Chapter 3 - Section A - Mathcad Solutions

3.1 $\beta = \frac{-1}{\rho}\cdot\left(\frac{d}{dT}\rho\right)_P$ $\kappa = \frac{1}{\rho}\cdot\left(\frac{d}{dP}\rho\right)_T$

At constant T, the 2nd equation can be written:

$\frac{d\rho}{\rho} = \kappa\cdot dP$ $\ln\left(\frac{\rho_2}{\rho_1}\right) = \kappa\Delta P$ $\kappa := 44.18\cdot 10^{-6}\cdot bar^{-1}$ $\rho_2 = 1.01\cdot\rho_1$

$\Delta P := \frac{\ln(1.01)}{\kappa}$ $\Delta P = 225.2\,bar$ $P_2 = 226.2\cdot bar$ **Ans.**

3.4 $b := 2700\cdot bar$ $c := 0.125\cdot\frac{cm^3}{gm}$ $P_1 := 1\cdot bar$ $P_2 := 500\cdot bar$

Since $Work = -\int_{V_1}^{V_2} P\,dV$ **a bit of algebra leads to**

$Work := c\cdot\int_{P_1}^{P_2}\frac{P}{P+b}\,dP$ $Work = 0.516\frac{J}{gm}$ **Ans.**

Alternatively, formal integration leads to

$Work := c\cdot\left(P_2 - P_1 - b\cdot\ln\left(\frac{P_2+b}{P_1+b}\right)\right)$ $Work = 0.516\frac{J}{gm}$ **Ans.**

3.5 $\kappa = a + b\cdot P$ $a := 3.9\cdot 10^{-6}\cdot atm^{-1}$ $b := -0.1\cdot 10^{-9}\cdot atm^{-2}$

$P_1 := 1\cdot atm$ $P_2 := 3000\cdot atm$ $V := 1\cdot ft^3$ **(assume const.)**

Combine Eqs. (1.3) and (3.3) for const. T:

$Work := V\cdot\int_{P_1}^{P_2}(a + b\cdot P)\cdot P\,dP$ $Work = 16.65\,atm\cdot ft^3$ **Ans.**

3.6 $\beta := 1.2\cdot10^{-3}\cdot degC^{-1}$ $C_P := 0.84\cdot\dfrac{kJ}{kg\cdot degC}$ $M := 5\cdot kg$

$V_1 := \dfrac{1}{1590}\cdot\dfrac{m^3}{kg}$ $P := 1\cdot bar$ $t_1 := 0\cdot degC$ $t_2 := 20\cdot degC$

With beta independent of T and with P=constant,

$\dfrac{dV}{V} = \beta\cdot dT$ $V_2 := V_1\cdot\exp\left[\beta\cdot\left(t_2 - t_1\right)\right]$ $\Delta V := V_2 - V_1$

$\Delta V_{total} := M\cdot\Delta V$ $\Delta V_{total} = 7.638\times10^{-5}\,m^3$ **Ans.**

$Work := -P\cdot\Delta V_{total}$ **(Const. P)** $Work = -7.638\,joule$ **Ans.**

$Q := M\cdot C_P\cdot\left(t_2 - t_1\right)$ $Q = 84\,kJ$ **Ans.**

$\Delta H_{total} := Q$ $\Delta H_{total} = 84\,kJ$ **Ans.**

$\Delta U_{total} := Q + Work$ $\Delta U_{total} = 83.99\,kJ$ **Ans.**

3.8 $P_1 := 8\cdot bar$ $P_2 := 1\cdot bar$ $T_1 := 600\cdot K$ $C_P := \dfrac{7}{2}\cdot R$ $C_V := \dfrac{5}{2}\cdot R$

(a) Constant V: $W = 0$ **and** $\Delta U = Q = C_V\cdot\Delta T$

$T_2 := T_1\cdot\dfrac{P_2}{P_1}$ $\Delta T := T_2 - T_1$ $\Delta T = -525\,K$

$\Delta U := C_V\cdot\Delta T$ **Q and** $\Delta U = -10.91\,\dfrac{kJ}{mol}$ **Ans.**

$\Delta H := C_P\cdot\Delta T$ $\Delta H = -15.28\,\dfrac{kJ}{mol}$ **Ans.**

(b) Constant T: $\Delta U = \Delta H = 0$ **and** $Q = W$

$Work := R\cdot T_1\cdot\ln\left(\dfrac{P_2}{P_1}\right)$ Q **and** $Work = -10.37\,\dfrac{kJ}{mol}$ **Ans.**

(c) Adiabatic: $Q = 0$ **and** $\Delta U = W = C_V\cdot\Delta T$

$\gamma := \dfrac{C_P}{C_V}$ $\qquad T_2 := T_1\cdot\left(\dfrac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$ $\qquad T_2 = 331.227\,K$ $\qquad \Delta T := T_2 - T_1$

$\Delta U := C_V\cdot\Delta T$ $\qquad \Delta H := C_P\cdot\Delta T$

W **and** $\Delta U = -5.586\,\dfrac{kJ}{mol}$ **Ans.** $\qquad \Delta H = -7.821\,\dfrac{kJ}{mol}$ **Ans.**

3.9 $P_4 := 2bar$ $\qquad C_P := \dfrac{7}{2}R$ $\qquad C_V := \dfrac{5}{2}R$

$P_1 := 10bar$ $\qquad T_1 := 600K$ $\qquad V_1 := \dfrac{R\cdot T_1}{P_1}$ $\qquad V_1 = 4.988\times10^{-3}\,\dfrac{m^3}{mol}$

Step 41: Adiabatic $\qquad T_4 := T_1\cdot\left(\dfrac{P_4}{P_1}\right)^{\frac{R}{C_P}}$ $\qquad T_4 = 378.831\,K$

$\Delta U_{41} := C_V\cdot(T_1 - T_4)$ $\qquad \Delta U_{41} = 4.597\times10^{3}\,\dfrac{J}{mol}$

$\Delta H_{41} := C_P\cdot(T_1 - T_4)$ $\qquad \Delta H_{41} = 6.436\times10^{3}\,\dfrac{J}{mol}$

$Q_{41} := 0\,\dfrac{J}{mol}$ $\qquad Q_{41} = 0\,\dfrac{J}{mol}$

$W_{41} := \Delta U_{41}$ $\qquad W_{41} = 4.597\times10^{3}\,\dfrac{J}{mol}$

$P_2 := 3bar$ $\qquad T_2 := 600K$ $\qquad V_2 := \dfrac{R\cdot T_2}{P_2}$ $\qquad V_2 = 0.017\,\dfrac{m^3}{mol}$

Step 12: Isothermal $\qquad \Delta U_{12} := 0\,\dfrac{J}{mol}$ $\qquad \Delta U_{12} = 0\,\dfrac{J}{mol}$

$\Delta H_{12} := 0\cdot\dfrac{J}{mol}$ $\qquad \Delta H_{12} = 0\,\dfrac{J}{mol}$

$Q_{12} := -R \cdot T_1 \cdot \ln\left(\frac{P_2}{P_1}\right)$ $Q_{12} = 6.006 \times 10^3 \frac{J}{mol}$

$W_{12} := -Q_{12}$ $W_{12} = -6.006 \times 10^3 \frac{J}{mol}$

$P_3 := 2bar$ $V_3 := V_2$ $T_3 := \frac{P_3 \cdot V_3}{R}$ $T_3 = 400 K$

Step 23: Isochoric $\Delta U_{23} := C_V \cdot (T_3 - T_2)$ $\Delta U_{23} = -4.157 \times 10^3 \frac{J}{mol}$

$\Delta H_{23} := C_P \cdot (T_3 - T_2)$ $\Delta H_{23} = -5.82 \times 10^3 \frac{J}{mol}$

$Q_{23} := C_V \cdot (T_3 - T_2)$ $Q_{23} = -4.157 \times 10^3 \frac{J}{mol}$

$W_{23} := 0 \frac{J}{mol}$ $W_{23} = 0 \frac{J}{mol}$

$P_4 = 2 bar$ $T_4 = 378.831 K$ $V_4 := \frac{R \cdot T_4}{P_4}$ $V_4 = 0.016 \frac{m^3}{mol}$

Step 34: Isobaric $\Delta U_{34} := C_V \cdot (T_4 - T_3)$ $\Delta U_{34} = -439.997 \frac{J}{mol}$

$\Delta H_{34} := C_P \cdot (T_4 - T_3)$ $\Delta H_{34} = -615.996 \frac{J}{mol}$

$Q_{34} := C_P \cdot (T_4 - T_3)$ $Q_{34} = -615.996 \frac{J}{mol}$

$W_{34} := -R \cdot (T_4 - T_3)$ $W_{34} = 175.999 \frac{J}{mol}$

3.10 For all parts of this problem: $T_2 = T_1$ **and**

$\Delta U = \Delta H = 0$ **Also** $Q = -Work$ **and all that remains is to calculate Work. Symbol V is used for total volume in this problem.**

$P_1 := 1 \cdot bar$ $P_2 := 12 \cdot bar$ $V_1 := 12 \cdot m^3$ $V_2 := 1 \cdot m^3$

(a) $\text{Work} = n\cdot R\cdot T\cdot\ln\left(\frac{P_2}{P_1}\right)$ $\text{Work} := P_1\cdot V_1\cdot\ln\left(\frac{P_2}{P_1}\right)$

$\text{Work} = 2982\,\text{kJ}$ **Ans.**

(b) Step 1: adiabatic compression to P_2

$\gamma := \frac{5}{3}$ $V_i := V_1\cdot\left(\frac{P_1}{P_2}\right)^{\frac{1}{\gamma}}$ **(intermediate V)** $V_i = 2.702\,\text{m}^3$

$W_1 := \frac{P_2\cdot V_i - P_1\cdot V_1}{\gamma - 1}$ $W_1 = 3063\,\text{kJ}$

Step 2: cool at const P_2 to V_2

$W_2 := -P_2\cdot\left(V_2 - V_i\right)$ $W_2 = 2042\,\text{kJ}$

$\text{Work} := W_1 + W_2$ $\text{Work} = 5106\,\text{kJ}$ **Ans.**

(c) Step 1: adiabatic compression to V_2

$P_i := P_1\cdot\left(\frac{V_1}{V_2}\right)^{\gamma}$ **(intermediate P)** $P_i = 62.898\,\text{bar}$

$W_1 := \frac{P_i\cdot V_2 - P_1\cdot V_1}{\gamma - 1}$ $W_1 = 7635\,\text{kJ}$

Step 2: No work. $\text{Work} := W_1$ $\text{Work} = 7635\,\text{kJ}$ **Ans.**

(d) Step 1: heat at const V_1 to P_2 $W_1 = 0$

Step 2: cool at const P_2 to V_2

$W_2 := -P_2\cdot\left(V_2 - V_1\right)$ $\text{Work} := W_2$ $\text{Work} = 13200\,\text{kJ}$ **Ans.**

(e) Step 1: cool at const P_1 to V_2

$W_1 := -P_1\cdot\left(V_2 - V_1\right)$ $W_1 = 1100\,\text{kJ}$

Step 2: heat at const V_2 to P_2 $W_2 = 0$

$\text{Work} := W_1$ $\text{Work} = 1100\,\text{kJ}$ **Ans.**

3.17 (a) No work is done; no heat is transferred.

$\Delta U^t = \Delta T = 0$ $T_2 = T_1 = 100\cdot\text{degC}$ **Not reversible**

(b) The gas is returned to its initial state by isothermal compression.

$\text{Work} = n\cdot R\cdot T\cdot\ln\left(\frac{V_1}{V_2}\right)$ **but** $n\cdot R\cdot T = P_2\cdot V_2$

$V_1 := 4\cdot m^3$ $V_2 := \frac{4}{3}\cdot m^3$ $P_2 := 6\cdot\text{bar}$

$\text{Work} := P_2\cdot V_2\cdot\ln\left(\frac{V_1}{V_2}\right)$ $\text{Work} = 878.9\,\text{kJ}$ **Ans.**

3.18 (a) $P_1 := 100\cdot\text{kPa}$ $P_2 := 500\cdot\text{kPa}$ $T_1 := 303.15\cdot K$

$C_P := \frac{7}{2}\cdot R$ $C_V := \frac{5}{2}\cdot R$ $\gamma := \frac{C_P}{C_V}$

Adiabatic compression from point 1 to point 2:

$Q_{12} := 0\cdot\frac{\text{kJ}}{\text{mol}}$ $\Delta U_{12} = W_{12} = C_V\cdot\Delta T_{12}$ $T_2 := T_1\cdot\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$

$\Delta U_{12} := C_V\cdot(T_2 - T_1)$ $\Delta H_{12} := C_P\cdot(T_2 - T_1)$ $W_{12} := \Delta U_{12}$

$\Delta U_{12} = 3.679\frac{\text{kJ}}{\text{mol}}$ $\Delta H_{12} = 5.15\frac{\text{kJ}}{\text{mol}}$ $W_{12} = 3.679\frac{\text{kJ}}{\text{mol}}$ **Ans.**

Cool at P_2 from point 2 to point 3:

$T_3 := T_1$ $\Delta H_{23} := C_P\cdot(T_3 - T_2)$ $Q_{23} := \Delta H_{23}$

$\Delta U_{23} := C_V\cdot(T_3 - T_2)$ $W_{23} := \Delta U_{23} - Q_{23}$

$\Delta H_{23} = -5.15\,\frac{kJ}{mol}$ $\Delta U_{23} = -3.679\,\frac{kJ}{mol}$ **Ans.**

$Q_{23} = -5.15\,\frac{kJ}{mol}$ $W_{23} = 1.471\,\frac{kJ}{mol}$ **Ans.**

Isothermal expansion from point 3 to point 1:

$\Delta U_{31} = \Delta H_{31} = 0$ $P_3 := P_2$ $W_{31} := R \cdot T_3 \cdot \ln\left(\frac{P_1}{P_3}\right)$

$Q_{31} := -W_{31}$

$W_{31} = -4.056\,\frac{kJ}{mol}$ $Q_{31} = 4.056\,\frac{kJ}{mol}$ **Ans.**

FOR THE CYCLE: $\Delta U = \Delta H = 0$

$Q := Q_{12} + Q_{23} + Q_{31}$ $\mathrm{Work} := W_{12} + W_{23} + W_{31}$

$Q = -1.094\,\frac{kJ}{mol}$ $\mathrm{Work} = 1.094\,\frac{kJ}{mol}$

(b) If each step that is 80% efficient accomplishes the same change of state, all property values are unchanged, and the delta H and delta U values are the same as in part (a). However, the Q and W values change.

Step 12: $W_{12} := \frac{W_{12}}{0.8}$ $W_{12} = 4.598\,\frac{kJ}{mol}$

$Q_{12} := \Delta U_{12} - W_{12}$ $Q_{12} = -0.92\,\frac{kJ}{mol}$

Step 23: $W_{23} := \frac{W_{23}}{0.8}$ $W_{23} = 1.839\,\frac{kJ}{mol}$

$Q_{23} := \Delta U_{23} - W_{23}$ $Q_{23} = -5.518\,\frac{kJ}{mol}$

Step 31: $W_{31} := W_{31} \cdot 0.8$ $W_{31} = -3.245\,\frac{kJ}{mol}$

$Q_{31} := -W_{31}$ $Q_{31} = 3.245\,\frac{kJ}{mol}$

FOR THE CYCLE:

$Q := Q_{12} + Q_{23} + Q_{31}$ $\qquad$ $Work := W_{12} + W_{23} + W_{31}$

$Q = -3.192\,\dfrac{kJ}{mol}$ $\qquad$ $Work = 3.192\,\dfrac{kJ}{mol}$

3.19 Here, V represents total volume.

$P_1 := 1000\cdot kPa$ $\qquad$ $V_1 := 1\cdot m^3$ $\qquad$ $V_2 := 5\cdot V_1$ $\qquad$ $T_1 := 600\cdot K$

$C_P := 21\cdot\dfrac{joule}{mol\cdot K}$ $\qquad$ $C_V := C_P - R$ $\qquad$ $\gamma := \dfrac{C_P}{C_V}$

(a) Isothermal: $\qquad$ $Work = n\cdot R\cdot T_1\cdot\ln\left(\dfrac{V_1}{V_2}\right)$ $\qquad$ $P_2 := P_1\cdot\dfrac{V_1}{V_2}$

$T_2 := T_1$ $\qquad$ $T_2 = 600\,K$ $\qquad$ $P_2 = 200\,kPa$ $\qquad$ **Ans.**

$Work := P_1\cdot V_1\cdot\ln\left(\dfrac{V_1}{V_2}\right)$ $\qquad$ $Work = -1609\,kJ$ $\qquad$ **Ans.**

(b) Adiabatic: $\qquad$ $P_2 := P_1\cdot\left(\dfrac{V_1}{V_2}\right)^{\gamma}$ $\qquad$ $T_2 := T_1\cdot\dfrac{P_2}{P_1}\cdot\dfrac{V_2}{V_1}$

$T_2 = 208.96\,K$ $\qquad$ $P_2 = 69.65\,kPa$ $\qquad$ **Ans.**

$Work := \dfrac{P_2\cdot V_2 - P_1\cdot V_1}{\gamma - 1}$ $\qquad$ $Work = -994.4\,kJ$ $\qquad$ **Ans,**

(c) Restrained adiabatic: $\qquad$ $Work = \Delta U = -P_{ext}\cdot\ V$

$P_{ext} := 100\cdot kPa$ $\qquad$ $Work := -P_{ext}\cdot\left(V_2 - V_1\right)$ $\qquad$ $Work = -400\,kJ$ $\qquad$ **Ans.**

$n := \dfrac{P_1\cdot V_1}{R\cdot T_1}$ $\qquad$ $\Delta U = n\cdot C_V\cdot\ T$

$T_2 := \dfrac{Work}{n\cdot C_V} + T_1$ $\qquad$ $T_2 = 442.71\,K$ $\qquad$ **Ans.**

$P_2 := P_1\cdot\dfrac{V_1}{V_2}\cdot\dfrac{T_2}{T_1}$ $\qquad$ $P_2 = 147.57\,kPa$ $\qquad$ **Ans.**

3.20 $T_1 := 423.15\cdot K$ $P_1 := 8\cdot bar$ $P_3 := 3\cdot bar$

$C_P := \frac{7}{2}\cdot R$ $C_V := \frac{5}{2}\cdot R$ $T_2 := T_1$ $T_3 := 323.15\cdot K$

Step 12: $\Delta H_{12} := 0\cdot\frac{kJ}{mol}$ $\Delta U_{12} := 0\cdot\frac{kJ}{mol}$

If $r = \frac{V_1}{V_2} = \frac{V_1}{V_3}$ **Then** $r := \frac{T_1}{T_3}\cdot\frac{P_3}{P_1}$ $W_{12} := R\cdot T_1\cdot \ln(r)$

$W_{12} = -2.502\frac{kJ}{mol}$ $Q_{12} := -W_{12}$ $Q_{12} = 2.502\frac{kJ}{mol}$

Step 23: $W_{23} := 0\cdot\frac{kJ}{mol}$ $\Delta U_{23} := C_V\cdot(T_3 - T_2)$

$Q_{23} := \Delta U_{23}$ $\Delta H_{23} := C_P\cdot(T_3 - T_2)$

$Q_{23} = -2.079\frac{kJ}{mol}$ $\Delta U_{23} = -2.079\frac{kJ}{mol}$ $\Delta H_{23} = -2.91\frac{kJ}{mol}$

Process: $Work := W_{12} + W_{23}$ $Work = -2.502\frac{kJ}{mol}$ **Ans.**

$Q := Q_{12} + Q_{23}$ $Q = 0.424\frac{kJ}{mol}$ **Ans.**

$\Delta H := \Delta H_{12} + \Delta H_{23}$ $\Delta H = -2.91\frac{kJ}{mol}$ **Ans.**

$\Delta U := \Delta U_{12} + \Delta U_{23}$ $\Delta U = -2.079\frac{kJ}{mol}$ **Ans.**

3.21 By Eq. (2.32a), unit-mass basis: $molwt := 28\,\frac{gm}{mol}$ $\Delta H + \frac{1}{2}\cdot\Delta u^2 = 0$

But $\Delta H = C_P\cdot\Delta T$ **Whence** $\Delta T = \frac{-\left(u_2{}^2 - u_1{}^2\right)}{2\cdot C_P}$

$C_P := \frac{7}{2}\cdot\frac{R}{molwt}$ $u_1 := 2.5\cdot\frac{m}{s}$ $u_2 := 50\cdot\frac{m}{s}$ $t_1 := 150\cdot degC$

$t_2 := t_1 - \frac{u_2{}^2 - u_1{}^2}{2\cdot C_P}$ $t_2 = 148.8\,degC$ **Ans.**

3.22 $C_P := \frac{7}{2}\cdot R$ $C_V := \frac{5}{2}\cdot R$ $T_1 := 303.15\cdot K$ $T_3 := 403.15\cdot K$

$P_1 := 1\cdot bar$ $P_3 := 10\cdot bar$

$\Delta U := C_V\cdot\left(T_3 - T_1\right)$ $\Delta H := C_P\cdot\left(T_3 - T_1\right)$

$\Delta U = 2.079\,\frac{kJ}{mol}$ **Ans.** $\Delta H = 2.91\,\frac{kJ}{mol}$ **Ans.**

Each part consists of two steps, 12 & 23.

(a) $T_2 := T_3$ $P_2 := P_1\cdot\frac{T_2}{T_1}$

$W_{23} := R\cdot T_2\cdot\ln\left(\frac{P_3}{P_2}\right)$ $Work := W_{23}$

$Work = 6.762\,\frac{kJ}{mol}$ **Ans.**

$Q := \Delta U - Work$

$Q = -4.684\,\frac{kJ}{mol}$ **Ans.**

(b) $P_2 := P_1$ $T_2 := T_3$ $\Delta U_{12} := C_V \cdot (T_2 - T_1)$

$\Delta H_{12} := C_P \cdot (T_2 - T_1)$ $Q_{12} := \Delta H_{12}$

$W_{12} := \Delta U_{12} - Q_{12}$ $W_{12} = -0.831 \frac{kJ}{mol}$

$W_{23} := R \cdot T_2 \cdot \ln\left(\frac{P_3}{P_2}\right)$ $W_{23} = 7.718 \frac{kJ}{mol}$

$Work := W_{12} + W_{23}$ $Work = 6.886 \frac{kJ}{mol}$ **Ans.**

$Q := \Delta U - Work$ $Q = -4.808 \frac{kJ}{mol}$ **Ans.**

(c) $T_2 := T_1$ $P_2 := P_3$ $W_{12} := R \cdot T_1 \cdot \ln\left(\frac{P_2}{P_1}\right)$

$\Delta H_{23} := C_P \cdot (T_3 - T_2)$ $Q_{23} := \Delta H_{23}$

$\Delta U_{23} := C_V \cdot (T_3 - T_2)$ $W_{23} := \Delta U_{23} - Q_{23}$

$Work := W_{12} + W_{23}$ $Work = 4.972 \frac{kJ}{mol}$ **Ans.**

$Q := \Delta U - Work$ $Q = -2.894 \frac{kJ}{mol}$ **Ans.**

For the second set of heat-capacity values, answers are (kJ/mol):

$\Delta U = 1.247$ $\Delta U = 2.079$

(a) $Work = 6.762$ $Q = -5.515$

(b) $Work = 6.886$ $Q = -5.639$

(c) $Work = 4.972$ $Q = -3.725$

3.23 $T_1 := 303.15 \cdot K$ $T_2 := T_1$ $T_3 := 393.15 \cdot K$

$P_1 := 1 \cdot bar$ $P_3 := 12 \cdot bar$ $C_P := \frac{7}{2} \cdot R$ $C_V := \frac{5}{2} \cdot R$

For the process: $\Delta U := C_V \cdot (T_3 - T_1)$ $\Delta H := C_P \cdot (T_3 - T_1)$

$\Delta U = 1.871 \frac{kJ}{mol}$ $\Delta H = 2.619 \frac{kJ}{mol}$ **Ans.**

Step 12: $P_2 := P_3 \cdot \frac{T_1}{T_3}$ $W_{12} := R \cdot T_1 \cdot \ln\left(\frac{P_2}{P_1}\right)$

$W_{12} = 5.608 \frac{kJ}{mol}$ $Q_{12} := -W_{12}$ $Q_{12} = -5.608 \frac{kJ}{mol}$

Step 23: $W_{23} := 0 \cdot \frac{kJ}{mol}$ $Q_{23} := \Delta U$

For the process: $Work := W_{12} + W_{23}$

$Q := Q_{12} + Q_{23}$ $Work = 5.608 \frac{kJ}{mol}$ $Q = -3.737 \frac{kJ}{mol}$ **Ans.**

3.24 $W_{12} = 0$ $Work = W_{23} = -P_2 (V_3 - V_2) = -R \cdot (T_3 - T_2)$

But $T_3 = T_1$ **So...** $Work = R \cdot (T_2 - T_1)$

Also $W = R \cdot T_1 \cdot \ln\left(\frac{P}{P_1}\right)$ **Therefore**

$\ln\left(\frac{P}{P_1}\right) = \frac{T_2 - T_1}{T_1}$ $T_2 := 350 \cdot K$ $T_1 := 800 \cdot K$ $P_1 := 4 \cdot bar$

$P := P_1 \cdot \exp\left(\frac{T_2 - T_1}{T_1}\right)$ $P = 2.279\,bar$ **Ans.**

3.25 $V_A := 256\cdot cm^3$ **Define:** $\frac{\Delta P}{P_1} = r$ $r := -0.0639$

Assume ideal gas; let V represent total volume:

$P_1\cdot V_B = P_2\cdot(V_A + V_B)$ **From this one finds:**

$\frac{\Delta P}{P_1} = \frac{-V_A}{V_A + V_B}$ $V_B := \frac{-V_A\cdot(r+1)}{r}$ $V_B = 3750.3\,cm^3$ **Ans.**

3.26 $T_1 := 300\cdot K$ $P_1 := 1\cdot atm$ $C_P := \frac{7}{2}\cdot R$ $C_V := C_P - R$ $\gamma := \frac{C_P}{C_V}$

The process occurring in section B is a reversible, adiabatic compression. Let

$P(final) = P_2$ $T_A(final) = T_A$ $T_B(final) = T_B$

$n_A = n_B$ **Since the total volume is constant,**

$\frac{2\cdot n_A\cdot R\cdot T_1}{P_1} = \frac{n_A\cdot R\cdot(T_A + T_B)}{P_2}$ **or** $\frac{2\cdot T_1}{P_1} = \frac{T_A + T_B}{P_2}$ **(1)**

(a) $P_2 := 1.25\cdot atm$ $T_B := T_1\cdot\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$ **(2)**

$T_A := 2\cdot T_1\cdot\frac{P_2}{P_1} - T_B$ $Q = n_A\cdot(\Delta U_A + \Delta U_B)$

Define $q = \frac{Q}{n_A}$ $q := C_V\cdot(T_A + T_B - 2\cdot T_1)$ **(3)**

$T_B = 319.75\,K$ $T_A = 430.25\,K$ $q = 3.118\,\frac{kJ}{mol}$ **Ans.**

(b) **Combine Eqs. (1) & (2) to eliminate the ratio of pressures:**

$T_A := 425\cdot K$ **(guess)** $T_B := 300\cdot K$

Given $T_B = T_1\cdot\left(\dfrac{T_A + T_B}{2\cdot T_1}\right)^{\frac{\gamma-1}{\gamma}}$ $T_B := \text{Find}(T_B)$

$T_B = 319.02\,K$ **Ans.**

$P_2 := P_1\cdot\left(\dfrac{T_A + T_B}{2\cdot T_1}\right)$ **(1)** $P_2 = 1.24\,atm$ **Ans.**

$q := C_V\cdot(T_A + T_B - 2\cdot T_1)$ $q = 2.993\,\dfrac{kJ}{mol}$ **Ans.**

(c) $T_B := 325\cdot K$ **By Eq. (2),**

$P_2 := P_1\cdot\left(\dfrac{T_B}{T_1}\right)^{\frac{\gamma}{\gamma-1}}$ $P_2 = 1.323\,atm$ **Ans.**

$T_A := 2\cdot T_1\cdot\dfrac{P_2}{P_1} - T_B$ **(1)** $T_A = 469\,K$ **Ans.**

$q := C_V\cdot(T_A + T_B - 2\cdot T_1)$ $q = 4.032\,\dfrac{kJ}{mol}$ **Ans.**

(d) **Eliminate** $T_A + T_B$ **from Eqs. (1) & (3):**

$q := 3\cdot\dfrac{kJ}{mol}$ $P_2 := \dfrac{q\cdot P_1}{2\cdot T_1\cdot C_V} + P_1$ $P_2 = 1.241\,atm$ **Ans.**

$T_B := T_1\cdot\left(\dfrac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$ **(2)** $T_B = 319.06\,K$ **Ans.**

$T_A := 2\cdot T_1\cdot\dfrac{P_2}{P_1} - T_B$ **(1)** $T_A = 425.28\,K$ **Ans.**

3.30 $B := -242.5 \cdot \frac{cm^3}{mol}$ $C := 25200 \cdot \frac{cm^6}{mol^2}$ $T := 373.15 \cdot K$

$P_1 := 1 \cdot bar$ $P_2 := 55 \cdot bar$

$B' := \frac{B}{R \cdot T}$ $B' = -7.817 \times 10^{-3} \frac{1}{bar}$

$C' := \frac{C - B^2}{R^2 \cdot T^2}$ $C' = -3.492 \times 10^{-5} \frac{1}{bar^2}$

(a) Solve virial eqn. for initial V.

Guess: $V_1 := \frac{R \cdot T}{P_1}$

Given $\frac{P_1 \cdot V_1}{R \cdot T} = 1 + \frac{B}{V_1} + \frac{C}{V_1{}^2}$ $V_1 := \mathrm{Find}(V_1)$ $V_1 = 30780 \frac{cm^3}{mol}$

Solve virial eqn. for final V.

Guess: $V_2 := \frac{R \cdot T}{P_2}$

Given $\frac{P_2 \cdot V_2}{R \cdot T} = 1 + \frac{B}{V_2} + \frac{C}{V_2{}^2}$ $V_2 := \mathrm{Find}(V_2)$ $V_2 = 241.33 \frac{cm^3}{mol}$

Eliminate P from Eq. (1.3) by the virial equation:

$$Work := -R \cdot T \cdot \int_{V_1}^{V_2} \left(1 + \frac{B}{V} + \frac{C}{V^2}\right) \cdot \frac{1}{V} \, dV$$ $Work = 12.62 \frac{kJ}{mol}$ **Ans.**

(b) Eliminate dV from Eq. (1.3) by the virial equation in P:

$$dV = R \cdot T \cdot \left(\frac{-1}{P^2} + C'\right) \cdot dP \qquad W := -R \cdot T \cdot \int_{P_1}^{P_2} \left(\frac{-1}{P} + C' \cdot P\right) dP$$

$W = 12.596 \frac{kJ}{mol}$ **Ans.**

Note: The answers to (a) & (b) differ because the relations between the two sets of parameters are exact only for infinite series.

3.32 $T_c := 282.3 \cdot K$ $\quad T := 298.15 \cdot K$ $\quad T_r := \frac{T}{T_c}$ $\quad T_r = 1.056$

$P_c := 50.4 \cdot bar$ $\quad P := 12 \cdot bar$ $\quad P_r := \frac{P}{P_c}$ $\quad P_r = 0.238$

$\omega := 0.087$

(guess)

(a) $B := -140 \cdot \frac{cm^3}{mol}$ $\quad C := 7200 \cdot \frac{cm^6}{mol^2}$ $\quad V := \frac{R \cdot T}{P}$ $\quad V = 2066 \frac{cm^3}{mol}$

Given $\frac{P \cdot V}{R \cdot T} = 1 + \frac{B}{V} + \frac{C}{V^2}$

$V := \text{Find}(V)$ $\quad V = 1919 \frac{cm^3}{mol}$ $\quad Z := \frac{P \cdot V}{R \cdot T}$ $\quad Z = 0.929$ **Ans.**

(b) $B_0 := 0.083 - \frac{0.422}{T_r^{1.6}}$ $\quad B_0 = -0.304$

$B_1 := 0.139 - \frac{0.172}{T_r^{4.2}}$ $\quad B_1 = 2.262 \times 10^{-3}$

$Z := 1 + \left(B_0 + \omega \cdot B_1\right) \cdot \frac{P_r}{T_r}$ $\quad Z = 0.932$ $\quad V := \frac{Z \cdot R \cdot T}{P}$ $\quad V = 1924 \frac{cm^3}{mol}$ **Ans.**

(c) For Redlich/Kwong EOS:

$\sigma := 1$ $\quad \varepsilon := 0$ $\quad \Omega := 0.08664$ $\quad \Psi := 0.42748$ **Table 3.1**

$\alpha(Tr) := T_r^{-0.5}$ **Table 3.1** $\quad q\left(T_r\right) := \frac{\Psi \alpha\left(T_r\right)}{\Omega \cdot T_r}$ **Eq. (3.54)**

$\beta\left(T_r, P_r\right) := \frac{\Omega \cdot P_r}{T_r}$ **Eq. (3.53)**

Calculate Z **Guess:** $Z := 0.9$

Given **Eq. (3.52)**

$$Z = 1 + \beta(T_r, P_r) - q(T_r) \cdot \beta(T_r, P_r) \cdot \frac{Z - \beta(T_r, P_r)}{(Z + \varepsilon\beta(T_r, P_r)) \cdot (Z + \sigma\beta(T_r, P_r))}$$

$Z := \mathrm{Find}(Z)$ $Z = 0.928$ $V := \frac{Z \cdot R \cdot T}{P}$ $V = 1916.5 \frac{cm^3}{mol}$ **Ans.**

(d) For SRK EOS:

$\sigma := 1$ $\varepsilon := 0$ $\Omega := 0.08664$ $\Psi := 0.42748$ **Table 3.1**

$$\alpha(T_r, \omega) := \left[1 + (0.480 + 1.574\omega - 0.176\omega^2) \cdot \left(1 - T_r^{\frac{1}{2}}\right)\right]^2$$ **Table 3.1**

$q(T_r) := \frac{\Psi\alpha(T_r, \omega)}{\Omega \cdot T_r}$ **Eq. (3.54)** $\beta(T_r, P_r) := \frac{\Omega \cdot P_r}{T_r}$ **Eq. (3.53)**

Calculate Z **Guess:** $Z := 0.9$

Given **Eq. (3.52)**

$$Z = 1 + \beta(T_r, P_r) - q(T_r) \cdot \beta(T_r, P_r) \cdot \frac{Z - \beta(T_r, P_r)}{(Z + \varepsilon\beta(T_r, P_r)) \cdot (Z + \sigma\beta(T_r, P_r))}$$

$Z := \mathrm{Find}(Z)$ $Z = 0.928$ $V := \frac{Z \cdot R \cdot T}{P}$ $V = 1918 \frac{cm^3}{mol}$ **Ans.**

(e) For Peng/Robinson EOS:

$\sigma := 1 + \sqrt{2}$ $\varepsilon := 1 - \sqrt{2}$ $\Omega := 0.07779$ $\Psi := 0.45724$ **Table 3.1**

$$\alpha(Tr, \omega) := \left[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2) \cdot \left(1 - T_r^{\frac{1}{2}}\right)\right]^2$$ **Table 3.1**

$q(T_r) := \frac{\Psi\alpha(T_r, \omega)}{\Omega \cdot T_r}$ **Eq. (3.54)** $\beta(T_r, P_r) := \frac{\Omega \cdot P_r}{T_r}$ **Eq. (3.53)**

Calculate Z **Guess:** $Z := 0.9$

Given **Eq. (3.52)**

$$Z = 1 + \beta(T_r, P_r) - q(T_r)\cdot\beta(T_r, P_r)\cdot\frac{Z - \beta(T_r, P_r)}{\left(Z + \varepsilon\beta(T_r, P_r)\right)\cdot\left(Z + \sigma\beta(T_r, P_r)\right)}$$

$Z := \mathrm{Find}(Z)$ $Z = 0.92$ $V := \frac{Z\cdot R\cdot T}{P}$ $V = 1900.6\,\frac{cm^3}{mol}$ **Ans.**

3.33 $T_c := 305.3\cdot K$ $T := 323.15\cdot K$ $T_r := \frac{T}{T_c}$ $T_r = 1.058$

$P_c := 48.72\cdot bar$ $P := 15\cdot bar$ $P_r := \frac{P}{P_c}$ $P_r = 0.308$

$\omega := 0.100$ **(guess)**

(a) $B := -156.7\cdot\frac{cm^3}{mol}$ $C := 9650\cdot\frac{cm^6}{mol^2}$ $V := \frac{R\cdot T}{P}$ $V = 1791\,\frac{cm^3}{mol}$

Given $\frac{P\cdot V}{R\cdot T} = 1 + \frac{B}{V} + \frac{C}{V^2}$

$V := \mathrm{Find}(V)$ $V = 1625\,\frac{cm^3}{mol}$ $Z := \frac{P\cdot V}{R\cdot T}$ $Z = 0.907$ **Ans.**

(b) $B_0 := 0.083 - \frac{0.422}{T_r^{\,1.6}}$ $B_0 = -0.302$

$B_1 := 0.139 - \frac{0.172}{T_r^{\,4.2}}$ $B_1 = 3.517\times 10^{-3}$

$Z := 1 + \left(B_0 + \omega\cdot B_1\right)\cdot\frac{P_r}{T_r}$ $Z = 0.912$ $V := \frac{Z\cdot R\cdot T}{P}$ $V = 1634\,\frac{cm^3}{mol}$ **Ans.**

(c) **For Redlich/Kwong EOS:**

$\sigma := 1$ $\varepsilon := 0$ $\Omega := 0.08664$ $\Psi := 0.42748$ **Table 3.1**

$\alpha(Tr) := T_r^{-0.5}$ **Table 3.1** $q(T_r) := \dfrac{\Psi\alpha(T_r)}{\Omega \cdot T_r}$ **Eq. (3.54)**

$\beta(T_r, P_r) := \dfrac{\Omega \cdot P_r}{T_r}$ **Eq. (3.53)**

Calculate Z **Guess:** $Z := 0.9$

Given **Eq. (3.52)**

$$Z = 1 + \beta(T_r, P_r) - q(T_r) \cdot \beta(T_r, P_r) \cdot \frac{Z - \beta(T_r, P_r)}{(Z + \epsilon\beta(T_r, P_r)) \cdot (Z + \sigma\beta(T_r, P_r))}$$

$Z := \mathrm{Find}(Z)$ $Z = 0.906$ $V := \dfrac{Z \cdot R \cdot T}{P}$ $V = 1622.7 \dfrac{cm^3}{mol}$ **Ans.**

(d) For SRK EOS:

$\sigma := 1$ $\epsilon := 0$ $\Omega := 0.08664$ $\Psi := 0.42748$ **Table 3.1**

$$\alpha(T_r, \omega) := \left[1 + \left(0.480 + 1.574\omega - 0.176\omega^2\right) \cdot \left(1 - T_r^{\frac{1}{2}}\right)\right]^2$$ **Table 3.1**

$q(T_r) := \dfrac{\Psi\alpha(T_r, \omega)}{\Omega \cdot T_r}$ **Eq. (3.54)** $\beta(T_r, P_r) := \dfrac{\Omega \cdot P_r}{T_r}$ **Eq. (3.53)**

Calculate Z **Guess:** $Z := 0.9$

Given **Eq. (3.52)**

$$Z = 1 + \beta(T_r, P_r) - q(T_r) \cdot \beta(T_r, P_r) \cdot \frac{Z - \beta(T_r, P_r)}{(Z + \epsilon\beta(T_r, P_r)) \cdot (Z + \sigma\beta(T_r, P_r))}$$

$Z := \mathrm{Find}(Z)$ $Z = 0.907$ $V := \dfrac{Z \cdot R \cdot T}{P}$ $V = 1624.8 \dfrac{cm^3}{mol}$ **Ans.**

(e) For Peng/Robinson EOS:

$\sigma := 1 + \sqrt{2}$ $\epsilon := 1 - \sqrt{2}$ $\Omega := 0.07779$ $\Psi := 0.45724$ **Table 3.1**

$$\alpha(T_r,\omega) := \left[1 + \left(0.37464 + 1.54226\omega - 0.26992\omega^2\right)\cdot\left(1 - T_r^{\frac{1}{2}}\right)\right]^2$$ **Table 3.1**

$$q(T_r) := \frac{\Psi\alpha(T_r,\omega)}{\Omega\cdot T_r}$$ **Eq. (3.54)**

$$\beta(T_r,P_r) := \frac{\Omega\cdot P_r}{T_r}$$ **Eq. (3.53)**

Calculate Z **Guess:** $Z := 0.9$

Given **Eq. (3.52)**

$$Z = 1 + \beta(T_r,P_r) - q(T_r)\cdot\beta(T_r,P_r)\cdot\frac{Z - \beta(T_r,P_r)}{\left(Z + \varepsilon\beta(T_r,P_r)\right)\cdot\left(Z + \sigma\beta(T_r,P_r)\right)}$$

$Z := \text{Find}(Z)$ $Z = 0.896$ $V := \frac{Z\cdot R\cdot T}{P}$ $V = 1605.5\,\frac{cm^3}{mol}$ **Ans.**

3.34 $T_c := 318.7\cdot K$ $T := 348.15\cdot K$ $T_r := \frac{T}{T_c}$ $T_r = 1.092$

$P_c := 37.6\cdot bar$ $P := 15\cdot bar$ $P_r := \frac{P}{P_c}$ $P_r = 0.399$

$\omega := 0.286$

(guess)

(a) $B := -194\cdot\frac{cm^3}{mol}$ $C := 15300\cdot\frac{cm^6}{mol^2}$ $V := \frac{R\cdot T}{P}$ $V = 1930\,\frac{cm^3}{mol}$

Given $\frac{P\cdot V}{R\cdot T} = 1 + \frac{B}{V} + \frac{C}{V^2}$

$V := \text{Find}(V)$ $V = 1722\,\frac{cm^3}{mol}$ $Z := \frac{P\cdot V}{R\cdot T}$ $Z = 0.893$ **Ans.**

(b) $B_0 := 0.083 - \frac{0.422}{T_r^{1.6}}$ $B_0 = -0.283$

$B_1 := 0.139 - \frac{0.172}{T_r^{4.2}}$ $B_1 = 0.02$

$Z := 1 + (B_0 + \omega \cdot B_1) \cdot \frac{P_r}{T_r}$ $Z = 0.899$ $V := \frac{Z \cdot R \cdot T}{P}$ $V = 1734 \frac{cm^3}{mol}$ **Ans.**

(c) For Redlich/Kwong EOS:

$\sigma := 1$ $\varepsilon := 0$ $\Omega := 0.08664$ $\Psi := 0.42748$ **Table 3.1**

$\alpha(Tr) := T_r^{-0.5}$ **Table 3.1** $q(T_r) := \frac{\Psi \alpha(T_r)}{\Omega \cdot T_r}$ **Eq. (3.54)**

$\beta(T_r, P_r) := \frac{\Omega \cdot P_r}{T_r}$ **Eq. (3.53)**

Calculate Z **Guess:** $Z := 0.9$

Given **Eq. (3.52)**

$$Z = 1 + \beta(T_r, P_r) - q(T_r) \cdot \beta(T_r, P_r) \cdot \frac{Z - \beta(T_r, P_r)}{(Z + \varepsilon\beta(T_r, P_r)) \cdot (Z + \sigma\beta(T_r, P_r))}$$

$Z := \mathrm{Find}(Z)$ $Z = 0.888$ $V := \frac{Z \cdot R \cdot T}{P}$ $V = 1714.1 \frac{cm^3}{mol}$ **Ans.**

(d) For SRK EOS:

$\sigma := 1$ $\varepsilon := 0$ $\Omega := 0.08664$ $\Psi := 0.42748$ **Table 3.1**

$$\alpha(T_r, \omega) := \left[1 + (0.480 + 1.574\omega - 0.176\omega^2) \cdot \left(1 - T_r^{\frac{1}{2}}\right)\right]^2$$ **Table 3.1**

$q(T_r) := \frac{\Psi \alpha(T_r, \omega)}{\Omega \cdot T_r}$ **Eq. (3.54)** $\beta(T_r, P_r) := \frac{\Omega \cdot P_r}{T_r}$ **Eq. (3.53)**

Calculate Z **Guess:** $Z := 0.9$

Given **Eq. (3.52)**

$$Z = 1 + \beta(T_r, P_r) - q(T_r)\cdot\beta(T_r, P_r)\cdot\frac{Z - \beta(T_r, P_r)}{(Z + \varepsilon\beta(T_r, P_r))\cdot(Z + \sigma\beta(T_r, P_r))}$$

$Z := \mathrm{Find}(Z)$ $Z = 0.895$ $V := \frac{Z\cdot R\cdot T}{P}$ $V = 1726.9\,\frac{cm^3}{mol}$ **Ans.**

(e) For Peng/Robinson EOS:

$\sigma := 1 + \sqrt{2}$ $\varepsilon := 1 - \sqrt{2}$ $\Omega := 0.07779$ $\Psi := 0.45724$ **Table 3.1**

$$\alpha(Tr, \omega) := \left[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)\cdot\left(1 - T_r^{\frac{1}{2}}\right)\right]^2$$ **Table 3.1**

$q(T_r) := \frac{\Psi\alpha(T_r, \omega)}{\Omega\cdot T_r}$ **Eq. (3.54)** $\beta(T_r, P_r) := \frac{\Omega\cdot P_r}{T_r}$ **Eq. (3.53)**

Calculate Z **Guess:** $Z := 0.9$

Given **Eq. (3.52)**

$$Z = 1 + \beta(T_r, P_r) - q(T_r)\cdot\beta(T_r, P_r)\cdot\frac{Z - \beta(T_r, P_r)}{(Z + \varepsilon\beta(T_r, P_r))\cdot(Z + \sigma\beta(T_r, P_r))}$$

$Z := \mathrm{Find}(Z)$ $Z = 0.882$ $V := \frac{Z\cdot R\cdot T}{P}$ $V = 1701.5\,\frac{cm^3}{mol}$ **Ans.**

3.35 $T := 523.15\cdot K$ $P := 1800\cdot kPa$

(a) $B := -152.5\cdot\frac{cm^3}{mol}$ $C := -5800\cdot\frac{cm^6}{mol^2}$ $V := \frac{R\cdot T}{P}$ **(guess)**

Given $\frac{P\cdot V}{R\cdot T} = 1 + \frac{B}{V} + \frac{C}{V^2}$ $V := \mathrm{Find}(V)$

$Z := \frac{P\cdot V}{R\cdot T}$ $V = 2250\,\frac{cm^3}{mol}$ $Z = 0.931$ **Ans.**

(b) $T_c := 647.1\cdot K$ $P_c := 220.55\cdot bar$ $\omega := 0.345$

$T_r := \frac{T}{T_c}$ $P_r := \frac{P}{P_c}$ $B_0 := 0.083 - \frac{0.422}{T_r^{1.6}}$

$T_r = 0.808$ $P_r = 0.082$ $B_0 = -0.51$

$B_1 := 0.139 - \frac{0.172}{T_r^{4.2}}$ $B_1 = -0.281$ $Z := 1 + \left(B_0 + \omega\cdot B_1\right)\cdot\frac{P_r}{T_r}$

$V := \frac{Z\cdot R\cdot T}{P}$ $Z = 0.939$ $V = 2268\,\frac{cm^3}{mol}$ **Ans.**

(c) Table F.2: $molwt := 18.015\cdot\frac{gm}{mol}$ $V := 124.99\cdot\frac{cm^3}{gm}\cdot molwt$

or $V = 2252\,\frac{cm^3}{mol}$ **Ans.**

3.37 $B := -53.4\cdot\frac{cm^3}{mol}$ $C := 2620\cdot\frac{cm^6}{mol^2}$ $D := 5000\cdot\frac{cm^9}{mol^3}$ $n := mol$

$T := 273.15\cdot K$

Given $\frac{P\cdot V}{R\cdot T} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3}$ $f(P,V) := \text{Find}(V)$

$i := 0..10$ $P_i := \left(10^{-10} + 20\cdot i\right)\cdot bar$ $V_i := \frac{R\cdot T}{P_i}$ **(guess)**

$Z_i := \frac{f\left(P_i, V_i\right)\cdot P_i}{R\cdot T}$ **Eq. (3.12)**

$Z1_i := 1 + \frac{B\cdot P_i}{R\cdot T}$ **Eq. (3.38)** $Z2_i := \frac{1}{2} + \sqrt{\frac{1}{4} + \frac{B\cdot P_i}{R\cdot T}}$ **Eq. (3.39)**

Chapter 3 - Section B - Non-Numerical Solutions

3.2 Differentiate Eq. (3.2) with respect to P and Eq. (3.3) with respect to T:

$$\left(\frac{\pi\xi}{\pi P}\right)_T = -\frac{1}{V^2}\left(\frac{\pi V}{\pi P}\right)_T\left(\frac{\pi V}{\pi T}\right)_P + \frac{1}{V}\left(\frac{\pi^2 V}{\pi P \pi T}\right) = \xi\,\epsilon + \left(\frac{\pi^2 V}{\pi P \pi T}\right)$$

$$\left(\frac{\pi\epsilon}{\pi T}\right)_P = \frac{1}{V^2}\left(\frac{\pi V}{\pi T}\right)_P\left(\frac{\pi V}{\pi P}\right)_T - \frac{1}{V}\left(\frac{\pi^2 V}{\pi T \pi P}\right) = -\xi\,\epsilon - \left(\frac{\pi^2 V}{\pi P \pi T}\right)$$

Addition of these two equations leads immediately to the given equation.

One could of course start with Eq. (3.4) and apply the condition for an exact differential, but this topic is not covered until Chapter 6.

3.3 The Tait equation is given as: $V = V_0\left(1 - \dfrac{AP}{B+P}\right)$

where V_0, A, and B are constants. Application of Eq. (3.3), the definition of ϵ, requires the derivative of this equation:

$$\left(\frac{\pi V}{\pi P}\right)_T = V_0\left[-\frac{A}{B+P} + \frac{AP}{(B+P)^2}\right] = \frac{AV_0}{B+P}\left(-1 + \frac{P}{B+P}\right)$$

Multiplication by $-1/V$ in accord with Eq. (3.3), followed by substitution for V_0/V by the Tait equation leads to:

$$\boxed{\epsilon = \frac{AB}{(B+P)[B+(1-A)P]}}$$

3.7 (*a*) For constant T, Eq. (3.4) becomes: $\dfrac{dV}{V} = -\epsilon\, dP$

Integration from the initial state (P_1, V_1) to an intermediate state (P, V) for constant ϵ gives:

$$\ln\frac{V}{V_1} = -\epsilon(P - P_1)$$

Whence, $V = V_1 \exp[-\epsilon(P - P_1)] = V_1 \exp(-\epsilon P)\exp(\epsilon P_1)$

If the given equation applies to the process, it must be valid for the initial state; then, $A(T) = V_1\exp(\epsilon P_1)$, and

$$\boxed{V = A(T)\exp(-\epsilon P)}$$

(*b*) Differentiate the preceding equation: $dV = -\epsilon A(T)\exp(-\epsilon P)dP$

Therefore,
$$W = -\int_{V_1}^{V_2} P\,dV = \epsilon A(T)\int_{P_1}^{P_2} P\exp(-\epsilon P)dP$$

$$= \frac{A(T)}{\epsilon}[(\epsilon P_1 + 1)\exp(-\epsilon P_1) - (\epsilon P_2 + 1)\exp(-\epsilon P_2)]$$

With $V_1 = A(T)\exp(-\kappa P_1)$ and $V_2 = A(T)\exp(-\kappa P_2)$, this becomes:

$$W = \frac{1}{\kappa}[(\kappa P_1 + 1)V_1 - (\kappa P_2 + 1)V_2]$$

or

$$\boxed{W = P_1V_1 - P_2V_2 + \frac{V_1 - V_2}{\kappa}}$$

3.11 Differentiate Eq. (3.35c) with respect to T:

$$T\left(\frac{1-\delta}{\delta}\right)P^{[(1-\delta)/\delta]-1}\frac{dP}{dz} + P^{(1-\delta)/\delta}\frac{dT}{dz} = T\left(\frac{1-\delta}{\delta}\right)\frac{P^{(1-\delta)/\delta}}{P}\frac{dP}{dz} + P^{(1-\delta)/\delta}\frac{dT}{dz} = 0$$

Algebraic reduction and substitution for dP/dz by the given equation yields:

$$\frac{T}{P}\left(\frac{1-\delta}{\delta}\right)(-\mathcal{M}\rho g) + \frac{dT}{dz} = 0$$

For an ideal gas $T\rho/P = 1/R$. This substitution reduces the preceding equation to:

$$\boxed{\frac{dT}{dz} = -\frac{\mathcal{M}g}{R}\left(\frac{\delta-1}{\delta}\right)}$$

3.12 Example 2.13 shows that $U_2 = H'$. If the gas is ideal,

$$H' = U' + P'V' = U' + RT' \qquad \text{and} \qquad U_2 - U' = RT'$$

For constant C_V, $\quad U_2 - U' = C_V(T_2 - T') \quad$ and $\quad C_V(T_2 - T') = RT'$

Whence,

$$\frac{T_2 - T'}{T'} = \frac{R}{C_V} = \frac{C_P - C_V}{C_V}$$

When C_P/C_V is set equal to γ, this reduces to: $\boxed{T_2 = \gamma T'}$

This result indicates that the final temperature is independent of the amount of gas admitted to the tank, a result strongly conditioned by the assumption of no heat transfer between gas and tank.

3.13 **Isobaric case** ($\delta = 0$). Here, Eqs. (3.36) and (3.37) reduce to:

$$W = -RT_1(1^{\infty} - 1) \qquad \text{and} \qquad Q = \frac{\gamma RT_1}{\gamma - 1}(1^{\infty} - 1)$$

Both are indeterminate. The easiest resolution is to write Eq. (3.36) and (3.37) in the alternative but equivalent forms:

$$W = \frac{RT_1}{\delta - 1}\left(\frac{T_2}{T_1} - 1\right) \qquad \text{and} \qquad Q = \frac{(\delta-\gamma)RT_1}{(\delta-1)(\gamma-1)}\left(\frac{T_2}{T_1} - 1\right)$$

from which we find immediately for $\delta = 0$ that:

$$W = -R(T_2 - T_1) \qquad \text{and} \qquad Q = \frac{\gamma R}{\gamma - 1}(T_2 - T_1) = C_P(T_2 - T_1)$$

Isothermal case ($\delta = 1$). Equations (3.36) and (3.37) are both indeterminate of form 0/0. Application of l'Hôpital's rule yields the appropriate results:

$$W = RT_1 \ln \frac{P_2}{P_1} \qquad \text{and} \qquad Q = -RT_1 \ln \frac{P_2}{P_1}$$

Note that if $\quad y \equiv \left(\frac{P_2}{P_1}\right)^{(\delta-1)/\delta} \quad$ then $\quad \frac{dy}{d\delta} = \frac{1}{\delta^2}\left(\frac{P_2}{P_1}\right)^{(\delta-1)/\delta} \ln \frac{P_2}{P_1}$

Adiabatic case ($\delta = \gamma$). In this case simple substitution yields:

$$W = \frac{RT_1}{\gamma - 1}\left[\left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma} - 1\right] \qquad \text{and} \qquad Q = 0$$

Isochoric case ($\delta = \infty$). Here, simple substitution yields:

$$W = 0 \qquad \text{and} \qquad Q = \frac{RT_1}{\gamma - 1}\left(\frac{P_2}{P_1} - 1\right) = \frac{RT_1}{\gamma - 1}\left(\frac{T_2}{T_1} - 1\right) = C_V(T_2 - T_1)$$

3.14 What is needed here is an equation relating the heat transfer to the quantity of air admitted to the tank and to its temperature change. For an ideal gas in a tank of total volume V^t at temperature T,

$$n_1 = \frac{P_1 V^t}{RT} \qquad \text{and} \qquad n_2 = \frac{P_2 V^t}{RT}$$

The quantity of air admitted to the tank is therefore:

$$n' = \frac{V^t(P_2 - P_1)}{RT} \tag{A}$$

The appropriate energy balance is given by Eq. (2.29), which here becomes:

$$\frac{d(nU)_{\text{tank}}}{dt} - \dot{n}'H' = \dot{Q}$$

where the prime ($'$) identifies the entrance stream of constant properties. Multiplying by dt and integrating over the time of the process yields:

$$n_2U_2 - n_1U_1 - n'H' = Q$$

With $n' = n_2 - n_1$, $\qquad n_2(U_2 - H') - n_1(U_1 - H') = Q$

Because $U_2 = H_2 - RT$ and $U_1 = H_1 - RT$, this becomes:

$$n_2(H_2 - H' - RT) - n_1(U_1 - H' - RT) = Q$$

or $\qquad n_2[C_P(T - T') - RT] - n_1[C_P(T - T') - RT] = Q$

Because $n' = n_2 - n_1$, this reduces to:

$$\boxed{Q = n'[C_P(T - T') - RT]}$$

Given: $V^t = 100,000 \text{ cm}^3$ $\quad T = 298.15 \text{ K}$ $\quad T' = 318.15 \text{ K}$ $\quad P_1 = 101.33 \text{ kPa}$ $\quad P_2 = 1500 \text{ kPa}$

By Eq. (A) with $R = 8,314$ cm^3 kPa mol^{-1} K^{-1},

$$n' = \frac{(100,000)(1500 - 101.33)}{(8,314)(298.15)} = 56.425 \text{ mol}$$

With $R = 8.314$ J mol^{-1} K^{-1} and $C_P = (7/2)R$, the energy equation gives:

$$Q = (56.425)(8.314)\left[\frac{7}{2}(298.15 - 318.15) - 298.15\right] = -172,705.6 \text{ J}$$

or $$\boxed{Q = -172.71 \text{ kJ}}$$

3.15 (a) The appropriate energy balance is given by Eq. (2.29), here written:

$$\frac{d(nU)_{\text{tank}}}{dt} - \dot{n}'H' = \dot{Q}$$

where the prime ($'$) identifies the entrance stream of constant properties. Multiplying by dt and integrating over the time of the process yields:

$$n_2U_2 - n_1U_1 - n'H' = Q$$

Since $n' = n_2 - n_1$, rearrangement gives:

$$\boxed{n_2(U_2 - H') - n_1(U_1 - H') = Q}$$

(b) If the gas is ideal, $\qquad H' = U' + P'V' = U' + RT'$

Whence for an ideal gas with constant heat capacities,

$$U_2 - H' = U_2 - U' - RT' = C_V(T_2 - T') - RT'$$

Substitute $R = C_P - C_V$: $\qquad U_2 - H' = C_VT_2 - C_VT' - C_PT' + C_VT' = C_VT_2 - C_PT'$

Similarly, $\qquad U_1 - H' = C_VT_1 - C_PT'$

and $$\boxed{n_2(C_VT_2 - C_PT') - n_1(C_VT_1 - C_PT') = Q}$$

Note also: $$n_2 = \frac{P_2V_{\text{tank}}}{RT_2} \qquad n_1 = \frac{P_1V_{\text{tank}}}{RT_1}$$

(c) If $n_1 = 0$, $$\boxed{n_2(C_VT_2 - C_PT') = Q}$$

(d) If in addition $Q = 0$, $\qquad C_VT_2 = C_PT' \qquad$ and $\qquad T_2 = \frac{C_P}{C_V}T$

Whence, $$\boxed{T_2 = \gamma T'}$$

(e) 1. Apply the result of Part (d), with $\gamma = 1.4$ and $T' = 298.15$ K:

$$T_2 = (1.4)(298.15) = 417.41 \text{ K}$$

Then, with $R = 83.14$ bar cm^3 mol^{-1} K^{-1}:

$$\boxed{n_2 = \frac{P_2 V_{\text{tank}}}{RT_2} = \frac{(3)(4 \times 10^6)}{(83.14)(417.41)} = 345.8 \text{ mol}}$$

2. Heat transfer between gas and tank is: $Q = -m_{\text{tank}}C(T_2 - T')$
   where C is the specific heat of the tank. The equation of Part (c) now becomes:

$$n_2(C_V T_2 - C_P T') = -m_{\text{tank}}C(T_2 - T')$$

Moreover $$n_2 = \frac{P_2 V_{\text{tank}}}{RT_2}$$

These two equations combine to give:

$$\frac{P_2 V_{\text{tank}}}{RT_2}(C_V T_2 - C_P T') = -m_{\text{tank}}C(T_2 - T')$$

With $C_P = (7/2)R$ and $C_V = C_P - R = (7/2)R - R = (5/2)R$, this equation becomes:

$$\frac{P_2 V_{\text{tank}}}{RT_2}(5T_2 - 7T')\frac{R}{2} = -m_{\text{tank}}C(T_2 - T')$$

Note: R in the denominator has the units of PV; R in the numerator has energy units. Given values in the appropriate units are:

$$m_{\text{tank}} = 400 \text{ kg} \qquad C = 460 \text{ J mol}^{-1} \text{ kg}^{-1} \qquad T' = 298.15 \text{ K}$$

$$P_2 = 3 \text{ bar} \qquad V_{\text{tank}} = 4 \times 10^6 \text{ cm}^3$$

Appropriate values for R are therefore:

$$R(\text{denominator}) = 83.14 \text{ bar cm}^3 \text{ mol}^{-1} \text{ K}^{-1} \qquad R(\text{numerator}) = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

Numerically,

$$\frac{(3)(4 \times 10^6)}{(83.14)(T_2)}[(5)(T_2) - (7)(298.15)]\frac{8.314}{2} = -(400)(460)(T_2 - 298.15)$$

Solution for T_2 is by trial, by an iteration scheme, or by the solve routine of a software package. The result is $T_2 = 304.217$ K. Then,

$$\boxed{n_2 = \frac{P_2 V_{\text{tank}}}{RT_2} = \frac{(3)(4 \times 10^6)}{(83.14)(304.217)} = 474.45 \text{ mol}}$$

3.16 The assumption made in solving this problem is that the gas is ideal with constant heat capacities. The appropriate energy balance is given by Eq. (2.29), here written:

$$\frac{d(nU)_{\text{tank}}}{dt} + H'\dot{n}' = \dot{Q}$$

Multiplied by dt it becomes: $$d(nU) + H'dn' = dQ$$

where n and U refer to the contents of the tank, and $H^{\equiv}$and $n^{\equiv}$refer to the exit stream. Since the stream bled from the tank is merely throttled, $H^{\equiv}= H$, where H is the enthalpy of the contents of the tank. By material balance, $dn^{\equiv}= -dn$. Thus,

$$n\,dU + U\,dn - H\,dn = Q \qquad \text{or} \qquad n\,dU - (H - U)dn = dQ$$

Also, $$dU = C_V\,dT \qquad H - U = PV = RT \qquad dQ = -mC\,dT$$

where m is the mass of the tank, and C is its specific heat.

Thus, $$nC_V\,dT - RT\,dn = -mC\,dT$$

or $$\frac{dT}{T} = \frac{R}{nC_V + mC}dn = \frac{R}{C_V}\frac{d(nC_V)}{nC_V + mC} = \frac{R}{C_V}\frac{d(nC_V + mC)}{nC_V + mC}$$

Integration yields: $$\ln\left(\frac{T_2}{T_1}\right) = \frac{R}{C_V}\ln\left(\frac{n_2C_V + mC}{n_1C_V + mC}\right)$$

or $$\boxed{\frac{T_2}{T_1} = \left(\frac{n_2C_V + mC}{n_1C_V + mC}\right)^{R/C_V}}$$

In addition, $$n_1 = \frac{P_1V_{\text{tank}}}{RT_1} \qquad \text{and} \qquad n_2 = \frac{P_2V_{\text{tank}}}{RT_2}$$

These equations may be solved for T_2 and n_2. If $mC >>> nC_V$, then $T_2 = T_1$. If $mC = 0$, then we recover the isentropic expansion formulas.

3.27 For an ideal gas, $$\Delta U = C_V\Delta T \qquad PV = RT \qquad \Delta(PV) = R\,\Delta T$$

Whence, $$\Delta U = \frac{C_V}{R}\Delta(PV)$$

But $$\frac{C_V}{R} = \frac{C_V}{C_P - C_V} = \frac{1}{\gamma - 1}$$ Therefore : $$\boxed{\Delta U = \frac{1}{\gamma - 1}\Delta(PV)}$$

3.28 Since $Z = PV/RT$ the given equation can be written: $$V = \frac{RT}{P} + B^{\equiv}RT$$

Differentiate at constant T: $$dV = -\frac{RT}{P^2}dP$$

The isothermal work is then: $$W = -\int_{V_1}^{V_2} P\,dV = RT\int_{P_1}^{P_2}\frac{1}{P}dP$$

Whence, $$\boxed{W = RT\ln\frac{P_2}{P_1}}$$ Compared with Eq. (3.27)

3.29 Solve the given equation of state for V: $$V = \frac{RT}{P} + b - \frac{\theta}{RT}$$

Whence, $$\left(\frac{\partial V}{\partial P}\right)_T = -\frac{RT}{P^2}$$

By definition [Eq. (3.3)]: $$\kappa \equiv \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

Substitution for both V and the derivative yields:

$$\boxed{\kappa = \frac{RT}{P^2\left(\dfrac{RT}{P} + b - \dfrac{\theta}{RT}\right)}}$$

Solve the given equation of state for P: $$P = \frac{RT}{V - b + \dfrac{\theta}{RT}}$$

Differentiate: $$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{\left(V - b + \dfrac{\theta}{RT}\right)} + \frac{\left(\dfrac{\theta}{T} - \dfrac{d\theta}{dT}\right)}{\left(V - b + \dfrac{\theta}{RT}\right)^2}$$

By the equation of state, the quantity in parentheses is RT/P; substitution leads to:

$$\boxed{\left(\frac{\partial P}{\partial T}\right)_V = \frac{P}{T} + \left(\frac{P}{RT}\right)^2\left(\frac{\theta}{T} - \frac{d\theta}{dT}\right)}$$

3.31 When multiplied by V/RT, Eq. (3.42) becomes:

$$Z = \frac{V}{V-b} - \frac{a(T)V/RT}{(V+\epsilon b)(V+\sigma b)} = \frac{V}{V-b} - \frac{a(T)V/RT}{V^2 + (\epsilon+\sigma)bV + \epsilon\sigma b^2}$$

Substitute $V = 1/\rho$: $$Z = \frac{1}{1-b\rho} - \frac{a(T)\rho}{RT}\,\frac{1}{1 + (\epsilon+\sigma)b\rho + \epsilon\sigma(b\rho)^2}$$

Expressed in series form, the first term on the right becomes: $$\frac{1}{1-b\rho} = 1 + b\rho + (b\rho)^2 + \cdots$$

The final fraction of the second term becomes:

$$\frac{1}{1 + (\epsilon+\sigma)b\rho + \epsilon\sigma(b\rho)^2} = 1 - (\epsilon+\sigma)b\rho + [(\epsilon+\sigma)^2 - \epsilon\sigma](b\rho)^2 + \cdots$$

Combining the last three equations gives, after reduction:

$$Z = 1 + \left(b - \frac{a(T)}{RT}\right)\rho + \left[b^2 + \frac{(\epsilon+\sigma)a(T)b}{RT}\right]\rho^2 + \cdots$$

Equation (3.12) may be written: $$Z = 1 + B\rho + C\rho^2 + \cdots$$

Comparison shows: $$\boxed{B = b - \frac{a(T)}{RT} \qquad \text{and} \qquad C = b^2 + \frac{(\epsilon+\sigma)ba(T)}{RT}}$$

For the Redlich/Kwong equation, the second equation becomes:

$$C = b^2 + \frac{ba(T)}{RT} = b\left(b + \frac{a(T)}{RT}\right)$$

Values for $a(T)$ and b are found from Eqs. (3.45) and (3.46), with numerical values from Table 3.1:

$$b = \frac{0.08664RT_c}{P_c} \qquad \frac{a(T)}{RT} = \frac{0.42748RT_c}{T_r^{1.5}P_c}$$

The numerical comparison is an open-ended problem, the scope of which must be decided by the instructor.

3.36 Differentiate Eq. (3.11): $\left(\frac{\partial Z}{\partial P}\right)_T = B' + 2C'P + 3D'P^2 + \cdots$

Whence,

$$\boxed{\left(\frac{\partial Z}{\partial P}\right)_{T,P=0} = B'}$$

Equation (3.12) with $V = 1/\rho$: $Z = 1 + B\rho + C\rho^2 + D\rho^3 + \cdots$

Differentiate:

$$\left(\frac{\partial Z}{\partial \rho}\right)_T = B + 2C\rho + 3D\rho^2 + \cdots$$

Whence,

$$\boxed{\left(\frac{\partial Z}{\partial \rho}\right)_{T,\rho=0} = B}$$

3.56 The compressibility factor is related to the measured quantities by:

$$Z = \frac{PV^t}{nRT} = \frac{MPV^t}{mRT} \qquad (A)$$

By Eq. (3.39),

$$B = (Z-1)V = \frac{(Z-1)MV^t}{m} \qquad (B)$$

(a) By Eq. (A),

$$\frac{dZ}{Z} = \frac{dM}{M} + \frac{dP}{P} + \frac{dV^t}{V^t} - \frac{dm}{m} - \frac{dT}{T} \qquad (C)$$

Thus

$$\text{Max}\,|\%\,\delta Z| \approx |\%\,\delta M| + |\%\,\delta P| + |\%\,\delta V^t| + |\%\,\delta m| + |\%\,\delta T|$$

Assuming approximately equal error in the five variables, a ±1% maximum error in Z requires errors in the variables of <0.2%.

(b) By Eq. (B),

$$\frac{dB}{B} = \frac{Z}{Z-1}\frac{dZ}{Z} + \frac{dV^t}{V^t} + \frac{dM}{M} - \frac{dm}{m}$$

By Eq. (C),

$$\frac{dB}{B} = \frac{Z}{Z-1}\left(\frac{dP}{P} - \frac{dT}{T}\right) + \frac{2Z-1}{Z-1}\left(\frac{dV^t}{V^t} + \frac{dM}{M} - \frac{dm}{m}\right)$$

Therefore

$$\text{Max}\,|\%\,\delta B| \approx \left|\frac{Z}{Z-1}\right|\big(|\%\,\delta P| + |\%\,\delta T|\big)$$

$$+ \left|\frac{2Z-1}{Z-1}\right|\big(|\%\,\delta V^t| + |\%\,\delta M| + |\%\,\delta m|\big)$$

For $Z \approx 0.9$ and for approximately equal error in the five variables, a $\pm 1\%$ maximum error in B requires errors in the variables of less than about 0.02%. This is because the divisor $Z - 1 \approx 0.1$. In the limit as $Z \rightarrow 1$, the error in B approaches infinity.

3.57 The Redlich/Kwong equation has the following equivalent forms, where a and b are constants:

$$Z = \frac{V}{V-b} - \frac{a}{RT^{3/2}(V+b)} \qquad\qquad P = \frac{RT}{V-b} - \frac{a}{T^{1/2}V(V+b)}$$

From these by differentiation,

$$\left(\frac{\partial Z}{\partial V}\right)_T = \frac{a(V-b)^2 - bRT^{3/2}(V+b)^2}{RT^{3/2}(V-b)^2(V+b)^2} \tag{A}$$

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{a(2V+b)(V-b)^2 - RT^{3/2}V^2(V+b)^2}{T^{1/2}V^2(V-b)^2(V+b)^2} \tag{B}$$

In addition, we have the mathematical relation:

$$\left(\frac{\partial Z}{\partial P}\right)_T = \frac{(\partial Z/\partial V)_T}{(\partial P/\partial V)_T} \tag{C}$$

Combining these three equations gives

$$\left(\frac{\partial Z}{\partial P}\right)_T = \frac{aV^2(V-b)^2 - bRT^{3/2}V^2(V+b)^2}{aRT(2V+b)(V-b)^2 - R^2T^{5/2}V^2(V+b)^2} \tag{D}$$

For $P \rightarrow 0$, $V \rightarrow \infty$, and Eq. (D) becomes: $\boxed{\lim_{P\to 0}\left(\frac{\partial Z}{\partial P}\right)_T = \frac{b - a/RT^{3/2}}{RT}}$

For $P \rightarrow \infty$, $V \rightarrow b$, and Eq. (D) becomes: $\boxed{\lim_{P\to \infty}\left(\frac{\partial Z}{\partial P}\right)_T = \frac{b}{RT}}$

3.60 (a) Differentiation of Eq. (3.11) gives:

$$\left(\frac{\partial Z}{\partial P}\right)_T = B' + 2C'P + 3D'P^2 + \cdot \qquad \text{whence} \qquad \lim_{P\to 0}\left(\frac{\partial Z}{\partial P}\right)_T = B'$$

If the limiting value of the derivative is zero, then $B' = 0$, and $\boxed{B = B'RT = 0}$

(b) For simple fluids, $\omega = 0$, and Eqs. (3.52) and (3.53) combine to give $B^0 = BP_c/RT_c$. If $B = 0$, then by Eq. (3.65),

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} = 0$$

and $$\boxed{T_r = \left(\frac{0.422}{0.083}\right)^{(1/1.6)} = 2.763}$$

3.63 Linear isochores require that $(\gamma P/\gamma T)_V =$ Constant.

(*a*) By Eq. (3.4) applied to a constant-V process: $\left(\dfrac{\gamma P}{\gamma T}\right)_V = \dfrac{\beta}{\kappa}$

(*b*) For an ideal gas $PV = RT$, and $\left(\dfrac{\gamma P}{\gamma T}\right)_V = \dfrac{R}{V}$

(*c*) Because a and b are constants, differentiation of Eq. (3.42) yields: $\left(\dfrac{\gamma P}{\gamma T}\right)_V = \dfrac{R}{V-b}$

In each case the quantities on the right are constant, and so therefore is the derivative.

3.64 (*a*) Ideal gas: Low P, or low ρ, or large V and/or high T. See Fig. 3.15 for quantitative guidance.

(*b*) Two-term virial equation: Low to modest P. See Fig. 3.14 for guidance.

(*c*) Cubic EOS: Gases at (in principle) any conditions.

(*d*) Lee/Kesler correlation: Same as (*c*), but often more accurate. Note that corresponding states correlations are strictly valid for non-polar fluids.

(*e*) Incompressible liquids: Liquids at normal Ts and Ps. Inappropriate where *changes* in V are required.

(*f*) Rackett equation: Saturated liquids; a corresponding states application.

(*g*) Constant β, κ liquids: Useful where changes in V are required. For absolute values of V, a reference volume is required.

(*h*) Lydersen correlation for liquids: a corresponding-states method applicable to liquids at extreme conditions.

3.66 Write Eq. (3.12) with $1/\rho$ substituted everywhere for V. Subtract 1 from each side of the equation and divide by ρ. Take the limit as $\rho \to 0$.

3.68 Follow the procedure laid out on p. 93 with respect to the van der Waals equation to obtain from Eq. (3.42) the following three more-general equations:

$$1 + (1 - \epsilon - \sigma)\Omega = 3Z_c$$

$$\epsilon\sigma\Omega^2 - (\epsilon + \sigma)\Omega(\Omega + 1) + \Psi = 3Z_c^2$$

$$\epsilon\sigma\Omega^2(\Omega + 1) + \Psi\Omega = Z_c^3$$

where by definition [see Eqs. (3.45) and (3.46)]:

$$\Omega \equiv \frac{bP_c}{RT_c} \qquad \text{and} \qquad \Psi \equiv \frac{a_c P_c}{R^2 T_c^2}$$

For a given EOS, ϵ and σ are fixed, and the above set represents 3 equations in 3 unknowns, Ω, Ψ, and Z_c. Thus, for a given EOS the value of Z_c is *preordained*, unrelated to experimental values of Z_c.

(*a, b*) For the Redlich/Kwong and Soave/Redlich/Kwong equations, $\epsilon = 0$ and $\sigma = 1$. Substitution of these values into the 3-equation set allows their solution to yield:

$$Z_c = \frac{1}{3} \qquad \Omega = 0.086640 \qquad \Psi = 0.427480$$

(*c*) For the Peng/Robinson equation, $\epsilon = 1 - \sqrt{2}$ and $\sigma = 1 + \sqrt{2}$. As for the Soave and SRK equations the 3-equation set can be solved (with considerably greater difficulty) to yield:

$$Z_c = 0.30740 \qquad \Omega = 0.077796 \qquad \Psi = 0.457236$$

3.69 Equation (3.12): $Z = 1 + B\rho + C\rho^2 + \ldots$ where $\rho = P/ZRT$

Eliminate ρ: $$Z = 1 + \frac{BP}{ZRT} + \frac{CP^2}{Z^2R^2T^2} + \ldots$$

$$Z = 1 + \frac{BP_c}{RT_c} \cdot \frac{P_r}{ZT_r} + \frac{CP_c^2}{R^2T_c^2} \cdot \frac{P_r^2}{Z^2T_r^2} + \ldots = 1 + \hat{B} \cdot \frac{P_r}{ZT_r} + \hat{C} \cdot \frac{P_r^2}{Z^2T_r^2} + \ldots$$

Rearrange: $$\frac{(Z-1)ZT_r}{P_r} = \hat{B} + \hat{C} \cdot \frac{P_r}{ZT_r} + \ldots$$

$$\boxed{\hat{B} = \lim_{P_r \to 0} (Z-1)ZT_r/P_r}$$

3.74 In a cylinder filled with 1 mole of an ideal gas, the molecules have kinetic energy only, and for a given T and P occupy a volume V^{ig}.

(*a*) For 1 mole of a gas with molecules having kinetic energy *and* purely attractive interactions at the same T and P, the intermolecular separations are smaller, and $V < V^{ig}$. In this case $Z < 1$.

(*b*) For 1 mole of a gas with molecules having kinetic energy *and* purely repulsive interactions at the same T and P, the intermolecular separations are larger, and $V > V^{ig}$. In this case $Z > 1$.

(*c*) If attractive and repulsive interactions are both present, they tend to cancel each other. If in balance, then the average separation is the same as for an ideal gas, and $V = V^{ig}$. In this case $Z = 1$.

3.75 van der Waals EOS: $$P = \frac{RT}{V-b} - \frac{a}{V^2} \qquad Z = \frac{V}{V-b} - \frac{a}{VRT}$$

Set $V = 1/\rho$: $$Z = \frac{1}{1-b\rho} - \frac{a\rho}{RT} = 1 + \frac{b\rho}{1-b\rho} - \frac{a\rho}{RT}$$

whence $$Z_{\text{rep}} = \frac{b\rho}{1-b\rho} \qquad Z_{\text{attr}} = \frac{a\rho}{RT}$$

3.76 Write each modification in "Z-form,"

(*a*) $$Z = \frac{V}{V-b} - \frac{a}{RT} \qquad \lim_{V\to\infty} Z = 1 - \frac{a}{RT}$$

The *required* behavior is: $\lim_{V\to\infty} Z = 1$

(*b*) $$Z = \frac{V}{(V-b)^2} - \frac{a}{RT} \qquad \lim_{V\to\infty} Z = -\frac{a}{RT}$$

The *required* behavior is: $\lim_{V\to\infty} Z = 1$

(*c*) $$Z = \frac{1}{V-b} - \frac{a}{VRT} \qquad \lim_{V\to\infty} Z = 0$$

The *required* behavior is: $\lim_{V\to\infty} Z = 1$

(*d*) $$Z = 1 - \frac{a}{VRT} = 1 - \frac{a\rho}{RT}$$

Although $\lim_{V\to\infty} Z = 1$ as required, the equation makes Z linear in ρ; i.e., a 2-term virial EOS in ρ. Such an equation is quite inappropriate at higher densities.

3.77 Refer to Pb. 2.43, where the general equation was developed; $\dot{Q} = -PV\dfrac{dn}{dt} + n\dfrac{dU}{dt}$

For an ideal gas, $n = \dfrac{PV^t}{RT}$ and $\dfrac{dn}{dt} = -\left(\dfrac{PV^t}{RT^2}\right)\dfrac{dT}{dt}$ Note that $PV^t/R = \text{const.}$

Also for an ideal gas, $dU = C_V\,dT$ whence $\dfrac{dU}{dt} = C_V\dfrac{dT}{dt}$

$$\dot{Q} = -RT\left(-\frac{PV^t}{RT^2}\right)\frac{dT}{dt} + \frac{PV^t}{RT}C_V\frac{dT}{dt} = C_P\frac{PV^t}{RT}\frac{dT}{dt}$$

Integration yields: $$\boxed{\ln\frac{T_2}{T_1} = \frac{R}{C_P PV^t}\int_{t_1}^{t_2}\dot{Q}\,dt}$$

3.78 By Eq. (3.4), $\dfrac{dV}{V} = \beta\,dT - \kappa\,dP$ where β and κ are average values

Integrate: $$\ln\frac{V_2}{V_1} = \ln\frac{V_2^t}{V_1^t} = \ln\frac{D_2^2}{D_1^2} = \ln\left(\frac{D_1+\delta D}{D_1}\right)^2 = \ln\left(1+\frac{\delta D}{D_1}\right)^2 = \beta(T_2-T_1) - \kappa(P_2-P_1)$$

$$\ln(1.0035)^2 = 250\times10^{-6}(40-10) - 45\times10^{-6}(P_2-6)$$

Solution for P_2 yields: $\boxed{P_2 = 17.4\text{ bar}}$