THERMODYNAMICS AND CHEMISTRY

SECOND EDITION

HOWARD DEVOE

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 $\cdot$ 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 $(\text{length})^6$. 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, $0.1 \times 10^{-3}\,\mathrm{g}/100\,\mathrm{g} = 1 \times 10^{-6}$
- micro balance, $0.1 \times 10^{-6}\,\mathrm{g}/20 \times 10^{-3}\,\mathrm{g} = 5 \times 10^{-6}$

Volume:
- pipet, $0.02\,\mathrm{ml}/10\,\mathrm{mL} = 2 \times 10^{-3}$
- volumetric flask, $0.3 \times 10^{-3}\,\mathrm{L}/1\,\mathrm{L} = 3 \times 10^{-4}$

Density:
- pycnometer, $2 \times 10^{-3}\,\mathrm{g\,mL^{-1}}/1\,\mathrm{g\,mL^{-1}} = 2 \times 10^{-3}$
- magnetic float densimeter, $0.1 \times 10^{-3}\,\mathrm{g\,mL^{-1}}/1\,\mathrm{g\,mL^{-1}} = 1 \times 10^{-4}$

Pressure:
- manometer or barometer, $0.001\,\mathrm{Torr}/760\,\mathrm{Torr} = 1 \times 10^{-6}$
- diaphragm gauge, $1\,\mathrm{Torr}/100\,\mathrm{Torr} = 1 \times 10^{-2}$

Temperature:
- gas thermometer, $0.001\,\mathrm{K}/10\,\mathrm{K} = 1 \times 10^{-4}$
- mercury thermometer, $0.01\,\mathrm{K}/300\,\mathrm{K} = 3 \times 10^{-5}$
- platinum resistance thermometer, $0.0001\,\mathrm{K}/300\,\mathrm{K} = 3 \times 10^{-7}$
- optical pyrometer, $0.03\,\mathrm{K}/1300\,\mathrm{K} = 2 \times 10^{-5}$

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 $T_1 = 7.1992\,\mathrm{K}$, 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

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

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[1] Ref. [13].

Table 1 Helium at a fixed temperature

$(1/V_m)/10^2\ \mathrm{mol\ m^{-3}}$	$(p_2 V_m/R)/K$
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

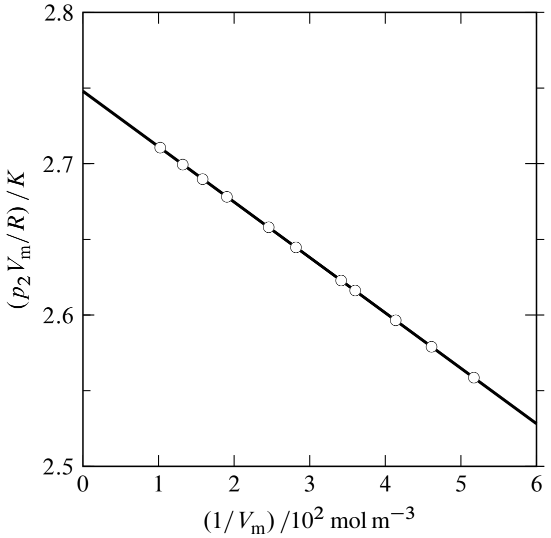

Figure 1

According to this equation, a plot of $p_2 V_m/R$ versus $1/V_m$ should be linear with an intercept at $1/V_m$=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 $-3.659 \times 10^{-4}\ \mathrm{K\,m^3\,mol^{-1}}$. The temperature and second virial coefficient therefore have the values

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

$$B = \frac{-3.659 \times 10^{-4}\ \mathrm{K\,m^3\,mol^{-1}}}{2.7478\ \mathrm{K}} = -1.332 \times 10^{-4}\ \mathrm{m^3\,mol^{-1}}$$

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:

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

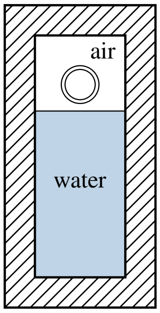

Figure 2

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.

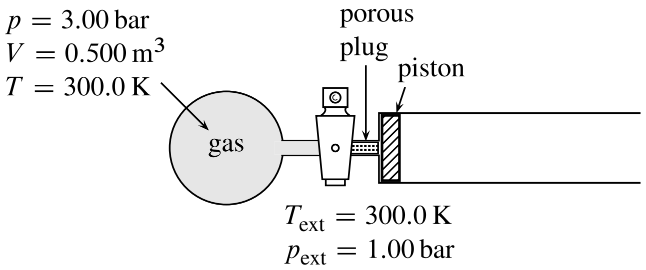

Figure 3

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 $p_1V_1 = p_2V_2$ 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:

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

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

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

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

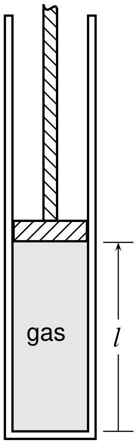

Figure 4

$\Delta\left(v_{\text{cm}}^2\right)$ 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 $w = w_{\text{lab}} - \frac{1}{2}mgl_1 = -nRT\ln 2 - \frac{1}{2}mgl_1$.

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

$$= \frac{1}{\dfrac{(2)(8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})(300\,\text{K})(\ln 2)}{(28.0\times10^{-3}\,\text{kg}\,\text{mol}^{-1})(9.81\,\text{m}\,\text{s}^{-2})(1\,\text{m})} + 1} = 7.9\times10^{-5}$$

which is 0.0079%.

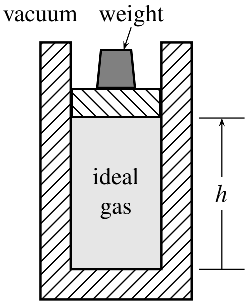

Figure 5

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: $pA_{\text{s}} - mg = 0$ (where A_{s} is the cross-section area of the cylinder). This gives $p = mg/A_{\text{s}} = mg/(V/h) = mgh/V$.

(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 $-m_2g\Delta h = -m_2g\Delta V/A_{\text{s}} = -p_2\Delta V$.

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: $V_2 = \dfrac{C_Vp_1 + nRp_2}{p_2(C_V + nR)}V_1$

(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 $V = 0.3000\,\text{dm}^3$ and $T = 300.0\,\text{K}$ and ending at $V = 0.1000\,\text{dm}^3$, find the final temperature to 0.1 K and the work.

Solution:

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

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

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

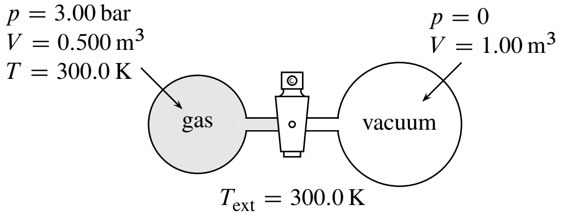

Figure 6

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 $m = 1.50$ 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:
$\Delta U = w = I^2 R_{\text{el}} t \quad \Delta\phi = I R_{\text{el}}$ (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, $\oint \text{đ}q/T$, 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: $w = -nRT \ln(V_0/V')$; $\oint \text{đ}q/T = q/T = nR \ln(V_0/V')$; $\oint \mathrm{d}S = 0$ because S is a state function. Note that $\oint \mathrm{d}S$ is greater than $\oint \text{đ}q/T$ 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 K and the other 310.00 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 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.

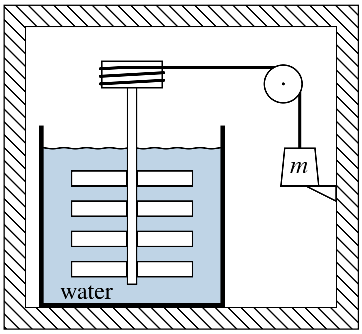

Figure 7

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:

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

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

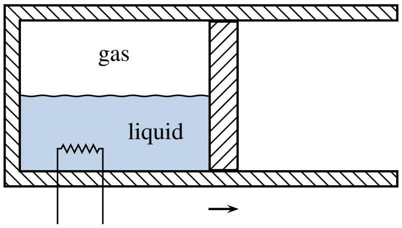

Figure 8

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

$$V_1 = 0.2200\,\mathrm{m}^3 \qquad T_1 = 300.0\,\mathrm{K} \qquad p_1 = 2.50 \times 10^5\,\mathrm{Pa}$$

A constant current $I = 0.5000\,\mathrm{A}$ is passed for 1600 s through the resistor, which has electric resistance $R_{\mathrm{el}} = 50.00\,\Omega$. 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

$$V_2 = 0.2400\,\mathrm{m}^3 \qquad T_2 = 300.0\,\mathrm{K} \qquad p_2 = 2.50 \times 10^5\,\mathrm{Pa}$$

(a) Calculate q, w, ΔU, and ΔH.

Solution:

$q = 0$ because the process is adiabatic.

$$\begin{aligned} w &= -p\Delta V + I^2 R_{\mathrm{el}}\Delta t \\ &= -(2.50 \times 10^5\,\mathrm{Pa})(0.0200\,\mathrm{m}^3) + (0.5000\,\mathrm{A})^2(50.00\,\Omega)(1600\,\mathrm{s}) \\ &= 1.50 \times 10^4\,\mathrm{J} \end{aligned}$$

$$\Delta U = q + w = 1.50 \times 10^4\,\mathrm{J}$$

$$\begin{aligned} \Delta H &= \Delta U + p\Delta V = 1.50 \times 10^4\,\mathrm{J} + (2.50 \times 10^5\,\mathrm{Pa})(0.0200\,\mathrm{m}^3) \\ &= 2.00 \times 10^4\,\mathrm{J} \end{aligned}$$

(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:

$$q = \Delta U - w = 1.50 \times 10^4\,\text{J} + (2.50 \times 10^5\,\text{Pa})(0.0200\,\text{m}^3) = 2.00 \times 10^4\,\text{J}$$

Calculate ΔS for this reversible process:

$$\Delta S = \frac{q}{T} = \frac{2.00 \times 10^4\,\text{J}}{300.0\,\text{K}} = 66.7\,\text{J}\,\text{K}^{-1}$$

(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 $-1.55 \times 10^{-8}\,\text{J}\,\text{K}^{-1}\,\text{cm}^{-2}$; thus, $(\partial S/\partial A_\text{s})_{T,p}$ is approximately $1.55 \times 10^{-8}\,\text{J}\,\text{K}^{-1}\,\text{cm}^{-2}$.

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 $p = 1$ bar. At the melting point, 161.11 K, the molar enthalpy of fusion is $\Delta_{\text{fus}}H = 4.39 \times 10^3\ \text{J mol}^{-1}$. 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 $p = 1$ 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:

$$\Delta_{\text{fus}}S = \frac{\Delta_{\text{fus}}H}{T_{\text{fus}}} = \frac{4.39 \times 10^3\ \text{J mol}^{-1}}{161.11\ \text{K}} = 27.2\ \text{J K}^{-1}\ \text{mol}^{-1}$$

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:

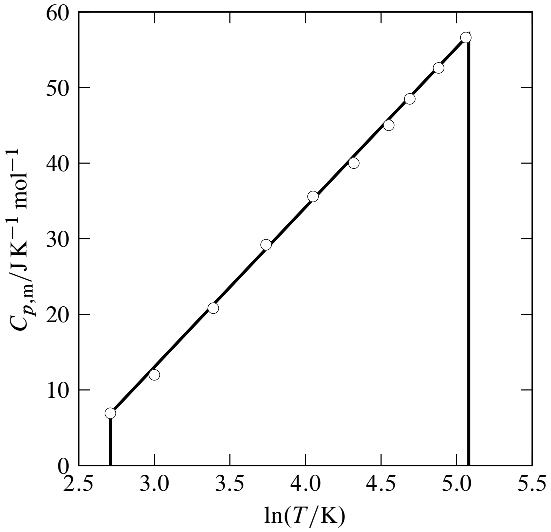

Figure 9

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

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:

$$\Delta H = n\int_{T_1}^{T_2} C_{p,\mathrm{m}}\,\mathrm{d}T = n\left[a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2)\right] = 5.001 \times 10^3\,\mathrm{J}$$

In the adiabatic enclosure, ΔH has the same value, and electrical work substitutes for heat: $w' = 5.001 \times 10^3$ 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

$$a = 44.2\,\mathrm{J\,K^{-1}\,mol^{-1}} \quad b = 8.8 \times 10^{-3}\,\mathrm{J\,K^{-2}\,mol^{-1}} \quad c = -8.6 \times 10^5\,\mathrm{J\,K\,mol^{-1}}$$

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:

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

$$= 2.27\times10^4\ \mathrm{J}$$

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

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

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

$$\begin{aligned} a' &= -521\ \mathrm{cm^3\,mol^{-1}} \\ b' &= 2.08\ \mathrm{cm^3\,K^{-1}\,mol^{-1}} \\ c' &= -2.89\times10^{-3}\ \mathrm{cm^3\,K^{-2}\,mol^{-1}} \\ d' &= 1.397\times10^{-6}\ \mathrm{cm^3\,K^{-3}\,mol^{-1}} \end{aligned}$$

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

Solution:

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

$$= 44.2\ \mathrm{J\,K^{-1}\,mol^{-1}} + (8.8\times10^{-3}\ \mathrm{J\,K^{-2}\,mol^{-1}})(400.0\ \mathrm{K}) + \frac{-8.6\times10^5\ \mathrm{J\,K\,mol^{-1}}}{(400.0\ \mathrm{K})^2}$$

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

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

Solution:

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

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

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

$$= 2(-2.89\times10^{-3}\ \mathrm{cm^3\,K^{-2}\,mol^{-1}})\left(\frac{10^{-2}\ \mathrm{m}}{1\ \mathrm{cm}}\right)^3$$

$$+ 6(1.397\times10^{-6}\ \mathrm{cm^3\,K^{-3}\,mol^{-1}})\left(\frac{10^{-2}\ \mathrm{m}}{1\ \mathrm{cm}}\right)^3(400.0\ \mathrm{K})$$

$$= (-5.78\times10^{-9} + 3.35\times10^{-9})\ \mathrm{m^3\,K^{-2}\,mol^{-1}}$$

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

$$\begin{aligned} C_{p,\text{m}} - C^{\circ}_{p,\text{m}} &\approx -pT\frac{\text{d}^2B}{\text{d}T^2} \\ &= -(100.0\,\text{bar})\left(\frac{10^5\,\text{Pa}}{1\,\text{bar}}\right)(400.0\,\text{K})(-2.43\times10^{-9}\,\text{m}^3\,\text{K}^{-2}\,\text{mol}^{-1}) \\ &= 9.7\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1} \end{aligned}$$

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

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 ($M = 26.9815\,\text{g}\,\text{mol}^{-1}$) 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:

$$\begin{aligned} \Delta H(\text{Al}) &= n\int_{T_1}^{T_2} C_{p,\text{m}}(\text{Al})\,\text{d}T = \frac{m}{M}\left[a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2)\right] \\ &= \frac{60.17\,\text{g}}{26.9815\,\text{g}\,\text{mol}^{-1}}\Big\{(20.67\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})(301.07\,\text{K} - 373.15\,\text{K}) \\ &\quad + \frac{1}{2}(0.01238\,\text{J}\,\text{K}^{-2}\,\text{mol}^{-1})\left[(301.07\,\text{K})^2 - (373.15\,\text{K})^2\right]\Big\} \\ &= -3.993\times10^3\,\text{J} \end{aligned}$$

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

$$C_p(\text{l}) = \frac{\Delta H(\text{l})}{\Delta T} = \frac{3.993\times10^3\,\text{J}}{301.07\,\text{K} - 297.95\,\text{K}} = 1.280\times10^3\,\text{J}\,\text{K}^{-1}$$

Specific heat capacity:

$$\frac{C_p(\text{l})}{m} = \frac{1.280\times10^3\,\text{J}\,\text{K}^{-1}}{500.0\,\text{g}} = 2.56\,\text{J}\,\text{K}^{-1}\,\text{g}^{-1}$$

(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

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

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:

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

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

(b) For $\mathrm{CO_2(g)}$ 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 $p = 20.0\,\mathrm{bar}$.

Solution:

$$\begin{aligned}\ln \phi &= B_p p + \frac{1}{2} C_p p^2 \\ &= (-6.67 \times 10^{-3}\,\mathrm{bar}^{-1})(20.0\,\mathrm{bar}) + \frac{1}{2}(-3.4 \times 10^{-5}\,\mathrm{bar}^{-2})(20.0\,\mathrm{bar})^2 \\ &= -0.140\end{aligned}$$

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

Table 5 Molar volume of $\mathrm{H_2O(g)}$ at 400.00 °C[a]

$p/10^5\,\mathrm{Pa}$	$V_\mathrm{m}/10^{-3}\,\mathrm{m^3\,mol^{-1}}$	$p/10^5\,\mathrm{Pa}$	$V_\mathrm{m}/10^{-3}\,\mathrm{m^3\,mol^{-1}}$
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 $\mathrm{H_2O}$ at 400.00 °C and 12 pressures.

(a) Evaluate the fugacity coefficient and fugacity of $\mathrm{H_2O(g)}$ 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

$p/10^5\,\text{Pa}$	$\left(\frac{V_\text{m}}{RT}-\frac{1}{p}\right)/10^{-8}\,\text{Pa}^{-1}$	$p/10^5\,\text{Pa}$	$\left(\frac{V_\text{m}}{RT}-\frac{1}{p}\right)/10^{-8}\,\text{Pa}^{-1}$
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

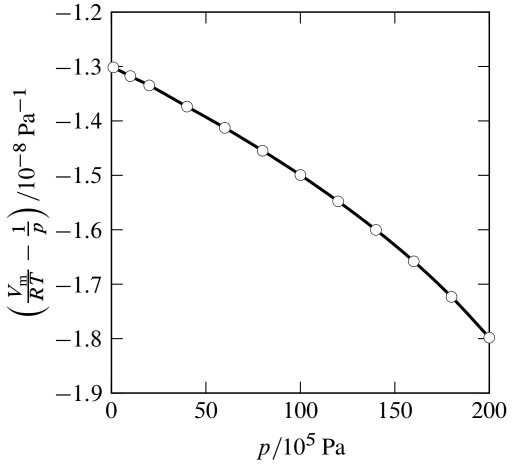

Figure 10

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

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

Use numerical integration to find the area under the curve:

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

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

(b) Show that the second virial coefficient B in the virial equation of state, $pV_\text{m} = RT(1 + B/V_\text{m} + C/V_\text{m}^2 + \cdots)$, is given by

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

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

Solution:

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

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

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

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

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 $T^{\text{g}} = T^{\text{l}}$, $\mu^{\text{g}} = \mu^{\text{l}}$, and $p^{\text{l}} = p^{\text{g}} + 2\gamma/r$, where γ is the surface tension.

Solution:

Internal energy change without constraints (Eq. 8.1.15):

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

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

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

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

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

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

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

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

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

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:

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

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

(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 $S^{\circ}_{\text{m}}(\text{l})$ to $S_{\text{m}}(\text{l})$ at the saturation vapor pressure.

Solution:

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

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

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

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

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 $\text{d}p/\text{d}T$ 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:

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

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

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

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 $\Delta_{\mathrm{vap}}H^\circ$ and $\Delta_{\mathrm{vap}}H$ 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 $\Delta_{\mathrm{vap}}H = 40.67\,\mathrm{kJ\,mol^{-1}}$. Estimate the value of $\Delta_{\mathrm{vap}}H^\circ$ 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:

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

Solution:

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

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

(c) Would you expect the values of $\Delta_{\mathrm{fus}}H$ and $\Delta_{\mathrm{fus}}H^\circ$ 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 $\Delta_{\mathrm{vap}}H = 40.67\,\mathrm{kJ\,mol^{-1}}$. The molar heat capacity of the liquid at temperatures close to this value is given by

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

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

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

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 $n_{\mathrm{B}}/n_{\mathrm{A}}$ in Eqs. 9.1.9 and 9.1.12 and solve for x_{B}:

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

Find x_{A}:

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

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

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

Solution:

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

Make the following substitutions:

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

The result is

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

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

x_{B}	$[\Delta V(\mathrm{mix})/n]/\mathrm{cm^3\,mol^{-1}}$	x_{B}	$[\Delta V(\mathrm{mix})/n]/\mathrm{cm^3\,mol^{-1}}$
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 $V^*_{\mathrm{A}} = 125.31\,\mathrm{cm^3\,mol^{-1}}$ and $V^*_{\mathrm{B}} =$

$157.85\,\mathrm{cm^3\,mol^{-1}}$. 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.

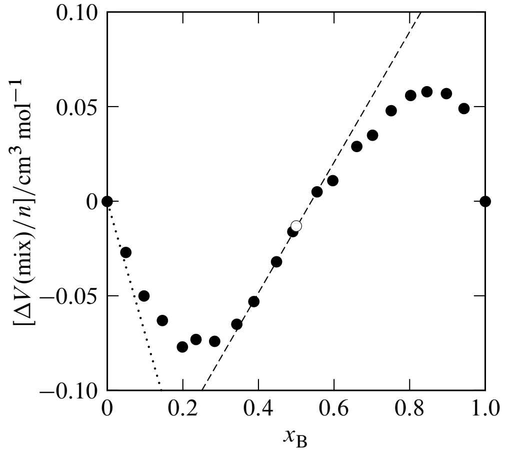

Figure 11 Molar volume of mixing as a function of x_B.

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

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

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

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 $-0.70\,\mathrm{cm^3\,mol^{-1}}$; this is also the value of the intercept at $x_B{=}1$. Therefore

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

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 $T^{\mathrm{g}} = T^{\mathrm{l}}$, $\mu_i^{\mathrm{g}} = \mu_i^{\mathrm{l}}$ (for each species i that can equilibrate between the two phases), and $p^{\mathrm{l}} = p^{\mathrm{g}} + 2\gamma/r$, 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

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

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]

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

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:

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

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

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

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	$\ln\gamma_B = -\int_{x_A=0}^{x_A} \frac{x_A}{x_B}\,d\ln\gamma_A$	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].

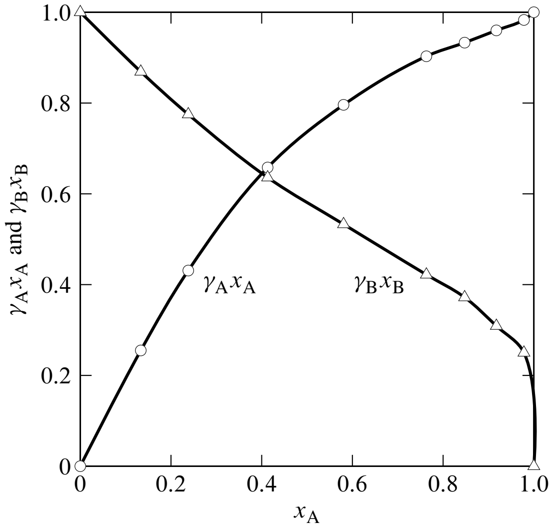

Figure 12 Results for Problem 9.8(b).

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

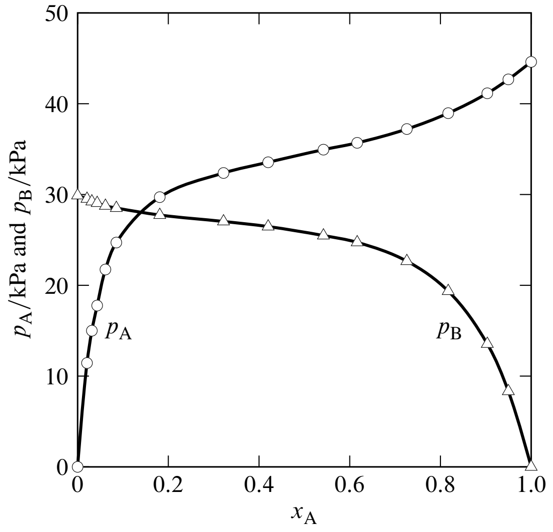

Figure 13 Results for Problem 9.9.

(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,

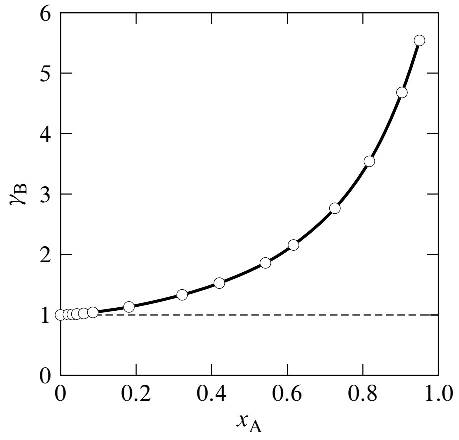

Figure 14 Activity coefficient of benzene in liquid methanol–benzene mixtures.

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 $k_{H,A} \approx 680\,\text{kPa}$.

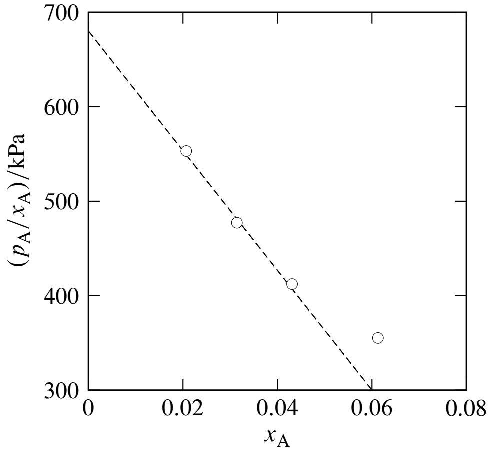

Figure 15 Estimate of the Henry's law constant of methanol in benzene.

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

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

where $\mu_{m,B}^{\text{ref}}$ 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 $d\mu_A = -(n_B/n_A)\, d\mu_B$ to obtain an expression for $\mu_A - \mu_A^*$ as a function of m_B in this solution.