Solution:

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

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

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

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

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

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

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

Solution:

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

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

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

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

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

$$\ln \gamma_{m,B}(m_B') = \phi_m - 1 + \int_0^{m_B'} \frac{\phi_m - 1}{m_B}\,dm_B$$

$$= -\frac{0.050 m_B'/m^\circ}{1.00 + 0.179 m_B'/m^\circ} - \int_0^{m_B'/m^\circ} \frac{0.050}{1.00 + 0.179 m_B/m^\circ}\,d(m_B/m^\circ)$$

$$= -\frac{0.050 m_B'/m^\circ}{1.00 + 0.179 m_B'/m^\circ} - 0.50 \ln(1.00 + 0.179 m_B'/m^\circ)$$

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

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

Solution:

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

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

[6] Ref. [160].

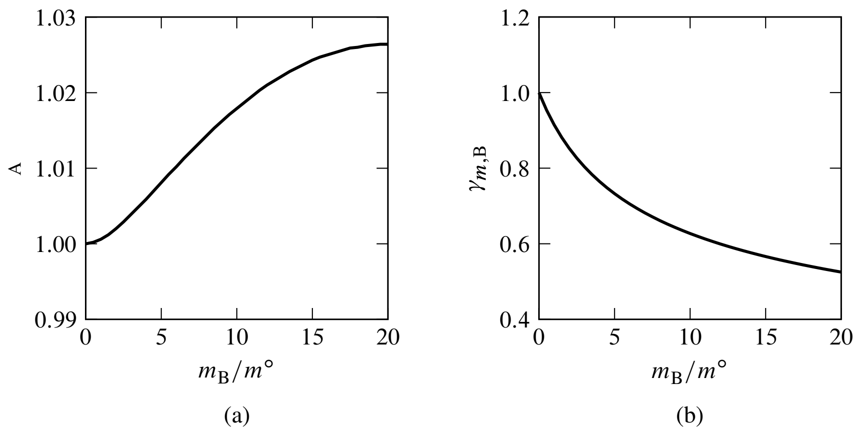

Figure 16 Activity coefficients in aqueous urea solutions at 25 °C.

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

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

Solution:

Partial pressures at sea level:

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

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

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

$$p_{N_2} = (0.788\,\text{bar})\exp\left[\frac{-(28.01\times 10^{-3}\,\text{kg mol}^{-1})(9.806\,65\,\text{m s}^{-2})(10.0\times 10^3\,\text{m})}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(273.15\,\text{K})}\right]$$
$$= 0.235\,\text{bar}$$

$$p_{O_2} = (0.212\,\text{bar})\exp\left[\frac{-(32.00\times 10^{-3}\,\text{kg mol}^{-1})(9.806\,65\,\text{m s}^{-2})(10.0\times 10^3\,\text{m})}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(273.15\,\text{K})}\right]$$
$$= 0.0532\,\text{bar}$$

The total pressure and mole fractions are found from

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

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

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

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

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

Solution:

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

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

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

Reversible elevation of small sample of mass m:

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

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

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

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

General relation:

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

At equilibrium:

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

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

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

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

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

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

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

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

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

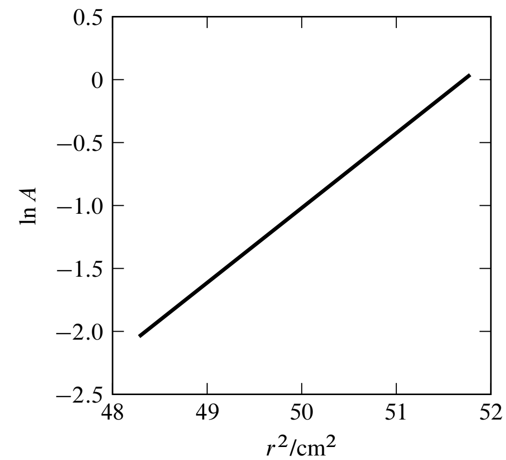

Figure 17 Sedimentation equilibrium of a dilute solution of the FhuA-dodecyl maltoside aggregate.

Solution:

$$\ln \frac{c_B(h)}{c_B(0)} = \ln 0.99 = -\frac{M_B g h \left(1 - v_B^\infty \rho\right)}{RT}$$

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

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

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

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

Solution:

$$p'' - p' = \frac{\omega^2 \rho}{2}\left[(r'')^2 - (r')^2\right] = \frac{(838\,\mathrm{s^{-1}})^2(1.004\,\mathrm{g\,cm^{-3}})(1\,\mathrm{kg}/10^3\,\mathrm{g})}{2}$$
$$\times \left[(7.20\,\mathrm{cm})^2 - (6.95\,\mathrm{cm})^2\right](1\,\mathrm{cm}/10^{-2}\,\mathrm{m})$$
$$= 1.2\times 10^5\,\mathrm{kg\,m^{-1}\,s^{-2}} = 1.2\,\mathrm{bar}$$

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

[7] Ref. [18].

Solution:

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

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

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

Chapter 10 Electrolyte Solutions

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

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

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

[a]Ref. [31].

Solution:

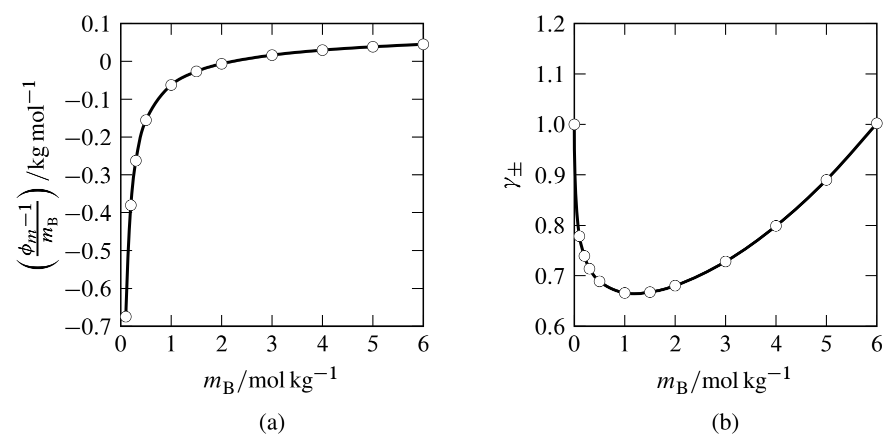

Figure 18 Aqueous NaCl at 298.15 K.

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

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

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

Table 13 Calculations for Prob. 10.1

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

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

Table 14 Osmotic coefficients of aqueous Na_2SO_4 at 298.15 K

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

Solution:

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

$$\begin{aligned}\ln\gamma_\pm &= -\frac{A_{DH}\,|z_+z_-|\,\sqrt{I_m}}{1 + B_{DH}a\sqrt{I_m}}\\ &= -\frac{(1.1744\,\text{kg}^{1/2}\,\text{mol}^{-1/2})(2)\sqrt{(3)(0.0126\,\text{mol kg}^{-1})}}{1 + (3.285\times10^{9}\,\text{m}^{-1}\,\text{kg}^{1/2}\,\text{mol}^{-1/2})(3.0\times10^{-10}\,\text{m})\sqrt{(3)(0.0126\,\text{mol kg}^{-1})}}\\ &= -0.3832\end{aligned}$$

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

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

$$\int_{m''_B}^{m'_B}\left(\frac{\phi_m - 1}{m_B}\right)dm_B = -0.426$$

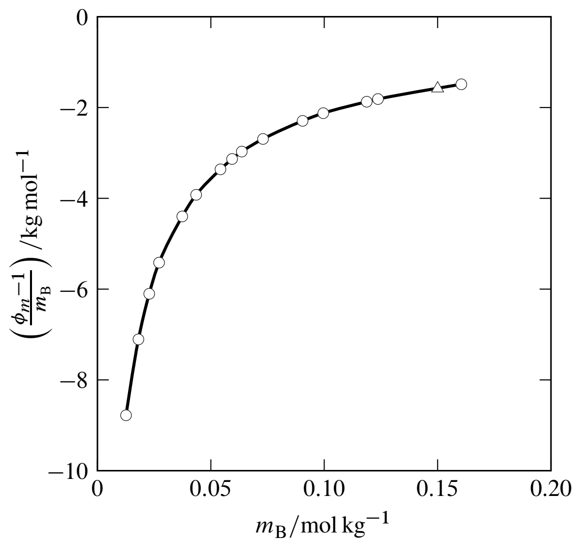

Figure 19 Aqueous Na_2SO_4 at 298.15 K.

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

$$\ln \gamma_\pm(m'_B) = \phi_m(m'_B) - \phi_m(m''_B) + \ln \gamma_\pm(m''_B) + \int_{m''_B}^{m'_B} \frac{\phi_m - 1}{m_B}\, dm_B$$

$$= 0.763 - 0.8893 - 0.3832 - 0.426$$

$$= -0.936$$

$\gamma_\pm = 0.392$

Chapter 11 Reactions and Other Chemical Processes

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

$$\tfrac{1}{2}N_2(g) + \tfrac{5}{4}O_2(g) + \tfrac{1}{2}H_2O(l) \rightarrow H^+(aq) + NO_3^-(aq)$$

Solution:

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

$$\Delta_r H° = -\tfrac{1}{2}\Delta_f H°(H_2O) + \Delta_f H°(NO_3^-)$$

$$= -\tfrac{1}{2}(-285.830\,\text{kJ mol}^{-1}) + (-206.85\,\text{kJ mol}^{-1}) = -63.94\,\text{kJ mol}^{-1}$$

$$\Delta_r G° = -\tfrac{1}{2}\Delta_f G°(H_2O) + \Delta_f G°(NO_3^-)$$

$$= -\tfrac{1}{2}(-237.16\,\text{kJ mol}^{-1}) + (-110.84\,\text{kJ mol}^{-1}) = 7.74\,\text{kJ mol}^{-1}$$

$$K = \exp(-\Delta_r G°/RT) = \exp\left[\frac{-7.74\times 10^3\,\text{J mol}^{-1}}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(298.15\,\text{K})}\right] = 4.41\times 10^{-2}$$

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

(a) Find the changes in $H°_m$, $S°_m$, and $G°_m$ for a gaseous substance when the standard pressure is changed isothermally from 1.01325 bar (1 atm) to exactly 1 bar. (Such a small pressure change has an entirely negligible effect on these quantities for a substance in a condensed phase.)

Solution:

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

$$\Delta H_m = \frac{\Delta H}{n} = 0$$

$$\Delta S_m = \frac{\Delta S}{n} = -R\ln\frac{p_2}{p_1} = -(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\ln\frac{1\,\text{bar}}{1.01325\,\text{bar}}$$

$$= 0.109\,\text{J K}^{-1}\,\text{mol}^{-1}$$

$$\Delta G_m = \frac{\Delta G}{n} = RT\ln\frac{p_2}{p_1} = (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})T\ln\frac{1\,\text{bar}}{1.01325\,\text{bar}}$$

$$= -(0.109\,\text{J K}^{-1}\,\text{mol}^{-1})T$$

(b) What are the values of the corrections that need to be made to the standard molar enthalpy of formation, the standard molar entropy of formation, and the standard molar Gibbs energy of formation of $N_2O_4(g)$ at 298.15 K when the standard pressure is changed from 1.01325 bar to 1 bar?

Solution:

The formation reaction is

$$N_2(g) + 2O_2(g) \rightarrow N_2O_4(g) \qquad \textstyle\sum_i \nu_i = -2$$

for which the standard molar enthalpy of formation is given by

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

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

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

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

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

Solution:

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

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

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

$$K = \frac{p}{p^\circ} = \exp\left(\frac{-\Delta_r G^\circ}{RT}\right) = \exp\left[\frac{-31.84\times 10^3\,\mathrm{J\,mol^{-1}}}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298.15\,\mathrm{K})}\right] = 2.6\times 10^{-6}$$

$$p = 2.6\times 10^{-6}\,p^\circ = 2.6\times 10^{-6}\,\mathrm{bar}$$

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

$$\ln\frac{p_2}{p_1} = -\frac{\Delta_{vap}H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = -\frac{61.38\times 10^3\,\mathrm{J\,mol^{-1}}}{8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}}\left(\frac{1}{273.15\,\mathrm{K}} - \frac{1}{298.15\,\mathrm{K}}\right)$$
$$= -2.2662$$

$p_2/p_1 = 0.1037$ $\qquad p_2 = (0.1037)(2.6\times 10^{-6}\,\mathrm{bar}) = 2.7\times 10^{-7}\,\mathrm{bar}$

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

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$	$\Delta_r H^\circ = -55.82\,\mathrm{kJ\,mol^{-1}}$
$Na(s) + H_2O(l) \rightarrow Na^+(aq) + OH^-(aq) + \frac{1}{2}H_2(g)$	$\Delta_r H^\circ = -184.52\,\mathrm{kJ\,mol^{-1}}$
$NaOH(s) \rightarrow NaOH(aq)$	$\Delta_{sol} H^\infty = -44.75\,\mathrm{kJ\,mol^{-1}}$
NaOH in 5 H_2O → NaOH in ∞ H_2O	$\Delta H_m(\mathrm{dil}) = -4.93\,\mathrm{kJ\,mol^{-1}}$
NaOH(s)	$\Delta_f H^\circ = -425.61\,\mathrm{kJ\,mol^{-1}}$

Using only these values, calculate:

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

Solution:

Add the first two reaction equations:

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$	$\Delta_r H^\circ = -55.82\,\mathrm{kJ\,mol^{-1}}$
$Na(s) + H_2O(l) \rightarrow Na^+(aq) + OH^-(aq) + \frac{1}{2}H_2(g)$	$\Delta_r H^\circ = -184.52\,\mathrm{kJ\,mol^{-1}}$
sum:	
$Na(s) + H^+(aq) \rightarrow Na^+(aq) + \frac{1}{2}H_2(g)$	$\Delta_r H^\circ = -240.34\,\mathrm{kJ\,mol^{-1}}$

From the relation $\Delta_r H^\circ = \sum_i \nu_i \Delta_f H^\circ(i)$ and because $\Delta_f H^\circ$ is zero for each species in the reaction except $Na^+(aq)$:

$\Delta_f H^\circ(Na^+, aq) = -240.34\,kJ\,mol^{-1}$

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

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

The resulting reaction is the formation of aqueous NaOH:

$\Delta_f H^\circ(NaOH, aq) = -470.36\,kJ\,mol^{-1}$

Apply the relation $\Delta_r H^\circ = \sum_i \nu_i \Delta_f H^\circ(i)$ to this reaction, setting the standard molar enthalpies of formation of the elements equal to zero:

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

$\Delta_f H^\circ(OH^-, aq) = -230.02\,kJ\,mol^{-1}$

(b) $\Delta_f H$ for NaOH in 5 H_2O;

Solution:

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

$\Delta_f H(\text{NaOH in 5 } H_2O) = (-470.36 + 4.93)\,kJ\,mol^{-1} = -465.43\,kJ\,mol^{-1}$

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

Solution:

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

$$\begin{aligned} \Delta_r H &= -\Delta_f H^\circ(NaOH, s) + \Delta_f H(\text{NaOH in 5 } H_2O) \\ &= (425.61 - 465.43)\,kJ\,mol^{-1} = -39.82\,kJ\,mol^{-1} \end{aligned}$$

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

$$\begin{aligned} \Delta_r H &= \Delta_{sol} H^\infty - \Delta H_m(\text{dil}) \\ &= (-44.75 + 4.93)\,kJ\,mol^{-1} = -39.82\,kJ\,mol^{-1} \end{aligned}$$

Table 15 Data for Problem 11.5[a]

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

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

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

Solution:

The amounts in the solution are

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

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

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

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

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

$Na_2S_2O_3{\cdot}5H_2O(s) \rightarrow 2\,Na(s) + 2\,S(s) + \frac{8}{2}O_2(g) + 5\,H_2(g)$
$2\,Na(s) + 2\,S(s) + \frac{3}{2}O_2(g) + 143\,H_2O(l) \rightarrow Na_2S_2O_3 \text{ in } 143\,H_2O$
$5\,H_2(g) + \frac{5}{2}O_2(g) \rightarrow 5\,H_2O(l)$
sum:
$Na_2S_2O_3{\cdot}5H_2O(s) + 138\,H_2O(l) \rightarrow Na_2S_2O_3 \text{ in } 143\,H_2O$

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

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

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

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

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

Solution:

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

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

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

[a]Ref. [167].

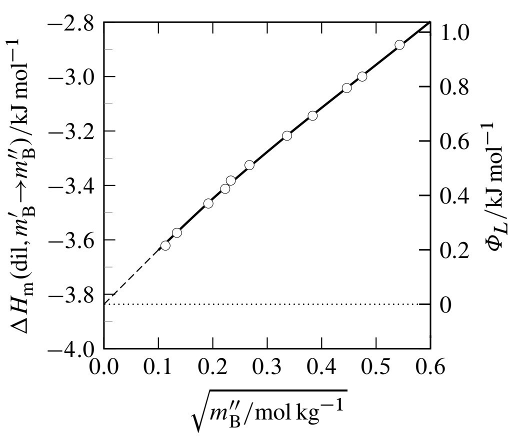

Figure 20 Plot for Problem 11.6. The dashed line has the theoretical slope $C_{\Phi_L} = 1.988 \times 10^3\,\mathrm{J\,kg^{1/2}\,mol^{-3/2}}$.

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

From Eq. 11.4.27:

$$L_\mathrm{B} = \Phi_L + \frac{\sqrt{m_\mathrm{B}}}{2}\,\frac{\mathrm{d}\Phi_L}{\mathrm{d}\sqrt{m_\mathrm{B}}}$$

$$= 0.560\,\mathrm{kg\,mol^{-1}} + \left(\frac{0.300\,\mathrm{mol^{1/2}\,kg^{-1/2}}}{2}\right)(1.670\,\mathrm{kJ\,kg^{1/2}\,mol^{-3/2}})$$

$$= 0.810\,\mathrm{kg\,mol^{-1}}$$

From Eq. 11.4.24:

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

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

Properties of the bomb vessel:	
internal volume	350.0 cm^3
mass of *n*-hexane placed in bomb	0.6741 g
mass of water placed in bomb	1.0016 g
Properties of liquid *n*-hexane:	
molar mass	$M = 86.177\,\mathrm{g\,mol^{-1}}$
density	$\rho = 0.6548\,\mathrm{g\,cm^{-3}}$
cubic expansion coefficient	$\alpha = 1.378\times10^{-3}\,\mathrm{K^{-1}}$
Properties of liquid H_2O:	
molar mass	$M = 18.0153\,\mathrm{g\,mol^{-1}}$
density	$\rho = 0.9970\,\mathrm{g\,cm^{-3}}$
cubic expansion coefficient	$\alpha = 2.59\times10^{-4}\,\mathrm{K^{-1}}$
standard molar energy of vaporization	$\Delta_{\mathrm{vap}}U^\circ = 41.53\,\mathrm{kJ\,mol^{-1}}$
Second virial coefficients, 298.15 K:	
B_{AA}	$-1158\,\mathrm{cm^3\,mol^{-1}}$
B_{BB}	$-16\,\mathrm{cm^3\,mol^{-1}}$
$\mathrm{d}B_{\mathrm{BB}}/\mathrm{d}T$	$0.21\,\mathrm{cm^3\,K^{-1}\,mol^{-1}}$
B_{CC}	$-127\,\mathrm{cm^3\,mol^{-1}}$
$\mathrm{d}B_{\mathrm{CC}}/\mathrm{d}T$	$0.97\,\mathrm{cm^3\,K^{-1}\,mol^{-1}}$
B_{AB}	$-40\,\mathrm{cm^3\,mol^{-1}}$
B_{AC}	$-214\,\mathrm{cm^3\,mol^{-1}}$
B_{BC}	$-43.7\,\mathrm{cm^3\,mol^{-1}}$
$\mathrm{d}B_{\mathrm{BC}}/\mathrm{d}T$	$0.4\,\mathrm{cm^3\,K^{-1}\,mol^{-1}}$
Henry's law constants at 1 bar (solvent = H_2O):	
O_2	$k_{m,\mathrm{B}} = 796\,\mathrm{bar\,kg\,mol^{-1}}$
CO_2	$k_{m,\mathrm{C}} = 29.7\,\mathrm{bar\,kg\,mol^{-1}}$
Partial molar volumes of solutes in water:	
O_2	$V_{\mathrm{B}}^{\infty} = 31\,\mathrm{cm^3\,mol^{-1}}$
CO_2	$V_{\mathrm{C}}^{\infty} = 33\,\mathrm{cm^3\,mol^{-1}}$
Standard molar energies of solution (solvent = H_2O):	
O_2	$\Delta_{\mathrm{sol}}U^\circ = -9.7\,\mathrm{kJ\,mol^{-1}}$
CO_2	$\Delta_{\mathrm{sol}}U^\circ = -17.3\,\mathrm{kJ\,mol^{-1}}$

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

$$\mathrm{C_6H_{14}(l)} + \tfrac{19}{2}\mathrm{O_2(g)} \rightarrow 6\,\mathrm{CO_2(g)} + 7\,\mathrm{H_2O(l)}$$

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

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

(a) Parts (a)–(c) consist of simple calculations of some quantities needed in later parts of the problem. Begin by using the masses of C_6H_{14} and H_2O placed in the bomb vessel, and their molar masses, to calculate the amounts (moles) of C_6H_{14} and H_2O present initially in the bomb vessel. Then use the stoichiometry of the combustion reaction to find the amount of O_2 consumed and the amounts of H_2O and CO_2 present in state 2. (There is not enough information at this stage to allow you to find the amount of O_2 present, just the change.) Also find the final mass of H_2O. Assume that oxygen is present in excess and the combustion reaction goes to completion.

Solution:

Initial amounts:

$$n_{C_6H_{14}} = \frac{0.6741\,\text{g}}{86.177\,\text{g mol}^{-1}} = 7.822 \times 10^{-3}\,\text{mol}$$

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

Change in amount of oxygen:

$$\Delta n_{O_2} = -(19/2)(7.822 \times 10^{-3}\,\text{mol}) = -0.07431\,\text{mol}$$

Final amounts (state 2):

$$n_{H_2O} = 0.05560\,\text{mol} + (7)(7.822 \times 10^{-3}\,\text{mol}) = 0.11035\,\text{mol}$$

$$n_{CO_2} = (6)(7.822 \times 10^{-3}\,\text{mol}) = 0.04693\,\text{mol}$$

Final mass of H_2O:

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

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

Solution:

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

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

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

Solution:

Initial volumes:

$$V(C_6H_{14}) = (7.822 \times 10^{-3}\,\text{mol})(131.61\,\text{cm}^3\text{mol}^{-1}) = 1.029\,\text{cm}^3$$
$$V(H_2O) = (0.05560\,\text{mol})(18.070\,\text{cm}^3\text{mol}^{-1}) = 1.005\,\text{cm}^3$$
$$V^\text{g} = (350.0 - 1.029 - 1.005)\,\text{cm}^3 = 348.0\,\text{cm}^3$$

Final volumes:

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

(d) When the bomb vessel is charged with oxygen and before the inlet valve is closed, the pressure at 298.15 K measured on an external gauge is found to be $p_1 = 30.00$ bar. To a good approximation, the gas phase of state 1 has the equation of state of pure O_2 (since the vapor pressure of water is only 0.1 % of 30.00 bar). Assume that this equation of state is given by $V_m = RT/p + B_{BB}$ (Eq. 2.2.8), where B_{BB} is the second virial coefficient of O_2 listed in Table 17. Solve for the amount of O_2 in the gas phase of state 1. The gas phase of state 2 is a mixture of O_2 and CO_2, again with a negligible partial pressure of H_2O. Assume that only small fractions of the total amounts of O_2 and CO_2 dissolve in the liquid water, and find the amount of O_2 in the gas phase of state 2 and the mole fractions of O_2 and CO_2 in this phase.

Solution:

In gas phase of state 1:

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

In gas phase of state 2:

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

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

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

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

(e) You now have the information needed to find the pressure in state 2, which cannot be measured directly. For the mixture of O_2 and CO_2 in the gas phase of state 2, use Eq. 9.3.23 on page 247 to calculate the second virial coefficient. Then solve the equation of state of Eq. 9.3.21 on page 246 for the pressure. Also calculate the partial pressures of the O_2 and CO_2 in the gas mixture.

Solution:

In gas phase of state 2:

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

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

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

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

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

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

The pressure at which the pure liquid and gas phases of H_2O are in equilibrium at 298.15 K (the saturation vapor pressure of water) is 0.03169 bar. Use Eq. 7.8.18 on page 187 to estimate the fugacity of $H_2O(g)$ in equilibrium with pure liquid water at this temperature and pressure. The effect of pressure on fugacity in a one-component liquid–gas system is discussed in Sec. 12.8.1; use Eq. 12.8.3 on page 400 to find the fugacity of H_2O in gas phases equilibrated with liquid water at the pressures of states 1 and 2 of the isothermal bomb process. (The mole fraction of O_2 dissolved in the liquid water is so small that you can ignore its effect on the chemical potential of the water.)

Solution:

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

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

$$\phi = 0.9985$$

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

Equation 12.8.3:

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

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

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

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

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

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

For state 1, in which the gas phase is practically-pure O_2, you can use Eq. 7.8.18 on page 187 to calculate ϕ_{O_2}. The other calculations require Eq. 9.3.29 on page 247, with the value of B'_i found from the formulas of Eq. 9.3.26 or Eqs. 9.3.27 and 9.3.28 (y_A is so small that you can set it equal to zero in these formulas).

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

Solution:

Gas phase of state 1:

$$B'_A = 2B_{AB} - B_{BB} = 2(-40\times10^{-6}\ \text{m}^3\ \text{mol}^{-1}) - (-16\times10^{-6}\ \text{m}^3\ \text{mol}^{-1})$$
$$= -64\times10^{-6}\ \text{m}^3\ \text{mol}^{-1}$$

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

$$\phi_A = 0.925$$

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

$$\phi_B = 0.981$$

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

Gas phase of state 2:

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

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

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

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

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

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

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

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

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

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

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

(h) From the values of the fugacity and fugacity coefficient of a constituent of a gas mixture, you can calculate the partial pressure with Eq. 9.3.17 on page 245, then the mole fraction with $y_i = p_i/p$, and finally the amount with $n_i = y_i n$. Use this method to find the amounts of H_2O in the gas phases of states 1 and 2, and also calculate the amounts of H_2O in the liquid phases of both states.

Solution:

H_2O in gas phase of state 1:

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

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

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

H_2O in gas phase of state 2:

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

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

$$n_A = y_A n^g = (0.00129)(0.402\,\text{mol}) = 5.19 \times 10^{-4}\,\text{mol}$$

H_2O in liquid phase of state 1:

$$n_A = 0.05560\,\text{mol} - 5.00 \times 10^{-4}\,\text{mol} = 0.05510\,\text{mol}$$

H_2O in liquid phase of state 2:

$$n_A = 0.11035\,\text{mol} - 5.19 \times 10^{-4}\,\text{mol} = 0.10983\,\text{mol}$$

(i) Next, consider the O_2 dissolved in the water of state 1 and the O_2 and CO_2 dissolved in the water of state 2. Treat the solutions of these gases as ideal dilute with the molality of solute i given by $m_i = f_i / k_{m,i}$ (Eq. 9.4.21). The values of the Henry's law constants of these gases listed in Table 17 are for the standard pressure of 1 bar. Use Eq. 12.8.35 on page 408 to find the appropriate values of $k_{m,i}$ at the pressures of states 1 and 2, and use these values to calculate the amounts of the dissolved gases in both states.

Solution:

Equation 12.8.35:

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

Dissolved O_2 in state 1:

$$k_{m,B} = (796\,\text{bar kg mol}^{-1})\exp\left[\frac{(31 \times 10^{-6}\,\text{m}^3\,\text{mol}^{-1})(30.00 - 1) \times 10^5\,\text{Pa}}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(298.15\,\text{K})}\right]$$

$$= 825\,\text{bar kg mol}^{-1}$$

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

$$n_B = (0.0356\,\text{mol kg}^{-1})(1.0016 \times 10^{-3}\,\text{kg}) = 3.57 \times 10^{-5}\,\text{mol}$$

Dissolved O_2 and CO_2 in state 2:

$$k_{m,B} = (796\,\text{bar kg mol}^{-1})\exp\left[\frac{(31 \times 10^{-6}\,\text{m}^3\,\text{mol}^{-1})(27.9 - 1) \times 10^5\,\text{Pa}}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(298.15\,\text{K})}\right]$$

$$= 823\,\text{bar kg mol}^{-1}$$

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

$$n_B = (0.0294\,\text{mol kg}^{-1})(1.9880 \times 10^{-3}\,\text{kg}) = 5.85 \times 10^{-5}\,\text{mol}$$

$$k_{m,C} = (29.7\,\text{bar kg mol}^{-1})\exp\left[\frac{(33 \times 10^{-6}\,\text{m}^3\,\text{mol}^{-1})(27.9 - 1) \times 10^5\,\text{Pa}}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(298.15\,\text{K})}\right]$$

$$= 30.8\,\text{bar kg mol}^{-1}$$

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

$$n_C = (0.096\,\text{mol kg}^{-1})(1.9880 \times 10^{-3}\,\text{kg}) = 1.92 \times 10^{-4}\,\text{mol}$$

(j) At this point in the calculations, you know the values of all properties needed to describe the initial and final states of the isothermal bomb process. You are now able to evaluate the various Washburn corrections. These corrections are the internal energy changes, at the reference temperature of 298.15 K, of processes that connect the standard states of substances with either state 1 or state 2 of the isothermal bomb process.
First, consider the gaseous H_2O. The Washburn corrections should be based on a pure-liquid standard state for the H_2O. Section 7.9 shows that the molar internal energy of a pure gas under ideal-gas conditions (low pressure) is the same as the molar internal energy of the gas in its standard state at the same temperature. Thus, the molar internal energy change when a substance in its pure-liquid standard state changes isothermally to an ideal gas is equal to the standard molar internal energy of vaporization, $\Delta_{\text{vap}}U^\circ$. Using the value of $\Delta_{\text{vap}}U^\circ$ for H_2O given in Table 17, calculate ΔU for the vaporization of liquid H_2O at pressure p° to ideal gas in the amount present in the gas phase of state 1. Also calculate ΔU for the condensation of ideal gaseous H_2O in the amount present in the gas phase of state 2 to liquid at pressure p°.
Solution:

Vaporization:

$$\Delta U = (5.00\times10^{-4}\,\text{mol})(41.53\times10^{3}\,\text{J mol}^{-1}) = 20.8\,\text{J}$$

Condensation:

$$\Delta U = -(5.19\times10^{-4}\,\text{mol})(41.53\times10^{3}\,\text{J mol}^{-1}) = -21.6\,\text{J}$$

(k) Next, consider the dissolved O_2 and CO_2, for which gas standard states are used. Assume that the solutions are sufficiently dilute to have infinite-dilution behavior; then the partial molar internal energy of either solute in the solution at the standard pressure $p^\circ = 1$ bar is equal to the standard partial molar internal energy based on a solute standard state (Sec. 9.7.1). Values of $\Delta_{\text{sol}}U^\circ$ are listed in Table 17. Find ΔU for the dissolution of O_2 from its gas standard state to ideal-dilute solution at pressure p° in the amount present in the aqueous phase of state 1. Find ΔU for the desolution (transfer from solution to gas phase) of O_2 and of CO_2 from ideal-dilute solution at pressure p°, in the amounts present in the aqueous phase of state 2, to their gas standard states.
Solution:

O_2 dissolution:

$$\Delta U = (3.57\times10^{-5}\,\text{mol})(-9.7\times10^{3}\,\text{J mol}^{-1}) = -0.35\,\text{J}$$

O_2 desolution:

$$\Delta U = (5.85\times10^{-5}\,\text{mol})(9.7\times10^{3}\,\text{J mol}^{-1}) = 0.57\,\text{J}$$

CO_2 desolution:

$$\Delta U = (1.92\times10^{-4}\,\text{mol})(17.3\times10^{3}\,\text{J mol}^{-1}) = 3.32\,\text{J}$$

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

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

C_6H_{14}(l) compression:

$$\Delta U = -(1.378\times10^{-3}\,\text{K}^{-1})(298.15\,\text{K})(1.029\times10^{-6}\,\text{m}^3)$$

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

Solution compression:

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

Solution decompression:

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

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

One of the internal energy changes is for the compression of gaseous O_2, starting at a pressure low enough for ideal-gas behavior ($U_\text{m} = U_\text{m}^\circ$) and ending at pressure p_1 to form the gas phase present in state 1. Use the approximate expression for $U_\text{m} - U_\text{m}^\circ(\text{g})$ in Table 7.5 to calculate $\Delta U = U(p_1) - nU_\text{m}^\circ(\text{g})$; a value of $\text{d}B/\text{d}T$ for pure O_2 is listed in Table 17.

The other internal energy change is for a process in which the gas phase of state 2 at pressure p_2 is expanded until the pressure is low enough for the gas to behave ideally, and the mixture is then separated into ideal-gas phases of pure O_2 and CO_2. The molar internal energies of the separated low-pressure O_2 and CO_2 gases are the same as the standard molar internal energies of these gases. The internal energy of unmixing ideal gases is zero (Eq. 11.1.11). The dependence of the internal energy of the gas mixture is given, to a good approximation, by $U = \sum_i U_i^\circ(\text{g}) - npT\,\text{d}B/\text{d}T$, where B is the second virial coefficient of the gas mixture; this expression is the analogy for a gas mixture of the approximate expression for $U_\text{m} - U_\text{m}^\circ(\text{g})$ in Table 7.5. Calculate the value of $\text{d}B/\text{d}T$ for the mixture of O_2 and CO_2 in state 2 (you need Eq. 9.3.23 on page 247 and the values of $\text{d}B_{ij}/\text{d}T$ in Table 17) and evaluate $\Delta U = \sum_i n_i U_i^\circ(\text{g}) - U(p_2)$ for the gas expansion.

Solution:

O_2 compression:

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

Gas mixture:

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

Gas mixture expansion:

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

$= 87\,\mathrm{J}$

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

Solution:

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

Table 18 Washburn corrections

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

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

Solution:

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

$$= \frac{-32.504\,\mathrm{kJ} + 8\times 10^{-3}\,\mathrm{kJ}}{7.822\times 10^{-3}\,\mathrm{mol}} = -4154.4\,\mathrm{kJ\,mol^{-1}}$$

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

Solution:

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

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

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

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

Solution:

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

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

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

11.9 Consider the combustion of methane:

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

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

Solution:

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

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

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

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

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

$x = T_2$

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

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

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

Solve with the quadratic formula:

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

Only the positive value is physically possible.

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

Solution:

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

$$\ln K = \frac{-\Delta_r G°}{RT} = \frac{-52.772\times 10^3\,\text{J mol}^{-1}}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(600.00\,\text{K})} = -10.578$$

$$K = 2.55\times 10^{-5}$$

$$K = \frac{a^2_{\text{Hg(l)}} f_{\text{O}_2}/p°}{a^2_{\text{HgO(s)}}} \approx p_{\text{O}_2}/p°$$

$$p_{\text{O}_2} = Kp° = 2.55\times 10^{-5}\,\text{bar}$$

11.11 The combustion of hydrogen is a reaction that is known to "go to completion."

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

$$\text{H}_2(\text{g}) + \tfrac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O(l)}$$

Solution:

$$\Delta_r G° = \Delta_f G°(\text{H}_2\text{O, l}) = -237.16\,\text{kJ mol}^{-1}$$

$$K = \exp(-\Delta_r G°/RT) = \exp\frac{237.16\times 10^3\,\text{J mol}^{-1}}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(298.15\,\text{K})} = 3.5\times 10^{41}$$

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

Solution:

$$K = \frac{a_{\text{H}_2\text{O(l)}}}{(f_{\text{H}_2}/p°)(f_{\text{O}_2}/p°)^{1/2}}$$

For ideal gas mixture, $p_{\text{O}_2} = 1.0\,\text{bar}$:

$$K = \frac{1}{(p_{\text{H}_2}/p°)(1.0)^{1/2}}$$

$$p_{\text{H}_2} = \frac{p°}{K} = \frac{1\,\text{bar}}{3.5\times 10^{41}} = 2.8\times 10^{-42}\,\text{bar}$$

$$N_{\text{H}_2} = \frac{N_{\text{A}}\,p_{\text{H}_2}V}{RT}$$

$$= \frac{(6.022\times 10^{23}\,\text{mol}^{-1})(2.8\times 10^{-42}\,\text{bar})(10^5\,\text{Pa/1 bar})(1.0\,\text{m}^3)}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(298.15\,\text{K})} = 6.9\times 10^{-17}$$

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

Solution:

$$t = (6.9\times 10^{-17})(1.0\times 10^{10}\,\text{years})(365\,\text{d year}^{-1})(24\,\text{h d}^{-1})(60\,\text{min h}^{-1})(60\,\text{s min}^{-1})$$

$$= 22\,\text{s}$$

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

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

Solution:

$$Q_{rxn} = a(D)/a(G) = \Gamma(D)/\Gamma(G)$$
$$\approx \frac{\exp[V_m(D)(p - p^\circ)/RT]}{\exp[V_m(G)(p - p^\circ)/RT]} = \exp\frac{[V_m(D) - V_m(G)](p - p^\circ)}{RT}$$

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

Solution:

Find the pressure at which Q_{rxn} is equal to K:

$$\ln Q_{rxn} \approx \frac{[V_m(D) - V_m(G)](p - p^\circ)}{RT}$$
$$= \frac{(3.4 - 5.3) \times 10^{-6}\ m^3\ mol^{-1}(p - p^\circ)}{(8.3145\ J\ K^{-1}\ mol^{-1})(298.15\ K)} = -7.7 \times 10^{-10}\ m^3\ J^{-1}(p - p^\circ)$$

At equilibrium, $\ln Q_{rxn} = \ln K = \ln(0.31) = -1.17$

$$p \approx \frac{-1.17}{-7.7 \times 10^{-10}\ m^3\ J^{-1}} = 1.5 \times 10^9\ Pa = 1.5 \times 10^4\ bar$$

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

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

Solution:

To simplify the nomenclature, write the reaction as A $\rightarrow$ 2 B. Use Eq. 11.7.19 on page 348, with $p = 0.0500p^\circ$, $y_{A,0} = 1$, $n_{B,0} = 0$, $\nu_A = -1$, and $\nu_B = 2$:

$$G(\xi) - G(0) = \xi\Delta_r G^\circ + n_A RT \ln y_A + n_B RT \ln y_B + RT\xi \ln(0.0500)$$

where

$$\Delta_r G^\circ = -\Delta_f G^\circ(N_2O_4) + 2\,\Delta_f G^\circ(NO_2) = -(97.72\ kJ\ mol^{-1}) + 2(51.22\ kJ\ mol^{-1})$$
$$= 4.72\ kJ\ mol^{-1}$$

$$y_A = \frac{n_A}{n_A + n_B} \qquad y_B = 1 - y_A$$

$$n_A = 1.000\ mol - \xi \qquad n_B = 2\xi$$

$$RT = (8.3145\ J\ K^{-1}\ mol^{-1})(298.15\ K) = 2.4790\ kJ\ mol^{-1}$$

See Table 19 for calculated values.

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

Table 19 Problem 11.13(a)

ξ/mol	n_A/mol	n_B/mol	y_A	y_B	$[G(\xi) - G(0)]$/kJ mol^{-1}
0	1.000	0	1	0	0
0.1	0.900	0.200	0.818	0.182	−1.56
0.2	0.800	0.400	0.667	0.333	−2.43
0.3	0.700	0.600	0.538	0.462	−3.04
0.4	0.600	0.800	0.429	0.571	−3.45
0.5	0.500	1.000	0.333	0.667	−3.72
0.6	0.400	1.200	0.250	0.750	−3.85
0.65	0.350	1.300	0.212	0.788	−3.87
0.7	0.300	1.400	0.176	0.824	−3.86
0.8	0.200	1.600	0.111	0.889	−3.72
0.9	0.100	1.800	0.053	0.947	−3.41
1	0	2.000	0	1	−2.71

Solution:

See Fig. 21.

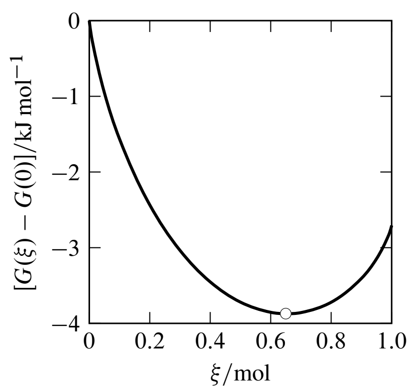

Figure 21 Problem 11.13(b). The open circle at $\xi = 0.65$ mol indicates the estimated position of ξ_{eq}.

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

Solution:

The curve minimum is at $\xi_{eq} = 0.65$ mol. The activities here are $a_A = y_A p/p^\circ = 0.0106$ and $a_B = y_B p/p^\circ = 0.0394$. The thermodynamic equilibrium constant has the value

$$K = \frac{a_B^2}{a_A} = \frac{(0.0394)^2}{0.0106} = 0.146$$

From Eq. 11.8.11:

$$K = \exp\left(-\frac{\Delta_r G^\circ}{RT}\right) = \exp\left[-\frac{4.72\times 10^3\ \text{J mol}^{-1}}{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(298.15\ \text{K})}\right] = 0.15$$

Chapter 12 Equilibrium Conditions in Multicomponent Systems

12.1 Consider the heterogeneous equilibrium $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$. Table 20 lists pressures measured over a range of temperatures for this system.

Table 20 Pressure of an equilibrium system containing $CaCO_3$(s), CaO(s), and CO_2(g)[a]

$t/°C$	p/Torr	$t/°C$	p/Torr
842.3	343.0	904.3	879.0
852.9	398.6	906.5	875.0
854.5	404.1	937.0	1350
868.9	510.9	937.0	1340

[a]Ref. [163].

(a) What is the approximate relation between p and K?
Solution:

$$K = \frac{a_{\text{CaO}} a_{\text{CO}_2}}{a_{\text{CaCO}_3}} = \frac{\Gamma_{\text{CaO}} f_{\text{CO}_2}/p^\circ}{\Gamma_{\text{CaCO}_3}}$$

Approximate the pressure coefficients of the solids by unity and the CO_2 fugacity by $f_{\text{CO}_2} \approx p_{\text{CO}_2} = p$:

$$K \approx p/p^\circ$$

(b) Plot these data in the form ln K versus $1/T$, or fit ln K to a linear function of $1/T$. Then, evaluate the temperature at which the partial pressure of the CO_2 is 1 bar, and the standard molar reaction enthalpy at this temperature.
Solution:

From the values of p/Torr, calculate p/p° using

$$p^\circ = (1\,\text{bar})\,\frac{10^5\,\text{Pa}\,\text{bar}^{-1}}{(101,325/760)\,\text{Pa}\,\text{Torr}^{-1}} = 750.06\,\text{Torr}$$

The values of $1/T$ and $\ln(p/p^\circ) \approx \ln K$ are listed in Table 21 and plotted in Fig. 22.

Table 21 Data for Problem 12.1(b)

$(1/T)/10^{-4}\,\text{K}^{-1}$	$\ln(p/p^\circ)$	$(1/T)/10^{-4}\,\text{K}^{-1}$	$\ln(p/p^\circ)$
8.965	−0.7824	8.493	0.1586
8.881	−0.6322	8.477	0.1894
8.868	−0.6185	8.263	0.5877
8.756	−0.3840	8.263	0.5803

From either the plot or the equation for the least-squares line, p_{CO_2} equals 1 bar and $\ln(p/p^\circ)$ is zero when $1/T$ equals $8.561 \times 10^{-4}\,\text{K}^{-1}$ and T is 1168 K. Use Eq. 12.1.14 to calculate $\Delta_r H^\circ$ from the slope of the least-squares line:

$$\Delta_r H^\circ = -R\frac{\text{d}\ln(p/p^\circ)}{\text{d}(1/T)} = -(8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})(-1.97 \times 10^4\,\text{K})$$

$$= 1.64 \times 10^5\,\text{J}\,\text{mol}^{-1}$$

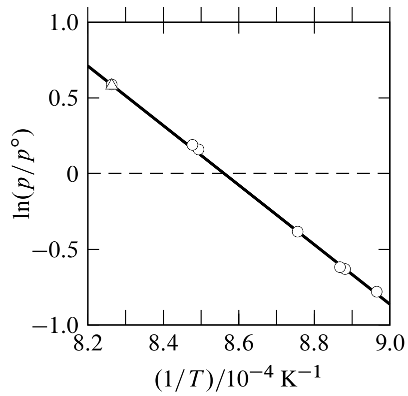

Figure 22 Graph for Problem 12.1(b). The solid line is the least-squares fit to the points: $\ln(p/p^\circ) = a + b(1/T)/10^{-4}\,\mathrm{K}^{-1}$ with $a = 16.839$, $b = -1.967$.

12.2 For a homogeneous reaction in which the reactants and products are solutes in a solution, write a rigorous relation between the standard molar reaction enthalpy and the temperature dependence of the thermodynamic equilibrium constant, with solute standard states based on concentration.

Solution:

Solve Eq. 12.1.11 for $\Delta_\mathrm{r}H^\circ$:

$$\Delta_\mathrm{r}H^\circ = RT^2\frac{\mathrm{d}\ln K}{\mathrm{d}T} + RT^2\alpha_\mathrm{A}^* \sum_{i\neq A}\nu_i$$

α_A^* is the cubic expansion coefficient of the pure solvent.

12.3 Derive an expression for the standard molar reaction entropy of a reaction that can be used to calculate its value from the thermodynamic equilibrium constant and its temperature derivative. Assume that no solute standard states are based on concentration.

Solution:

Combine the relations $\Delta_\mathrm{r}G^\circ = -RT\ln K$ (Eq. 11.8.10) and $\Delta_\mathrm{r}G^\circ = \Delta_\mathrm{r}H^\circ - T\Delta_\mathrm{r}S^\circ$ (Eq. 11.8.21):

$$\Delta_\mathrm{r}S^\circ = R\ln K + (1/T)\Delta_\mathrm{r}H^\circ$$

From Eq. 12.1.13, substitute

$$\Delta_\mathrm{r}H^\circ = RT^2\frac{\mathrm{d}\ln K}{\mathrm{d}T}$$

to obtain the relation

$$\Delta_\mathrm{r}S^\circ = R\ln K + RT\frac{\mathrm{d}\ln K}{\mathrm{d}T}$$

<u>**12.4**</u> Use the data in Table 22 on the next page to evaluate the molal freezing-point depression constant and the molal boiling-point elevation constant for H_2O at a pressure of 1 bar.

Table 22 Properties of H_2O at 1 bar

M	t_f	t_b	$\Delta_{fus}H$	$\Delta_{vap}H$
18.0153 g mol^{-1}	0.00 °C	99.61 °C	6.010 kJ mol^{-1}	40.668 kJ mol^{-1}

Solution:

$$K_f = \frac{M_A R(T_f^*)^2}{\Delta_{fus,A}H} = \frac{(18.0153\times10^{-3}\,\text{kg mol}^{-1})(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(273.15\,\text{K})^2}{6.010\times10^3\,\text{J mol}^{-1}}$$

$$= 1.860\,\text{K kg mol}^{-1}$$

$$K_b = \frac{M_A R(T_b^*)^2}{\Delta_{vap,A}H} = \frac{(18.0153\times10^{-3}\,\text{kg mol}^{-1})(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(372.76\,\text{K})^2}{40.668\times10^3\,\text{J mol}^{-1}}$$

$$= 0.5118\,\text{K kg mol}^{-1}$$

12.5 An aqueous solution of the protein bovine serum albumin, containing 2.00×10^{-2} g of protein per cubic centimeter, has an osmotic pressure of 8.1×10^{-3} bar at 0 °C. Estimate the molar mass of this protein.

Solution:

From van't Hoff's equation for osmotic pressure:

$$c_B \approx \frac{\Pi}{\nu RT} = \frac{(8.1\times10^{-3}\,\text{bar})(10^5\,\text{Pa bar}^{-1})}{(1)(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(273\,\text{K})} = 0.36\,\text{mol m}^{-3}$$

$$n_B \approx (0.36\,\text{mol m}^{-3})(1\,\text{cm}^3)(10^{-2}\,\text{m cm}^{-1})^3 = 3.6\times10^{-7}\,\text{mol}$$

$$M_B \approx \frac{2.00\times10^{-2}\,\text{g}}{3.6\times10^{-7}\,\text{mol}} = 5.6\times10^4\,\text{g mol}^{-1}$$

12.6 Figure 12.8 on page 393 shows a curve fitted to experimental points for the aqueous solubility of n-butylbenzene. The curve has the equation $\ln x_B = a(t/°\text{C} - b)^2 + c$, where the constants have the values $a = 3.34\times10^{-4}$, $b = 12.13$, and $c = -13.25$. Assume that the saturated solution behaves as an ideal-dilute solution, use a solute standard state based on mole fraction, and calculate $\Delta_{sol,B}H°$ and $\Delta_{sol,B}S°$ at 5.00 °C, 12.13 °C (the temperature of minimum solubility), and 25.00 °C.

Solution:

Rewrite the equation for the curve using thermodynamic temperature:

$$\ln x_B = A(T-B)^2 + C$$

where $A = 3.34\times10^{-4}\,\text{K}^{-2}$ $\quad B = (12.13 + 273.15)\,\text{K} = 285.28\,\text{K}$ $\quad C = c = -13.25$

From Sec. 12.6.2, with $K = x_B$:

$$\Delta_{sol,B}H° = RT^2\frac{d\,\ln x_B}{dT} = [RT^2][2A(T-B)]$$

$$\Delta_{sol,B}G° = -RT\ln x_B = -RT[A(T-B)^2 + C]$$

$$\Delta_{sol,B}S° = \frac{\Delta_{sol,B}H° - \Delta_{sol,B}G°}{T}$$

The formula of Prob. 12.3 can also be used, with K replaced with x_B:

$$\Delta_{\rm sol,B}S^\circ = R\ln x_{\rm B} + RT\frac{{\rm d}\ln x_{\rm B}}{{\rm d}T}$$

The values calculated at the three temperatures are listed in Table 23.

Table 23 Problem 12.6

$t/°{\rm C}$	$T/{\rm K}$	$\dfrac{\Delta_{\rm sol,B}H^\circ}{\rm kJ\,mol^{-1}}$	$\dfrac{\Delta_{\rm sol,B}G^\circ}{\rm kJ\,mol^{-1}}$	$\dfrac{\Delta_{\rm sol,B}S^\circ}{\rm J\,K^{-1}\,mol^{-1}}$
5.00	278.15	−3.06	30.60	−121.0
12.13	285.28	0	31.43	−110.2
25.00	298.15	6.35	32.71	−88.4

12.7 Consider a hypothetical system in which two aqueous solutions are separated by a semipermeable membrane. Solution α is prepared by dissolving 1.00×10^{-5} mol KCl in 10.0 g water. Solution β is prepared from 1.00×10^{-5} mol KCl and 1.00×10^{-6} mol of the potassium salt of a polyelectrolyte dissolved in 10.0 g water. All of solution β is used to fill a dialysis bag, which is then sealed and placed in solution α.

Each polyelectrolyte ion has a charge of −10. The membrane of the dialysis bag is permeable to the water molecules and to the K^+ and Cl^- ions, but not to the polyelectrolyte. The system comes to equilibrium at 25.00 °C. Assume that the volume of the dialysis bag remains constant. Also make the drastic approximation that both solutions behave as ideal-dilute solutions.

(a) Find the equilibrium molality of each solute species in the two solution phases.

Solution:

Polyelectrolyte molality: $m_{\rm P} = \dfrac{1.00\times10^{-6}\,{\rm mol}}{10.0\times10^{-3}\,{\rm kg}} = 1.00\times10^{-4}\,{\rm mol\,kg^{-1}}$

Calculate the initial molalities of K^+ and Cl^-:

$$m_+^\alpha = m_-^\alpha = m_-^\beta = \frac{1.00\times10^{-5}\,{\rm mol}}{10.0\times10^{-3}\,{\rm kg}} = 1.00\times10^{-3}\,{\rm mol\,kg^{-1}}$$

$$m_+^\beta = 1.00\times10^{-3}\,{\rm mol\,kg^{-1}} + (10)(1.00\times10^{-4}\,{\rm mol\,kg^{-1}}) = 2.00\times10^{-3}\,{\rm mol\,kg^{-1}}$$

Simultaneously solve the following equations for m_-^α and m_-^β in the equilibrium system:

$$m_-^\alpha + m_-^\beta = 2.00\times10^{-3}\,{\rm mol\,kg^{-1}}$$

$$(m_-^\alpha)^2 = (m_-^\beta + z m_{\rm P})m_-^\beta = (m_-^\beta + 1.00\times10^{-3}\,{\rm mol\,kg^{-1}})m_-^\beta$$

The resulting equilibrium molalities are

$$m_-^\alpha = 1.20\times10^{-3}\,{\rm mol\,kg^{-1}} \qquad m_-^\beta = 0.80\times10^{-3}\,{\rm mol\,kg^{-1}}$$

Find the equilibrium values of m_+^α and m_+^β from the requirement of electroneutrality in each phase:

$$m_+^\alpha = m_-^\alpha = 1.20\times10^{-3}\,{\rm mol\,kg^{-1}}$$

$$m_+^\beta = m_-^\beta + z m_{\rm P} = 1.80\times10^{-3}\,{\rm mol\,kg^{-1}}$$

(b) Describe the amounts and directions of any macroscopic transfers of ions across the membrane that are required to establish the equilibrium state.

Solution:

The change in the amount of KCl in phase α is

$(1.20 \times 10^{-3}\,\text{mol kg}^{-1})(10.0 \times 10^{-3}\,\text{kg}) - 1.00 \times 10^{-5}\,\text{mol} = 2.0 \times 10^{-6}\,\text{mol}$

Thus, 2.0×10^{-6} mol KCl has transferred from phase β to phase α.

(c) Estimate the Donnan potential, $\phi^{\alpha} - \phi^{\beta}$.

Solution:

Apply Eq. 12.7.15:

$$\phi^{\alpha} - \phi^{\beta} \approx \frac{RT}{F} \ln \frac{m_+^{\beta}}{m_+^{\alpha}} = \frac{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(298.15\,\text{K})}{(96,485\,\text{C mol}^{-1})} \ln \frac{1.80 \times 10^{-3}\,\text{mol kg}^{-1}}{1.20 \times 10^{-3}\,\text{mol kg}^{-1}}$$

$$= 0.0104\,\text{V}$$

(d) Estimate the pressure difference across the membrane at equilibrium. (The density of liquid H_2O at 25.00 °C is $0.997\,\text{g cm}^{-3}$.)

Solution:

From Eq. 12.7.11: $p^{\beta} - p^{\alpha} \approx \rho_A^* RT[(m_+^{\beta} + m_-^{\beta} + m_P) - (m_+^{\alpha} + m_-^{\alpha})]$

$$= (0.997\,\text{g cm}^{-3})(10^{-3}\,\text{kg g}^{-1})(10^{6}\,\text{cm}^3\,\text{m}^{-3})$$

$$\times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(298.15\,\text{K})$$

$$\times [(1.80 + 0.80 + 0.100 - 1.20 - 1.20)10^{-3}\,\text{mol kg}^{-1}]$$

$$= 7.4 \times 10^{2}\,\text{Pa}$$

12.8 The derivation of Prob. 9.3 on page 42 shows that the pressure in a liquid droplet of radius r is greater than the pressure of the surrounding equilibrated gas phase by a quantity $2\gamma/r$, where γ is the surface tension.

(a) Consider a droplet of water of radius 1.00×10^{-6} m at 25 °C suspended in air of the same temperature. The surface tension of water at this temperature is $0.07199\,\text{J m}^{-2}$. Find the pressure in the droplet if the pressure of the surrounding air is 1.00 bar.

Solution:

$$p^{\text{l}} = p^{\text{g}} + \frac{2\gamma}{r} = 1.00\,\text{bar} + \frac{2(0.07199\,\text{J m}^{-2})}{1.00 \times 10^{-6}\,\text{m}} = 2.44 \times 10^{5}\,\text{Pa} = 2.44\,\text{bar}$$

(b) Calculate the difference between the fugacity of H_2O in the air of pressure 1.00 bar equilibrated with this water droplet, and the fugacity in air equilibrated at the same temperature and pressure with a pool of liquid water having a flat surface. Liquid water at 25 °C and 1 bar has a vapor pressure of 0.032 bar and a molar volume of $1.807 \times 10^{-5}\,\text{m}^3\,\text{mol}^{-1}$.

Solution:

From Eq. 12.8.3:

$$f(p_2) = f(p_1) \exp\left[\frac{V_{\text{m}}(\text{l})(p_2 - p_1)}{RT}\right]$$

$$= f(p_1) \exp\left[\frac{(1.807 \times 10^{-5}\,\text{m}^3\,\text{mol}^{-1})(1.44 \times 10^{5}\,\text{Pa})}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(298.15\,\text{K})}\right]$$

$$= 1.00105 f(p_1)$$

$$f(p_2) - f(p_1) = (1.00105 - 1) f(p_1) = (0.00105)(0.032\,\text{bar}) = 3.4 \times 10^{-5}\,\text{bar}$$

12.9 For a solution process in which species B is transferred from a gas phase to a liquid solution, find the relation between $\Delta_{\text{sol}}G^{\circ}$ (solute standard state based on mole fraction) and the Henry's law constant $k_{\text{H,B}}$.

Solution:

$\Delta_{\text{sol}}G^{\circ} = -RT \ln K$

From Eq. 12.8.30: $K = \dfrac{\Gamma_{x,\text{B}}\, p^{\circ}}{k_{\text{H,B}}}$

Under standard state conditions, $p = p^{\circ}$ and $\Gamma_{x,\text{B}} = 1$

Therefore $\Delta_{\text{sol}}G^{\circ} = RT \ln[k_{\text{H,B}}(p^{\circ})/p^{\circ}]$

12.10 Crovetto[10] reviewed the published data for the solubility of gaseous CO_2 in water, and fitted the Henry's law constant $k_{\text{H,B}}$ to a function of temperature. Her recommended values of $k_{\text{H,B}}$ at five temperatures are 1233 bar at 15.00 °C, 1433 bar at 20.00 °C, 1648 bar at 25.00 °C, 1874 bar at 30.00 °C, and 2111 bar at 35 °C.

(a) The partial pressure of CO_2 in the atmosphere is typically about 3×10^{-4} bar. Assume a fugacity of 3.0×10^{-4} bar, and calculate the aqueous solubility at 25.00 °C expressed both as a mole fraction and as a molality.

Solution:

From Table 9.4: $x_{\text{B}} = f_{\text{B}}/\gamma_{x,\text{B}}\, k_{\text{H,B}}$. Assume that $\gamma_{x,\text{B}}$ is 1:

$$x_{\text{B}} = \frac{f_{\text{B}}}{k_{\text{H,B}}} = \frac{3.0 \times 10^{-4}\ \text{bar}}{1648\ \text{bar}} = 1.8 \times 10^{-7}$$

From Eq. 9.1.14, at high dilution:

$$m_{\text{B}} = \frac{x_{\text{B}}}{M_{\text{A}}} = \frac{1.8 \times 10^{-7}}{18.0153 \times 10^{-3}\ \text{kg mol}^{-1}} = 1.0 \times 10^{-5}\ \text{mol kg}^{-1}$$

(b) Find the standard molar enthalpy of solution at 25.00 °C.

Solution:

From Eq. 12.8.32:

$$\Delta_{\text{sol,B}}H^{\circ} = R\frac{\text{d}\ln(k_{\text{H,B}}/p^{\circ})}{\text{d}(1/T)}$$

The values of $1/T$ and $\ln k_{\text{H,B}}/p^{\circ}$ are listed in Table 24.

Table 24 Data for Problem 12.10

$t/{}^{\circ}\text{C}$	T/K	$(1/T)/10^{-3}\ \text{K}^{-1}$	$\ln(k_{\text{H,B}}/p^{\circ})$
15.00	288.15	3.4704	7.117
20.00	293.15	3.4112	7.268
25.00	298.15	3.3540	7.407
30.00	303.15	3.2987	7.536
35.00	308.15	3.2452	7.655

The points are plotted in Fig. 23 on the next page. The tangent to the curve at the point for 298.15 K (dashed line) has the slope $\text{d}\ln(k_{\text{H,B}}/p^{\circ})/\,\text{d}(1/T) = -2.39 \times 10^{3}$ K. The same value may be obtained from the slope of a line between the two end points.

$\Delta_{\text{sol,B}}H^{\circ} = (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(-2.39 \times 10^{3}\ \text{K}) = -1.99 \times 10^{4}\ \text{J mol}^{-1}$

(c) Dissolved carbon dioxide exists mostly in the form of CO_2 molecules, but a small fraction exists as H_2CO_3 molecules, and there is also some ionization:

[10] Ref. [40].

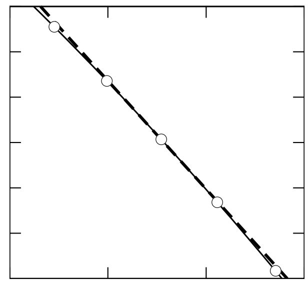

Figure 23 Plot for Problem 12.10(b).

$CO_2(aq) + H_2O(l) \rightarrow H^+(aq) + HCO_3^-(aq)$

(The equilibrium constant of this reaction is often called the first ionization constant of carbonic acid.) Combine the $k_{H,B}$ data with data in Appendix H to evaluate K and $\Delta_r H^\circ$ for the ionization reaction at 25.00 °C. Use solute standard states based on molality, which are also the solute standard states used for the values in Appendix H.

Solution:

The ionization reaction is the difference of the reaction
$CO_2(g) + H_2O(l) \rightarrow H^+(aq) + HCO_3^-(aq)$ and the solution process
$CO_2(g) \rightarrow CO_2(aq)$. Calculate the standard molar reaction Gibbs energy and standard molar reaction enthalpy of the first reaction:

$$\Delta_r G^\circ/\text{kJ mol}^{-1} = \sum_i \nu_i \Delta_f G^\circ(i)/\text{kJ mol}^{-1}$$
$$= -(-394.41) - (-237.16) + (0) + (-586.90) = 44.67$$

$$\Delta_r H^\circ/\text{kJ mol}^{-1} = \sum_i \nu_i \Delta_f H^\circ(i)/\text{kJ mol}^{-1}$$
$$= -(-393.51) - (-285.830) + (0) + (-689.93) = -10.59$$

From Eq. 12.8.30, the equilibrium constant for the solution process, with standard state based on mole fraction, is related to $k_{H,B}$ by $K = \Gamma_{x,B}\, p^\circ/k_{H,B}$. Approximate $\Gamma_{x,B}$ by 1 and take $k_{H,B}$ at 25.00 °C: $K = p^\circ/k_{H,B} = 1/1648 = 6.07 \times 10^{-4}$. Since the solute standard states used in Appendix H are based on molality, convert the value using Eq. 11.8.19:

$$K(m\text{ basis}) = \frac{K(x\text{ basis})}{M_A m^\circ} = \frac{6.07 \times 10^{-4}}{(18.0153 \times 10^{-3}\text{ kg mol}^{-1})(1\text{ mol kg}^{-1})} = 3.37 \times 10^{-2}$$

Calculate the standard molar reaction Gibbs energy of the solution process:

$$\Delta_{\text{sol,B}} G^\circ = -RT \ln K(m\text{ basis}) = -(8.3145\text{ J K}^{-1}\text{ mol}^{-1})(298.15\text{ K}) \ln(3.37 \times 10^{-2})$$
$$= 8.41 \times 10^3\text{ J mol}^{-1}$$

For the overall ionization reaction:

$$\Delta_r G^\circ/\text{kJ mol}^{-1} = 44.67 - (8.41) = 36.26$$

$$K = \exp\left(-\frac{\Delta_r G^\circ}{RT}\right) = \exp\left[-\frac{36.26 \times 10^3\text{ J mol}^{-1}}{(8.3145\text{ J K}^{-1}\text{ mol}^{-1})(298.15\text{ K})}\right] = 4.4 \times 10^{-7}$$

$$\Delta_r H^\circ/\text{kJ mol}^{-1} = (-10.59) - (-19.9) = 9.3$$

12.11 The solubility of gaseous O_2 at a partial pressure of 1.01 bar and a temperature of 310.2 K, expressed as a concentration, is 1.07×10^{-3} mol dm^{-3} in pure water and 4.68×10^{-4} mol dm^{-3} in a 3.0 M aqueous solution of KCl.[11] This solubility decrease is the *salting-out effect*. Calculate the activity coefficient $\gamma_{c,\mathrm{B}}$ of O_2 in the KCl solution.

Solution:

The equation for solubility expressed as a concentration analogous to Eq. 12.8.23 is

$$c_{\mathrm{B}} = \frac{K c^\circ f_{\mathrm{B}}/p^\circ}{\Gamma_{c,\mathrm{B}}\,\gamma_{c,\mathrm{B}}}$$

Assume that $\gamma_{c,\mathrm{B}}$ is equal to 1 when no KCl is present, and that $\Gamma_{c,\mathrm{B}}$ is not affected by the presence of KCl:

$$\gamma_{c,\mathrm{B}}(3.0\ \mathrm{M\ KCl}) = \gamma_{c,\mathrm{B}}(0\ \mathrm{M\ KCl})\frac{c_{\mathrm{B}}(0\ \mathrm{M\ KCl})}{c_{\mathrm{B}}(3.0\ \mathrm{M\ KCl})} = (1)\frac{1.07\times10^{-3}\ \mathrm{mol\,dm^{-3}}}{4.68\times10^{-4}\ \mathrm{mol\,dm^{-3}}} = 2.29$$

12.12 At 298.15 K, the partial molar volume of CO_2(aq) is 33 cm^3 mol^{-1}. Use Eq. 12.8.35 to estimate the percent change in the value of the Henry's law constant $k_{\mathrm{H,B}}$ for aqueous CO_2 at 298.15 K when the total pressure is changed from 1.00 bar to 10.00 bar.

Solution:

From Eq. 12.8.35:

$$k_{\mathrm{H,B}}(p_2) \approx k_{\mathrm{H,B}}(p_1)\exp\left[\frac{V_{\mathrm{B}}^{\infty}(p_2 - p_1)}{RT}\right]$$

$$k_{\mathrm{H,B}}(10.00\ \mathrm{bar}) \approx k_{\mathrm{H,B}}(1.00\ \mathrm{bar})\exp\left[\frac{(33\times10^{-6}\ \mathrm{m^3\,mol^{-1}})(10.00-1.00)\times10^5\ \mathrm{Pa}}{(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})(298.15\ \mathrm{K})}\right]$$

$$\approx 1.012\,k_{\mathrm{H,B}}(1.00\ \mathrm{bar})$$

percent change $\approx 1.2\%$

12.13 Rettich et al[12] made high-precision measurements of the solubility of gaseous oxygen (O_2) in water. Each measurement was made by equilibrating water and oxygen in a closed vessel for a period of up to two days, at a temperature controlled within ± 0.003 K. The oxygen was extracted from samples of known volume of the equilibrated liquid and gas phases, and the amount of O_2 in each sample was determined from p-V-T measurements taking gas nonideality into account. It was then possible to evaluate the mole fraction x_{B} of O_2 in the liquid phase and the ratio $(n_{\mathrm{B}}^{\mathrm{g}}/V^{\mathrm{g}})$ for the O_2 in the gas phase.

Table 25 Data for Problem 12.13 (A = H_2O, B = O_2)

$T = 298.152$ K	Second virial coefficients:
$x_{\mathrm{B}} = 2.02142\times10^{-5}$	$B_{\mathrm{AA}} = -1152\times10^{-6}$ m^3 mol^{-1}
$(n_{\mathrm{B}}^{\mathrm{g}}/V^{\mathrm{g}}) = 35.9957$ mol m^{-3}	$B_{\mathrm{BB}} = -16.2\times10^{-6}$ m^3 mol^{-1}
$p_{\mathrm{A}}^{*} = 3167.13$ Pa	$B_{\mathrm{AB}} = -27.0\times10^{-6}$ m^3 mol^{-1}
$V_{\mathrm{A}}^{*} = 18.069\times10^{-6}$ m^3 mol^{-1}	
$V_{\mathrm{B}}^{\infty} = 31.10\times10^{-6}$ m^3 mol^{-1}	

Table 25 gives values of physical quantities at $T = 298.152$ K needed for this problem. The values of x_{B} and $(n_{\mathrm{B}}^{\mathrm{g}}/V^{\mathrm{g}})$ were obtained by Rettich et al from samples of liquid and gas phases

[11] Ref. [112]. [12] Ref. [152].

equilibrated at temperature T, as explained above. p_A^* is the saturation vapor pressure of pure liquid water at this temperature.

Your calculations will be similar to those used by Rettich et al to obtain values of the Henry's law constant of oxygen to six significant figures. Your own calculations should also be carried out to six significant figures. For the gas constant, use the value $R = 8.31447\,\mathrm{J\,K^{-1}\,mol^{-1}}$.

The method you will use to evaluate the Henry's law constant $k_{H,B} = f_B/x_B$ at the experimental temperature and pressure is as follows. The value of x_B is known, and you need to find the fugacity f_B of the O_2 in the gas phase. f_B can be calculated from ϕ_B and p_B. These in turn can be calculated from the pressure p, the mole fraction y_B of O_2 in the gas phase, and known values of second virial coefficients. You will calculate p and y_B by an iterative procedure. Assume the gas has the virial equation of state $(V^g/n^g) = (RT/p) + B$ (Eq. 9.3.21) and use relevant relations in Sec. 9.3.4.

(a) For the equilibrated liquid-gas system, calculate initial approximate values of p and y_B by assuming that p_A is equal to p_A^* and p_B is equal to $(n_B^g/V^g)RT$.

Solution:

$$p_B = (n_B^g/V^g)RT = (35.9957\,\mathrm{mol\,m^{-3}})(8.31447\,\mathrm{J\,K^{-1}\,mol^{-1}})(298.152\,\mathrm{K})$$

$$= 89232.5\,\mathrm{Pa}$$

$$p = p_A + p_B = 3167.13\,\mathrm{Pa} + 89232.5\,\mathrm{Pa} = 92399.6\,\mathrm{Pa}$$

$$y_B = \frac{p_B}{p} = 0.965724$$

(b) Use your approximate values of p and y_B from part (a) to calculate ϕ_A, the fugacity coefficient of A in the gas mixture.

Solution:

From Eq. 9.3.27: $B'_A = B_{AA} + (-B_{AA} + 2B_{AB} - B_{BB})y_B^2 = -112.9\times10^{-6}\,\mathrm{m^3\,mol^{-1}}$

From Eq. 9.3.29: $\phi_A = \exp(B'_A p/RT) = 0.995801$

(c) Evaluate the fugacity f_A of the H_2O in the gas phase. Assume p, y_B, and ϕ_A have the values you calculated in parts (a) and (b). Hint: start with the value of the saturation vapor pressure of pure water.

Solution:

From Eq. 9.3.27, with y_B set equal to 1: $B'_A = B_{AA} = -1152\times10^{-6}\,\mathrm{m^3\,mol^{-1}}$

From Eq. 9.3.29, with p set equal to p_A^*: $\phi_A^*(p_A^*) = \exp(B'_A p_A^*/RT) = 0.998529$

$f_A^*(p_A^*) = \phi_A^*(p_A^*)p_A^* = (0.998529)(3167.13\,\mathrm{Pa}) = 3162.47\,\mathrm{Pa}$

From Eq. 12.8.3:

$$f_A^*(p) = f_A^*(p_A^*)\exp\left[\frac{V_A^*(p-p_A^*)}{RT}\right]$$

$$= (3162.47\,\mathrm{Pa})\exp\left[\frac{(18.069\times10^{-6}\,\mathrm{m^3\,mol^{-1}})(92399.6\,\mathrm{Pa} - 3167.13\,\mathrm{Pa})}{(8.31447\,\mathrm{J\,K^{-1}\,mol^{-1}})(298.152\,\mathrm{K})}\right]$$

$$= 3164.53\,\mathrm{Pa}$$

From Raoult's law for fugacity:

$$f_A(p) = (1-x_B)f_A^*(p) = (0.999980)(3164.53\,\mathrm{Pa}) = 3164.47\,\mathrm{Pa}$$

(d) Use your most recently calculated values of p, ϕ_A, and f_A to calculate an improved value of y_B.

Solution:

$p_A = f_A/\phi_A = (3164.47\,\text{Pa})/(0.995801) = 3177.81\,\text{Pa}$

$y_B = 1 - y_A = 1 - p_A/p = 1 - (3177.81\,\text{Pa})/(92399.6\,\text{Pa}) = 0.965608$

(e) Use your current values of p and y_B to evaluate the compression factor Z of the gas mixture, taking nonideality into account.

Solution:

$y_A = 1 - y_B = 1 - 0.965608 = 0.034392$

From Eq. 9.3.23:

$$\begin{aligned} B &= y_A^2 B_{AA} + 2y_A y_B B_{AB} + y_B^2 B_{BB} \\ &= (0.034392)^2 B_{AA} + 2(0.034392)(0.965608) B_{AB} + (0.965608)^2 B_{BB} \\ &= -18.2608 \times 10^{-6}\,\text{m}^3\,\text{mol}^{-1} \end{aligned}$$

From Eq. 9.3.22:

$$Z = 1 + \frac{Bp}{RT} = 1 + \frac{(-18.2608 \times 10^{-6}\,\text{m}^3\,\text{mol}^{-1})(92399.6\,\text{Pa})}{(8.31447\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})(298.152\,\text{K})} = 0.999319$$

(f) Derive a general expression for p as a function of (n_B^g/V^g), T, y_B, and Z. Use this expression to calculate an improved value of p.

Solution:

$$Z \stackrel{\text{def}}{=} \frac{pV^g}{n^g RT} \qquad n^g = n_B^g/y_B$$

$$\begin{aligned} p &= \frac{n^g RTZ}{V^g} = \left(\frac{n_B^g}{V^g}\right)\frac{RTZ}{y_B} \\ &= (35.9957\,\text{mol}\,\text{m}^{-3})\frac{(8.31447\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})(298.152\,\text{K})(0.999319)}{0.965608} \\ &= 92347.7\,\text{Pa} \end{aligned}$$

(g) Finally, use the improved values of p and y_B to evaluate the Henry's law constant $k_{H,B}$ at the experimental T and p.

Solution:

From Eq. 9.3.28:

$$B'_B = B_{BB} + (-B_{AA} + 2B_{AB} - B_{BB})(1 - y_B)^2 = -14.88 \times 10^{-6}\,\text{m}^3\,\text{mol}^{-1}$$

From Eq. 9.3.29:

$$\phi_B = \exp\left(B'_B p/RT\right) = \exp\left[\frac{(-14.88 \times 10^{-6}\,\text{m}^3\,\text{mol}^{-1})(92347.7\,\text{Pa})}{(8.31447\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})(298.152\,\text{K})}\right] = 0.999446$$

$$\begin{aligned} k_{H,B} &= \frac{f_B}{x_B} = \frac{\phi_B y_B p}{x_B} = \frac{(0.999446)(0.965608)(92347.7\,\text{Pa})}{2.02142 \times 10^{-5}} \\ &= 4.40890 \times 10^9\,\text{Pa} \end{aligned}$$

12.14 The method described in Prob. 12.13 has been used to obtain high-precision values of the Henry's law constant, $k_{H,B}$, for gaseous methane dissolved in water.[13] Table 26 lists values of $\ln(k_{H,B}/p^\circ)$ at eleven temperatures in the range 275 K–328 K and at pressures close to 1 bar. Use these data to evaluate $\Delta_{sol,B}H^\circ$ and $\Delta_{sol,B}C_p^\circ$ at $T = 298.15\,\text{K}$. This can be done by a

[13] Ref. [153].

Table 26 Data for Prob. 12.14

$1/(T/\text{K})$	$\ln(k_{\text{H,B}}/p^\circ)$	$1/(T/\text{K})$	$\ln(k_{\text{H,B}}/p^\circ)$
0.00363029	10.0569	0.00329870	10.6738
0.00359531	10.1361	0.00319326	10.8141
0.00352175	10.2895	0.00314307	10.8673
0.00347041	10.3883	0.00309444	10.9142
0.00341111	10.4951	0.00304739	10.9564
0.00335390	10.5906		

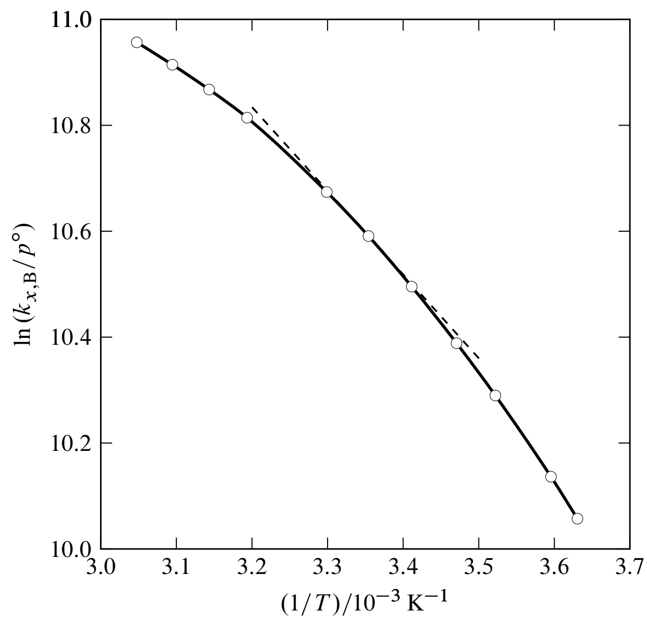

Figure 24 Plot for Prob. 12.14. Open circles: data points from Table 12.26. Dashed line: tangent to curve at $1/T = 1/298.15\,\text{K}$.

graphical method. Better precision will be obtained by making a least-squares fit of the data to the three-term polynomial

$$\ln(k_{\text{H,B}}/p^\circ) = a + b(1/T) + c(1/T)^2$$

and using the values of the coefficients a, b, and c for the evaluations.

Solution:

For the *graphical method*, make a plot of ln $k_{\text{H,B}}$ versus $1/T$ as in Fig. 24. The tangent to the curve at $1/T = 1/298.15\,\text{K}$ (dashed line) has a slope of $-1.58\times10^3\,\text{K}$.

From Eq. 12.8.32:

$$\Delta_{\text{sol,B}}H^\circ = R\,\frac{\text{d}\ln(k_{\text{H,B}}/p^\circ)}{\text{d}(1/T)} = (8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})(-1.58\times10^3\,\text{K}) = -13.1\,\text{kJ}\,\text{mol}^{-1}$$

From Eq. 11.3.6:

$$\Delta_{\text{sol,B}}C_p^\circ = \text{d}\Delta_{\text{sol,B}}H^\circ/\,\text{d}T$$

From the slope between the first two points on the graph:

$\Delta_{\text{sol,B}} H^\circ = (-897\,\text{K})R$ at $T \approx 325.6\,\text{K}$

From the slope between the last two points on the graph:

$\Delta_{\text{sol,B}} H^\circ = (-2264\,\text{K})R$ at $T \approx 276.8\,\text{K}$

$$\Delta_{\text{sol,B}} C_p^\circ \approx \frac{(-897\,\text{K} + 2264\,\text{K})(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})}{325.6\,\text{K} - 276.8\,\text{K}} = 233\,\text{J K}^{-1}\,\text{mol}^{-1}$$

Using a *least-squares fit* to $\ln(k_{\text{H,B}}/p^\circ) = a + b(1/T) + c(1/T)^2$:

$a = 1.6755 \qquad b = 6896.86\,\text{K} \qquad c = -1.263836 \times 10^6\,\text{K}^2$

$$\Delta_{\text{sol,B}} H^\circ = R\,\frac{\mathrm{d}\ln(k_{\text{H,B}}/p^\circ)}{\mathrm{d}(1/T)} = R[b + 2c(1/T)] = -13.145\,\text{kJ mol}^{-1}$$

$$\Delta_{\text{sol,B}} C_p^\circ = \mathrm{d}\Delta_{\text{sol,B}} H^\circ/\,\mathrm{d}T = -2Rc(1/T)^2 = 236.42\,\text{J K}^{-1}\,\text{mol}^{-1}$$

12.15 Liquid water and liquid benzene have very small mutual solubilities. Equilibria in the binary water–benzene system were investigated by Tucker, Lane, and Christian[14] as follows. A known amount of distilled water was admitted to an evacuated, thermostatted vessel. Part of the water vaporized to form a vapor phase. Small, precisely measured volumes of liquid benzene were then added incrementally from the sample loop of a liquid-chromatography valve. The benzene distributed itself between the liquid and gaseous phases in the vessel. After each addition, the pressure was read with a precision pressure gauge. From the known amounts of water and benzene and the total pressure, the liquid composition and the partial pressure of the benzene were calculated. The fugacity of the benzene in the vapor phase was calculated from its partial pressure and the second virial coefficient.

At a fixed temperature, for mole fractions x_{B} of benzene in the liquid phase up to about 3×10^{-4} (less than the solubility of benzene in water), the fugacity of the benzene in the equilibrated gas phase was found to have the following dependence on x_{B}:

$$\frac{f_{\text{B}}}{x_{\text{B}}} = k_{\text{H,B}} - A x_{\text{B}}$$

Here $k_{\text{H,B}}$ is the Henry's law constant and A is a constant related to deviations from Henry's law. At 30 °C, the measured values were $k_{\text{H,B}} = 385.5$ bar and $A = 2.24 \times 10^4$ bar.

(a) Treat benzene (B) as the solute and find its activity coefficient on a mole fraction basis, $\gamma_{x,\text{B}}$, at 30 °C in the solution of composition $x_{\text{B}} = 3.00 \times 10^{-4}$.

Solution:

From Table 9.5, with the pressure factor of unity:

$$a_{x,\text{B}} = \gamma_{x,\text{B}}\, x_{\text{B}} = \frac{f_{\text{B}}}{k_{\text{H,B}}}$$

$$\gamma_{x,\text{B}} = \frac{f_{\text{B}}}{k_{\text{H,B}}\, x_{\text{B}}} = 1 - \frac{A x_{\text{B}}}{k_{\text{H,B}}} = 1 - \frac{(2.24 \times 10^4\,\text{bar})(3.00 \times 10^{-4})}{385.5\,\text{bar}} = 0.9826$$

(b) The fugacity of benzene vapor in equilibrium with pure liquid benzene at 30 °C is $f_{\text{B}}^* = 0.1576$ bar. Estimate the mole fraction solubility of liquid benzene in water at this temperature.

Solution:

Assume that the fugacity of benzene vapor in equilibrium with a saturated aqueous solution of benzene is 0.1576 bar, and solve the equation $f_{\text{B}}/x_{\text{B}} = k_{\text{H,B}} - A x_{\text{B}}$ for x_{B}:

[14] Ref. [171].

$$Ax_B^2 - k_{H,B}x_B + f_B = 0$$

$$x_B = \frac{k_{H,B} \pm \sqrt{k_{H,B}^2 - 4Af_B}}{2A} = 1.68\times 10^{-2} \quad \text{or} \quad 4.19\times 10^{-4}$$

As x_B is increased in the unsaturated solution the saturation condition is reached at the lower of the two values: $x_B = 4.19\times 10^{-4}$.

(c) The calculation of $\gamma_{x,B}$ in part (a) treated the benzene as a single solute species with deviations from infinite-dilution behavior. Tucker et al suggested a dimerization model to explain the observed negative deviations from Henry's law. (Classical thermodynamics, of course, cannot prove such a molecular interpretation of observed macroscopic behavior.) The model assumes that there are two solute species, a monomer (M) and a dimer (D), in reaction equilibrium: 2M $\rightleftharpoons$ D. Let n_B be the total amount of C_6H_6 present in solution, and define the mole fractions

$$x_B \stackrel{\text{def}}{=} \frac{n_B}{n_A + n_B} \approx \frac{n_B}{n_A}$$

$$x_M \stackrel{\text{def}}{=} \frac{n_M}{n_A + n_M + n_D} \approx \frac{n_M}{n_A} \qquad x_D \stackrel{\text{def}}{=} \frac{n_D}{n_A + n_M + n_D} \approx \frac{n_D}{n_A}$$

where the approximations are for dilute solution. In the model, the individual monomer and dimer particles behave as solutes in an ideal-dilute solution, with activity coefficients of unity. The monomer is in transfer equilibrium with the gas phase: $x_M = f_B/k_{H,B}$. The equilibrium constant expression (using a mole fraction basis for the solute standard states and setting pressure factors equal to 1) is $K = x_D/x_M^2$. From the relation $n_B = n_M + 2n_D$, and because the solution is very dilute, the expression becomes

$$K = \frac{x_B - x_M}{2x_M^2}$$

Make individual calculations of K from the values of f_B measured at $x_B = 1.00\times 10^{-4}$, $x_B = 2.00\times 10^{-4}$, and $x_B = 3.00\times 10^{-4}$. Extrapolate the calculated values of K to x_B=0 in order to eliminate nonideal effects such as higher aggregates. Finally, find the fraction of the benzene molecules present in the dimer form at $x_B = 3.00\times 10^{-4}$ if this model is correct.

Solution:

Use the formulas

$$x_M = \frac{f_B}{k_{H,B}} = x_B - \frac{Ax_B^2}{k_{H,B}} \quad \text{and} \quad K = \frac{x_B - x_M}{2x_M^2}$$

The results are $K = 29.4$ at $x_B = 1.00\times 10^{-4}$, $K = 29.7$ at $x_B = 2.00\times 10^{-4}$, and $K = 30.1$ at $x_B = 3.00\times 10^{-4}$. The extrapolated value is $K \approx 29.1$. At $x_B = 3.00\times 10^{-4}$, the fraction of benzene molecules in the dimer form is

$$\frac{2n_D}{n_B} = 1 - \frac{n_M}{n_B} \approx 1 - \frac{x_M}{x_B} = 1 - \frac{2.95\times 10^{-4}}{3.00\times 10^{-4}} = 0.017$$

12.16 Use data in Appendix H to evaluate the thermodynamic equilibrium constant at 298.15 K for the limestone reaction

$$CaCO_3(\text{cr, calcite}) + CO_2(\text{g}) + H_2O(\text{l}) \rightarrow Ca^{2+}(\text{aq}) + 2HCO_3^{\;-}(\text{aq})$$

Solution:

$\Delta_r G^\circ/\text{kJ mol}^{-1} = \sum_i \nu_i \Delta_f G^\circ(i)/\text{kJ mol}^{-1}$

$$= -(-1128.8) - (-394.41) - (-237.16) + (-552.8) + 2(-586.90)$$

$$= 33.8$$

$$K = \exp\left(-\frac{\Delta_r G^\circ}{RT}\right) = \exp\left[-\frac{33.8\times 10^3\,\mathrm{J\,mol^{-1}}}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298.15\,\mathrm{K})}\right] = 1.2\times 10^{-6}$$

12.17 For the dissociation equilibrium of formic acid, $HCO_2H(aq) \rightleftharpoons H^+(aq) + HCO_2{}^-(aq)$, the acid dissociation constant at 298.15 K has the value $K_a = 1.77\times 10^{-4}$.

(a) Use Eq. 12.9.7 to find the degree of dissociation and the hydrogen ion molality in a 0.01000 molal formic acid solution. You can safely set Γ_r and $\gamma_{m,\mathrm{HA}}$ equal to 1, and use the Debye–Hückel limiting law (Eq. 10.4.8) to calculate $\gamma_\pm$. You can do this calculation by iteration: Start with an initial estimate of the ionic strength (in this case 0), calculate $\gamma_\pm$ and α, and repeat these steps until the value of α no longer changes.

Solution:

Equation 12.9.7:

$$K_a = \Gamma_r \frac{\gamma_\pm^2\,\alpha^2 m_B/m^\circ}{\gamma_{m,\mathrm{HA}}(1-\alpha)} \approx \frac{\gamma_\pm^2\,\alpha^2 m_B/m^\circ}{1-\alpha}$$

Solve for α:

$$\alpha = \frac{-K_a + \left[K_a^2 + 4\gamma_\pm^2(m_B/m^\circ)K_a\right]^{1/2}}{2\gamma_\pm^2(m_B/m^\circ)}$$

Calculate $\gamma_\pm$ from Eq. 10.4.8:

$$\ln\gamma_\pm = -A\,|z_+z_-|\,\sqrt{I_m} = -1.1744(\alpha m_B/m^\circ)^{1/2}$$

First estimate ($I_m = 0, \gamma_\pm = 1$):

$$\alpha = \frac{-1.77\times 10^{-4} + \left[(1.77\times 10^{-4})^2 + 4(0.01000)(1.77\times 10^{-4})\right]^{1/2}}{2(0.01000)} = 0.124$$

$$\ln\gamma_\pm = -(1.1744)(0.00124)^{1/2} = -0.0414 \qquad \gamma_\pm = 0.9594$$

Second estimate:

$$\alpha = \frac{-1.77\times 10^{-4} + \left[(1.77\times 10^{-4})^2 + 4(0.9594)^2(0.01000)(1.77\times 10^{-4})\right]^{1/2}}{2(0.9594)^2(0.01000)}$$

$$= 0.129$$

$$\ln\gamma_\pm = -(1.1744)(0.00129)^{1/2} = -0.0422 \qquad \gamma_\pm = 0.9586$$

Third estimate:

$$\alpha = \frac{-1.77\times 10^{-4} + \left[(1.77\times 10^{-4})^2 + 4(0.9586)^2(0.01000)(1.77\times 10^{-4})\right]^{1/2}}{2(0.9586)^2(0.01000)}$$

$$= 0.129$$

The calculated degree of dissociation has become constant at $\alpha = 0.129$; the hydrogen ion molality is $m_+ = \alpha m_B = 1.29\times 10^{-3}\,\mathrm{mol\,kg^{-1}}$.

(b) Estimate the degree of dissociation of formic acid in a solution that is 0.01000 molal in both formic acid and sodium nitrate, again using the Debye–Hückel limiting law for $\gamma_\pm$. Compare with the value in part (a).

Solution:

Use same formula for α as in part (a); calculate $\gamma_\pm$ from

$$\ln\gamma_\pm = -A\,|z_+z_-|\,\sqrt{I_m} = -1.1744(\alpha m_{\rm B}/m^\circ + 0.01000)^{1/2}$$

First estimate:

$$\ln\gamma_\pm = -1.1744(0.01000)^{1/2} = -0.1174 \qquad \gamma_\pm = 0.8892$$

$$\alpha = \frac{-1.77\times10^{-4} + \left[(1.77\times10^{-4})^2 + 4(0.8892)^2(0.01000)(1.77\times10^{-4})\right]^{1/2}}{2(0.8892)^2(0.01000)}$$

$$= 0.139$$

$$\ln\gamma_\pm = -(1.1744)(0.00139 + 0.01000)^{1/2} = -0.1253 \qquad \gamma_\pm = 0.8822$$

Second estimate:

$$\alpha = \frac{-1.77\times10^{-4} + \left[(1.77\times10^{-4})^2 + 4(0.8822)^2(0.01000)(1.77\times10^{-4})\right]^{1/2}}{2(0.8822)^2(0.01000)}$$

$$= 0.140$$

$$\ln\gamma_\pm = -(1.1744)(0.00140 + 0.01000)^{1/2} = -0.1254 \qquad \gamma_\pm = 0.8822$$

This value of $\gamma_\pm$ will give the same value of the degree of dissociation as before: $\alpha = 0.140$. The increased ionic strength causes the degree of dissociation to increase.

12.18 Use the following experimental information to evaluate the standard molar enthalpy of formation and the standard molar entropy of the aqueous chloride ion at 298.15 K, based on the conventions $\Delta_{\rm f}H^\circ({\rm H^+, aq}) = 0$ and $S^\circ_{\rm m}({\rm H^+, aq}) = 0$ (Secs. 11.3.2 and 11.8.4). (Your calculated values will be close to, but not exactly the same as, those listed in Appendix H, which are based on the same data combined with data of other workers.)

- For the reaction $\frac{1}{2}{\rm H_2(g)} + \frac{1}{2}{\rm Cl_2(g)} \rightarrow {\rm HCl(g)}$, the standard molar enthalpy of reaction at 298.15 K measured in a flow calorimeter[15] is $\Delta_{\rm r}H^\circ = -92.312\ {\rm kJ\,mol^{-1}}$.
- The standard molar entropy of gaseous HCl at 298.15 K calculated from spectroscopic data is $S^\circ_{\rm m} = 186.902\ {\rm J\,K^{-1}\,mol^{-1}}$.
- From five calorimetric runs,[16] the average experimental value of the standard molar enthalpy of solution of gaseous HCl at 298.15 K is $\Delta_{\rm sol,B}H^\circ = -74.84\ {\rm kJ\,mol^{-1}}$.
- From vapor pressure measurements of concentrated aqueous HCl solutions,[17] the value of the ratio $f_{\rm B}/a_{m,{\rm B}}$ for gaseous HCl in equilibrium with aqueous HCl at 298.15 K is 5.032×10^{-7} bar.

Solution:

The sum of the reactions $\frac{1}{2}{\rm H_2(g)} + \frac{1}{2}{\rm Cl_2(g)} \rightarrow {\rm HCl(g)}$ and ${\rm HCl(g)} \rightarrow {\rm H^+(aq)} + {\rm Cl^-(aq)}$ is the net reaction

$$\tfrac{1}{2}{\rm H_2(g)} + \tfrac{1}{2}{\rm Cl_2(g)} \rightarrow {\rm H^+(aq)} + {\rm Cl^-(aq)}$$

with standard molar reaction enthalpy equal to the sum of the corresponding standard molar enthalpy changes:

$$\Delta_{\rm r}H^\circ = (-92.312 - 74.84)\ {\rm kJ\,mol^{-1}} = -167.15\ {\rm kJ\,mol^{-1}}$$

Since $\Delta_{\rm r}H^\circ$ for the net reaction is equal to the sum of the standard molar enthalpies of formation of ${\rm H^+(aq)}$ and ${\rm Cl^-(aq)}$, and $\Delta_{\rm f}H^\circ({\rm H^+, aq})$ is zero, we have

[15]Ref. [155]. [16]Ref. [77]. [17]Ref. [148].

$\Delta_f H°(Cl^-, aq) = -167.15\,kJ\,mol^{-1}$

For the dissolution reaction

$HCl(g) \rightarrow H^+(aq) + Cl^-(aq)$

the equilibrium constant is given by $K = a_{m,B}/(f_B/p°)$, and the standard molar reaction Gibbs energy is

$$\Delta_r G° = -RT \ln K = -(8.3145\,J\,K^{-1}\,mol^{-1})(298.15\,K) \ln\left(\frac{1}{5.032 \times 10^{-7}}\right)$$
$$= 3.595 \times 10^4\,J\,mol^{-1}$$

The standard molar reaction entropy is then

$$\Delta_r S° = \frac{\Delta_r H° - \Delta_r G°}{T} = \frac{(-74.84 \times 10^3 + 3.595 \times 10^4)\,J\,mol^{-1}}{298.15\,K}$$
$$= -130.44\,J\,K^{-1}\,mol^{-1}$$

Use Eq. 11.8.22 on page 355:

$$\Delta_r S° = \textstyle\sum_i \nu_i S_i° = -S_m°(HCl, g) + S_m°(H^+, aq) + S_m°(Cl^-, aq)$$

Since $S_m°(H^+, aq)$ is zero, we have

$$S_m°(Cl^-, aq) = \Delta_r S° + S_m°(HCl, g) = (-130.44 + 186.902)\,J\,K^{-1}\,mol^{-1}$$
$$= 56.46\,J\,K^{-1}\,mol^{-1}$$

12.19 The solubility of crystalline AgCl in ultrapure water has been determined from the electrical conductivity of the saturated solution.[18] The average of five measurements at 298.15 K is $s_B = 1.337 \times 10^{-5}\,mol\,dm^{-3}$. The density of water at this temperature is $\rho_A^* = 0.9970\,kg\,dm^{-3}$.

(a) From these data and the Debye–Hückel limiting law, calculate the solubility product K_s of AgCl at 298.15 K.

Solution:

From Eq. 9.1.14 for a dilute solution:

$$m_B = \frac{c_B}{\rho_A^*} = \frac{1.337 \times 10^{-5}\,mol\,dm^{-3}}{0.9970\,kg\,dm^{-3}} = 1.341 \times 10^{-5}\,mol\,kg^{-1}$$

Find the mean ionic activity coefficient from the Debye–Hückel limiting law, Eq. 10.4.8:

$$\ln \gamma_\pm = -A\sqrt{I_m} = -(1.1744\,kg^{1/2}\,mol^{-1/2})(1.341 \times 10^{-5}\,mol\,kg^{-1})^{1/2}$$
$$= -4.301 \times 10^{-3}$$

$$\gamma_\pm = 0.996$$

Use Eq. 12.5.26 with $\Gamma_r = 1$:

$$K_s = \gamma_\pm^2 (m_B/m°)^2 = (0.996)^2 (1.341 \times 10^{-5})^2 = 1.783 \times 10^{-10}$$

(b) Evaluate the standard molar Gibbs energy of formation of aqueous Ag^+ ion at 298.15 K, using the results of part (a) and the values $\Delta_f G°(Cl^-, aq) = -131.22\,kJ\,mol^{-1}$ and $\Delta_f G°(AgCl, s) = -109.77\,kJ\,mol^{-1}$ from Appendix H.

Solution:

Calculate $\Delta_{sol} G°$ for the dissolution reaction $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$:

[18] Ref. [72].

$$\Delta_{sol}G^\circ = -RT \ln K_s = -(8.3145\,J\,K^{-1}\,mol^{-1})(298.15\,K)\ln(1.783\times 10^{-10})$$
$$= 5.5647\times 10^4\,J\,mol^{-1}$$

Apply the general relation $\Delta_r G^\circ = \sum_i \nu_i \Delta_f G^\circ(i)$ to the dissolution reaction:

$$\Delta_{sol}G^\circ = -\Delta_f G^\circ(AgCl, s) + \Delta_f G^\circ(Ag^+, aq) + \Delta_f G^\circ(Cl^-, aq)$$

Rearrange to

$$\Delta_f G^\circ(Ag^+, aq) = \Delta_{sol}G^\circ + \Delta_f G^\circ(AgCl, s) - \Delta_f G^\circ(Cl^-, aq)$$

$$\Delta_f G^\circ(Ag^+, aq)/kJ\,mol^{-1} = 55.647 + (-109.77) - (-131.22) = 77.10$$

12.20 The following reaction was carried out in an adiabatic solution calorimeter by Wagman and Kilday:[19]

$$AgNO_3(s) + KCl(aq, m_B = 0.101\,mol\,kg^{-1}) \rightarrow AgCl(s) + KNO_3(aq)$$

The reaction can be assumed to go to completion, and the amount of KCl was in slight excess, so the amount of AgCl formed was equal to the initial amount of $AgNO_3$. After correction for the enthalpies of diluting the solutes in the initial and final solutions to infinite dilution, the standard molar reaction enthalpy at 298.15 K was found to be $\Delta_r H^\circ = -43.042\,kJ\,mol^{-1}$. The same workers used solution calorimetry to obtain the molar enthalpy of solution at infinite dilution of crystalline $AgNO_3$ at 298.15 K: $\Delta_{sol,B}H^\infty = 22.727\,kJ\,mol^{-1}$.

(a) Show that the difference of these two values is the standard molar reaction enthalpy for the precipitation reaction

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

and evaluate this quantity.

Solution:

The reaction $AgNO_3(s) + KCl(aq) \rightarrow AgCl(s) + KNO_3(aq)$ is equivalent to $AgNO_3(s) + Cl^-(aq) \rightarrow AgCl(s) + NO_3{}^-(aq)$. Subtracting the equation for the dissolution of $AgNO_3$, $AgNO_3(s) \rightarrow Ag^+(aq) + Cl^-(aq)$, gives the equation for precipitation, $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$. Thus, the standard molar reaction enthalpy for the precipitation reaction is the difference

$$\Delta_r H^\circ = [(-43.042) - (22.727)]\,kJ\,mol^{-1} = -65.769\,kJ\,mol^{-1}$$

(b) Evaluate the standard molar enthalpy of formation of aqueous Ag^+ ion at 298.15 K, using the results of part (a) and the values $\Delta_f H^\circ(Cl^-, aq) = -167.08\,kJ\,mol^{-1}$ and $\Delta_f H^\circ(AgCl, s) = -127.01\,kJ\,mol^{-1}$ from Appendix H. (These values come from calculations similar to those in Probs. 12.18 and 14.4.) The calculated value will be close to, but not exactly the same as, the value listed in Appendix H, which is based on the same data combined with data of other workers.

Solution:

Apply the relation $\Delta_r H^\circ = \sum_i \Delta_f H^\circ(i)$ to the precipitation reaction:

$$\Delta_r H^\circ = -\Delta_f H^\circ(Ag^+, aq) - \Delta_f H^\circ(Cl^-, aq) + \Delta_f H^\circ(AgCl, s)$$

$$\Delta_f H^\circ(Ag^+, aq) = -\Delta_r H^\circ - \Delta_f H^\circ(Cl^-, aq) + \Delta_f H^\circ(AgCl, s)$$
$$= [-(-65.769) - (-167.08) + (-127.01)]\,kJ\,mol^{-1}$$
$$= 105.84\,kJ\,mol^{-1}$$

[19]Ref. [176].

Chapter 13 The Phase Rule and Phase Diagrams

13.1 Consider a single-phase system that is a gaseous mixture of N_2, H_2, and NH_3. For each of the following cases, find the number of degrees of freedom and give an example of the independent intensive variables that could be used to specify the equilibrium state, apart from the total amount of gas.

(a) There is no reaction.

Solution:

There are three components: N_2, H_2, and NH_3. The number of degrees of freedom is

$F = 2 + C - P = 2 + 3 - 1 = 4$

The equilibrium state could be specified by T, p, and the mole fractions of two of the substances; or by T and the partial pressures of each of the substances.

(b) The reaction $N_2(g) + 3\,H_2(g) \rightarrow 2\,NH_3(g)$ is at equilibrium.

Solution:

There are three species and one independent relation for reaction equilibrium, $-\mu_{N_2} - 3\mu_{H_2} + 2\mu_{NH_3} = 0$.

$F = 2 + s - r - P = 2 + 3 - 1 - 1 = 3$

One possibility would be to specify the equilibrium state by values of T and the partial pressures of two of the gases; the partial pressure of the third gas would be determined by the thermodynamic equilibrium constant and the fugacity coefficients, and p would be the sum of the three partial pressures.

(c) The reaction is at equilibrium and the system is prepared from NH_3 only.

Solution:

There are three species and two independent relations among intensive variables: $-\mu_{N_2} - 3\mu_{H_2} + 2\mu_{NH_3} = 0$ and $y_{H_2} = 3y_{N_2}$.

$F = 2 + s - r - P = 2 + 3 - 2 - 1 = 2$

The equilibrium state could be specified by T and p. The partial pressures of the three gases would be those that satisfy the relations $-\mu_{N_2} - 3\mu_{H_2} + 2\mu_{NH_3} = 0$, $y_{H_2} = 3y_{N_2}$, and $p_{N_2} + p_{H_2} + p_{NH_3} = p$.

13.2 How many components has a mixture of water and deuterium oxide in which the equilibrium $H_2O + D_2O \rightleftharpoons 2\,HDO$ exists?

Solution:

There are three species and one relation among intensive variables, $-\mu_{H_2O} - \mu_{D_2O} + 2\mu_{HDO} = 0$.

$C = s - r = 3 - 1 = 2$

13.3 Consider a system containing only $NH_4Cl(s)$, $NH_3(g)$, and $HCl(g)$. Assume that the equilibrium $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$ exists.

(a) Suppose you prepare the system by placing solid NH_4Cl in an evacuated flask and heating to 400 K. Use the phase rule to decide whether you can vary the pressure while both phases remain in equilibrium at 400 K.

Solution:

There are three species and two relations among intensive variables:
$-\mu_{NH_4Cl} + \mu_{NH_3} + \mu_{HCl} = 0$ and $y_{NH_3} = y_{HCl}$ (or $p_{NH_3} = p_{HCl}$).

$F = 2 + s - r - P = 2 + 3 - 2 - 2 = 1$

The two phases cannot remain in equilibrium while p is varied and T is fixed.

(b) According to the phase rule, if the system is not prepared as described in part (a) could you vary the pressure while both phases remain in equilibrium at 400 K? Explain.

Solution:

Yes, because y_{NH_3} no longer has to equal y_{HCl} and F is increased to 2. T and p can be varied independently, and the pressure can be varied while the temperature is fixed at an arbitrary value.

(c) Rationalize your conclusions for these two cases on the basis of the thermodynamic equilibrium constant. Assume that the gas phase is an ideal gas mixture and use the approximate expression $K = p_{NH_3} p_{HCl}/(p^\circ)^2$.

Solution:

At a fixed temperature, K has a fixed value. If the system is prepared from $NH_4Cl(s)$ only, then the following relations hold

$$p = p_{NH_3} + p_{HCl} \qquad p_{NH_3} = p_{HCl} = p/2 \qquad K = (p/2)^2/(p^\circ)^2 \qquad p = 2\sqrt{K}\,p^\circ$$

and therefore p can have only one value at each temperature. If, however, p_{NH_3} and p_{HCl} can be varied independently, then the relation $K = p_{NH_3} p_{HCl}/(p^\circ)^2$ can be satisfied for a fixed value of K and a varying value of $p = p_{NH_3} + p_{HCl}$.

13.4 Consider the lime-kiln process $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$. Find the number of intensive variables that can be varied independently in the equilibrium system under the following conditions:

(a) The system is prepared by placing calcium carbonate, calcium oxide, and carbon dioxide in a container.

Solution:

There are three species, three phases, and one relation among intensive variables:

$-\mu_{CaCO_3} + \mu_{CaO} + \mu_{CO_2} = 0$

$F = 2 + s - r - P = 2 + 3 - 1 - 3 = 1$

Only one intensive variable, such as T, can be varied independently while the three phases remain in equilibrium.

(b) The system is prepared from calcium carbonate only.

Solution:

Only one intensive variable can be varied, as before; the initial condition leads to no relation among intensive variables.

(c) The temperature is fixed at 1000 K.

Solution:

If T is fixed, no other intensive variable can be varied.

13.5 What are the values of C and F in systems consisting of solid AgCl in equilibrium with an aqueous phase containing H_2O, $Ag^+(aq)$, $Cl^-(aq)$, $Na^+(aq)$, and $NO_3^-(aq)$ prepared in the following ways? Give examples of intensive variables that could be varied independently.

(a) The system is prepared by equilibrating excess solid AgCl with an aqueous solution of $NaNO_3$.

Solution:

Both phases were prepared from either the first or all three of the substances AgCl, H_2O, and $NaNO_3$; thus, there are three components:

$C = 3 \qquad F = 2 + C - P = 2 + 3 - 2 = 3.$

T, p, and m_{Na^+} could be varied independently.

(b) The system is prepared by mixing aqueous solutions of $AgNO_3$ and NaCl in arbitrary proportions; some solid AgCl forms by precipitation.

Solution:

There are six species and two independent relations among intensive variables:

$-\mu_{AgCl} + \mu_{Ag^+} + \mu_{Cl^-} = 0$

$m_{Ag^+} + m_{Na^+} = m_{Cl^-} + m_{NO_3^-}$

From the phase rule we find

$C = s - r = 4 \qquad F = 2 + C - P = 2 + 4 - 2 = 4$

T, p, and the molalities of any two of the aqueous ions could be varied independently.

13.6 How many degrees of freedom has a system consisting of solid NaCl in equilibrium with an aqueous phase containing H_2O, Na^+(aq), Cl^-(aq), H^+(aq), and OH^-(aq)? Would it be possible to independently vary T, p, and m_{OH^-}? If so, explain how you could do this.

Solution:

There are six species, two phases, and three independent relations among intensive variables:

$-\mu_{NaCl} + \mu_{Na^+} + \mu_{Cl^-} = 0$

$-\mu_{H_2O} + \mu_{H^+} + \mu_{OH^-} = 0$

$m_{Na^+} + m_{H^+} = m_{Cl^-} + m_{OH^-}$

The system has three degrees of freedom:

$F = 2 + s - r - P = 2 + 6 - 3 - 2 = 3$

m_{OH^-} may be varied at any given T and p by dissolving HCl or NaOH in the aqueous phase.

13.7 Consult the phase diagram shown in Fig. 13.4 on page 430. Suppose the system contains 36.0 g (2.00 mol) H_2O and 58.4 g (1.00 mol) NaCl at 25 °C and 1 bar.

(a) Describe the phases present in the equilibrium system and their masses.

Solution:

The mass percent NaCl in the system as a whole is

$$\frac{58.4\,\text{g}}{36.0\,\text{g} + 58.4\,\text{g}} \times 100 = 61.9\%$$

The system point at 61.9% NaCl by mass and 25 °C lies in the two-phase area labeled sln + NaCl(s). The left end of the tie line drawn through the system point is at 26% NaCl by mass. The lever rule gives the relation

$$\frac{m^{\text{sln}}}{m^{\text{s}}} = \frac{100 - 61.9}{61.9 - 26} = 1.06$$

where m is mass. Solve this equation simultaneously with $m^s + m^{sln} = 94.4$ g:

$m^{sln} = 48.6$ g $\qquad m^s = 45.8$ g

The system contains approximately 49 g solution of composition 26% NaCl by mass, and 46 g solid NaCl.

(b) Describe the changes that occur at constant pressure if the system is placed in thermal contact with a heat reservoir at −30 °C.

Solution:

As the temperature decreases, some NaCl precipitates from the solution. The temperature drop halts at 0 °C while the system is converted completely to solid $NaCl{\cdot}2H_2O$; then the solid cools to −30 °C.

(c) Describe the changes that occur if the temperature is raised from 25 °C to 120 °C at constant pressure.

Solution:

As the temperature increases, some of the solid NaCl dissolves in the solution. The temperature rise halts at 109 °C until all the water vaporizes. At 120 °C the system contains 1.00 mol of solid NaCl and 2.00 mol of gaseous H_2O.

(d) Describe the system after 200 g H_2O is added at 25 °C.

Solution:

The solid NaCl dissolves to give a single phase, an unsaturated solution of composition 19.8% NaCl by mass.

Table 27 Aqueous solubilities of sodium sulfate decahydrate and anhydrous sodium sulfate[a]

$Na_2SO_4{\cdot}10H_2O$		Na_2SO_4	
$t/°C$	x_B	$t/°C$	x_B
10	0.011	40	0.058
15	0.016	50	0.056
20	0.024		
25	0.034		
30	0.048		

[a]Ref. [59], p. 179–180.

13.8 Use the following information to draw a temperature–composition phase diagram for the binary system of H_2O (A) and Na_2SO_4 (B) at $p = 1$ bar, confining t to the range −20 to 50 °C and z_B to the range 0–0.2. The solid decahydrate, $Na_2SO_4{\cdot}10H_2O$, is stable below 32.4 °C. The anhydrous salt, Na_2SO_4, is stable above this temperature. There is a peritectic point for these two solids and the solution at $x_B = 0.059$ and $t = 32.4$ °C. There is a eutectic point for ice, $Na_2SO_4{\cdot}10H_2O$, and the solution at $x_B = 0.006$ and $t = -1.3$ °C. Table 27 gives the temperature dependence of the solubilities of the ionic solids.

Solution:

See Fig. 25.

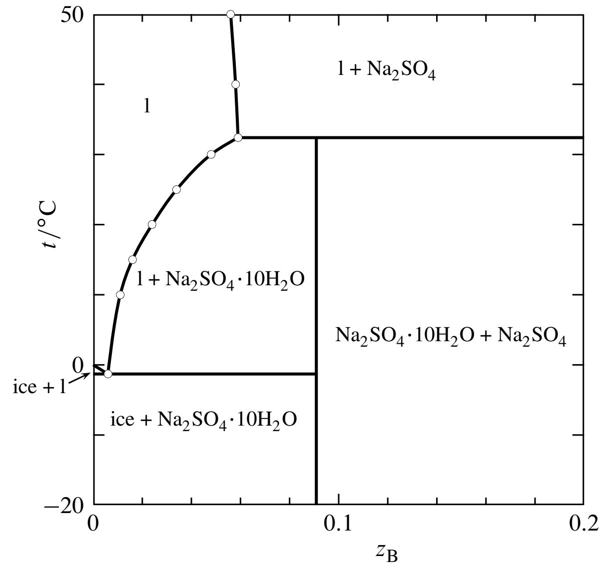

Figure 25 Phase diagram for the binary system of H_2O (A) and Na_2SO_4 (B) at $p =$ 1 bar. Open circles are data points given in problem.

Table 28 Data for Problem 13.9. Temperatures of saturated solutions of aqueous iron(III) chloride at $p =$ 1 bar (A = $FeCl_3$, B = H_2O)[a]

x_A	$t/°C$	x_A	$t/°C$	x_A	$t/°C$
0.000	0.0	0.119	35.0	0.286	56.0
0.020	−10.0	0.143	37.0	0.289	55.0
0.032	−20.5	0.157	36.0	0.293	60.0
0.037	−27.5	0.173	33.0	0.301	69.0
0.045	−40.0	0.183	30.0	0.318	72.5
0.052	−55.0	0.195	27.4	0.333	73.5
0.053	−41.0	0.213	32.0	0.343	72.5
0.056	−27.0	0.222	32.5	0.358	70.0
0.076	0.0	0.232	30.0	0.369	66.0
0.083	10.0	0.238	35.0	0.369	80.0
0.093	20.0	0.259	50.0	0.373	100.0
0.106	30.0	0.277	55.0		

[a]Data from Ref. [59], page 193.

13.9 Iron(III) chloride forms various solid hydrates, all of which melt congruently. Table 28 lists the temperatures t of aqueous solutions of various compositions that are saturated with respect to a solid phase.

(a) Use these data to construct a t–z_B phase diagram for the binary system of $FeCl_3$ (A) and H_2O (B). Identify the formula and melting point of each hydrate. Hint: derive a formula for the mole ratio n_B/n_A as a function of x_A in a binary mixture.

Solution:

See Fig. 26.

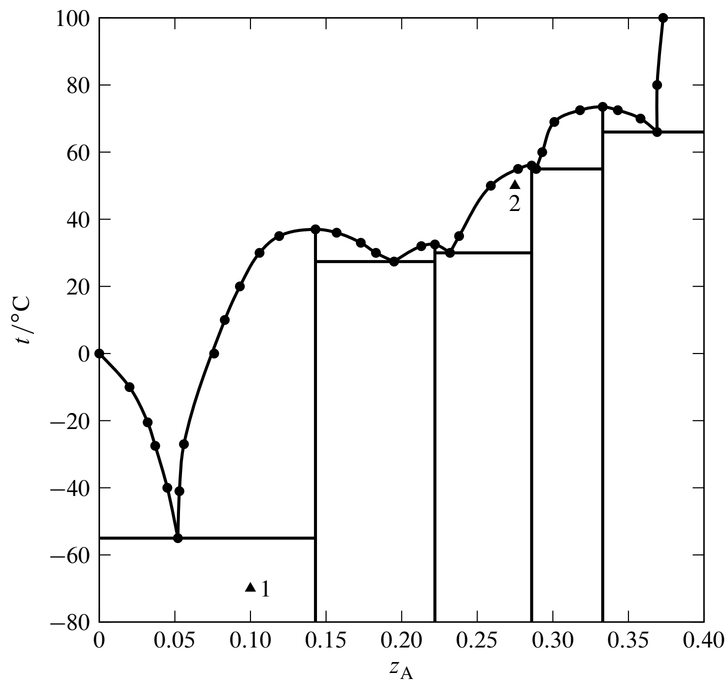

Figure 26 Phase diagram for the binary system of $FeCl_3$ (A) and H_2O (B). Solid circles: data points.

$$\frac{n_B}{n_A} = \frac{x_B}{x_A} = \frac{1 - x_A}{x_A}$$

The stoichiometry of each hydrate is given by the mole ratio of the liquid mixture with the same composition:

$x_A = 0.143$, $n_B/n_A = 5.99$: AB_6 or $FeCl_3 \cdot 6H_2O$

$x_A = 0.222$, $n_B/n_A = 3.50$: A_2B_7 or $(FeCl_3)_2 \cdot 7H_2O$

$x_A = 0.286$, $n_B/n_A = 2.50$: A_2B_5 or $(FeCl_3)_2 \cdot 5H_2O$

$x_A = 0.333$, $n_B/n_A = 2.00$: AB_2 or $FeCl_3 \cdot 2H_2O$

(b) For the following conditions, determine the phase or phases present at equilibrium and the composition of each.

1. $t = -70.0°C$ and $z_A = 0.100$
2. $t = 50.0°C$ and $z_A = 0.275$

Solution:

See points 1 and 2 on the phase diagram.

At $t = -70.0°C$ and $z_A = 0.100$, the phases are solid H_2O (ice) and solid hydrate AB_6.

At $t = 50.0°C$ and $z_A = 0.275$, the phases are solution of composition $x_B = 0.259$ and solid hydrate A_2B_5.

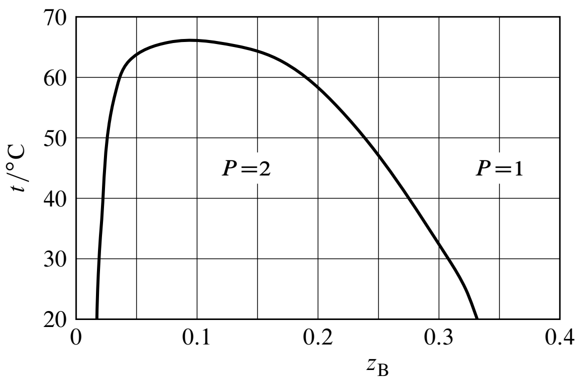

Figure 27 Temperature–composition phase diagram for the binary system of water (A) and phenol (B) at 1 bar.[a] Only liquid phases are present.

[a]Ref. [59], p. 95.

13.10 Figure 27 is a temperature–composition phase diagram for the binary system of water (A) and phenol (B) at 1 bar. These liquids are partially miscible below 67 °C. Phenol is more dense than water, so the layer with the higher mole fraction of phenol is the bottom layer. Suppose you place 4.0 mol of H_2O and 1.0 mol of phenol in a beaker at 30 °C and gently stir to allow the layers to equilibrate.

(a) What are the compositions of the equilibrated top and bottom layers?

Solution:

The system point is at $z_B = (1.0\,\text{mol})/(5.0\,\text{mol}) = 0.20$ and $t = 30\,°\text{C}$, in the two-phase area. The ends of the tie line through this point give the compositions $x_B(\text{top}) = 0.02$ and $x_B(\text{bottom}) = 0.31$.

(b) Find the amount of each component in the bottom layer.

Solution:

The lever rule gives the relation

$$\frac{n(\text{bottom})}{n(\text{top})} = \frac{0.20 - 0.02}{0.31 - 0.20} = 1.6$$

Solve simultaneously with $n(\text{bottom}) + n(\text{top}) = 5.0\,\text{mol}$ to get $n(\text{bottom}) = 3.1\,\text{mol}$. Then, in the bottom layer we have

$$n_B = x_B n = (0.31)(3.1\,\text{mol}) = 1.0\,\text{mol} \qquad n_A = 3.1\,\text{mol} - 1.0\,\text{mol} = 2.1\,\text{mol}$$

(c) As you gradually stir more phenol into the beaker, maintaining the temperature at 30 °C, what changes occur in the volumes and compositions of the two layers? Assuming that one layer eventually disappears, what additional amount of phenol is needed to cause this to happen?

Solution:

The volume of the bottom layer increases and that of the top layer decreases. There is no change in the compositions of the two phases. When the overall system composition reaches $z_B = 0.31$, the top layer disappears; the amount of phenol in the system at this point is calculated from

$$z_B = \frac{n_B}{n_A + n_B} \qquad n_B = \frac{z_B n_A}{1 - z_B} = \frac{(0.31)(4.0\,\text{mol})}{1 - 0.31} = 1.8\,\text{mol}$$

Since 1.0 mol phenol was present initially, the top layer disappears when an additional 0.8 mol phenol has been added.

Table 29 Saturation vapor pressures of propane (A) and *n*-butane (B)

$t/°C$	p_A^*/bar	p_B^*/bar
−10.0	3.360	0.678
−20.0	2.380	0.441
−30.0	1.633	0.275

13.11 The standard boiling point of propane is −41.8 °C and that of *n*-butane is −0.2 °C. Table 29 lists vapor pressure data for the pure liquids. Assume that the liquid mixtures obey Raoult's law.

(a) Calculate the compositions, x_A, of the liquid mixtures with boiling points of −10.0 °C, −20.0 °C, and −30.0 °C at a pressure of 1 bar.

Solution:

Solve Eq. 13.2.4 for x_A:

$$x_A = \frac{p - p_B^*}{p_A^* - p_B^*}$$

Set p equal to 1 bar and take values of p_A^* and p_B^* from the table.

at −10 °C: $x_A = 0.120$

at −20 °C: $x_A = 0.288$

at −30 °C: $x_A = 0.534$

(b) Calculate the compositions, y_A, of the equilibrium vapor at these three temperatures.

Solution:

Use Eq. 13.2.7: $y_A = x_A p_A^*/p$.

at −10 °C: $y_A = 0.403$

at −20 °C: $y_A = 0.686$

at −30 °C: $y_A = 0.872$

(c) Plot the temperature–composition phase diagram at $p = 1$ bar using these data, and label the areas appropriately.

Solution:

See Fig. 28.

(d) Suppose a system containing 10.0 mol propane and 10.0 mol *n*-butane is brought to a pressure of 1 bar and a temperature of −25 °C. From your phase diagram, estimate the compositions and amounts of both phases.

Solution:

From the ends of the tie line (dashed line) in Fig. 28:

$x_A = 0.39$, $y_A = 0.79$

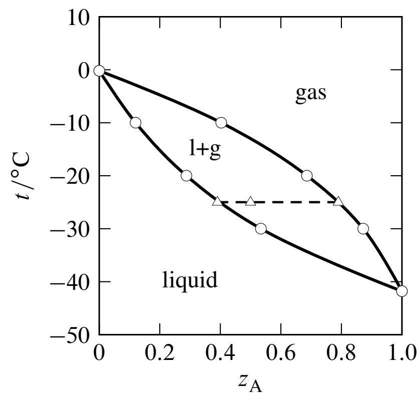

Figure 28 Phase diagram for the binary system of propane (A) and *n*-butane at 1 bar.

Use the lever rule:

$$\frac{n^g}{n^l} = \frac{z_A - x_A}{y_A - z_A} = \frac{0.50 - 0.39}{0.79 - 0.50} = 0.38$$

Solve this equation simultaneously with $n^l + n^g = 20.0\,\text{mol}$:

$n^l = 14.5\,\text{mol}$, $n^g = 5.5\,\text{mol}$

Table 30 Liquid and gas compositions in the two-phase system of 2-propanol (A) and benzene at 45 °C [a]

x_A	y_A	p/kPa	x_A	y_A	p/kPa
0	0	29.89	0.5504	0.3692	35.32
0.0472	0.1467	33.66	0.6198	0.3951	34.58
0.0980	0.2066	35.21	0.7096	0.4378	33.02
0.2047	0.2663	36.27	0.8073	0.5107	30.28
0.2960	0.2953	36.45	0.9120	0.6658	25.24
0.3862	0.3211	36.29	0.9655	0.8252	21.30
0.4753	0.3463	35.93	1.0000	1.0000	18.14

[a] Ref. [24].

13.12 Use the data in Table 30 to draw a pressure–composition phase diagram for the 2-propanol–benzene system at 45 °C. Label the axes and each area.

Solution:

See Fig. 29. The system exhibits a minimum-boiling azeotrope.

13.13 Use the data in Table 31 on the next page to draw a pressure–composition phase diagram for the acetone–chloroform system at 35.2 °C. Label the axes and each area.

Solution:

See Fig. 30. The system exhibits a maximum-boiling azeotrope.

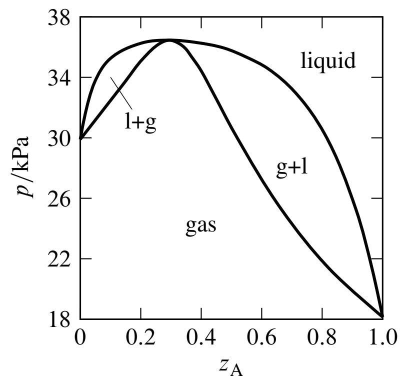

Figure 29 Phase diagram for the binary system of 2-propanol (A) and benzene at 45 °C.

Table 31 Liquid and gas compositions in the two-phase system of acetone (A) and chloroform at 35.2 °C[a]

x_A	y_A	p/kPa	x_A	y_A	p/kPa
0	0	39.08	0.634	0.727	36.29
0.083	0.046	37.34	0.703	0.806	38.09
0.200	0.143	34.92	0.815	0.896	40.97
0.337	0.317	33.22	0.877	0.936	42.62
0.413	0.437	33.12	0.941	0.972	44.32
0.486	0.534	33.70	1.000	1.000	45.93
0.577	0.662	35.09			

[a]Ref. [179], p. 286.

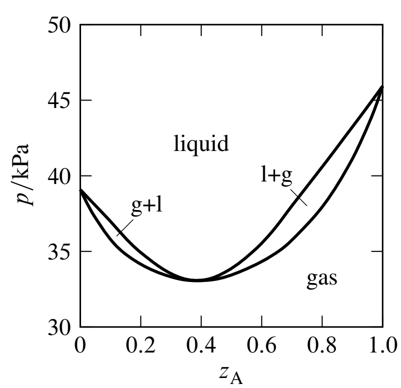

Figure 30 Phase diagram for the binary system of acetone (A) and chloroform at 35.2 °C.

Chapter 14 Galvanic Cells

14.1 The state of a galvanic cell without liquid junction, when its temperature and pressure are uniform, can be fully described by values of the variables T, p, and ξ. Find an expression for dG during a reversible advancement of the cell reaction, and use it to derive the relation $\Delta_r G_{\text{cell}} = -zFE_{\text{cell, eq}}$ (Eq. 14.3.8). (Hint: Eq. 3.8.8.)

Solution:

Equation 3.8.8 is a general formula for electrical work when the cell is part of an electrical circuit:

$$đw_{\text{el}} = E_{\text{cell}}\, đQ_{\text{sys}}$$

Combine this relation with $đQ_{\text{sys}} = -zF\,\text{d}\xi$ (Eq. 14.1.1):

$$đw_{\text{el}} = -zFE_{\text{cell}}\,\text{d}\xi$$

The intermediate states of a reversible cell reaction have uniform T and p and an equilibrium cell potential: $E_{\text{cell}} = E_{\text{cell, eq}}$. d$G$ during a reversible process of a closed system with nonexpansion work is given by the equality of Eq. 5.8.6. In this equality, replace $đw'$ by $đw_{\text{el}} = -zFE_{\text{cell, eq}}\,\text{d}\xi$:

$$\text{d}G = -S\,\text{d}T + V\,\text{d}p - zFE_{\text{cell, eq}}\,\text{d}\xi$$

This is an expression for the total differential of G with T, p, and ξ as the independent variables. Identify the coefficient of dξ as the partial derivative $(\partial G/\partial \xi)_{T,p}$, which is the molar reaction Gibbs energy of the cell reaction:

$$\Delta_r G_{\text{cell}} = -zFE_{\text{cell, eq}}$$

14.2 Before 1982 the standard pressure was usually taken as 1 atm. For the cell shown in Fig. 14.1, what correction is needed, for a value of $E^\circ_{\text{cell, eq}}$ obtained at 25 °C and using the older convention, to change the value to one corresponding to a standard pressure of 1 bar? Equation 14.3.15 can be used for this calculation.

Solution:

From Eq. 14.3.15:

$$E^\circ_{\text{cell, eq}} = -\frac{\Delta_r G^\circ}{zF}$$

where the standard molar reaction Gibbs energy is given by $\Delta_r G^\circ = \sum_i \nu_i \mu_i^\circ$ (Eq. 11.8.3). The effect of a small pressure change on the chemical potential of a solid or solute is negligible. The standard state of the gaseous H_2 is the pure gas behaving as an ideal gas. Apply Eq. 7.8.4 to the isothermal pressure change of an ideal gas:

$$\left(\frac{\partial \mu}{\partial p}\right)_T = V_{\text{m}} = \frac{RT}{p} \qquad \mu(p_2) - \mu(p_1) = RT\int_{p_1}^{p_2} \frac{\text{d}p}{p} = RT \ln \frac{p_2}{p_1}$$

For a pressure change from 1 atm to 1 bar the change of chemical potential is

$$\begin{aligned}\mu(1\,\text{bar}) - \mu(1\,\text{atm}) &= (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(298.15\,\text{K}) \ln \frac{1\,\text{bar}}{1.01325\,\text{bar}} \\ &= -32.63\,\text{J mol}^{-1}\end{aligned}$$

Therefore for the cell reaction $H_2(g) + 2\,AgCl(s) \rightarrow 2\,Ag(s) + 2\,H^+(aq) + 2\,Cl^-(aq)$ the pressure change causes $E^\circ_{\text{cell, eq}}$ to change by

$$E^\circ_{\text{cell, eq}}(p^\circ = 1\,\text{bar}) - E^\circ_{\text{cell, eq}}(p^\circ = 1\,\text{atm}) = -\frac{-(-32.63\,\text{J mol}^{-1})}{(2)(96,485\,\text{C mol}^{-1})} = -1.691 \times 10^{-4}\,\text{V}$$

The correction to $E^\circ_{\text{cell, eq}}$ based on the older convention is $-0.17\,\text{mV}$.

14.3 Careful measurements[20] of the equilibrium cell potential of the cell

$$\text{Pt} \mid \text{H}_2(\text{g}) \mid \text{HCl(aq)} \mid \text{AgCl(s)} \mid \text{Ag}$$

yielded, at 298.15 K and using a standard pressure of 1 bar, the values $E^\circ_{\text{cell, eq}} = 0.22217\,\text{V}$ and $\text{d}E^\circ_{\text{cell, eq}}/\,\text{d}T = -6.462 \times 10^{-4}\,\text{V K}^{-1}$. (The requested calculated values are close to, but not exactly the same as, the values listed in Appendix H, which are based on the same data combined with data of other workers.)

(a) Evaluate $\Delta_\text{r}G^\circ$, $\Delta_\text{r}S^\circ$, and $\Delta_\text{r}H^\circ$ at 298.15 K for the reaction

$$\tfrac{1}{2}\text{H}_2(\text{g}) + \text{AgCl(s)} \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq}) + \text{Ag(s)}$$

Solution:

From Eq. 14.3.15:

$$\Delta_\text{r}G^\circ = -zFE^\circ_{\text{cell, eq}} = -(1)(96,485\,\text{C mol}^{-1})(0.22217\,\text{V}) = -21.436\,\text{kJ mol}^{-1}$$

From Eq. 14.3.18:

$$\Delta_\text{r}S^\circ = zF\frac{\text{d}E^\circ_{\text{cell, eq}}}{\text{d}T} = (1)(96,485\,\text{C mol}^{-1})(-6.462 \times 10^{-4}\,\text{V K}^{-1})$$
$$= -62.35\,\text{J K}^{-1}\,\text{mol}^{-1}$$

$$\Delta_\text{r}H^\circ = T\Delta_\text{r}S^\circ + \Delta_\text{r}G^\circ$$
$$= (298.15\,\text{K})(-62.35\,\text{J K}^{-1}\,\text{mol}^{-1}) + (-21.436 \times 10^3\,\text{J mol}^{-1})$$
$$= -40.03\,\text{kJ mol}^{-1}$$

The value of $\Delta_\text{r}H^\circ$ may also be calculated with Eq. 14.3.17.

(b) Problem 12.18 showed how the standard molar enthalpy of formation of the aqueous chloride ion may be evaluated based on the convention $\Delta_\text{f}H^\circ(\text{H}^+, \text{aq}) = 0$. If this value is combined with the value of $\Delta_\text{r}H^\circ$ obtained in part (a) of the present problem, the standard molar enthalpy of formation of crystalline silver chloride can be evaluated. Carry out this calculation for $T = 298.15\,\text{K}$ using the value $\Delta_\text{f}H^\circ(\text{Cl}^-, \text{aq}) = -167.08\,\text{kJ mol}^{-1}$ (Appendix H).

Solution:

Apply the general relation $\Delta_\text{r}H^\circ = \sum_i \nu_i \Delta_\text{f}H^\circ(i)$ (Eq. 11.3.3) to the reaction of part (a):

$$\Delta_\text{r}H^\circ = -\tfrac{1}{2}\Delta_\text{f}H^\circ(\text{H}_2, \text{g}) - \Delta_\text{f}H^\circ(\text{AgCl, s}) + \Delta_\text{f}H^\circ(\text{H}^+, \text{aq})$$
$$+ \Delta_\text{f}H^\circ(\text{Cl}^-, \text{aq}) + \Delta_\text{f}H^\circ(\text{Ag, s})$$
$$= -\tfrac{1}{2}(0) - \Delta_\text{f}H^\circ(\text{AgCl, s}) + 0 + \Delta_\text{f}H^\circ(\text{Cl}^-, \text{aq}) + 0$$

$$\Delta_\text{f}H^\circ(\text{AgCl, s}) = -\Delta_\text{r}H^\circ + \Delta_\text{f}H^\circ(\text{Cl}^-, \text{aq})$$
$$= -(-40.03\,\text{kJ mol}^{-1}) + (-167.08\,\text{kJ mol}^{-1}) = -127.05\,\text{kJ mol}^{-1}$$

[20] Ref. [4].

(c) By a similar procedure, evaluate the standard molar entropy, the standard molar entropy of formation, and the standard molar Gibbs energy of formation of crystalline silver chloride at 298.15 K. You need the following standard molar entropies evaluated from spectroscopic and calorimetric data:

$S^\circ_m(H_2, g) = 130.68\,J\,K^{-1}\,mol^{-1}$ $S^\circ_m(Cl_2, g) = 223.08\,J\,K^{-1}\,mol^{-1}$

$S^\circ_m(Cl^-, aq) = 56.60\,J\,K^{-1}\,mol^{-1}$ $S^\circ_m(Ag, s) = 42.55\,J\,K^{-1}\,mol^{-1}$

Solution:

For the standard molar reaction entropy, apply the general relation $\Delta_r S^\circ = \sum_i \nu_i S^\circ_i$ (Eq. 11.8.22) to the reaction of part (a):

$$\Delta_r S^\circ = -\tfrac{1}{2} S^\circ_m(H_2, g) - S^\circ_m(AgCl, s) + S^\circ_m(H^+, aq) + S^\circ_m(Cl^-, aq) + S^\circ_m(Ag, s)$$

By convention, $S^\circ_m(H^+, aq)$ is zero.

$$S^\circ_m(AgCl, s) = -\Delta_r S^\circ - \tfrac{1}{2} S^\circ_m(H_2, g) + S^\circ_m(Cl^-, aq) + S^\circ_m(Ag, s)$$

$$S^\circ_m(AgCl, s)/J\,K^{-1}\,mol^{-1} = -(-62.35) - \tfrac{1}{2}(130.68) + 56.60 + 42.55 = 96.16$$

The formation reaction of AgCl is $Ag(s) + \tfrac{1}{2}Cl_2(g) \rightarrow AgCl(s)$:

$$\Delta_f S^\circ(AgCl, s) = -S^\circ_m(Ag, s) - \tfrac{1}{2} S^\circ_m(Cl_2, g) + S^\circ_m(AgCl, s)$$

$$\Delta_f S^\circ(AgCl, s)/J\,K^{-1}\,mol^{-1} = -(42.55) - \tfrac{1}{2}(223.08) + 96.16 = -57.93$$

$$\begin{aligned}\Delta_f G^\circ(AgCl, s) &= \Delta_f H^\circ(AgCl, s) - T\Delta_f S^\circ(AgCl, s)\\ &= -127.05 \times 10^3\,J\,mol^{-1} - (298.15\,K)(-57.93\,J\,K^{-1}\,mol^{-1})\\ &= -109.78\,kJ\,mol^{-1}\end{aligned}$$

14.4 The standard cell potential of the cell

$$Ag \mid AgCl(s) \mid HCl(aq) \mid Cl_2(g) \mid Pt$$

has been determined over a range of temperature.[21] At T=298.15 K, the standard cell potential was found to be $E^\circ_{cell,\,eq} = 1.13579\,V$, and its temperature derivative was found to be $dE^\circ_{cell,\,eq}/dT = -5.9863 \times 10^{-4}\,V\,K^{-1}$.

(a) Write the cell reaction for this cell.

Solution:

left electrode reaction (oxidation)	$2\,[Ag(s) + Cl^-(aq) \rightarrow AgCl(s) + e^-]$
right electrode reaction (reduction)	$Cl_2(g) + 2\,e^- \rightarrow 2\,Cl^-(aq)$
cell reaction	$2\,Ag(s) + Cl_2(g) \rightarrow 2\,AgCl(s)$

(b) Use the data to evaluate the standard molar enthalpy of formation and the standard molar Gibbs energy of formation of crystalline silver chloride at 298.15 K. (Note that this calculation provides values of quantities also calculated in Prob. 14.3 using independent data.)

Solution:

The cell reaction is the formation reaction of AgCl(s). As written in the solution for part (a), the electron number is $z = 2$. To simplify the calculation, divide the coefficients by 2:

$$Ag(s) + \tfrac{1}{2}Cl_2(g) \rightarrow AgCl(s) \qquad z = 1$$

[21] Ref. [55].

Then we have, from Eq. 14.3.17:

$$\Delta_f H^\circ(\text{AgCl, s}) = \Delta_r H^\circ = zF\left(T\frac{dE^\circ_{\text{cell, eq}}}{dT} - E^\circ_{\text{cell, eq}}\right)$$

$$= (1)(96{,}485\ \text{C mol}^{-1})\left[(298.15\ \text{K})(-5.9863\times10^{-4}\ \text{V K}^{-1}) - 1.13579\ \text{V}\right]$$

$$= -126.81\ \text{kJ mol}^{-1}$$

and from Eq. 14.3.15:

$$\Delta_f G^\circ(\text{AgCl, s}) = \Delta_r G^\circ = -zFE^\circ_{\text{cell, eq}} = -(1)(96{,}485\ \text{C mol}^{-1})(1.13579\ \text{V})$$

$$= -109.59\ \text{kJ mol}^{-1}$$

14.5 Use data in Sec. 14.3.3 to evaluate the solubility product of silver chloride at 298.15 K.

Solution:

From Eq. 14.3.16:

$$\ln K_s = \frac{zF}{RT}E^\circ_{\text{cell, eq}} = \frac{(1)(96{,}485\ \text{C mol}^{-1})}{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(298.15\ \text{K})}(-0.5770\ \text{V}) = -22.46$$

$K_s = 1.76\times10^{-10}$

14.6 The equilibrium cell potential of the galvanic cell

$$\text{Pt} \mid \text{H}_2(\text{g}, f = 1\ \text{bar}) \mid \text{HCl}(\text{aq}, 0.500\ \text{mol kg}^{-1}) \mid \text{Cl}_2(\text{g}, f = 1\ \text{bar}) \mid \text{Pt}$$

is found to be $E_{\text{cell, eq}} = 1.410\ \text{V}$ at 298.15 K. The standard cell potential is $E^\circ_{\text{cell, eq}} = 1.360\ \text{V}$.

(a) Write the cell reaction and calculate its thermodynamic equilibrium constant at 298.15 K.

Solution:

left electrode reaction (oxidation)	$H_2(g) \rightarrow 2\,H^+(aq) + 2\,e^-$
right electrode reaction (reduction)	$Cl_2(g) + 2\,e^- \rightarrow 2\,Cl^-(aq)$
cell reaction	$H_2(g) + Cl_2(g) \rightarrow 2\,H^+(aq) + 2\,Cl^-(aq)$

From Eq. 14.3.16:

$$\ln K_s = \frac{zF}{RT}E^\circ_{\text{cell, eq}} = \frac{(2)(96{,}485\ \text{C mol}^{-1})}{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(298.15\ \text{K})}(1.360\ \text{V}) = 105.9$$

$K_s = 9\times10^{45}$

(b) Use the cell measurement to calculate the mean ionic activity coefficient of aqueous HCl at 298.15 K and a molality of $0.500\ \text{mol kg}^{-1}$.

Solution:

From Eq. 14.4.2:

$$E_{\text{cell, eq}} = E^\circ_{\text{cell, eq}} - \frac{0.02569\ \text{V}}{z}\ln Q_{\text{rxn}} = E^\circ_{\text{cell, eq}} - \frac{0.02569\ \text{V}}{z}\ln\frac{\gamma_\pm^4\,(m_B/m^\circ)^4}{(f_{H_2}/p^\circ)(f_{Cl_2}/p^\circ)}$$

$$= E^\circ_{\text{cell, eq}} - \frac{0.02569\ \text{V}}{2}\ln\frac{\gamma_\pm^4(0.500)^4}{(1)(1)}$$

$$\ln(0.500\gamma_\pm) = \frac{E^\circ_{\text{cell, eq}} - E_{\text{cell, eq}}}{2\times0.02569\ \text{V}} = \frac{(1.360 - 1.410)\ \text{V}}{2\times0.02569\ \text{V}} = -0.973$$

$\gamma_\pm = 0.756$

14.7 Consider the following galvanic cell, which combines a hydrogen electrode and a calomel electrode:

$$\mathrm{Pt}\,|\,\mathrm{H_2(g)}\,|\,\mathrm{HCl(aq)}\,|\,\mathrm{Hg_2Cl_2(s)}\,|\,\mathrm{Hg(l)}\,|\,\mathrm{Pt}$$

(a) Write the cell reaction.

Solution:

left electrode reaction (oxidation) $\quad \mathrm{H_2(g) \rightarrow 2\,H^+(aq) + 2\,e^-}$

right electrode reaction (reduction) $\quad \mathrm{Hg_2Cl_2(s) + 2\,e^- \rightarrow 2\,Hg(l) + 2\,Cl^-(aq)}$

cell reaction: $\mathrm{H_2(g) + Hg_2Cl_2(s) \rightarrow 2\,H^+(aq) + 2\,Cl^-(aq) + 2\,Hg(l)}$

(b) At 298.15 K, the standard cell potential of this cell is $E^\circ_{\mathrm{cell,\,eq}} = 0.2680\,\mathrm{V}$. Using the value of $\Delta_\mathrm{f} G^\circ$ for the aqueous chloride ion in Appendix H, calculate the standard molar Gibbs energy of formation of crystalline mercury(I) chloride (calomel) at 298.15 K.

Solution:

From Eq. 14.3.15:

$$\Delta_\mathrm{r} G^\circ = -zFE^\circ_{\mathrm{cell,\,eq}} = -(2)(96,485\,\mathrm{C\,mol^{-1}})(0.2680\,\mathrm{V}) = -5.172\times10^4\,\mathrm{J\,mol^{-1}}$$

$$\Delta_\mathrm{r} G^\circ = \sum \nu_i \Delta_\mathrm{f} G^\circ(i) = -(0) - \Delta_\mathrm{f} G^\circ(\mathrm{Hg_2Cl_2,s}) + 2(0) + 2\Delta_\mathrm{f} G^\circ(\mathrm{Cl^-,aq}) + 2(0)$$

$$\begin{aligned}\Delta_\mathrm{f} G^\circ(\mathrm{Hg_2Cl_2,s}) &= -\Delta_\mathrm{r} G^\circ + 2\Delta_\mathrm{f} G^\circ(\mathrm{Cl^-,aq})\\ &= -(-5.172\times10^4\,\mathrm{J\,mol^{-1}}) + 2(-131.22\times10^3\,\mathrm{J\,mol^{-1}})\\ &= -210.72\,\mathrm{kJ\,mol^{-1}}\end{aligned}$$

(c) Calculate the solubility product of mercury(I) chloride at 298.15 K. The dissolution equilibrium is $\mathrm{Hg_2Cl_2(s) \rightleftharpoons {Hg_2}^{2+}(aq) + 2\,Cl^-(aq)}$. Take values for the standard molar Gibbs energies of formation of the aqueous ions from Appendix H.

Solution:

$$\Delta_\mathrm{r} G^\circ = \sum \nu_i \Delta_\mathrm{f} G^\circ(i) = -\Delta_\mathrm{f} G^\circ(\mathrm{Hg_2Cl_2,s}) + \Delta_\mathrm{f} G^\circ(\mathrm{{Hg_2}^{2+},aq}) + 2\Delta_\mathrm{f} G^\circ(\mathrm{Cl^-,aq})$$

$$\Delta_\mathrm{r} G^\circ/\mathrm{kJ\,mol^{-1}} = -(-210.72) + (153.57) + 2(-131.22) = 101.85$$

$$K_\mathrm{s} = \exp\left(-\frac{\Delta_\mathrm{r} G^\circ}{RT}\right) = \exp\left[-\frac{101.85\times10^3\,\mathrm{J\,mol^{-1}}}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298.15\,\mathrm{K})}\right] = 1.4\times10^{-18}$$

Table 32 Equilibrium cell potential as a function of HBr molality m_B.

$m_\mathrm{B}\,/\,(\mathrm{mol\,kg^{-1}})$	$E_{\mathrm{cell,\,eq}}\,/\,\mathrm{V}$
0.0004042	0.47381
0.0008444	0.43636
0.0008680	0.43499
0.0013554	0.41243
0.001464	0.40864
0.001850	0.39667
0.002396	0.38383
0.003719	0.36173

14.8 Table 32 lists equilibrium cell potentials obtained with the following cell at 298.15 K:[22]

$$\mathrm{Pt}\,|\,\mathrm{H_2(g,\,1.01\,bar)}\,|\,\mathrm{HBr}(\mathrm{aq},m_\mathrm{B})\,|\,\mathrm{AgBr(s)}\,|\,\mathrm{Ag}$$

[22] Ref. [98].

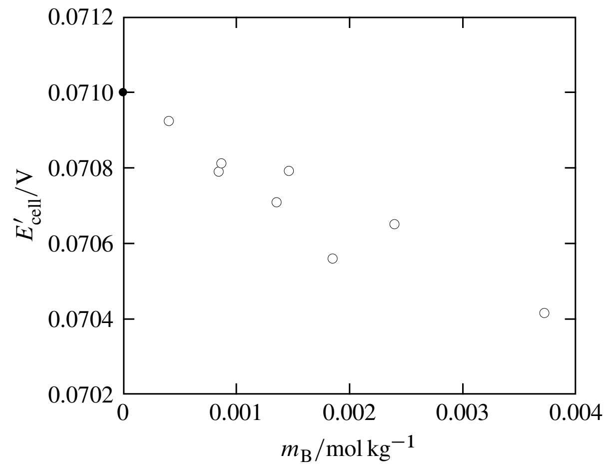

Figure 31 Graph for Problem 14.8.

Use these data to evaluate the standard electrode potential of the silver-silver bromide electrode at this temperature to the nearest millivolt. (Since the electrolyte solutions are quite dilute, you may ignore the term $Ba\sqrt{m_B}$ in Eq. 14.5.2.)

Solution:

The cell has a hydrogen electrode at the left and a silver-silver bromide electrode at the right. The standard electrode potential E° of the silver-silver bromide electrode is therefore equal to the standard cell potential $E^\circ_{\text{cell, eq}}$ of this cell.

Figure 31 shows values of E'_{cell} plotted versus m_B (open circles), where the function E'_{cell} is defined by Eq. 14.5.2 with a set equal to zero:

$$\begin{aligned} E'_{\text{cell}} &= E_{\text{cell, eq}} + \frac{2RT}{F}(-A\sqrt{m_B}) + \frac{2RT}{F}\ln\frac{m_B}{m^\circ} - \frac{RT}{2F}\ln\frac{f_{H_2}}{p^\circ} \\ &= E_{\text{cell, eq}} + \frac{RT}{F}\left(-2A\sqrt{m_B} + 2\ln\frac{m_B}{m^\circ} - \frac{1}{2}\ln\frac{f_{H_2}}{p^\circ}\right) \\ &= E_{\text{cell, eq}} + \frac{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(298.15\,\text{K})}{96,485\,\text{C mol}^{-1}} \\ &\qquad \times \left[-(2)(1.1744\,\text{kg}^{1/2}\,\text{mol}^{-1/2})\sqrt{m_B} + 2\ln(m_B\,/\,\text{mol kg}^{-1}) - \frac{1}{2}\ln(1.01)\right] \end{aligned}$$

To the nearest millivolt, E'_{cell} extrapolated to $m_B = 0$ (filled circle) has the value $E^\circ = E^\circ_{\text{cell, eq}} = 0.071\,\text{V}$.

14.9 The cell diagram of a mercury cell can be written

$$\text{Zn(s)} \mid \text{ZnO(s)} \mid \text{NaOH(aq)} \mid \text{HgO(s)} \mid \text{Hg(l)}$$

(a) Write the electrode reactions and cell reaction with electron number $z = 2$.

Solution:

At the left electrode: $\text{Zn(s)} + 2\,\text{OH}^-\text{(aq)} \rightarrow \text{ZnO(s)} + \text{H}_2\text{O(l)} + 2\,\text{e}^-$

At the right electrode: $\text{HgO(s)} + \text{H}_2\text{O(l)} + 2\,\text{e}^- \rightarrow \text{Hg(l)} + 2\,\text{OH}^-\text{(aq)}$

Cell reaction: $\mathrm{Zn(s) + HgO(s) \rightarrow ZnO(s) + Hg(l)}$

(b) Use data in Appendix H to calculate the standard molar reaction quantities $\Delta_r H^\circ$, $\Delta_r G^\circ$, and $\Delta_r S^\circ$ for the cell reaction at 298.15 K.

Solution:

$$\begin{aligned}\Delta_r H^\circ &= \Delta_f H^\circ(\mathrm{ZnO}) + \Delta_f H^\circ(\mathrm{Hg}) - \Delta_f H^\circ(\mathrm{Zn}) - \Delta_f H^\circ\mathrm{HgO})\\ &= [(-350.46) + 0 - 0 - (-90.79)]\ \mathrm{kJ\ mol^{-1}}\\ &= -259.67\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

$$\begin{aligned}\Delta_r G^\circ &= \Delta_f G^\circ(\mathrm{ZnO}) + \Delta_f G^\circ(\mathrm{Hg}) - \Delta_f G^\circ(\mathrm{Zn}) - \Delta_f G^\circ\mathrm{HgO})\\ &= [(-320.48) + 0 - 0 - (-58.54)]\ \mathrm{kJ\ mol^{-1}}\\ &= -261.94\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

$$T\Delta_r S^\circ = \Delta_r H^\circ - \Delta_r G^\circ = 2.27\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta_r S^\circ = \frac{2.27 \times 10^3\ \mathrm{J\ mol^{-1}}}{298.15\ \mathrm{K}} = 7.61\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

(c) Calculate the standard cell potential of the mercury cell at 298.15 K to the nearest 0.01 V.

Solution:

$$E^\circ_{\mathrm{cell,\,eq}} = -\frac{\Delta_r G^\circ}{zF} = -\frac{(-261.94 \times 10^3\ \mathrm{J\ mol^{-1}})}{(2)(96,485\ \mathrm{C\ mol^{-1}})} = 1.36\ \mathrm{V}$$

(d) Evaluate the ratio of heat to advancement, $đq/\,\mathrm{d}\xi$, at a constant temperature of 298.15 K and a constant pressure of 1 bar, for the cell reaction taking place in two different ways: reversibly in the cell, and spontaneously in a reaction vessel that is not part of an electrical circuit.

Solution:

In the cell:

$$\frac{đq}{\mathrm{d}\xi} = T\Delta_r S^\circ = 2.27\ \mathrm{kJ\ mol^{-1}}$$

In a reaction vessel, from Eq. 11.3.1:

$$đq/\,\mathrm{d}\xi = \Delta_r H^\circ = -259.67\ \mathrm{kJ\ mol^{-1}}$$

(e) Evaluate $\mathrm{d}E^\circ_{\mathrm{cell,\,eq}}/\,\mathrm{d}T$, the temperature coefficient of the standard cell potential.

Solution:

From Eq. 14.3.18:

$$\frac{\mathrm{d}E^\circ_{\mathrm{cell,\,eq}}}{\mathrm{d}T} = \frac{\Delta_r S^\circ}{zF} = \frac{7.61\ \mathrm{J\ K^{-1}\ mol^{-1}}}{(2)(96,485\ \mathrm{C\ mol^{-1}})} = 3.9 \times 10^{-5}\ \mathrm{V\ K^{-1}}$$