limiting law for $\gamma_\pm$. Compare with the value in part (a).

Solution:

Use same formula for α as in part (a); calculate $\gamma_\pm$ from

$$\ln\gamma_\pm = -A\,|z_+z_-|\,\sqrt{I_m} = -1.1744(\alpha m_\mathrm{B}/m^\circ + 0.01000)^{1/2}$$

First estimate:

$$\ln\gamma_\pm = -1.1744(0.01000)^{1/2} = -0.1174 \qquad \gamma_\pm = 0.8892$$

$$\alpha = \frac{-1.77\times10^{-4} + \left[(1.77\times10^{-4})^2 + 4(0.8892)^2(0.01000)(1.77\times10^{-4})\right]^{1/2}}{2(0.8892)^2(0.01000)}$$

$$= 0.139$$

$$\ln\gamma_\pm = -(1.1744)(0.00139 + 0.01000)^{1/2} = -0.1253 \qquad \gamma_\pm = 0.8822$$

Second estimate:

$$\alpha = \frac{-1.77\times10^{-4} + \left[(1.77\times10^{-4})^2 + 4(0.8822)^2(0.01000)(1.77\times10^{-4})\right]^{1/2}}{2(0.8822)^2(0.01000)}$$

$$= 0.140$$

$$\ln\gamma_\pm = -(1.1744)(0.00140 + 0.01000)^{1/2} = -0.1254 \qquad \gamma_\pm = 0.8822$$

This value of $\gamma_\pm$ will give the same value of the degree of dissociation as before: $\alpha = 0.140$. The increased ionic strength causes the degree of dissociation to increase.

12.18 Use the following experimental information to evaluate the standard molar enthalpy of formation and the standard molar entropy of the aqueous chloride ion at 298.15 K, based on the conventions $\Delta_\mathrm{f}H^\circ(\mathrm{H^+, aq}) = 0$ and $S^\circ_\mathrm{m}(\mathrm{H^+, aq}) = 0$ (Secs. 11.3.2 and 11.8.4). (Your calculated values will be close to, but not exactly the same as, those listed in Appendix H, which are based on the same data combined with data of other workers.)

- For the reaction $\frac{1}{2}\mathrm{H_2(g)} + \frac{1}{2}\mathrm{Cl_2(g)} \rightarrow \mathrm{HCl(g)}$, the standard molar enthalpy of reaction at 298.15 K measured in a flow calorimeter[15] is $\Delta_\mathrm{r}H^\circ = -92.312\,\mathrm{kJ\,mol^{-1}}$.
- The standard molar entropy of gaseous HCl at 298.15 K calculated from spectroscopic data is $S^\circ_\mathrm{m} = 186.902\,\mathrm{J\,K^{-1}\,mol^{-1}}$.
- From five calorimetric runs,[16] the average experimental value of the standard molar enthalpy of solution of gaseous HCl at 298.15 K is $\Delta_\mathrm{sol,B}H^\circ = -74.84\,\mathrm{kJ\,mol^{-1}}$.
- From vapor pressure measurements of concentrated aqueous HCl solutions,[17] the value of the ratio $f_\mathrm{B}/a_{m,\mathrm{B}}$ for gaseous HCl in equilibrium with aqueous HCl at 298.15 K is 5.032×10^{-7} bar.

Solution:

The sum of the reactions $\frac{1}{2}\mathrm{H_2(g)} + \frac{1}{2}\mathrm{Cl_2(g)} \rightarrow \mathrm{HCl(g)}$ and $\mathrm{HCl(g)} \rightarrow \mathrm{H^+(aq)} + \mathrm{Cl^-(aq)}$ is the net reaction

$$\tfrac{1}{2}\mathrm{H_2(g)} + \tfrac{1}{2}\mathrm{Cl_2(g)} \rightarrow \mathrm{H^+(aq)} + \mathrm{Cl^-(aq)}$$

with standard molar reaction enthalpy equal to the sum of the corresponding standard molar enthalpy changes:

$$\Delta_\mathrm{r}H^\circ = (-92.312 - 74.84)\,\mathrm{kJ\,mol^{-1}} = -167.15\,\mathrm{kJ\,mol^{-1}}$$

Since $\Delta_\mathrm{r}H^\circ$ for the net reaction is equal to the sum of the standard molar enthalpies of formation of $\mathrm{H^+(aq)}$ and $\mathrm{Cl^-(aq)}$, and $\Delta_\mathrm{f}H^\circ(\mathrm{H^+, aq})$ is zero, we have

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[15] Ref. [155]. [16] Ref. [77]. [17] Ref. [148].

$\Delta_f H^\circ(\text{Cl}^-, \text{aq}) = -167.15\,\text{kJ mol}^{-1}$

For the dissolution reaction

$\text{HCl(g)} \rightarrow \text{H}^+\text{(aq)} + \text{Cl}^-\text{(aq)}$

the equilibrium constant is given by $K = a_{m,\text{B}}/(f_\text{B}/p^\circ)$, and the standard molar reaction Gibbs energy is

$$\Delta_r G^\circ = -RT \ln K = -(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(298.15\,\text{K}) \ln \left(\frac{1}{5.032 \times 10^{-7}}\right)$$

$$= 3.595 \times 10^4\,\text{J mol}^{-1}$$

The standard molar reaction entropy is then

$$\Delta_r S^\circ = \frac{\Delta_r H^\circ - \Delta_r G^\circ}{T} = \frac{(-74.84 \times 10^3 + 3.595 \times 10^4)\,\text{J mol}^{-1}}{298.15\,\text{K}}$$

$$= -130.44\,\text{J K}^{-1}\,\text{mol}^{-1}$$

Use Eq. 11.8.22 on page 355:

$$\Delta_r S^\circ = \textstyle\sum_i \nu_i S_i^\circ = -S_\text{m}^\circ(\text{HCl, g}) + S_\text{m}^\circ(\text{H}^+, \text{aq}) + S_\text{m}^\circ(\text{Cl}^-, \text{aq})$$

Since $S_\text{m}^\circ(\text{H}^+, \text{aq})$ is zero, we have

$$S_\text{m}^\circ(\text{Cl}^-, \text{aq}) = \Delta_r S^\circ + S_\text{m}^\circ(\text{HCl, g}) = (-130.44 + 186.902)\,\text{J K}^{-1}\,\text{mol}^{-1}$$

$$= 56.46\,\text{J K}^{-1}\,\text{mol}^{-1}$$

12.19 The solubility of crystalline AgCl in ultrapure water has been determined from the electrical conductivity of the saturated solution.[18] The average of five measurements at 298.15 K is $s_\text{B} = 1.337 \times 10^{-5}\,\text{mol dm}^{-3}$. The density of water at this temperature is $\rho_\text{A}^* = 0.9970\,\text{kg dm}^{-3}$.

(a) From these data and the Debye–Hückel limiting law, calculate the solubility product K_s of AgCl at 298.15 K.

Solution:

From Eq. 9.1.14 for a dilute solution:

$$m_\text{B} = \frac{c_\text{B}}{\rho_\text{A}^*} = \frac{1.337 \times 10^{-5}\,\text{mol dm}^{-3}}{0.9970\,\text{kg dm}^{-3}} = 1.341 \times 10^{-5}\,\text{mol kg}^{-1}$$

Find the mean ionic activity coefficient from the Debye–Hückel limiting law, Eq. 10.4.8:

$$\ln \gamma_\pm = -A\sqrt{I_m} = -(1.1744\,\text{kg}^{1/2}\,\text{mol}^{-1/2})(1.341 \times 10^{-5}\,\text{mol kg}^{-1})^{1/2}$$

$$= -4.301 \times 10^{-3}$$

$$\gamma_\pm = 0.996$$

Use Eq. 12.5.26 with $\mathit{\Gamma}_\text{r} = 1$:

$$K_\text{s} = \gamma_\pm^2 (m_\text{B}/m^\circ)^2 = (0.996)^2 (1.341 \times 10^{-5})^2 = 1.783 \times 10^{-10}$$

(b) Evaluate the standard molar Gibbs energy of formation of aqueous Ag^+ ion at 298.15 K, using the results of part (a) and the values $\Delta_f G^\circ(\text{Cl}^-, \text{aq}) = -131.22\,\text{kJ mol}^{-1}$ and $\Delta_f G^\circ(\text{AgCl, s}) = -109.77\,\text{kJ mol}^{-1}$ from Appendix H.

Solution:

Calculate $\Delta_\text{sol} G^\circ$ for the dissolution reaction $\text{AgCl(s)} \rightleftharpoons \text{Ag}^+\text{(aq)} + \text{Cl}^-\text{(aq)}$:

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[18] Ref. [72].

$$\Delta_{\mathrm{sol}}G^\circ = -RT \ln K_{\mathrm{s}} = -(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298.15\,\mathrm{K}) \ln(1.783 \times 10^{-10})$$
$$= 5.5647 \times 10^{4}\,\mathrm{J\,mol^{-1}}$$

Apply the general relation $\Delta_{\mathrm{r}}G^\circ = \sum_i \nu_i \Delta_{\mathrm{f}}G^\circ(i)$ to the dissolution reaction:

$$\Delta_{\mathrm{sol}}G^\circ = -\Delta_{\mathrm{f}}G^\circ(\mathrm{AgCl, s}) + \Delta_{\mathrm{f}}G^\circ(\mathrm{Ag^+, aq}) + \Delta_{\mathrm{f}}G^\circ(\mathrm{Cl^-, aq})$$

Rearrange to

$$\Delta_{\mathrm{f}}G^\circ(\mathrm{Ag^+, aq}) = \Delta_{\mathrm{sol}}G^\circ + \Delta_{\mathrm{f}}G^\circ(\mathrm{AgCl, s}) - \Delta_{\mathrm{f}}G^\circ(\mathrm{Cl^-, aq})$$

$$\Delta_{\mathrm{f}}G^\circ(\mathrm{Ag^+, aq})/\mathrm{kJ\,mol^{-1}} = 55.647 + (-109.77) - (-131.22) = 77.10$$

12.20 The following reaction was carried out in an adiabatic solution calorimeter by Wagman and Kilday:[19]

$$\mathrm{AgNO_3(s) + KCl(aq}, m_{\mathrm{B}} = 0.101\,\mathrm{mol\,kg^{-1}}) \rightarrow \mathrm{AgCl(s) + KNO_3(aq)}$$

The reaction can be assumed to go to completion, and the amount of KCl was in slight excess, so the amount of AgCl formed was equal to the initial amount of $\mathrm{AgNO_3}$. After correction for the enthalpies of diluting the solutes in the initial and final solutions to infinite dilution, the standard molar reaction enthalpy at 298.15 K was found to be $\Delta_{\mathrm{r}}H^\circ = -43.042\,\mathrm{kJ\,mol^{-1}}$. The same workers used solution calorimetry to obtain the molar enthalpy of solution at infinite dilution of crystalline $\mathrm{AgNO_3}$ at 298.15 K: $\Delta_{\mathrm{sol,B}}H^\infty = 22.727\,\mathrm{kJ\,mol^{-1}}$.

(a) Show that the difference of these two values is the standard molar reaction enthalpy for the precipitation reaction

$$\mathrm{Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)}$$

and evaluate this quantity.

Solution:

The reaction $\mathrm{AgNO_3(s) + KCl(aq) \rightarrow AgCl(s) + KNO_3(aq)}$ is equivalent to $\mathrm{AgNO_3(s) + Cl^-(aq) \rightarrow AgCl(s) + NO_3{}^-(aq)}$. Subtracting the equation for the dissolution of $\mathrm{AgNO_3}$, $\mathrm{AgNO_3(s) \rightarrow Ag^+(aq) + Cl^-(aq)}$, gives the equation for precipitation, $\mathrm{Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)}$. Thus, the standard molar reaction enthalpy for the precipitation reaction is the difference

$$\Delta_{\mathrm{r}}H^\circ = [(-43.042) - (22.727)]\,\mathrm{kJ\,mol^{-1}} = -65.769\,\mathrm{kJ\,mol^{-1}}$$

(b) Evaluate the standard molar enthalpy of formation of aqueous $\mathrm{Ag^+}$ ion at 298.15 K, using the results of part (a) and the values $\Delta_{\mathrm{f}}H^\circ(\mathrm{Cl^-, aq}) = -167.08\,\mathrm{kJ\,mol^{-1}}$ and $\Delta_{\mathrm{f}}H^\circ(\mathrm{AgCl, s}) = -127.01\,\mathrm{kJ\,mol^{-1}}$ from Appendix H. (These values come from calculations similar to those in Probs. 12.18 and 14.4.) The calculated value will be close to, but not exactly the same as, the value listed in Appendix H, which is based on the same data combined with data of other workers.

Solution:

Apply the relation $\Delta_{\mathrm{r}}H^\circ = \sum_i \Delta_{\mathrm{f}}H^\circ(i)$ to the precipitation reaction:

$$\Delta_{\mathrm{r}}H^\circ = -\Delta_{\mathrm{f}}H^\circ(\mathrm{Ag^+, aq}) - \Delta_{\mathrm{f}}H^\circ(\mathrm{Cl^-, aq}) + \Delta_{\mathrm{f}}H^\circ(\mathrm{AgCl, s})$$

$$\Delta_{\mathrm{f}}H^\circ(\mathrm{Ag^+, aq}) = -\Delta_{\mathrm{r}}H^\circ - \Delta_{\mathrm{f}}H^\circ(\mathrm{Cl^-, aq}) + \Delta_{\mathrm{f}}H^\circ(\mathrm{AgCl, s})$$
$$= [-(-65.769) - (-167.08) + (-127.01)]\,\mathrm{kJ\,mol^{-1}}$$
$$= 105.84\,\mathrm{kJ\,mol^{-1}}$$

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[19] Ref. [176].

Chapter 13 The Phase Rule and Phase Diagrams

13.1 Consider a single-phase system that is a gaseous mixture of N_2, H_2, and NH_3. For each of the following cases, find the number of degrees of freedom and give an example of the independent intensive variables that could be used to specify the equilibrium state, apart from the total amount of gas.

(a) There is no reaction.

Solution:

There are three components: N_2, H_2, and NH_3. The number of degrees of freedom is

$F = 2 + C - P = 2 + 3 - 1 = 4$

The equilibrium state could be specified by T, p, and the mole fractions of two of the substances; or by T and the partial pressures of each of the substances.

(b) The reaction $N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g)$ is at equilibrium.

Solution:

There are three species and one independent relation for reaction equilibrium, $-\mu_{N_2} - 3\mu_{H_2} + 2\mu_{NH_3} = 0$.

$F = 2 + s - r - P = 2 + 3 - 1 - 1 = 3$

One possibility would be to specify the equilibrium state by values of T and the partial pressures of two of the gases; the partial pressure of the third gas would be determined by the thermodynamic equilibrium constant and the fugacity coefficients, and p would be the sum of the three partial pressures.

(c) The reaction is at equilibrium and the system is prepared from NH_3 only.

Solution:

There are three species and two independent relations among intensive variables: $-\mu_{N_2} - 3\mu_{H_2} + 2\mu_{NH_3} = 0$ and $y_{H_2} = 3y_{N_2}$.

$F = 2 + s - r - P = 2 + 3 - 2 - 1 = 2$

The equilibrium state could be specified by T and p. The partial pressures of the three gases would be those that satisfy the relations $-\mu_{N_2} - 3\mu_{H_2} + 2\mu_{NH_3} = 0$, $y_{H_2} = 3y_{N_2}$, and $p_{N_2} + p_{H_2} + p_{NH_3} = p$.

13.2 How many components has a mixture of water and deuterium oxide in which the equilibrium $H_2O + D_2O \rightleftharpoons 2\,HDO$ exists?

Solution:

There are three species and one relation among intensive variables, $-\mu_{H_2O} - \mu_{D_2O} + 2\mu_{HDO} = 0$.

$C = s - r = 3 - 1 = 2$

13.3 Consider a system containing only $NH_4Cl(s)$, $NH_3(g)$, and $HCl(g)$. Assume that the equilibrium $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$ exists.

(a) Suppose you prepare the system by placing solid NH_4Cl in an evacuated flask and heating to 400 K. Use the phase rule to decide whether you can vary the pressure while both phases remain in equilibrium at 400 K.

Solution:

There are three species and two relations among intensive variables:
$-\mu_{NH_4Cl} + \mu_{NH_3} + \mu_{HCl} = 0$ and $y_{NH_3} = y_{HCl}$ (or $p_{NH_3} = p_{HCl}$).

$F = 2 + s - r - P = 2 + 3 - 2 - 2 = 1$

The two phases cannot remain in equilibrium while p is varied and T is fixed.

(b) According to the phase rule, if the system is not prepared as described in part (a) could you vary the pressure while both phases remain in equilibrium at 400 K? Explain.

Solution:

Yes, because y_{NH_3} no longer has to equal y_{HCl} and F is increased to 2. T and p can be varied independently, and the pressure can be varied while the temperature is fixed at an arbitrary value.

(c) Rationalize your conclusions for these two cases on the basis of the thermodynamic equilibrium constant. Assume that the gas phase is an ideal gas mixture and use the approximate expression $K = p_{NH_3} p_{HCl}/(p^\circ)^2$.

Solution:

At a fixed temperature, K has a fixed value. If the system is prepared from $NH_4Cl(s)$ only, then the following relations hold

$$p = p_{NH_3} + p_{HCl} \qquad p_{NH_3} = p_{HCl} = p/2 \qquad K = (p/2)^2/(p^\circ)^2 \qquad p = 2\sqrt{K}p^\circ$$

and therefore p can have only one value at each temperature. If, however, p_{NH_3} and p_{HCl} can be varied independently, then the relation $K = p_{NH_3} p_{HCl}/(p^\circ)^2$ can be satisfied for a fixed value of K and a varying value of $p = p_{NH_3} + p_{HCl}$.

13.4 Consider the lime-kiln process $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$. Find the number of intensive variables that can be varied independently in the equilibrium system under the following conditions:

(a) The system is prepared by placing calcium carbonate, calcium oxide, and carbon dioxide in a container.

Solution:

There are three species, three phases, and one relation among intensive variables:

$-\mu_{CaCO_3} + \mu_{CaO} + \mu_{CO_2} = 0$

$F = 2 + s - r - P = 2 + 3 - 1 - 3 = 1$

Only one intensive variable, such as T, can be varied independently while the three phases remain in equilibrium.

(b) The system is prepared from calcium carbonate only.

Solution:

Only one intensive variable can be varied, as before; the initial condition leads to no relation among intensive variables.

(c) The temperature is fixed at 1000 K.

Solution:

If T is fixed, no other intensive variable can be varied.

13.5 What are the values of C and F in systems consisting of solid AgCl in equilibrium with an aqueous phase containing H_2O, $Ag^+(aq)$, $Cl^-(aq)$, $Na^+(aq)$, and $NO_3^-(aq)$ prepared in the following ways? Give examples of intensive variables that could be varied independently.

(a) The system is prepared by equilibrating excess solid AgCl with an aqueous solution of $NaNO_3$.

Solution:

Both phases were prepared from either the first or all three of the substances AgCl, H_2O, and $NaNO_3$; thus, there are three components:

$$C = 3 \qquad F = 2 + C - P = 2 + 3 - 2 = 3.$$

T, p, and m_{Na^+} could be varied independently.

(b) The system is prepared by mixing aqueous solutions of $AgNO_3$ and NaCl in arbitrary proportions; some solid AgCl forms by precipitation.

Solution:

There are six species and two independent relations among intensive variables:

$$-\mu_{AgCl} + \mu_{Ag^+} + \mu_{Cl^-} = 0$$

$$m_{Ag^+} + m_{Na^+} = m_{Cl^-} + m_{NO_3^-}$$

From the phase rule we find

$$C = s - r = 4 \qquad F = 2 + C - P = 2 + 4 - 2 = 4$$

T, p, and the molalities of any two of the aqueous ions could be varied independently.

13.6 How many degrees of freedom has a system consisting of solid NaCl in equilibrium with an aqueous phase containing H_2O, $Na^+(aq)$, $Cl^-(aq)$, $H^+(aq)$, and $OH^-(aq)$? Would it be possible to independently vary T, p, and m_{OH^-}? If so, explain how you could do this.

Solution:

There are six species, two phases, and three independent relations among intensive variables:

$$-\mu_{NaCl} + \mu_{Na^+} + \mu_{Cl^-} = 0$$

$$-\mu_{H_2O} + \mu_{H^+} + \mu_{OH^-} = 0$$

$$m_{Na^+} + m_{H^+} = m_{Cl^-} + m_{OH^-}$$

The system has three degrees of freedom:

$$F = 2 + s - r - P = 2 + 6 - 3 - 2 = 3$$

m_{OH^-} may be varied at any given T and p by dissolving HCl or NaOH in the aqueous phase.

13.7 Consult the phase diagram shown in Fig. 13.4 on page 430. Suppose the system contains 36.0 g (2.00 mol) H_2O and 58.4 g (1.00 mol) NaCl at 25 °C and 1 bar.

(a) Describe the phases present in the equilibrium system and their masses.

Solution:

The mass percent NaCl in the system as a whole is

$$\frac{58.4\,\text{g}}{36.0\,\text{g} + 58.4\,\text{g}} \times 100 = 61.9\%$$

The system point at 61.9% NaCl by mass and 25 °C lies in the two-phase area labeled sln + NaCl(s). The left end of the tie line drawn through the system point is at 26% NaCl by mass. The lever rule gives the relation

$$\frac{m^{\text{sln}}}{m^{\text{s}}} = \frac{100 - 61.9}{61.9 - 26} = 1.06$$

where m is mass. Solve this equation simultaneously with $m^{\mathrm{s}} + m^{\mathrm{sln}} = 94.4\,\mathrm{g}$:

$m^{\mathrm{sln}} = 48.6\,\mathrm{g} \qquad m^{\mathrm{s}} = 45.8\,\mathrm{g}$

The system contains approximately 49 g solution of composition 26% NaCl by mass, and 46 g solid NaCl.

(b) Describe the changes that occur at constant pressure if the system is placed in thermal contact with a heat reservoir at −30 °C.

Solution:

As the temperature decreases, some NaCl precipitates from the solution. The temperature drop halts at 0 °C while the system is converted completely to solid $NaCl{\cdot}2H_2O$; then the solid cools to −30 °C.

(c) Describe the changes that occur if the temperature is raised from 25 °C to 120 °C at constant pressure.

Solution:

As the temperature increases, some of the solid NaCl dissolves in the solution. The temperature rise halts at 109 °C until all the water vaporizes. At 120 °C the system contains 1.00 mol of solid NaCl and 2.00 mol of gaseous H_2O.

(d) Describe the system after 200 g H_2O is added at 25 °C.

Solution:

The solid NaCl dissolves to give a single phase, an unsaturated solution of composition 19.8% NaCl by mass.

Table 27 Aqueous solubilities of sodium sulfate decahydrate and anhydrous sodium sulfate[a]

$Na_2SO_4{\cdot}10H_2O$		Na_2SO_4	
$t/°C$	x_B	$t/°C$	x_B
10	0.011	40	0.058
15	0.016	50	0.056
20	0.024		
25	0.034		
30	0.048		

[a] Ref. [59], p. 179–180.

13.8 Use the following information to draw a temperature–composition phase diagram for the binary system of H_2O (A) and Na_2SO_4 (B) at $p = 1$ bar, confining t to the range −20 to 50 °C and z_B to the range 0–0.2. The solid decahydrate, $Na_2SO_4{\cdot}10H_2O$, is stable below 32.4 °C. The anhydrous salt, Na_2SO_4, is stable above this temperature. There is a peritectic point for these two solids and the solution at $x_B = 0.059$ and $t = 32.4$ °C. There is a eutectic point for ice, $Na_2SO_4{\cdot}10H_2O$, and the solution at $x_B = 0.006$ and $t = -1.3$ °C. Table 27 gives the temperature dependence of the solubilities of the ionic solids.

Solution:

See Fig. 25.

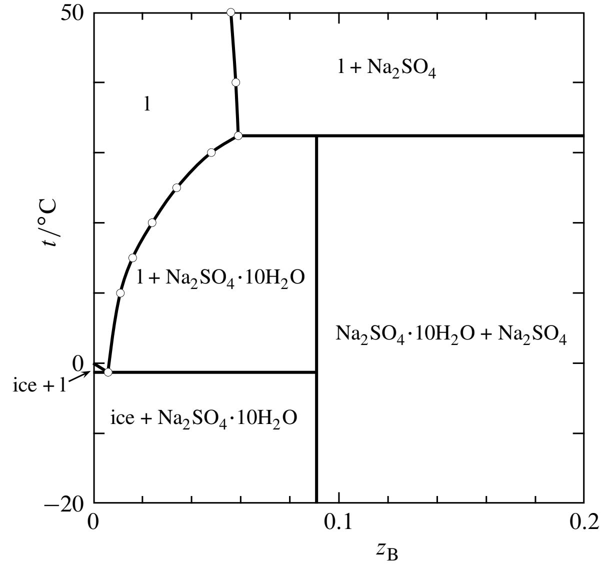

Figure 25 Phase diagram for the binary system of H_2O (A) and Na_2SO_4 (B) at $p =$ 1 bar. Open circles are data points given in problem.

Table 28 Data for Problem 13.9. Temperatures of saturated solutions of aqueous iron(III) chloride at $p =$ 1 bar (A = $FeCl_3$, B = H_2O)[a]

x_A	t/°C	x_A	t/°C	x_A	t/°C
0.000	0.0	0.119	35.0	0.286	56.0
0.020	−10.0	0.143	37.0	0.289	55.0
0.032	−20.5	0.157	36.0	0.293	60.0
0.037	−27.5	0.173	33.0	0.301	69.0
0.045	−40.0	0.183	30.0	0.318	72.5
0.052	−55.0	0.195	27.4	0.333	73.5
0.053	−41.0	0.213	32.0	0.343	72.5
0.056	−27.0	0.222	32.5	0.358	70.0
0.076	0.0	0.232	30.0	0.369	66.0
0.083	10.0	0.238	35.0	0.369	80.0
0.093	20.0	0.259	50.0	0.373	100.0
0.106	30.0	0.277	55.0		

[a] Data from Ref. [59], page 193.

13.9 Iron(III) chloride forms various solid hydrates, all of which melt congruently. Table 28 lists the temperatures t of aqueous solutions of various compositions that are saturated with respect to a solid phase.

(a) Use these data to construct a t–z_B phase diagram for the binary system of $FeCl_3$ (A) and H_2O (B). Identify the formula and melting point of each hydrate. Hint: derive a formula for the mole ratio n_B/n_A as a function of x_A in a binary mixture.

Solution:

See Fig. 26.

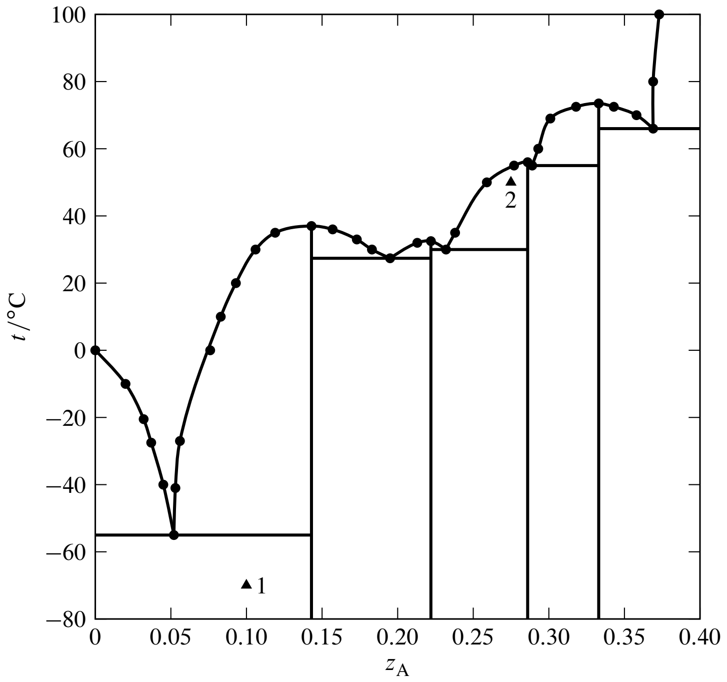

Figure 26 Phase diagram for the binary system of $FeCl_3$ (A) and H_2O (B). Solid circles: data points.

$$\frac{n_B}{n_A} = \frac{x_B}{x_A} = \frac{1 - x_A}{x_A}$$

The stoichiometry of each hydrate is given by the mole ratio of the liquid mixture with the same composition:

$x_A = 0.143, n_B/n_A = 5.99$: AB_6 or $FeCl_3 \cdot 6H_2O$

$x_A = 0.222, n_B/n_A = 3.50$: A_2B_7 or $(FeCl_3)_2 \cdot 7H_2O$

$x_A = 0.286, n_B/n_A = 2.50$: A_2B_5 or $(FeCl_3)_2 \cdot 5H_2O$

$x_A = 0.333, n_B/n_A = 2.00$: AB_2 or $FeCl_3 \cdot 2H_2O$

(b) For the following conditions, determine the phase or phases present at equilibrium and the composition of each.

1. $t = -70.0$°C and $z_A = 0.100$
2. $t = 50.0$°C and $z_A = 0.275$

Solution:

See points 1 and 2 on the phase diagram.

At $t = -70.0$°C and $z_A = 0.100$, the phases are solid H_2O (ice) and solid hydrate AB_6.

At $t = 50.0$°C and $z_A = 0.275$, the phases are solution of composition $x_B = 0.259$ and solid hydrate A_2B_5.

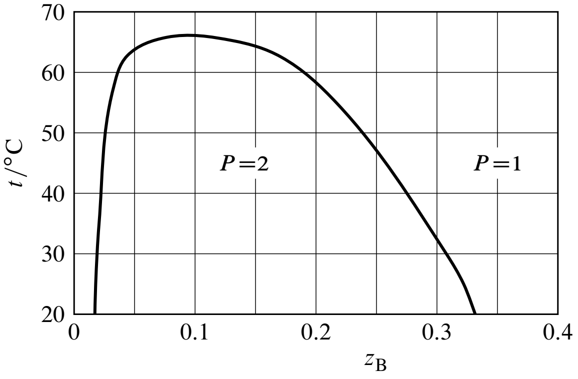

Figure 27 Temperature–composition phase diagram for the binary system of water (A) and phenol (B) at 1 bar.[a] Only liquid phases are present.

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[a] Ref. [59], p. 95.

13.10 Figure 27 is a temperature–composition phase diagram for the binary system of water (A) and phenol (B) at 1 bar. These liquids are partially miscible below 67 °C. Phenol is more dense than water, so the layer with the higher mole fraction of phenol is the bottom layer. Suppose you place 4.0 mol of H_2O and 1.0 mol of phenol in a beaker at 30 °C and gently stir to allow the layers to equilibrate.

(a) What are the compositions of the equilibrated top and bottom layers?

Solution:

The system point is at $z_B = (1.0\,\text{mol})/(5.0\,\text{mol}) = 0.20$ and $t = 30\,°\text{C}$, in the two-phase area. The ends of the tie line through this point give the compositions $x_B(\text{top}) = 0.02$ and $x_B(\text{bottom}) = 0.31$.

(b) Find the amount of each component in the bottom layer.

Solution:

The lever rule gives the relation

$$\frac{n(\text{bottom})}{n(\text{top})} = \frac{0.20 - 0.02}{0.31 - 0.20} = 1.6$$

Solve simultaneously with $n(\text{bottom}) + n(\text{top}) = 5.0\,\text{mol}$ to get $n(\text{bottom}) = 3.1\,\text{mol}$. Then, in the bottom layer we have

$$n_B = x_B n = (0.31)(3.1\,\text{mol}) = 1.0\,\text{mol} \qquad n_A = 3.1\,\text{mol} - 1.0\,\text{mol} = 2.1\,\text{mol}$$

(c) As you gradually stir more phenol into the beaker, maintaining the temperature at 30 °C, what changes occur in the volumes and compositions of the two layers? Assuming that one layer eventually disappears, what additional amount of phenol is needed to cause this to happen?

Solution:

The volume of the bottom layer increases and that of the top layer decreases. There is no change in the compositions of the two phases. When the overall system composition reaches $z_B = 0.31$, the top layer disappears; the amount of phenol in the system at this point is calculated from

$$z_B = \frac{n_B}{n_A + n_B} \qquad n_B = \frac{z_B n_A}{1 - z_B} = \frac{(0.31)(4.0\,\text{mol})}{1 - 0.31} = 1.8\,\text{mol}$$

Since 1.0 mol phenol was present initially, the top layer disappears when an additional 0.8 mol phenol has been added.

Table 29 Saturation vapor pressures of propane (A) and *n*-butane (B)

$t/°\text{C}$	p_A^*/bar	p_B^*/bar
−10.0	3.360	0.678
−20.0	2.380	0.441
−30.0	1.633	0.275

13.11 The standard boiling point of propane is −41.8 °C and that of *n*-butane is −0.2 °C. Table 29 lists vapor pressure data for the pure liquids. Assume that the liquid mixtures obey Raoult's law.

(a) Calculate the compositions, x_A, of the liquid mixtures with boiling points of −10.0 °C, −20.0 °C, and −30.0 °C at a pressure of 1 bar.

Solution:

Solve Eq. 13.2.4 for x_A:

$$x_A = \frac{p - p_B^*}{p_A^* - p_B^*}$$

Set p equal to 1 bar and take values of p_A^* and p_B^* from the table.

at −10 °C: $x_A = 0.120$

at −20 °C: $x_A = 0.288$

at −30 °C: $x_A = 0.534$

(b) Calculate the compositions, y_A, of the equilibrium vapor at these three temperatures.

Solution:

Use Eq. 13.2.7: $y_A = x_A p_A^*/p$.

at −10 °C: $y_A = 0.403$

at −20 °C: $y_A = 0.686$

at −30 °C: $y_A = 0.872$

(c) Plot the temperature–composition phase diagram at $p = 1$ bar using these data, and label the areas appropriately.

Solution:

See Fig. 28.

(d) Suppose a system containing 10.0 mol propane and 10.0 mol *n*-butane is brought to a pressure of 1 bar and a temperature of −25 °C. From your phase diagram, estimate the compositions and amounts of both phases.

Solution:

From the ends of the tie line (dashed line) in Fig. 28:

$x_A = 0.39$, $y_A = 0.79$

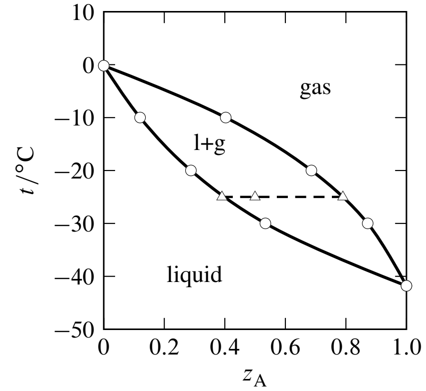

Figure 28 Phase diagram for the binary system of propane (A) and *n*-butane at 1 bar.

Use the lever rule:

$$\frac{n^{\mathrm{g}}}{n^{\mathrm{l}}} = \frac{z_{\mathrm{A}} - x_{\mathrm{A}}}{y_{\mathrm{A}} - z_{\mathrm{A}}} = \frac{0.50 - 0.39}{0.79 - 0.50} = 0.38$$

Solve this equation simultaneously with $n^{\mathrm{l}} + n^{\mathrm{g}} = 20.0\,\mathrm{mol}$:

$n^{\mathrm{l}} = 14.5\,\mathrm{mol}$, $n^{\mathrm{g}} = 5.5\,\mathrm{mol}$

Table 30 Liquid and gas compositions in the two-phase system of 2-propanol (A) and benzene at 45 °C[a]

x_A	y_A	p/kPa	x_A	y_A	p/kPa
0	0	29.89	0.5504	0.3692	35.32
0.0472	0.1467	33.66	0.6198	0.3951	34.58
0.0980	0.2066	35.21	0.7096	0.4378	33.02
0.2047	0.2663	36.27	0.8073	0.5107	30.28
0.2960	0.2953	36.45	0.9120	0.6658	25.24
0.3862	0.3211	36.29	0.9655	0.8252	21.30
0.4753	0.3463	35.93	1.0000	1.0000	18.14

[a] Ref. [24].

13.12 Use the data in Table 30 to draw a pressure–composition phase diagram for the 2-propanol–benzene system at 45 °C. Label the axes and each area.

Solution:

See Fig. 29. The system exhibits a minimum-boiling azeotrope.

13.13 Use the data in Table 31 on the next page to draw a pressure–composition phase diagram for the acetone–chloroform system at 35.2 °C. Label the axes and each area.

Solution:

See Fig. 30. The system exhibits a maximum-boiling azeotrope.

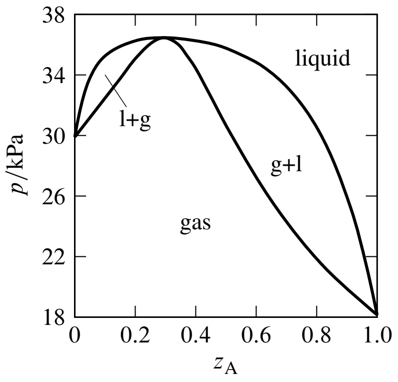

Figure 29 Phase diagram for the binary system of 2-propanol (A) and benzene at 45 °C.

Table 31 Liquid and gas compositions in the two-phase system of acetone (A) and chloroform at 35.2 °C[a]

x_A	y_A	p/kPa	x_A	y_A	p/kPa
0	0	39.08	0.634	0.727	36.29
0.083	0.046	37.34	0.703	0.806	38.09
0.200	0.143	34.92	0.815	0.896	40.97
0.337	0.317	33.22	0.877	0.936	42.62
0.413	0.437	33.12	0.941	0.972	44.32
0.486	0.534	33.70	1.000	1.000	45.93
0.577	0.662	35.09			

[a] Ref. [179], p. 286.

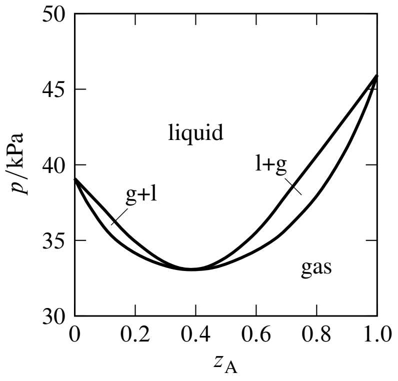

Figure 30 Phase diagram for the binary system of acetone (A) and chloroform at 35.2 °C.

Chapter 14 Galvanic Cells

14.1 The state of a galvanic cell without liquid junction, when its temperature and pressure are uniform, can be fully described by values of the variables T, p, and ξ. Find an expression for $\mathrm{d}G$ during a reversible advancement of the cell reaction, and use it to derive the relation $\Delta_\mathrm{r}G_\mathrm{cell} = -zFE_\mathrm{cell,\,eq}$ (Eq. 14.3.8). (Hint: Eq. 3.8.8.)

Solution:

Equation 3.8.8 is a general formula for electrical work when the cell is part of an electrical circuit:

$$\text{đ}w_\mathrm{el} = E_\mathrm{cell}\,\text{đ}Q_\mathrm{sys}$$

Combine this relation with $\text{đ}Q_\mathrm{sys} = -zF\,\mathrm{d}\xi$ (Eq. 14.1.1):

$$\text{đ}w_\mathrm{el} = -zFE_\mathrm{cell}\,\mathrm{d}\xi$$

The intermediate states of a reversible cell reaction have uniform T and p and an equilibrium cell potential: $E_\mathrm{cell} = E_\mathrm{cell,\,eq}$. $\mathrm{d}G$ during a reversible process of a closed system with nonexpansion work is given by the equality of Eq. 5.8.6. In this equality, replace $\text{đ}w'$ by $\text{đ}w_\mathrm{el} = -zFE_\mathrm{cell,\,eq}\,\mathrm{d}\xi$:

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p - zFE_\mathrm{cell,\,eq}\,\mathrm{d}\xi$$

This is an expression for the total differential of G with T, p, and ξ as the independent variables. Identify the coefficient of $\mathrm{d}\xi$ as the partial derivative $(\partial G/\partial\xi)_{T,p}$, which is the molar reaction Gibbs energy of the cell reaction:

$$\Delta_\mathrm{r}G_\mathrm{cell} = -zFE_\mathrm{cell,\,eq}$$

14.2 Before 1982 the standard pressure was usually taken as 1 atm. For the cell shown in Fig. 14.1, what correction is needed, for a value of $E^\circ_\mathrm{cell,\,eq}$ obtained at 25 °C and using the older convention, to change the value to one corresponding to a standard pressure of 1 bar? Equation 14.3.15 can be used for this calculation.

Solution:

From Eq. 14.3.15:

$$E^\circ_\mathrm{cell,\,eq} = -\frac{\Delta_\mathrm{r}G^\circ}{zF}$$

where the standard molar reaction Gibbs energy is given by $\Delta_\mathrm{r}G^\circ = \sum_i \nu_i\mu_i^\circ$ (Eq. 11.8.3). The effect of a small pressure change on the chemical potential of a solid or solute is negligible. The standard state of the gaseous H_2 is the pure gas behaving as an ideal gas. Apply Eq. 7.8.4 to the isothermal pressure change of an ideal gas:

$$\left(\frac{\partial\mu}{\partial p}\right)_T = V_\mathrm{m} = \frac{RT}{p} \qquad \mu(p_2) - \mu(p_1) = RT\int_{p_1}^{p_2}\frac{\mathrm{d}p}{p} = RT\ln\frac{p_2}{p_1}$$

For a pressure change from 1 atm to 1 bar the change of chemical potential is

$$\begin{aligned}\mu(1\,\mathrm{bar}) - \mu(1\,\mathrm{atm}) &= (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298.15\,\mathrm{K})\ln\frac{1\,\mathrm{bar}}{1.01325\,\mathrm{bar}}\\ &= -32.63\,\mathrm{J\,mol^{-1}}\end{aligned}$$

Therefore for the cell reaction $H_2(g) + 2\,AgCl(s) \rightarrow 2\,Ag(s) + 2\,H^+(aq) + 2\,Cl^-(aq)$ the pressure change causes $E^\circ_\mathrm{cell,\,eq}$ to change by

$$E^\circ_{\text{cell, eq}}(p^\circ = 1\,\text{bar}) - E^\circ_{\text{cell, eq}}(p^\circ = 1\,\text{atm}) = -\frac{-(-32.63\,\text{J mol}^{-1})}{(2)(96,485\,\text{C mol}^{-1})} = -1.691 \times 10^{-4}\,\text{V}$$

The correction to $E^\circ_{\text{cell, eq}}$ based on the older convention is -0.17 mV.

14.3 Careful measurements[20] of the equilibrium cell potential of the cell

$$\text{Pt} \mid \text{H}_2(\text{g}) \mid \text{HCl(aq)} \mid \text{AgCl(s)} \mid \text{Ag}$$

yielded, at 298.15 K and using a standard pressure of 1 bar, the values $E^\circ_{\text{cell, eq}} = 0.22217\,\text{V}$ and $\text{d}E^\circ_{\text{cell, eq}}/\,\text{d}T = -6.462 \times 10^{-4}\,\text{V K}^{-1}$. (The requested calculated values are close to, but not exactly the same as, the values listed in Appendix H, which are based on the same data combined with data of other workers.)

(a) Evaluate $\Delta_\text{r}G^\circ$, $\Delta_\text{r}S^\circ$, and $\Delta_\text{r}H^\circ$ at 298.15 K for the reaction

$$\tfrac{1}{2}\text{H}_2(\text{g}) + \text{AgCl(s)} \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq}) + \text{Ag(s)}$$

Solution:

From Eq. 14.3.15:

$$\Delta_\text{r}G^\circ = -zFE^\circ_{\text{cell, eq}} = -(1)(96,485\,\text{C mol}^{-1})(0.22217\,\text{V}) = -21.436\,\text{kJ mol}^{-1}$$

From Eq. 14.3.18:

$$\begin{aligned}\Delta_\text{r}S^\circ &= zF\frac{\text{d}E^\circ_{\text{cell, eq}}}{\text{d}T} = (1)(96,485\,\text{C mol}^{-1})(-6.462 \times 10^{-4}\,\text{V K}^{-1})\\ &= -62.35\,\text{J K}^{-1}\,\text{mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta_\text{r}H^\circ &= T\Delta_\text{r}S^\circ + \Delta_\text{r}G^\circ\\ &= (298.15\,\text{K})(-62.35\,\text{J K}^{-1}\,\text{mol}^{-1}) + (-21.436 \times 10^3\,\text{J mol}^{-1})\\ &= -40.03\,\text{kJ mol}^{-1}\end{aligned}$$

The value of $\Delta_\text{r}H^\circ$ may also be calculated with Eq. 14.3.17.

(b) Problem 12.18 showed how the standard molar enthalpy of formation of the aqueous chloride ion may be evaluated based on the convention $\Delta_\text{f}H^\circ(\text{H}^+, \text{aq}) = 0$. If this value is combined with the value of $\Delta_\text{r}H^\circ$ obtained in part (a) of the present problem, the standard molar enthalpy of formation of crystalline silver chloride can be evaluated. Carry out this calculation for $T = 298.15\,\text{K}$ using the value $\Delta_\text{f}H^\circ(\text{Cl}^-, \text{aq}) = -167.08\,\text{kJ mol}^{-1}$ (Appendix H).

Solution:

Apply the general relation $\Delta_\text{r}H^\circ = \sum_i \nu_i \Delta_\text{f}H^\circ(i)$ (Eq. 11.3.3) to the reaction of part (a):

$$\begin{aligned}\Delta_\text{r}H^\circ &= -\tfrac{1}{2}\Delta_\text{f}H^\circ(\text{H}_2, \text{g}) - \Delta_\text{f}H^\circ(\text{AgCl, s}) + \Delta_\text{f}H^\circ(\text{H}^+, \text{aq})\\ &\quad + \Delta_\text{f}H^\circ(\text{Cl}^-, \text{aq}) + \Delta_\text{f}H^\circ(\text{Ag, s})\\ &= -\tfrac{1}{2}(0) - \Delta_\text{f}H^\circ(\text{AgCl, s}) + 0 + \Delta_\text{f}H^\circ(\text{Cl}^-, \text{aq}) + 0\end{aligned}$$

$$\begin{aligned}\Delta_\text{f}H^\circ(\text{AgCl, s}) &= -\Delta_\text{r}H^\circ + \Delta_\text{f}H^\circ(\text{Cl}^-, \text{aq})\\ &= -(-40.03\,\text{kJ mol}^{-1}) + (-167.08\,\text{kJ mol}^{-1}) = -127.05\,\text{kJ mol}^{-1}\end{aligned}$$

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[20] Ref. [4].

(c) By a similar procedure, evaluate the standard molar entropy, the standard molar entropy of formation, and the standard molar Gibbs energy of formation of crystalline silver chloride at 298.15 K. You need the following standard molar entropies evaluated from spectroscopic and calorimetric data:

$S^\circ_\mathrm{m}(\mathrm{H_2, g}) = 130.68\,\mathrm{J\,K^{-1}\,mol^{-1}}$ $\quad$ $S^\circ_\mathrm{m}(\mathrm{Cl_2, g}) = 223.08\,\mathrm{J\,K^{-1}\,mol^{-1}}$
$S^\circ_\mathrm{m}(\mathrm{Cl^-, aq}) = 56.60\,\mathrm{J\,K^{-1}\,mol^{-1}}$ $\quad$ $S^\circ_\mathrm{m}(\mathrm{Ag, s}) = 42.55\,\mathrm{J\,K^{-1}\,mol^{-1}}$

Solution:

For the standard molar reaction entropy, apply the general relation $\Delta_\mathrm{r}S^\circ = \sum_i \nu_i S^\circ_i$ (Eq. 11.8.22) to the reaction of part (a):

$$\Delta_\mathrm{r}S^\circ = -\tfrac{1}{2}S^\circ_\mathrm{m}(\mathrm{H_2, g}) - S^\circ_\mathrm{m}(\mathrm{AgCl, s}) + S^\circ_\mathrm{m}(\mathrm{H^+, aq}) + S^\circ_\mathrm{m}(\mathrm{Cl^-, aq}) + S^\circ_\mathrm{m}(\mathrm{Ag, s})$$

By convention, $S^\circ_\mathrm{m}(\mathrm{H^+, aq})$ is zero.

$$S^\circ_\mathrm{m}(\mathrm{AgCl, s}) = -\Delta_\mathrm{r}S^\circ - \tfrac{1}{2}S^\circ_\mathrm{m}(\mathrm{H_2, g}) + S^\circ_\mathrm{m}(\mathrm{Cl^-, aq}) + S^\circ_\mathrm{m}(\mathrm{Ag, s})$$

$$S^\circ_\mathrm{m}(\mathrm{AgCl, s})/\mathrm{J\,K^{-1}\,mol^{-1}} = -(-62.35) - \tfrac{1}{2}(130.68) + 56.60 + 42.55 = 96.16$$

The formation reaction of AgCl is $\mathrm{Ag(s)} + \tfrac{1}{2}\mathrm{Cl_2(g)} \rightarrow \mathrm{AgCl(s)}$:

$$\Delta_\mathrm{f}S^\circ(\mathrm{AgCl, s}) = -S^\circ_\mathrm{m}(\mathrm{Ag, s}) - \tfrac{1}{2}S^\circ_\mathrm{m}(\mathrm{Cl_2, g}) + S^\circ_\mathrm{m}(\mathrm{AgCl, s})$$

$$\Delta_\mathrm{f}S^\circ(\mathrm{AgCl, s})/\mathrm{J\,K^{-1}\,mol^{-1}} = -(42.55) - \tfrac{1}{2}(223.08) + 96.16 = -57.93$$

$$\begin{aligned}\Delta_\mathrm{f}G^\circ(\mathrm{AgCl, s}) &= \Delta_\mathrm{f}H^\circ(\mathrm{AgCl, s}) - T\Delta_\mathrm{f}S^\circ(\mathrm{AgCl, s})\\ &= -127.05\times10^3\,\mathrm{J\,mol^{-1}} - (298.15\,\mathrm{K})(-57.93\,\mathrm{J\,K^{-1}\,mol^{-1}})\\ &= -109.78\,\mathrm{kJ\,mol^{-1}}\end{aligned}$$

14.4 The standard cell potential of the cell

$$\mathrm{Ag} \mid \mathrm{AgCl(s)} \mid \mathrm{HCl(aq)} \mid \mathrm{Cl_2(g)} \mid \mathrm{Pt}$$

has been determined over a range of temperature.[21] At T=298.15 K, the standard cell potential was found to be $E^\circ_\mathrm{cell,\,eq} = 1.13579\,\mathrm{V}$, and its temperature derivative was found to be $\mathrm{d}E^\circ_\mathrm{cell,\,eq}/\,\mathrm{d}T = -5.9863\times10^{-4}\,\mathrm{V\,K^{-1}}$.

(a) Write the cell reaction for this cell.

Solution:

left electrode reaction (oxidation)	$2\,[\mathrm{Ag(s)} + \mathrm{Cl^-(aq)} \rightarrow \mathrm{AgCl(s)} + \mathrm{e^-}]$
right electrode reaction (reduction)	$\mathrm{Cl_2(g)} + 2\,\mathrm{e^-} \rightarrow 2\,\mathrm{Cl^-(aq)}$
cell reaction	$2\,\mathrm{Ag(s)} + \mathrm{Cl_2(g)} \rightarrow 2\,\mathrm{AgCl(s)}$

(b) Use the data to evaluate the standard molar enthalpy of formation and the standard molar Gibbs energy of formation of crystalline silver chloride at 298.15 K. (Note that this calculation provides values of quantities also calculated in Prob. 14.3 using independent data.)

Solution:

The cell reaction is the formation reaction of AgCl(s). As written in the solution for part (a), the electron number is $z = 2$. To simplify the calculation, divide the coefficients by 2:

$\mathrm{Ag(s)} + \tfrac{1}{2}\mathrm{Cl_2(g)} \rightarrow \mathrm{AgCl(s)} \qquad z = 1$

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[21] Ref. [55].

Then we have, from Eq. 14.3.17:

$$\begin{aligned}\Delta_f H^\circ(\text{AgCl, s}) &= \Delta_r H^\circ = zF\left(T\frac{dE^\circ_{\text{cell, eq}}}{dT} - E^\circ_{\text{cell, eq}}\right)\\ &= (1)(96{,}485\,\text{C mol}^{-1})\left[(298.15\,\text{K})(-5.9863\times10^{-4}\,\text{V K}^{-1}) - 1.13579\,\text{V}\right]\\ &= -126.81\,\text{kJ mol}^{-1}\end{aligned}$$

and from Eq. 14.3.15:

$$\begin{aligned}\Delta_f G^\circ(\text{AgCl, s}) = \Delta_r G^\circ = -zFE^\circ_{\text{cell, eq}} &= -(1)(96{,}485\,\text{C mol}^{-1})(1.13579\,\text{V})\\ &= -109.59\,\text{kJ mol}^{-1}\end{aligned}$$

14.5 Use data in Sec. 14.3.3 to evaluate the solubility product of silver chloride at 298.15 K.

Solution:

From Eq. 14.3.16:

$$\ln K_s = \frac{zF}{RT}E^\circ_{\text{cell, eq}} = \frac{(1)(96{,}485\,\text{C mol}^{-1})}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(298.15\,\text{K})}(-0.5770\,\text{V}) = -22.46$$

$$K_s = 1.76\times10^{-10}$$

14.6 The equilibrium cell potential of the galvanic cell

$$\text{Pt} \mid \text{H}_2(\text{g}, f{=}1\,\text{bar}) \mid \text{HCl}(\text{aq}, 0.500\,\text{mol kg}^{-1}) \mid \text{Cl}_2(\text{g}, f{=}1\,\text{bar}) \mid \text{Pt}$$

is found to be $E_{\text{cell, eq}} = 1.410\,\text{V}$ at 298.15 K. The standard cell potential is $E^\circ_{\text{cell, eq}} = 1.360\,\text{V}$.

(a) Write the cell reaction and calculate its thermodynamic equilibrium constant at 298.15 K.

Solution:

left electrode reaction (oxidation)	$H_2(g) \rightarrow 2H^+(aq) + 2e^-$
right electrode reaction (reduction)	$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$
cell reaction	$H_2(g) + Cl_2(g) \rightarrow 2H^+(aq) + 2Cl^-(aq)$

From Eq. 14.3.16:

$$\ln K_s = \frac{zF}{RT}E^\circ_{\text{cell, eq}} = \frac{(2)(96{,}485\,\text{C mol}^{-1})}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(298.15\,\text{K})}(1.360\,\text{V}) = 105.9$$

$$K_s = 9\times10^{45}$$

(b) Use the cell measurement to calculate the mean ionic activity coefficient of aqueous HCl at 298.15 K and a molality of 0.500 mol kg^{-1}.

Solution:

From Eq. 14.4.2:

$$\begin{aligned}E_{\text{cell, eq}} = E^\circ_{\text{cell, eq}} - \frac{0.02569\,\text{V}}{z}\ln Q_{\text{rxn}} &= E^\circ_{\text{cell, eq}} - \frac{0.02569\,\text{V}}{z}\ln\frac{\gamma_\pm^4(m_B/m^\circ)^4}{(f_{H_2}/p^\circ)(f_{Cl_2}/p^\circ)}\\ &= E^\circ_{\text{cell, eq}} - \frac{0.02569\,\text{V}}{2}\ln\frac{\gamma_\pm^4(0.500)^4}{(1)(1)}\end{aligned}$$

$$\ln(0.500\gamma_\pm) = \frac{E^\circ_{\text{cell, eq}} - E_{\text{cell, eq}}}{2\times0.02569\,\text{V}} = \frac{(1.360 - 1.410)\,\text{V}}{2\times0.02569\,\text{V}} = -0.973$$

$$\gamma_\pm = 0.756$$

14.7 Consider the following galvanic cell, which combines a hydrogen electrode and a calomel electrode:

$$\mathrm{Pt} \mid \mathrm{H_2(g)} \mid \mathrm{HCl(aq)} \mid \mathrm{Hg_2Cl_2(s)} \mid \mathrm{Hg(l)} \mid \mathrm{Pt}$$

(a) Write the cell reaction.

Solution:

left electrode reaction (oxidation) $\mathrm{H_2(g)} \rightarrow 2\,\mathrm{H^+(aq)} + 2\,\mathrm{e^-}$

right electrode reaction (reduction) $\mathrm{Hg_2Cl_2(s)} + 2\,\mathrm{e^-} \rightarrow 2\,\mathrm{Hg(l)} + 2\,\mathrm{Cl^-(aq)}$

cell reaction: $\mathrm{H_2(g)} + \mathrm{Hg_2Cl_2(s)} \rightarrow 2\,\mathrm{H^+(aq)} + 2\,\mathrm{Cl^-(aq)} + 2\,\mathrm{Hg(l)}$

(b) At 298.15 K, the standard cell potential of this cell is $E^\circ_{\text{cell, eq}} = 0.2680\,\mathrm{V}$. Using the value of $\Delta_\mathrm{f}G^\circ$ for the aqueous chloride ion in Appendix H, calculate the standard molar Gibbs energy of formation of crystalline mercury(I) chloride (calomel) at 298.15 K.

Solution:

From Eq. 14.3.15:

$$\Delta_\mathrm{r}G^\circ = -zFE^\circ_{\text{cell, eq}} = -(2)(96{,}485\,\mathrm{C\,mol^{-1}})(0.2680\,\mathrm{V}) = -5.172\times10^4\,\mathrm{J\,mol^{-1}}$$

$$\Delta_\mathrm{r}G^\circ = \sum \nu_i\,\Delta_\mathrm{f}G^\circ(i) = -(0) - \Delta_\mathrm{f}G^\circ(\mathrm{Hg_2Cl_2,s}) + 2(0) + 2\Delta_\mathrm{f}G^\circ(\mathrm{Cl^-,aq}) + 2(0)$$

$$\begin{aligned}\Delta_\mathrm{f}G^\circ(\mathrm{Hg_2Cl_2,s}) &= -\Delta_\mathrm{r}G^\circ + 2\Delta_\mathrm{f}G^\circ(\mathrm{Cl^-,aq})\\ &= -(-5.172\times10^4\,\mathrm{J\,mol^{-1}}) + 2(-131.22\times10^3\,\mathrm{J\,mol^{-1}})\\ &= -210.72\,\mathrm{kJ\,mol^{-1}}\end{aligned}$$

(c) Calculate the solubility product of mercury(I) chloride at 298.15 K. The dissolution equilibrium is $\mathrm{Hg_2Cl_2(s)} \rightleftharpoons \mathrm{Hg_2}^{2+}\mathrm{(aq)} + 2\,\mathrm{Cl^-(aq)}$. Take values for the standard molar Gibbs energies of formation of the aqueous ions from Appendix H.

Solution:

$$\Delta_\mathrm{r}G^\circ = \sum \nu_i\,\Delta_\mathrm{f}G^\circ(i) = -\Delta_\mathrm{f}G^\circ(\mathrm{Hg_2Cl_2,s}) + \Delta_\mathrm{f}G^\circ(\mathrm{Hg_2}^{2+},\mathrm{aq}) + 2\Delta_\mathrm{f}G^\circ(\mathrm{Cl^-,aq})$$

$$\Delta_\mathrm{r}G^\circ/\mathrm{kJ\,mol^{-1}} = -(-210.72) + (153.57) + 2(-131.22) = 101.85$$

$$K_\mathrm{s} = \exp\left(-\frac{\Delta_\mathrm{r}G^\circ}{RT}\right) = \exp\left[-\frac{101.85\times10^3\,\mathrm{J\,mol^{-1}}}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298.15\,\mathrm{K})}\right] = 1.4\times10^{-18}$$

Table 32 Equilibrium cell potential as a function of HBr molality m_B.

$m_\mathrm{B}\,/\,(\mathrm{mol\,kg^{-1}})$	$E_{\text{cell, eq}}\,/\,\mathrm{V}$
0.0004042	0.47381
0.0008444	0.43636
0.0008680	0.43499
0.0013554	0.41243
0.001464	0.40864
0.001850	0.39667
0.002396	0.38383
0.003719	0.36173

14.8 Table 32 lists equilibrium cell potentials obtained with the following cell at 298.15 K:[22]

$$\mathrm{Pt} \mid \mathrm{H_2(g, 1.01\,bar)} \mid \mathrm{HBr}(\mathrm{aq}, m_\mathrm{B}) \mid \mathrm{AgBr(s)} \mid \mathrm{Ag}$$

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[22] Ref. [98].

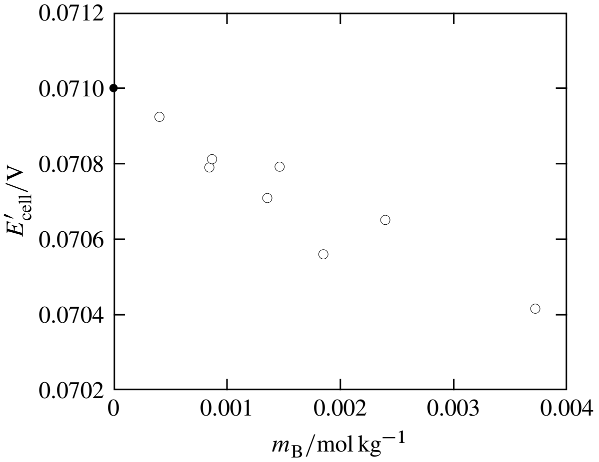

Figure 31 Graph for Problem 14.8.

Use these data to evaluate the standard electrode potential of the silver-silver bromide electrode at this temperature to the nearest millivolt. (Since the electrolyte solutions are quite dilute, you may ignore the term $Ba\sqrt{m_B}$ in Eq. 14.5.2.)

Solution:

The cell has a hydrogen electrode at the left and a silver-silver bromide electrode at the right. The standard electrode potential E° of the silver-silver bromide electrode is therefore equal to the standard cell potential $E^\circ_{\text{cell, eq}}$ of this cell.

Figure 31 shows values of E'_{cell} plotted versus m_B (open circles), where the function E'_{cell} is defined by Eq. 14.5.2 with a set equal to zero:

$$\begin{aligned}
E'_{\text{cell}} &= E_{\text{cell, eq}} + \frac{2RT}{F}(-A\sqrt{m_B}) + \frac{2RT}{F}\ln\frac{m_B}{m^\circ} - \frac{RT}{2F}\ln\frac{f_{H_2}}{p^\circ} \\
&= E_{\text{cell, eq}} + \frac{RT}{F}\left(-2A\sqrt{m_B} + 2\ln\frac{m_B}{m^\circ} - \frac{1}{2}\ln\frac{f_{H_2}}{p^\circ}\right) \\
&= E_{\text{cell, eq}} + \frac{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(298.15\,\text{K})}{96,485\,\text{C mol}^{-1}} \\
&\qquad \times \left[-(2)(1.1744\,\text{kg}^{1/2}\,\text{mol}^{-1/2})\sqrt{m_B} + 2\ln(m_B\,/\,\text{mol kg}^{-1}) - \frac{1}{2}\ln(1.01)\right]
\end{aligned}$$

To the nearest millivolt, E'_{cell} extrapolated to $m_B = 0$ (filled circle) has the value $E^\circ = E^\circ_{\text{cell, eq}} = 0.071\,\text{V}$.

14.9 The cell diagram of a mercury cell can be written

$$\text{Zn(s)}\mid\text{ZnO(s)}\mid\text{NaOH(aq)}\mid\text{HgO(s)}\mid\text{Hg(l)}$$

(a) Write the electrode reactions and cell reaction with electron number $z = 2$.

Solution:

At the left electrode: $\text{Zn(s)} + 2\,\text{OH}^-(\text{aq}) \rightarrow \text{ZnO(s)} + \text{H}_2\text{O(l)} + 2\,\text{e}^-$

At the right electrode: $\text{HgO(s)} + \text{H}_2\text{O(l)} + 2\,\text{e}^- \rightarrow \text{Hg(l)} + 2\,\text{OH}^-(\text{aq})$

Cell reaction: $\mathrm{Zn(s)} + \mathrm{HgO(s)} \rightarrow \mathrm{ZnO(s)} + \mathrm{Hg(l)}$

(b) Use data in Appendix H to calculate the standard molar reaction quantities $\Delta_\mathrm{r}H^\circ$, $\Delta_\mathrm{r}G^\circ$, and $\Delta_\mathrm{r}S^\circ$ for the cell reaction at 298.15 K.

Solution:

$$\begin{aligned}\Delta_\mathrm{r}H^\circ &= \Delta_\mathrm{f}H^\circ(\mathrm{ZnO}) + \Delta_\mathrm{f}H^\circ(\mathrm{Hg}) - \Delta_\mathrm{f}H^\circ(\mathrm{Zn}) - \Delta_\mathrm{f}H^\circ\mathrm{HgO})\\ &= [(-350.46) + 0 - 0 - (-90.79)]\,\mathrm{kJ\,mol^{-1}}\\ &= -259.67\,\mathrm{kJ\,mol^{-1}}\end{aligned}$$

$$\begin{aligned}\Delta_\mathrm{r}G^\circ &= \Delta_\mathrm{f}G^\circ(\mathrm{ZnO}) + \Delta_\mathrm{f}G^\circ(\mathrm{Hg}) - \Delta_\mathrm{f}G^\circ(\mathrm{Zn}) - \Delta_\mathrm{f}G^\circ\mathrm{HgO})\\ &= [(-320.48) + 0 - 0 - (-58.54)]\,\mathrm{kJ\,mol^{-1}}\\ &= -261.94\,\mathrm{kJ\,mol^{-1}}\end{aligned}$$

$$T\Delta_\mathrm{r}S^\circ = \Delta_\mathrm{r}H^\circ - \Delta_\mathrm{r}G^\circ = 2.27\,\mathrm{kJ\,mol^{-1}}$$

$$\Delta_\mathrm{r}S^\circ = \frac{2.27\times10^{3}\,\mathrm{J\,mol^{-1}}}{298.15\,\mathrm{K}} = 7.61\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

(c) Calculate the standard cell potential of the mercury cell at 298.15 K to the nearest 0.01 V.

Solution:

$$E^\circ_\text{cell, eq} = -\frac{\Delta_\mathrm{r}G^\circ}{zF} = -\frac{(-261.94\times10^{3}\,\mathrm{J\,mol^{-1}})}{(2)(96,485\,\mathrm{C\,mol^{-1}})} = 1.36\,\mathrm{V}$$

(d) Evaluate the ratio of heat to advancement, $đq/\,\mathrm{d}\xi$, at a constant temperature of 298.15 K and a constant pressure of 1 bar, for the cell reaction taking place in two different ways: reversibly in the cell, and spontaneously in a reaction vessel that is not part of an electrical circuit.

Solution:

In the cell:

$$\frac{đq}{\mathrm{d}\xi} = T\Delta_\mathrm{r}S^\circ = 2.27\,\mathrm{kJ\,mol^{-1}}$$

In a reaction vessel, from Eq. 11.3.1:

$$đq/\,\mathrm{d}\xi = \Delta_\mathrm{r}H^\circ = -259.67\,\mathrm{kJ\,mol^{-1}}$$

(e) Evaluate $\mathrm{d}E^\circ_\text{cell, eq}/\,\mathrm{d}T$, the temperature coefficient of the standard cell potential.

Solution:

From Eq. 14.3.18:

$$\frac{\mathrm{d}E^\circ_\text{cell, eq}}{\mathrm{d}T} = \frac{\Delta_\mathrm{r}S^\circ}{zF} = \frac{7.61\,\mathrm{J\,K^{-1}\,mol^{-1}}}{(2)(96,485\,\mathrm{C\,mol^{-1}})} = 3.9\times10^{-5}\,\mathrm{V\,K^{-1}}$$