7.10: Chapter 7 Problems

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

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

$$\alpha = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p \quad \kappa_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_T \tag{7.10.1}$$

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

$$\alpha = 1/T \quad \kappa_T = 1/p \tag{7.10.2}$$

7.3 For a gas with the simple equation of state

$$V_m = \frac{RT}{p} + B \tag{7.10.3}$$

(Eq. 2.2.8), where B is the second virial coefficient (a function of T), find expressions for α, κ_T, and $(\partial U_m/\partial V)_T$ in terms of dB/dT and other state functions.

7.4 Show that when the virial equation $pV_m = RT\left(1 + B_p p + C_p p^2 + \cdots\right)$ (Eq. 2.2.3) adequately represents the equation of state of a real gas, the Joule-Thomson coefficient is given by

$$\mu_{JT} = \frac{RT^2\left[\,dB_p/dT + (dC_p/dT)\,p + \cdots\right]}{C_{p,\,m}} \tag{7.10.4}$$

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

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

$$\frac{p - \alpha T/\kappa_T}{C_V} \tag{7.10.5}$$

7.6 $p - V - T$ data for several organic liquids were measured by Gibson and Loeffler. [11] The following formulas describe the results for aniline.
Molar volume as a function of temperature at $p = 1$ bar $(298 - 358\text{ K})$:

$$V_m = a + bT + cT^2 + dT^3 \tag{7.10.6}$$

where the parameters have the values

$$\begin{aligned}
a &= 69.287\text{ cm}^3\text{ mol}^{-1} & c &= -1.0443 \times 10^{-4}\text{ cm}^3\text{ K}^{-2}\text{ mol}^{-1}\\
b &= 0.08852\text{ cm}^3\text{ K}^{-1}\text{ mol}^{-1} & d &= 1.940 \times 10^{-7}\text{ cm}^3\text{ K}^{-3}\text{ mol}^{-1}
\end{aligned} \tag{7.10.7}$$

Molar volume as a function of pressure at $T = 298.15$ K (1-1000 bar):

$$V_m = e - f\ln(g + p/\text{ bar}) \tag{7.10.8}$$

where the parameter values are

$$e = 156.812\text{ cm}^3\text{ mol}^{-1} \quad f = 8.5834\text{ cm}^3\text{ mol}^{-1} \quad g = 2006.6 \tag{7.10.9}$$

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

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

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

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

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

(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 1.2×10^{-3} K^{-1} at $25°$C and 1 bar. (Use information from Fig. 7.2 on page 168.)

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

(a) Show that the van der Waals equation of state $\left(p + a/V_m^2\right)\left(V_m - b\right) = RT$ (where a and b are constants) is of this form.

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

7.10 Suppose that the molar heat capacity at constant pressure of a substance has a temperature dependence given by $C_{p,\,m} = a + bT + cT^2$, 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.

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

$$C_{p,\,m} = a + bT \tag{7.10.10}$$

where the constants have the values

$$a = 20.67\text{ J K}^{-1}\text{ mol}^{-1} \quad b = 0.01238\text{JK}^{-2}\text{ mol}^{-1} \tag{7.10.11}$$

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.

7.12 The temperature dependence of the standard molar heat capacity of gaseous carbon dioxide in the temperature range 298 K $- 2000$ K is given by

$$C_{p,\,m}^\circ = a + bT + \frac{c}{T^2} \tag{7.10.12}$$

where the constants have the values

$$a = 44.2\text{JK}^{-1}\text{ mol}^{-1} \quad b = 8.8 \times 10^{-3}\text{ J K}^{-2}\text{ mol}^{-1} \quad c = -8.6 \times 10^5\text{ J K mol}^{-1} \tag{7.10.13}$$

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 $C_{p,\,m}$ is practically equal to $C_{p,\,m}^\circ$.

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 $300\ \mathrm{K} - 800\ \mathrm{K}$ the dependence of B on temperature is given by

$$B = a' + b'T + c'T^2 + d'T^3 \tag{7.10.14}$$

where the constants have the values

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

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

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

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 $\left(M = 26.9815\ \mathrm{g\ mol^{-1}}\right)$ 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.

(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

$$\frac{\int_{T_1}^{T_2} \left(C_p/m \right) \mathrm{d}T}{T_2 - T_1} \tag{7.10.15}$$

7.15 Suppose a gas has the virial equation of state $pV_\mathrm{m} = RT\left(1 + B_p p + C_p p^2\right)$, 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.
(b) For $CO_2(\mathrm{g})$ at 0.00°C, the virial coefficients have the values $B_p = -6.67 \times 10^{-3}\ \mathrm{bar^{-1}}$ and $C_p = -3.4 \times 10^{-5}\mathrm{bar^{-2}}$. Evaluate the fugacity f at 0.00°C and $p = 20.0$ bar.

7.16 Table 7.6 on the next page lists values of the molar volume of gaseous H_2O at 400.00°C and 12 pressures.
(a) Evaluate the fugacity coefficient and fugacity of $H_2O(\mathrm{g})$ at 400.00°C and 200 bar.
(b) Show that the second virial coefficient B in the virial equation of state, $pV_\mathrm{m} = RT(1 + B/V_\mathrm{m} + C/V_\mathrm{m}^2 + \cdots)$, is given by

$$B = RT \lim_{p \to 0} \left(\frac{V_\mathrm{m}}{RT} - \frac{1}{p} \right) \tag{7.10.16}$$

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

Table 7.6 Molar volume of $H_2O(\mathrm{g})$ 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]