# 4

# Fundamental Equations of Thermodynamics

4.1 One mole of nitrogen is allowed to expand from 0.5 to 10 L. Calculate the change in entropy using (a) the ideal gas law and (b) the van der Waals equation.

SOLUTION

(a) $$\Delta\bar{S} = R\ln(\bar{V}_2/\bar{V}_1)$$
$$= (8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})\ln(10/0.5)$$
$$= 24.91\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

(b) $$\Delta\bar{S} = R\ln\left[(\bar{V}_2 - b)/(\bar{V}_1 - b)\right]$$
$$= (8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})\ln\left[\frac{(10 - 0.039)}{(0.5 - 0.039)}\right]$$
$$= 25.55\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

4.2 Derive the relation for $\bar{C}_P - \bar{C}_V$ for a gas that follows van der Waals' equation.

SOLUTION

$$\bar{C}_P - \bar{C}_V = T\bar{V}\alpha^2/\kappa = -T\left(\frac{\partial\bar{V}}{\partial T}\right)_P^2\left(\frac{\partial P}{\partial\bar{V}}\right)_T$$

The van der Waals equation can be written in the following form:

$$T = \frac{P\bar{V}}{R} - \frac{bP}{R} + \frac{a}{\bar{V}R} - \frac{ab}{R\bar{V}^2}$$

$$\left(\frac{\partial T}{\partial\bar{V}}\right)_P = \frac{P}{R} - \frac{a}{R\bar{V}^2} + \frac{2ab}{R\bar{V}^3}$$

$$\alpha^{-1} = \bar{V}\left(\frac{\partial T}{\partial \bar{V}}\right)_P = \frac{P\bar{V}}{R} - \frac{a}{R\bar{V}} + \frac{2ab}{R\bar{V}^2}$$

Eliminating $P$ with the van der Waals equation yields

$$\alpha^{1} = \frac{T\bar{V}}{\bar{V} - b} - \frac{2a}{R\bar{V}^2}(\bar{V} - b)$$

$\kappa$ is calculated from

$$\left(\frac{\partial P}{\partial \bar{V}}\right)_T = -\frac{RT}{(\bar{V} - b)^2} + \frac{2a}{\bar{V}^3}$$

$$\bar{C}_P - \bar{C}_V = \frac{R}{1 - \frac{2a}{RT}\frac{(\bar{V} - b)^2}{\bar{V}^3}}$$

4.3 Earlier we derived the expression for the entropy of an ideal gas as a function of $T$ and $P$. Now that we have the Maxwell relations, derive the expression for d$S$ for any fluid.

SOLUTION

$$\begin{aligned} \mathrm{d}S &= (\partial S/\partial T)_P\,\mathrm{d}T + (\partial S/\partial P)_T\,\mathrm{d}P \\ &= (C_P/T)\,\mathrm{d}T - (\partial V/\partial T)_P\,\mathrm{d}P \\ &= (C_P/T)\,\mathrm{d}T - \alpha V\mathrm{d}P \end{aligned}$$

4.4 What is the change in molar entropy of liquid benzene at 25 °C when the pressure is raised from 1 to 1000 bar? The coefficient of thermal expansion $\alpha$ is $1.237 \times 10^{-3}$ $\mathrm{K}^{-1}$, the density is $0.879\ \mathrm{g\ cm^{-3}}$, and the molar mass is $78.11\ \mathrm{g\ mol^{-1}}$.

SOLUTION

Equation 4.50 can be written as

$$\left(\frac{\Delta\bar{S}}{\Delta P}\right)_T = -\left(\frac{\partial \bar{V}}{\partial T}\right)_P = -\bar{V}\alpha$$

where $\alpha$ is defined by equation 1.36.

$$\begin{aligned} \Delta\bar{S} &= -\bar{V}\alpha\Delta P \\ &= -\frac{78.11\ \mathrm{g\ mol^{-1}}}{0.879\ \mathrm{g\ cm^{-3}}}(10^{-2}\ \mathrm{m\ cm^{-1}})^3\,(1.237 \times 10^{-3}\ \mathrm{K^{-1}})(1000\ \mathrm{bar}) \\ &= -10.99\ \mathrm{J\ K^{-1}\ mol^{-1}} \end{aligned}$$

4.5 Derive the expression for $\bar{C}_P - \bar{C}_V$ for a gas with the following equation of state.

$$[P + (a/\bar{V}^2)]\bar{V} = RT$$

SOLUTION

$$\bar{C}_P - \bar{C}_V = T\bar{V}\alpha^2/\kappa = -T\left(\frac{\partial \bar{V}}{\partial T}\right)_P^2\left(\frac{\partial P}{\partial \bar{V}}\right)_T$$

$$P = \frac{RT}{\bar{V}} - \frac{a}{\bar{V}^2}$$

$$\left(\frac{\partial P}{\partial \bar{V}}\right)_T = -\frac{RT}{\bar{V}^2} + \frac{2a}{\bar{V}^3}$$

$$\left(\frac{\partial \bar{V}}{\partial T}\right)_P = \frac{R\bar{V}}{2P\bar{V} - RT}$$

$$\bar{C}_P - \bar{C}_V = R\left(1 - \frac{2a}{\bar{V}RT}\right)^{-1}$$

4.6 What is the difference between the molar heat capacity of iron at constant pressure and constant volume at 25 °C? Given: $\alpha = 35.1 \times 10^{-6}\ \text{K}^{-1}$, $\kappa = 0.52 \times 10^{-6}\ \text{bar}^{-1}$, and the density is 7.86 g cm$^{-3}$.

SOLUTION

$$\bar{V} = \frac{55.847\ \text{g mol}^{-1}}{7.86\ \text{g cm}^{-3}} = \frac{7.11\ \text{cm}^3\ \text{mol}^{-1}}{(10^2\ \text{cm m}^{-1})^3} = 7.11 \times 10^{-6}\ \text{m}^3\ \text{mol}^{-}$$

$$\bar{C}_P - \bar{C}_V = \alpha^2 T\bar{V}/\kappa$$

$$= \frac{(35.1 \times 10^{-6}\ \text{K}^{-1})^2(298\ \text{K})(7.11 \times 10^{-6}\ \text{m}^3\ \text{mol}^{-1})(10^5\ \text{Pa bar}^{-1})}{(0.52 \times 10^{-6}\ \text{bar}^{-1})}$$

$$= 0.51\ \text{J K}^{-1}\ \text{mol}^{-1}$$

4.7 In equation 1.27 we saw that the compressibility factor of a van der Waals gas can be written as

$$Z = 1 + \frac{1}{RT}\left(b - \frac{a}{RT}\right)P + $$

where terms in $P^2$ and higher are negligible. (a) To this degree of approximation, derive the expression for $(\partial \bar{H}/\partial P)_T$ for a van der Waals gas. (b) Calculate $(\partial \bar{H}/\partial P)_T$

for $CO_2(g)$ in J $bar^{-1}$ $mol^{-1}$ at 298 K. Given: $a = 3.640$ $L^2$ bar $mol^{-2}$ and $b = 0.04267$ L $mol^{-1}$.

SOLUTION

(a) $(\partial\bar{H}/\partial P)_T = \bar{V} - T(\partial\bar{V}/\partial T)_P$

$$P\bar{V} \cong RT + (b - a/RT)P$$

$$\bar{V} \cong RT/P + b - a/RT$$

$$(\partial\bar{V}/\partial T)_P \cong R/P + a/RT^2$$

$$(\partial\bar{H}/\partial P)_T \cong \bar{V} - RT/P - a/RT$$

$$\cong b - 2a/RT$$

(b) $$(\partial\bar{H}/\partial P)_T \cong 0.04267 \text{ L mol}^{-1} - \frac{2(3.64 \text{ L}^2 \text{ bar mol}^{-2})}{(0.08314 \text{ L bar K}^{-1} \text{ mol}^{-1})(298 \text{ K})}$$

$$\cong -0.251 \text{ L mol}^{-1}$$

$$\cong \frac{-0.251 \text{ L mol}^{-1}}{0.01 \text{ L bar J}^{-1}} = -25 \text{ J bar}^{-1} \text{ mol}^{-1}$$

Since $R = 8.314$ J $K^{-1}$ $mol^{-1}$ = 0.08314 L bar $K^{-1}$ $mol^{-1}$
Therefore, 1 J = 0.01 L bar or 0.01 L bar $J^{-1}$ = 1.

4.8 Derive the expression for $(\partial U/\partial V)_T$ (the internal pressure) for a gas following the virial equation with $Z = 1 + B/\bar{V}$.

SOLUTION

$$P = \frac{RT}{\bar{V}} + \frac{BRT}{\bar{V}^2}$$

$$\left(\frac{\partial P}{\partial T}\right)_{\bar{V}} = \frac{R}{\bar{V}} + \frac{BR}{\bar{V}^2} + \frac{RT}{\bar{V}^2}\left(\frac{\partial B}{\partial T}\right)_{\bar{V}}$$

$$(\partial\bar{U}/\partial\bar{V})_T = T\left(\frac{\partial P}{\partial T}\right)_{\bar{V}} - P$$

$$= \frac{RT^2}{\bar{V}^2}\left(\frac{\partial B}{\partial T}\right)_{\bar{V}}$$

4.9 In Section 3.9 we calculated that the enthalpy of freezing water at - 10 °C is -5619 J $mol^{-1}$, and we calculated that the entropy of freezing water is - 20.54 J $K^{-1}$ $mol^{-1}$ at - 10 °C. What is the Gibbs energy of freezing water at - 10 °C?

SOLUTION

$$\begin{aligned}\Delta G^{o} &= \Delta H^{o} - T\Delta S^{o}\\ &= -\,5619\ \mathrm{J\ mol^{-1}} - (263.15\ \mathrm{K})(-\,20.54\ \mathrm{J\ K^{-1}\ mol^{-1}})\\ &= -\,213.9\ \mathrm{J\ mol^{-1}}\end{aligned}$$

This is negative, as expected for a spontaneous process at constant $T$ and $P$. If the water was at -10 °C in an isolated system, the temperature would rise, but part of the water would freeze. In this case the increase in order due to the crystallization of part of the ice is more than compensated for by the increase in disorder of the system as a whole by the rise in temperature.

4.10 (a) Integrate the Gibbs-Helmholtz equation to obtain an expression for $\Delta G_2$ at temperature $T_2$ in terms of $\Delta G_1$ at $T_1$, assuming $\Delta H$ is independent of temperature. (b) Obtain an expression for $\Delta G_2$ using the more accurate approximation that $\Delta H = \Delta H_1 + (T - T_1)\Delta C_P$ where $T_1$ is an arbitrary reference temperature.

SOLUTION

(a) Using equation 4.62

$$\int_{\Delta G_1/T}^{\Delta G_2/T} \mathrm{d}(\Delta G/T) = -\int_{T_1}^{T_2} (\Delta H/T^2)\mathrm{d}T$$

$$\frac{\Delta G_2}{T_2}\ \frac{\Delta G_1}{T_1} = -\,\Delta H\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\Delta G_2 = \Delta G_1 T_2/T_1 + \Delta H[1 - (T_2/T_1)]$$

(b)

$$\int \mathrm{d}(\Delta G/T) = -\int \frac{\Delta H_1}{T^2}\,\mathrm{d}T + \Delta C_P \int \frac{(T - T_1)}{T^2}\,\mathrm{d}T$$

$$\frac{\Delta G_2}{T_2} - \frac{\Delta G_1}{T_1} = -\,\Delta H\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + \Delta C_P \ln\left(\frac{T_2}{T_1}\right) - T_1\Delta C_P\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\Delta G_2 = \Delta G_1 T_2/T_1 + (\Delta H_1 + T_1\Delta C_P)\left(1 - \frac{T_2}{T_1}\right) + T_2\Delta C_P \ln\left(\frac{T_2}{T_1}\right)$$

4.11 When a liquid is compressed its Gibbs energy is increased. To a first approximation the increase in molar Gibbs energy can be calculated using $(\partial\bar{G}/\partial P)_T = \bar{V}$, assuming a constant molar volume. What is the change in the molar Gibbs energy for liquid water when it is compressed to 1000 bar?

SOLUTION

$$\int_{\bar{G}_1}^{\bar{G}_2} \mathrm{d}\bar{G} = \int_{P_1}^{P_2} \bar{V}\mathrm{d}P$$

$$\begin{aligned}\Delta\bar{G} = \bar{V}\Delta P &= (18 \times 10^{-6}\ \mathrm{m^{-3}\ mol^{-1}})(999\ \mathrm{bar})(10^{5}\ \mathrm{Pa\ bar^{-1}})\\ &= 1.8\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

4.12 An ideal gas is allowed to expand reversibly and isothermally (25 °C) from a pressure of 1 bar to a pressure of 0.1 bar. (a) What is the change in molar Gibbs energy? (b) What would be the change in molar Gibbs energy if the process occurred irreversibly?

SOLUTION

(a) $$\left(\frac{\partial \bar{G}}{\partial P}\right)_T = \bar{V} = \frac{RT}{P}$$

$$\Delta\bar{G} = RT \ln \frac{P_2}{P_1} = (8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K}) \ln 0.1$$
$$= - 5708 \text{ J mol}^{-1}$$

(b) $\Delta\bar{G} = - 5708 \text{ J mol}^{-1}$ because $G$ is a state function and depends only on the initial state and the final state.

4.13 The standard entropy of $O_2$(g) at 1 bar is listed in Appendix C.2 as 205.138 J K$^{-1}$ mol$^{-1}$ at 298 K, and the standard Gibbs energy of formation is listed as 0 kJ mol$^{-1}$ Assuming $O_2$ is an ideal gas, what will be the molar entropy and molar Gibbs energy of formation at 100 bar?

SOLUTION

$$\bar{S} = \bar{S}^o - R \ln \frac{P}{P^o} = 205.137 - 8.314 \ln 100 = 166.848 \text{ J K}^{-1} \text{ mol}^{-1}$$
$$\Delta_f G^o = 0 + RT \ln (P/P^o) = (8.314 \times 10^{-3})(298) \ln 100 = 11.41 \text{ kJ mol}^{-1}$$

4.14 Helium is compressed isothermally and reversibly at 100 °C from a pressure of 2 to 10 bar. Calculate (a) $q$ per mole, (b) $w$ per mole, (c) $\Delta\bar{G}$, (d) $\Delta\bar{A}$, (e) $\Delta\bar{H}$, (f) $\Delta\bar{U}$, and (g) $\Delta\bar{S}$, assuming helium is an ideal gas.

SOLUTION

(a) $$\Delta\bar{U} = q + w = 0$$
$$q = - w = - RT \ln \frac{P_2}{P_1}$$
$$= - (8.314 \text{ J K}^{-1} \text{ mol}^{-1})(373.15 \text{ K}) \ln \frac{10 \text{ bar}}{2 \text{ bar}} = - 4993 \text{ J mol}^{-1}$$

(b) $$w = - q = 4993 \text{ J mol}^{-1}$$

(c) $$\Delta\bar{G} = \int_{P_1}^{P_2} \bar{V} dP = RT \ln \frac{P_2}{P_1} = 4993 \text{ J mol}^{-1}$$

(d) $$\Delta\bar{A} = w_{max} = 4993 \text{ J mol}^{-1}$$

(e) $$\Delta\bar{H} = \Delta\bar{U} + \Delta (P\bar{V}) = 0$$

(f) $\Delta \bar{U} = 0$

(g) $\Delta \bar{S} = \Delta \bar{H} - \frac{\Delta \bar{G}}{T} = 0 - \frac{4933 \text{ J mol}^{-1}}{373.15 \text{ K}} = -13.38 \text{ J K}^{-1} \text{ mol}^{-1}$

4.15 Toluene is vaporized at its boiling point, 111 °C. The heat of vaporization at this temperature is 361.9 J $g^{-1}$. For the vaporization of toluene, calculate (a) $w$ per mole, (b) $q$ per mole, (c) $\Delta \bar{H}$, (d) $\Delta \bar{U}$, (e) $\Delta \bar{G}$, and (f) $\Delta \bar{S}$.

SOLUTION

(a) Assuming that toluene vapor is an ideal gas and that the volume of the liquid is negligible, the work on the toluene is

$$w = -P\Delta \bar{V} = -RT = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(384 \text{ K})$$
$$= -3193 \text{ J mol}^{-1}$$

(b) $q_p = \Delta \bar{H} = (361.9 \text{ J g}^{-1})(92.13 \text{ g mol}^{-1}) = 33{,}340 \text{ J mol}^{-1}$.

(c) $\Delta \bar{H} = 33{,}340 \text{ J mol}^{-1}$

(d) $\Delta \bar{U} = q + w = 33{,}340 - 3193 = 30{,}147 \text{ J mol}^{-1}$

(e) $\Delta \bar{G} = 0$ because the evaporation is reversible at the boiling point and 1 atm.

(f) $\Delta \bar{S} = \frac{q_{\text{rev}}}{T} = \frac{33\,340 \text{ J mol}^{-1}}{384 \text{ K}} = 86.8 \text{ J K}^{-1} \text{ mol}^{-1}$

4.16 If the Gibbs energy varies with temperature according to

$$G/T = a + b/T + c/T^2$$

How will the enthalpy and entropy vary with temperature? Check that these three equations are consistent.

SOLUTION

$$G = aT + b + c/T$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S = a - c/T^2$$

$$S = -a + c/T^2$$

$$\left[\frac{\partial (G/T)}{\partial T}\right]_P = -H/T^2 = -b/T^2 - 2c/T^3$$

$$H = b + 2c/T$$

$$G = H - TS = aT + b + c/T$$

4.17 Calculate the change in molar Gibbs energy $\bar{G}$ when supercooled water at -3 °C freezes at constant $T$ and $P$. The density of ice at -3 °C is $0.917 \times 10^3$ kg m$^{-3}$, and its vapor pressure is 475 Pa. The density of supercooled water at -3 °C is 0.9996 kg m$^{-3}$ and its vapor pressure is 489 Pa.

SOLUTION

$$\bar{V}_s = \frac{(18.015 \times 10^{-3}\ \text{kg mol}^{-1})}{(0.917 \times 10^3\ \text{kg m}^{-3})}$$
$$= 1.965 \times 10^{-5}\ \text{m}^3\ \text{mol}^{-1}$$
$$\bar{V}_l = \frac{(18.015 \times 10^{-3}\ \text{kg mol}^{-1})}{(0.9996 \times 10^3\ \text{kg m}^{-3})}$$
$$= 1.802 \times 10^{-5}\ \text{m}^3\ \text{mol}^{-1}$$

Since the actual process is irreversible, the calculation uses the following reversible isothermal path:

$H_2O(l, 270.15\ \text{K}, 10^5\ \text{Pa})$ $H_2O(s, 270.15\ \text{K}, 10^5\ \text{Pa})$

$\downarrow \Delta\bar{G}_1 = \int_{10^5}^{489} \bar{V}_l\, dP = -1.7\ \text{J mol}^{-1}$ $\uparrow \Delta\bar{G}_5 = \int_{475}^{10^5} \bar{V}_s\, dP = -1.9\ \text{J mol}^{-1}$

$H_2O(l, 270.15\ \text{K}, 489\ \text{Pa})$ $H_2O(s, 270.15\ \text{K}, 475\ \text{Pa})$

$\downarrow \Delta\bar{G}_2 = 0$ $\uparrow \Delta\bar{G}_4 = 0$

$H_2O(g, 270.15\ \text{K}, 489\ \text{Pa}) = H_2O(g, 270.15\ \text{K}, 475\ \text{Pa})$

$$\Delta\bar{G}_3 = RT \ln (475/489) = -65.2\ \text{J mol}^{-1}$$

$$\Delta\bar{G} = \Delta\bar{G}_1 + \Delta\bar{G}_2 + \Delta\bar{G}_3 + \Delta\bar{G}_4 + \Delta\bar{G}_5$$
$$= -1.7 + 0 - 65.2 + 1.9$$
$$= -65.0\ \text{J mol}^{-1}$$

4.18 Calculate the molar Gibbs energy of fusion when supercooled water at -3 °C freezes at constant $T$ and $P$. The molar enthalpy of fusion of ice is 6000 J mol$^{-1}$ at 0 °C. The heat capacities of water and ice in the vicinity of the freezing point are 75.3 and 38 J K$^{-1}$ mol$^{-1}$, respectively.

SOLUTION

Since the actual process in irreversible, the calculation uses the following reversible isobaric path.

$$\begin{tikzcd}
H_2O(l, 273.15\text{ K}, 1\text{ bar}) \arrow[r] & H_2O(s, 273.15, 1\text{ bar}) \arrow[d] \\
H_2O(l, 270.15\text{ K}, 1\text{ bar}) \arrow[u] \arrow[r] & H_2O(s, 270.15, 1\text{ bar})
\end{tikzcd}$$

To obtain $\Delta_{fus}G$ (270.15 K), we have to calculate $\Delta_{fus}H$ (270.15 K) and $\Delta_{fus}S$ (270.15 K) separately and use
$\Delta_{fus}G = \Delta_{fus}H - 270.15\,\Delta_{fus}S$.

$$\Delta_{fus}H(270.15\text{ K}) = \Delta_{fus}H(273.15\text{ K}) + \int_{273.15}^{270.15} \Delta_{fus}C_P\, dT$$

$$= -6000 + (38 - 75.3)(-3)$$

$$= -5888\text{ J mol}^{-1}$$

$$\Delta_{fus}S(270.15\text{ K}) = -6000/273.15 + \Delta_{fus}C_P \ln(270.15/273.15)$$

$$= -21.56\text{ J mol}^{-1}$$

$$\Delta_{fus}G = \Delta_{fus}H - T\Delta_{fus}S = -5888 - (270.15)(-21.56)$$

$$= -63.6\text{ J mol}^{-1}$$

4.19 At 298.15 K and a particular pressure, a real gas has a fugacity coefficient $\phi$ of 2.00. At this pressure, what is the difference in the chemical potential of this real gas and an ideal gas?

SOLUTION

$$\mu(\text{ideal}) = \mu^o + RT\ln(P/P^o)$$

$$\mu(\text{real}) = \mu^o + RT\ln(\phi P/P^o)$$

$$\mu(\text{real}) - \mu(\text{ideal}) = RT\ln\phi = (8.314\text{ J K}^{-1}\text{ mol}^{-1})(298.15\text{ K})\ln 2$$

$$= 1.72\text{ kJ mol}^{-1}$$

4.20 As shown in Example 4.7, the fugacity of a van der Waals gas is given by a fairly simple expression if only the second virial coefficient is used. To this degree of approximation derive the expressions for $\bar{G}$, $\bar{S}$, $\bar{A}$, $\bar{U}$, $\bar{H}$, and $\bar{V}$.

SOLUTION

$$\bar{G} = \bar{G}^o + RT\ln\left(\frac{f}{P^o}\right) = \bar{G}^o + RT\ln\left(\frac{P}{P^o}\right) + \left(b - \frac{a}{RT}\right)P$$

$$\bar{S} = -\left(\frac{\partial \bar{G}}{\partial T}\right)_P = \bar{S}^o - R\ln\left(\frac{P}{P^o}\right) + \frac{aP}{RT^2}$$

$$\bar{A} = \bar{G} - P\left(\frac{\partial \bar{G}}{\partial P}\right)_T = \bar{G}^o + RT\ln\left(\frac{P}{P^o}\right) - RT$$

$$\bar{U} = \bar{G} - T\left(\frac{\partial \bar{G}}{\partial T}\right)_P - P\left(\frac{\partial \bar{G}}{\partial P}\right)_T = \bar{G}^o + T\bar{S}^o - RT - \frac{aP}{RT}$$

$$= \bar{H}^o - RT - \frac{aP}{RT} = \bar{U}^o - \frac{aP}{RT}$$

Since the second term is small, we can use the ideal gas law to obtain

$$\bar{U} = \bar{U}^o - (a/\bar{V})$$

Note that this agrees with the earlier result (Section 4.4) that

$$\left(\partial\bar{U}/\partial\bar{V}\right)_T = a/\bar{V}^2$$

$$\bar{H} = \bar{U} + P\bar{V} = \bar{U}^o + \frac{aP}{RT} + RT + bP - \frac{aP}{RT}$$

$$= \bar{H}^o + (b - \frac{2a}{RT})P$$

$$\bar{V} = \left(\frac{\partial \bar{G}}{\partial P}\right)_T = \frac{RT}{P} + b - \frac{a}{RT}$$

4.21 Using the relation derived in Example 4.7, calculate the fugacity of $H_2(g)$ at 100 bar at 298 K.

SOLUTION

$$f = P\exp\left[\left(b - \frac{a}{RT}\right)\frac{P}{RT}\right]$$

$$= (100\text{ bar})\exp\left\{[0.02661 - 0.2476/(0.08314)(298)]100/(0.08314)(298)\right\}$$

$$= 106.9\text{ bar}$$

4.22 Show that if the compressibility factor is given by $Z = 1 + BP/RT$ the fugacity is given by $f = Pe^{Z-1}$. If $Z$ is not very different from unity, $e^{Z-1} = 1 + (Z - 1) + \cdots \equiv Z$ so that $f = PZ$. Using this approximation, what is the fugacity of $H_2(g)$ at 50 bar and 298 K using its van der Waals constants?

SOLUTION

Substituting this expression for the compressibility factor in equation 4.78,

$$\frac{f}{P} = \exp\left[\int_0^P (B/RT)\mathrm{d}P\right]$$

$$= \exp(BP/RT)$$

$$= \exp(Z - 1)$$

If $Z$ is not very different from unity, $f = PZ$.

For $H_2(g)$ at 50 bar and 298 K,

$$Z = 1 + (b - a/RT)\,P/RT$$

$$= 1 + \left(0.02661\text{ L mol}^{-1} - \frac{0.02476\text{ L}^2\text{ bar mol}^{-2}}{0.08314\text{ L bar K}^{-1}\text{ mol}^{-1}}\right)\frac{50\text{ bar}}{(0.08314)(298)}$$

$$= 1.0335$$

$$f = (50\text{ bar})(1.0335) = 5.17\text{ bar}$$

*4.23 Calculate the partial molar volume of zinc chloride in 1-molal $ZnCl_2$ solution using the following data.

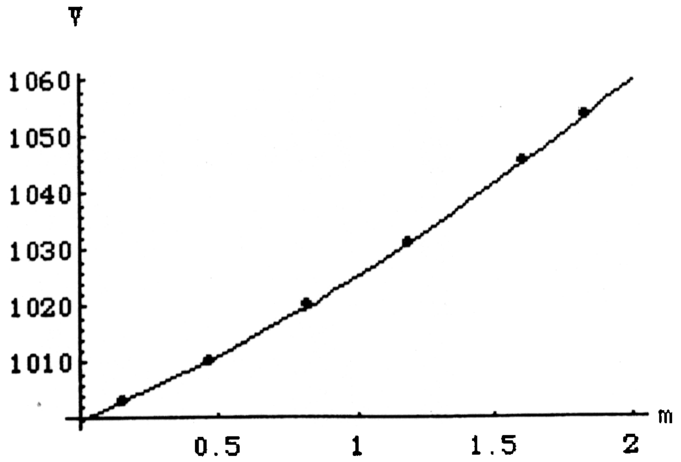
| % by weight of $ZnCl_2$ | 2 | 6 | 10 | 14 | 18 |
|---|---|---|---|---|---|
| Density/g cm$^{-3}$ | 1.0167 | 1.0532 | 1.0891 | 1.1275 | 1.1665 |

SOLUTION

Consider a kilogram of solution that is 2% by weight $ZnCl_2$, so that it contains 20 g of $ZnCl_2$ and 980 g of $H_2O$. Since there are (20 g/136.28 g mol$^{-1}$) mol for 980 g $H_2O$, the molality is given by $m(ZnCl_2) = 20 \times 1000/136.58 \times 980 = 0.14975$ mol kg$^{-1}$. The volume of solution containing 1000 g of $H_2O$ is given by

$$\frac{1020.4\text{ g}}{1.0167\text{ g cm}^{-3}} = 1003.6\text{ cm}^3$$

| Wt % | Molality | Volume Containing 1000 g of $H_2O$ |
|---|---|---|
| 2 | 0.1497 m | 1003.2 |
| 6 | 0.4683 | 1010.1 |
| 10 | 0.8152 | 1020.2 |
| 14 | 1.194 | 1031.3 |
| 18 | 1.610 | 1045.5 |



The slope of this plot at $m = 1$ molar can be obtained by drawing a tangent at $m = 1$ and calculating its slope. This yields 29.3 $\text{cm}^3\ \text{mol}^{-1}$, and so this is the partial molar volume of $ZnCl_2$. *Mathematica* ™ was used to obtain a quadratic fit of the data. This yielded

$V = 999.706 + 21.1601\ m + 4.4639\ m^2$

so that the slope is $21.1601 + (2)(4.4639)m$. At $m = 1$ molal, this yields 30.06 $\text{cm}^3\ \text{mol}^{-1}$.

4.24 Calculate $\Delta_{\text{mix}}G$ and $\Delta_{\text{mix}}S$ for the formation of a quantity of air containing 1 mol of gas by mixing nitrogen and oxygen at 298.15 K. Air may be taken to be 80% nitrogen and 20% oxygen by volume.

SOLUTION

$$\begin{aligned}\Delta_{\text{mix}}G &= RT(y_1 \ln y_1 + y_2 \ln y_2)\\ &= (8.314\ \text{J K}^{-1}\ \text{mol}^{-1})(298.15\ \text{K})(0.8 \ln 0.8 + 0.2 \ln 0.2)\\ &= -\ 1239\ \text{J mol}^{-1}\end{aligned}$$

$$\Delta_{\text{mix}}S = -\ R(y_1 \ln y_1 + y_2 \ln y_2) = 4.159\ \text{J K}^{-1}\ \text{mol}^{-1}$$

4.25 A mole of gas A is mixed with a mole of gas B at 1 bar and 298 K. How much work is required to separate these gases to produce a container of each at 1 bar and 298 K?

SOLUTION

The mixture can be separated by diffusion through a perfect semipermeable membrane. The highest partial pressure of each that can be reached is 1/2 bar. These gases then have to be compressed to 1 bar.

$$\begin{aligned}w &= (2\ \text{mol}) \int_{1/2}^{1} \bar{V}\text{d}P = (2\ \text{mol}) \int_{1/2}^{1} (RT/P)\text{d}P = (2\ \text{mol})\ RT \ln 2\\ &= 2(8.314)(298) \ln 2\\ &= 3.4\ \text{kJ}\end{aligned}$$

The actual process will require more work.

4.26 In studying statistical mechanics we will find (see Table 16.1) that for a monatomic ideal gas, the molar Gibbs energy is given by

$$\bar{G} = -T\ln\frac{T^{5/2}}{P}$$

where numerical constants have been omitted so that only the functional dependence on the natural variables of $\bar{G}$, that is $T$ and $P$, is shown. Derive the corresponding equations for $\bar{S}$, $\bar{H}$, $\bar{V}$, $\bar{U}$, and $\bar{A}$.

SOLUTION

The fundamental equation for $\bar{G}$ is

$$d\bar{G} = -\bar{S}dT + \bar{V}dP$$

Since

$$\bar{G} = -\frac{5}{2}T\ln T + T\ln P$$

the molar entropy is given by

$$\bar{S} = -\left(\frac{\partial\bar{G}}{\partial T}\right)_P = \frac{5}{2} + \frac{5}{2}\ln T - \ln P = \frac{5}{2} + \ln\frac{T^{5/2}}{P}$$

and the molar volume is given by

$$\bar{V} = \left(\frac{\partial\bar{G}}{\partial P}\right)_T = \frac{T}{P}$$

The expressions for the molar enthalpy, internal energy, and Helmholtz energy can be calculated from the following Legendre transforms:

$$\bar{H} = \bar{G} - T\bar{S} = \frac{5}{2}T$$

$$\bar{U} = \bar{H} - P\bar{V} = \frac{3}{2}T$$

$$\bar{A} = \bar{G} - P\bar{V} = -\frac{5}{2}T\ln T + T\ln P - T = -T\ln\frac{T^{5/2}}{P} - T$$

4.27 Statistical mechanics shows that for a monatomic ideal gas, the molar Gibbs energy is given by

$$\bar{G} = -\frac{5}{2}T\ln T + T\ln P$$

where the numerical factors have been omitted so that only the functional dependence on the natural variables, $T$ and $P$, is shown. If we want to treat the thermodynamics of an ideal monatomic gas at specified $T$ and $\bar{V}$ without losing any information, we cannot simply replace $P$ with $T/\bar{V}$ and use

$$\bar{G} = -\frac{5}{2}T \ln T + T \ln \frac{T}{\bar{V}}$$

even though this relation is correct. If we want to treat the thermodynamics of an ideal monatomic gas at specified $T$ and $\bar{V}$ without losing any information, we have to use the following Legendre transform to define the molar Helmholtz energy $\bar{A}$.

$$\bar{A} = \bar{G} - P\bar{V}$$

Use the expression for $\bar{A}$ obtained in this way to calculate $\bar{S}$, $\bar{V}$, $\bar{H}$, and $\bar{U}$ for an ideal monatomic gas as a function of $T$ and $\bar{V}$. Show that these expressions agree with the expressions obtained in the preceding problem.

SOLUTION

Substitute the expressions for $\bar{G}$ and $P$ into the Legendre transform to obtain

$$\bar{A} = -\frac{3}{2}T \ln T - T \ln \bar{V} - T$$

The fundamental equation for the molar Helmholtz energy is

$$d\bar{A} = -\bar{S}dT - Pd\bar{V}$$

Thus the molar entropy is given by

$$\bar{S} = -\left(\frac{\partial \bar{A}}{\partial T}\right)_{\bar{V}} = \frac{5}{2} + \frac{3}{2}\ln T + \ln \bar{V} = \frac{5}{2} + \ln T^{3/2}\bar{V}$$

and the molar volume is given by

$$P = -\left(\frac{\partial \bar{A}}{\partial \bar{V}}\right)_T = \frac{T}{\bar{V}}$$

The values of the molar enthalpy and molar internal energy are given by the following Legendre transforms:

$$\bar{H} = \bar{A} + T\bar{S} + P\bar{V} = \frac{5}{2}T$$

$$\bar{U} = \bar{A} + T\bar{S} = \frac{3}{2}T$$

Substituting $\bar{V} = T/P$ in these expressions yields the same equations obtained in the previous problem for these thermodynamic properties. The moral is that we can change the variables in the expression for a thermodynamic property, but we cannot differentiate this expression to obtain other thermodynamic properties unless the variables in the expression are the natural variables for the thermodynamic potential.

4.28 We already know enough about the thermodynamics of a monatomic ideal gas to express $V$, $U$, and $S$ in terms of the natural variables of $G$, namely $T$, $P$, and $n$.

$$V = nRT/P$$

$$U = \frac{3}{2}nRT$$

$$S = nR\left\{\frac{\bar{S}^o}{R} + \ln\left[\left(\frac{T}{T^o}\right)^{5/2}\left(\frac{P^o}{P}\right)\right]\right\}$$

The last equation is the Sackur-Tetrode equation, where $\bar{S}^o$ is the molar entropy at the standard temperature $T^o$(298.15 K) and standard pressure $P^o$(1 bar). The Gibbs energy $G(T,P,n)$ of the ideal monatomic gas can be calculated by using the Legendre transform

$$G = U + PV - TS$$

The fundamental equation for $G$ is

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P + \mu\mathrm{d}n$$

Show that the correct expressions for $S$, $V$, and $\mu$ are obtained by using the partial derivatives of $G$ indicated by this fundamental equation.

SOLUTION

$$G = \frac{3}{2}nRT + nRT - nRT\left\{\frac{\bar{S}^o}{R} + \ln\left[\left(\frac{T}{T^o}\right)^{5/2}\left(\frac{P^o}{P}\right)\right]\right\}$$

$$\begin{aligned} S &= -\left(\frac{\partial G}{\partial T}\right)_{P,n} \\ &= -\frac{3}{2}nRT - nR + nR\left\{\frac{\bar{S}^o}{R} + \ln\left[\left(\frac{T}{T^o}\right)^{5/2}\left(\frac{P^o}{P}\right)\right]\right\} + nRT\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{5}{2}\ln T\right) \\ &= nR\left\{\frac{\bar{S}^o}{R} + \ln\left[\left(\frac{T}{T^o}\right)^{5/2}\left(\frac{P^o}{P}\right)\right]\right\} \end{aligned}$$

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,n} = nRT/P$$

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{T,P} = RT\left(\frac{5}{2} - \bar{S}^o\right) + RT\ln\left[\left(\frac{T}{T^o}\right)^{5/2}\left(\frac{P}{P^o}\right)\right]$$

Thus the correct expressions are obtained for $S$ and $V$ and the equation for the chemical potential is consistent with $\mu = \mu^o + RT\ln(P/P^o)$.

4.30 $\mathrm{d}S = (C_V/T)\mathrm{d}T + (\alpha/\kappa)\mathrm{d}V$

4.31 $-0.0252\ \mathrm{J\ K^{-1}\ mol^{-1}}$

4.32 $(\partial S/\partial P)_T = 0$, $(\partial H/P)_T = V$, $(\partial U/\partial P)_T = 0$

4.36 $88.2\ \mathrm{J\ mol^{-1}}$

4.37 (a) 4993, (b) 3655 J mol$^{-1}$

4.38 168.97 J K$^{-1}$ mol$^{-1}$, 0, -11.42 kJ mol$^{-1}$

4.39 (a) 6820 J mol$^{-1}$ (b) 6072 J mol$^{-1}$ (c) 75.9 J K$^{-1}$ mol$^{-1}$ (d) 0

4.40 (a) - 5229 J mol$^{-1}$, (b) 5229 J mol$^{-1}$, (c) 0, (d) - 5229 J mol$^{-1}$,
(e) 19.14 J K$^{-1}$ mol$^{-1}$, (f) 0, (g) 0, (h) 0, (i) - 5229 J mol$^{-1}$, (j) 19.14 J K$^{-1}$ mol$^{-1}$,
(k) 0, (l) 19.14 J K$^{-1}$ mol$^{-1}$

4.41 3100 J mol$^{-1}$, - 40,690 J mol$^{-1}$, - 37.6 kJ mol$^{-1}$, - 34.5 kJ mol$^{-1}$,
3.1 kJ mol$^{-1}$, - 109.0 J K$^{-1}$ mol$^{-1}$, 0 kJ mol$^{-1}$

4.42 (a) - 6.754 kJ mol$^{-1}$, (b) 0, (c) 0, (d) -6.754 kJ mol$^{-1}$, (e) 22.51 J K$^{-1}$ mol$^{-1}$

4.43 0, 19.16 J K$^{-1}$ mol$^{-1}$

4.44 0, -13.38 J K$^{-1}$ mol$^{-1}$, 4991 J mol$^{-1}$

4.45 33.34 kJ mol$^{-1}$, 73.52 J K$^{-1}$ mol$^{-1}$, 0

4.46 - 2121 J mol$^{-1}$

4.47 $\Delta\bar{G} = RT \ln (P_2/P_1) + (b - a/RT)(P_2 - P_1)$

4.49 0.79 x 10$^{-3}$ m$^3$ kg$^{-1}$

4.50 (a) 0.2033 x 10$^{-3}$ m$^{-3}$ kg$^{-1}$ (b) 19.36 x 10$^{-6}$ m$^3$ mol$^{-1}$

4.51 - 4731 J, 15.88 J K$^{-1}$

4.52 $\Delta_{\text{vap}}S$ = 109.3 J K$^{-1}$ mol$^{-1}$

$\Delta_{\text{vap}}H$ = 39.9 kJ mol$^{-1}$

$\Delta_{\text{vap}}G$ = - 3.6 kJ mol$^{-1}$