15.9: Appendix I- Answers to Selected Problems

3.3(b)
$q = -w = 1.00 \times 10^5\ \text{J}$

3.4(c)
$w = 1.99 \times 10^3\ \text{J}$, $q = -1.99 \times 10^3\ \text{J}$.

3.5
0.0079%

3.6(c)
$V_2 \to nRV_1/(C_V + nR)$, $T_2 \to \infty$. For $C_V = (3/2)nR$, $V_2/V_1 \to 0.4$.

3.11
$9.58 \times 10^3\ \text{s}\,(2\ \text{hr}\ 40\ \text{min})$

4.4
$\Delta S = 0.054\ \text{J K}^{-1}$

4.5
$\Delta S = 549\ \text{J K}^{-1}$ for both processes; $\int đq/T_{\text{ext}} = 333\ \text{J K}^{-1}$ and 0.

5.4(a)
$$S = nR \ln\left[cT^{3/2}\left(\frac{V}{n} - b\right)\right] + \left(\frac{5}{2}\right)nR$$

5.5(a)
$q = 0$, $w = 1.50 \times 10^4\ \text{J}$, $\Delta U = 1.50 \times 10^4\ \text{J}$, $\Delta H = 2.00 \times 10^4\ \text{J}$

5.5(c)
$\Delta S = 66.7\ \text{J K}^{-1}$

6.1
$S_{\text{m}} \approx 151.6\ \text{J K}^{-1}\ \text{mol}^{-1}$

7.6(a)
$\alpha = 8.519 \times 10^{-4}\ \text{K}^{-1}$
$\kappa_t = 4.671 \times 10^{-5}\ \text{bar}^{-1}$
$(\partial p/\partial T)_V = 18.24\ \text{bar K}^{-1}$
$(\partial U/\partial V)_T = 5437\ \text{bar}$

7.6(b)
$\Delta p \approx 1.8\ \text{bar}$

7.7(b)
$(\partial C_{p,\text{m}}/\partial p)_T = -4.210 \times 10^{-8}\ \text{J K}^{-1}\ \text{Pa}^{-1}\ \text{mol}^{-1}$

7.8(b)
$8 \times 10^{-4}\ \text{K}^{-1}$

7.11
$5.001 \times 10^3\ \text{J}$

7.12
$\Delta H = 2.27 \times 10^4\ \text{J}$, $\Delta S = 43.6\ \text{J K}^{-1}$

7.13(a)
$C^{\circ}_{p,\text{m}} = 42.3\ \text{J K}^{-1}\ \text{mol}^{-1}$

7.13(b)
$C_{p,\text{m}} \approx 52.0\ \text{J K}^{-1}\ \text{mol}^{-1}$

7.14(a)
$2.56\ \mathrm{J\ K^{-1}\ g^{-1}}$

7.15(b)
$f = 17.4\ \mathrm{bar}$

7.16(a)
$\phi = 0.739$, $f = 148\ \mathrm{bar}$

7.16(b)
$B = -7.28 \times 10^{-5}\ \mathrm{m^3\ mol^{-1}}$

8.2(a)
$S^\circ_\mathrm{m}(\mathrm{l}) = 253.6\ \mathrm{J\ K^{-1}\ mol^{-1}}$

8.2(b)
$\Delta_\mathrm{vap}S^\circ = 88.6\ \mathrm{J\ K^{-1}\ mol^{-1}}$, $\Delta_\mathrm{vap}H^\circ = 2.748 \times 10^4\ \mathrm{J\ mol^{-1}}$

8.4
$4.5 \times 10^{-3}\ \mathrm{bar}$

8.5
$19\ \mathrm{J\ mol^{-1}}$

8.6(a)
$352.82\ \mathrm{K}$

8.6(b)
$3.4154 \times 10^4\ \mathrm{J\ mol^{-1}}$

8.7(a)
$3.62 \times 10^3\ \mathrm{Pa\ K^{-1}}$

8.7(b)
$3.56 \times 10^3\ \mathrm{Pa\ K^{-1}}$

8.7(c)
$99.60\ ^\circ\mathrm{C}$

8.8(b)
$\Delta_\mathrm{vap}H^\circ = 4.084 \times 10^4\ \mathrm{J\ mol^{-1}}$

8.9
$0.93\ \mathrm{mol}$

9.2(b)
$V_\mathrm{A}(x_\mathrm{B} = 0.5) \approx 125.13\ \mathrm{cm^3\ mol^{-1}}$
$V_\mathrm{B}(x_\mathrm{B} = 0.5) \approx 158.01\ \mathrm{cm^3\ mol^{-1}}$
$V_\mathrm{B}^\infty \approx 157.15\ \mathrm{cm^3\ mol^{-1}}$

9.4
real gas: $p = 1.9743\ \mathrm{bar}$
ideal gas: $p = 1.9832\ \mathrm{bar}$

9.5(a)
$x_{\mathrm{N_2}} = 8.83 \times 10^{-6}$
$x_{\mathrm{O_2}} = 4.65 \times 10^{-6}$
$y_{\mathrm{N_2}} = 0.763$
$y_{\mathrm{O_2}} = 0.205$

9.5(b)
$x_{\mathrm{N_2}} = 9.85 \times 10^{-6}$
$x_{\mathrm{O_2}} = 2.65 \times 10^{-6}$

$y_{N_2} = 0.851$
$y_{O_2} = 0.117$

9.7(b)
$f_A = 0.03167$ bar, $f_A = 0.03040$ bar

9.8(a)
In the mixture of composition $x_A = 0.9782$, the activity coefficient is $\gamma_B \approx 11.5$.

9.9(d)
$k_{H,A} \approx 680\,\text{kPa}$

9.11
Values for $m_B/m^\circ = 20$: $\gamma_A = 1.026$, $\gamma_{m,B} = 0.526$; the limiting slopes are $\mathrm{d}\gamma_A/\,\mathrm{d}(m_B/m^\circ) = 0$, $\mathrm{d}\gamma_{m,B}/\,\mathrm{d}(m_B/m^\circ) = -0.09$

9.13
$p_{N_2} = 0.235$ bar
$y_{N_2} = 0.815$
$p_{O_2} = 0.0532$ bar
$y_{O_2} = 0.185$
$p = 0.288$ bar

9.14(b)
$h = 1.2\,\text{m}$

9.15(a)
$p(7.20\,\text{cm}) - p(6.95\,\text{cm}) = 1.2$ bar

9.15(b)
$M_B = 187\,\text{kg mol}^{-1}$
mass binding ratio $= 1.37$

10.2
$\gamma\pm = 0.392$

11.1
$\Delta_r H^\circ = -63.94\,\text{kJ mol}^{-1}$
$K = 4.41 \times 10^{-2}$

11.2(b)
$\Delta_f H^\circ$: no change
$\Delta_f S^\circ$: subtract $0.219\,\text{J K}^{-1}\,\text{mol}^{-1}$
$\Delta_f G^\circ$: add $65\,\text{J mol}^{-1}$

11.3
$p(298.15\,\text{K}) = 2.6 \times 10^{-6}$ bar
$p(273.15\,\text{K}) = 2.7 \times 10^{-7}$ bar

11.4(a)
$-240.34\,\text{kJ mol}^{-1}$, $-470.36\,\text{kJ mol}^{-1}$, $-230.02\,\text{kJ mol}^{-1}$

11.4(b)
$-465.43\,\text{kJ mol}^{-1}$

11.4(c)
$-39.82\,\text{kJ mol}^{-1}$

11.5
$\Delta H = 0.92\,\text{kJ}$

11.6
$L_A = -0.405\,\text{J mol}^{-1}$

$L_{\mathrm{B}} = 0.810\ \mathrm{kJ\ mol^{-1}}$

11.7(a)

State 1:

$n_{\mathrm{C_6H_{14}}} = 7.822 \times 10^{-3}\ \mathrm{mol}$

$n_{\mathrm{H_2O}} = 0.05560\ \mathrm{mol}$

amount of $\mathrm{O_2}$ consumed: $0.07431\ \mathrm{mol}$

State 2:

$n_{\mathrm{H_2O}} = 0.11035\ \mathrm{mol}$

$n_{\mathrm{CO_2}} = 0.04693\ \mathrm{mol}$

\tx{mass of $\mathrm{H_2O}$}=1.9880 g

11.7(b)

$V_{\mathrm{m}}(\mathrm{C_6H_{14}}) = 131.61\ \mathrm{cm^3\ mol^{-1}}$

$V_{\mathrm{m}}(\mathrm{H_2O}) = 18.070\ \mathrm{cm^3\ mol^{-1}}$

11.7(c)

State 1: $V(\mathrm{C_6H_{14}}) = 1.029\ \mathrm{cm^3}$

$V(\mathrm{H_2O}) = 1.005\ \mathrm{cm^3}$

$V^{\mathrm{g}} = 348.0\ \mathrm{cm^3}$

State 2:

$V(\mathrm{H_2O}) = 1.994\ \mathrm{cm^3}$

$V^{\mathrm{g}} = 348.0\ \mathrm{cm^3}$

11.7(d)

State 1:

$n_{\mathrm{O_2}} = 0.429\ \mathrm{mol}$

State 2:

$n_{\mathrm{O_2}} = 0.355\ \mathrm{mol}$

$y_{\mathrm{O_2}} = 0.883$

$y_{\mathrm{CO_2}} = 0.117$

11.7(e)

State 2:

$p_2 = 27.9\ \mathrm{bar}$

$p_{\mathrm{O_2}} = 24.6\ \mathrm{bar}$

$p_{\mathrm{CO_2}} = 3.26\ \mathrm{bar}$

11.7(f)

$f_{\mathrm{H_2O}}(0.03169\ \mathrm{bar}) = 0.03164\ \mathrm{bar}$

State 1: $f_{\mathrm{H_2O}} = 0.03234\ \mathrm{bar}$

State 2: $f_{\mathrm{H_2O}} = 0.03229\ \mathrm{bar}$

11.7(g)

State 1:

$\phi_{\mathrm{H_2O}} = 0.925$

$\phi_{\mathrm{O_2}} = 0.981$

$f_{\mathrm{O_2}} = 29.4\ \mathrm{bar}$

State 2:

$\phi_{\mathrm{H_2O}} = 0.896$

$\phi_{\mathrm{O_2}} = 0.983$

$\phi_{\mathrm{CO_2}} = 0.910$

$f_{\mathrm{O_2}} = 24.2\ \mathrm{bar}$

$f_{\mathrm{CO_2}} = 2.97\ \mathrm{bar}$

11.7(h)

State 1:

$n^{\mathrm{g}}_{\mathrm{H_2O}} = 5.00 \times 10^{-4}\ \mathrm{mol}$
$n^{\mathrm{l}}_{\mathrm{H_2O}} = 0.05510\ \mathrm{mol}$
State 2:
$n^{\mathrm{g}}_{\mathrm{H_2O}} = 5.19 \times 10^{-4}\ \mathrm{mol}$
$n^{\mathrm{l}}_{\mathrm{H_2O}} = 0.10983\ \mathrm{mol}$

11.7(i)
State 1:
$k_{m,\mathrm{O_2}} = 825\ \mathrm{bar\ kg\ mol^{-1}}$
$n_{\mathrm{O_2}} = 3.57 \times 10^{-5}\ \mathrm{mol}$
State 2:
$k_{m,\mathrm{O_2}} = 823\ \mathrm{bar\ kg\ mol^{-1}}$
$k_{m,\mathrm{CO_2}} = 30.8\ \mathrm{bar\ kg\ mol^{-1}}$
$n_{\mathrm{O_2}} = 5.85 \times 10^{-5}\ \mathrm{mol}$
$n_{\mathrm{CO_2}} = 1.92 \times 10^{-4}\ \mathrm{mol}$

11.7(j)
$\mathrm{H_2O}$ vaporization: $\Delta U = +20.8\ \mathrm{J}$
$\mathrm{H_2O}$ condensation: $\Delta U = -21.6\ \mathrm{J}$

11.7(k)
$\mathrm{O_2}$ dissolution: $\Delta U = -0.35\ \mathrm{J}$
$\mathrm{O_2}$ desolution: $\Delta U = 0.57\ \mathrm{J}$
$\mathrm{CO_2}$ desolution: $\Delta U = 3.32\ \mathrm{J}$

11.7(l)
$\mathrm{C_6H_{14}}$(l) compression: $\Delta U = -1.226\ \mathrm{J}$
solution compression: $\Delta U = -0.225\ \mathrm{J}$
solution decompression: $\Delta U = 0.414\ \mathrm{J}$

11.7(m)
$\mathrm{O_2}$ compression: $\Delta U = -81\ \mathrm{J}$
gas mixture: $\mathrm{d}B/\,\mathrm{d}T = 0.26 \times 10^{-6}\ \mathrm{m^3 K^{-1}\ mol^{-1}}$
gas mixture expansion: $\Delta U = 87\ \mathrm{J}$

11.7(n)
$\Delta U = 8\ \mathrm{J}$

11.7(o)
$\Delta_{\mathrm{c}} U^\circ = -4154.4\ \mathrm{kJ\ mol^{-1}}$

11.7(p)
$\Delta_{\mathrm{c}} H^\circ = -4163.1\ \mathrm{kJ\ mol^{-1}}$

11.8
$\Delta_{\mathrm{f}} H^\circ = -198.8\ \mathrm{kJ\ mol^{-1}}$

11.9
$T_2 = 2272\ \mathrm{K}$

11.10
$p(\mathrm{O_2}) = 2.55 \times 10^{-5}\ \mathrm{bar}$

11.11(a)
$K = 3.5 \times 10^{41}$

11.11(b)
$p_{\mathrm{H_2}} = 2.8 \times 10^{-42}\ \mathrm{bar}$
$N_{\mathrm{H_2}} = 6.9 \times 10^{-17}$

11.11(c)
$t = 22\,\mathrm{s}$

11.12(b)
$p \approx 1.5 \times 10^4\,\mathrm{bar}$

11.13(c)
$K = 0.15$

12.1(b)
$T = 1168\,\mathrm{K}$
$\Delta_\mathrm{r} H^\circ = 1.64 \times 10^5\,\mathrm{J\,mol^{-1}}$

12.4
$K_\mathrm{f} = 1.860\,\mathrm{K\,kg\,mol^{-1}}$
$K_\mathrm{b} = 0.5118\,\mathrm{K\,kg\,mol^{-1}}$

12.5
$M_\mathrm{B} \approx 5.6 \times 10^4\,\mathrm{g\,mol^{-1}}$

12.6
$\Delta_{\mathrm{sol,B}} H^\circ/\mathrm{kJ\,mol^{-1}} = -3.06, 0, 6.35$
$\Delta_{\mathrm{sol,B}} S^\circ/\mathrm{J\,K^{-1}\,mol^{-1}} = -121.0, -110.2, -88.4$

12.7(a)
$m_+^\alpha = m_-^\alpha = 1.20 \times 10^{-3}\,\mathrm{mol\,kg^{-1}}$
$m_+^\beta = 1.80 \times 10^{-3}\,\mathrm{mol\,kg^{-1}}$
$m_-^\beta = 0.80 \times 10^{-3}\,\mathrm{mol\,kg^{-1}}$
$m_\mathrm{P} = 2.00 \times 10^{-6}\,\mathrm{mol\,kg^{-1}}$

12.8(a)
$p^\mathrm{l} = 2.44\,\mathrm{bar}$

12.8(b)
$f(2.44\,\mathrm{bar}) - f(1.00\,\mathrm{bar}) = 3.4 \times 10^{-5}\,\mathrm{bar}$

12.10(a)
$x_\mathrm{B} = 1.8 \times 10^{-7}$
$m_\mathrm{B} = 1.0 \times 10^{-5}\,\mathrm{mol\,kg^{-1}}$

12.10(b)
$\Delta_{\mathrm{sol,B}} H^\circ = -1.99 \times 10^4\,\mathrm{J\,mol^{-1}}$

12.10(c)
$K = 4.4 \times 10^{-7}$
$\Delta_\mathrm{r} H^\circ = 9.3\,\mathrm{kJ\,mol^{-1}}$

12.13(a)
$p = 92399.6\,\mathrm{Pa}$, $y_\mathrm{B} = 0.965724$

12.13(b)
$\phi_\mathrm{A} = 0.995801$

12.13(c)
$f_\mathrm{A} = 3164.47\,\mathrm{Pa}$

12.13(d)
$y_\mathrm{B} = 0.965608$

12.13(e)
$Z = 0.999319$

12.13(f)
$p = 92347.7\,\mathrm{Pa}$

12.13(g)
$k_{\mathrm{H,B}} = 4.40890 \times 10^{9}\,\mathrm{Pa}$

12.15(a)
$\gamma_{x,\mathrm{B}} = 0.9826$

12.15(b)
$x_{\mathrm{B}} = 4.19 \times 10^{-4}$

12.16
$K = 1.2 \times 10^{-6}$

12.17(a)
$\alpha = 0.129$
$m_{+} = 1.29 \times 10^{-3}\,\mathrm{mol\,kg^{-1}}$

12.17(b)
$\alpha = 0.140$

12.18
$\Delta_{\mathrm{f}}H^{\circ}(\mathrm{Cl^{-}},\mathrm{aq}) = -167.15\,\mathrm{kJ\ mol^{-1}}$
$S^{\circ}_{\mathrm{m}}(\mathrm{Cl^{-}},\mathrm{aq}) = 56.46\,\mathrm{J\ K^{-1}\ mol^{-1}}$

12.19(a)
$K_{\mathrm{s}} = 1.783 \times 10^{-10}$

12.20(a)
$\Delta_{\mathrm{r}}H^{\circ} = -65.769\,\mathrm{kJ\ mol^{-1}}$

12.20(b)
$\Delta_{\mathrm{f}}H^{\circ}(\mathrm{Ag^{+}},\mathrm{aq}) = 105.84\,\mathrm{kJ\ mol^{-1}}$

13.1(a)
$F = 4$

13.1(b)
$F = 3$

13.1(c)
$F = 2$

13.10(a)
$x_{\mathrm{B}}(\mathrm{top}) = 0.02,\ x_{\mathrm{B}}(\mathrm{bottom}) = 0.31$

13.10(b)
$n_{\mathrm{A}} = 2.1\,\mathrm{mol},\ n_{\mathrm{B}} = 1.0\,\mathrm{mol}$

14.3(a)
$\Delta_{\mathrm{r}}G^{\circ} = -21.436\,\mathrm{kJ\ mol^{-1}}$
$\Delta_{\mathrm{r}}S^{\circ} = -62.35\,\mathrm{J\ K^{-1}\ mol^{-1}}$
$\Delta_{\mathrm{r}}H^{\circ} = -40.03\,\mathrm{kJ\ mol^{-1}}$

14.3(b)
$\Delta_{\mathrm{f}}H^{\circ}(\mathrm{AgCl},\mathrm{s}) = -127.05\,\mathrm{kJ\ mol^{-1}}$

14.3(c)
$S^{\circ}_{\mathrm{m}}(\mathrm{AgCl},\mathrm{s}) = 96.16\,\mathrm{J\ K^{-1}\ mol^{-1}}$
$\Delta_{\mathrm{f}}S^{\circ}(\mathrm{AgCl},\mathrm{s}) = -57.93\backslash\mathrm{units}\{\mathrm{J\ K^{-1}\ mol^{-1}}\}$
$\Delta_{\mathrm{f}}G^{\circ}(\mathrm{AgCl},\mathrm{s}) = -109.78\,\mathrm{kJ\ mol^{-1}}$

14.4(b)
$\Delta_\mathrm{f}H^\circ(\mathrm{AgCl,\,s}) = -126.81\,\mathrm{kJ\ mol^{-1}}$
$\Delta_\mathrm{f}G^\circ(\mathrm{AgCl,\,s}) = -109.59\,\mathrm{kJ\ mol^{-1}}$

14.5
$K_\mathrm{s} = 1.76 \times 10^{-10}$

14.6(b)
$\gamma_\pm = 0.756$

14.7(b)
$\Delta_\mathrm{f}G^\circ = -210.72\,\mathrm{kJ\ mol^{-1}}$

14.7(c)
$K_\mathrm{s} = 1.4 \times 10^{-18}$

14.8
$E^\circ = 0.071\,\mathrm{V}$

14.9(c)
$E^\circ_{\mathrm{cell,\,eq}} = 1.36\,\mathrm{V}$

14.9(d)
In the cell:
$đq/\,\mathrm{d}\xi = 2.27\,\mathrm{kJ\ mol^{-1}}$
In a reaction vessel:
$đq/\,\mathrm{d}\xi = -259.67\,\mathrm{kJ\ mol^{-1}}$

14.9(e)
$\mathrm{d}E^\circ_{\mathrm{cell,\,eq}}/\,\mathrm{d}T = 3.9 \times 10^{-5}\,\mathrm{V\ K^{-1}}$
