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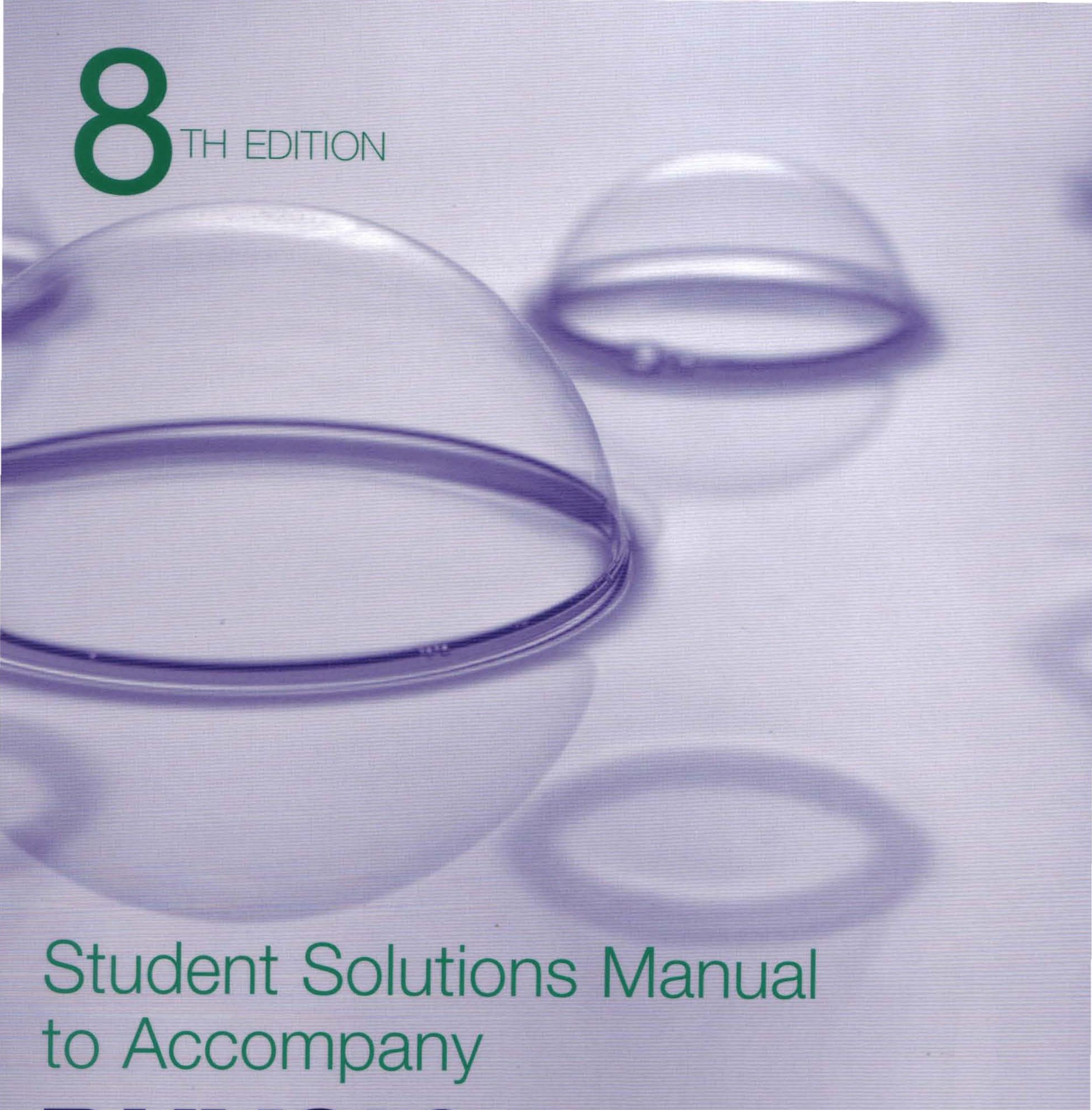

Student Solutions Manual to Accompany

PHYSICAL CHEMISTRY

PETER ATKINS • CHARLES TRAPP
CARMEN GIUNTA • MARSHALL CADY

STUDENT'S SOLUTIONS
MANUAL TO ACCOMPANY

PHYSICAL CHEMISTRY

EIGHTH EDITION

STUDENT'S SOLUTIONS MANUAL TO ACCOMPANY

PHYSICAL CHEMISTRY

Eighth Edition

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Preface

This manual provides detailed solutions to all the end-of-chapter (**b**) Exercises, and to the odd-numbered Discussion Questions and Problems. Solutions to Exercises and Problems carried over from previous editions have been reworked, modified, or corrected when needed.

The solutions to the Problems in this edition rely more heavily on the mathematical and molecular modelling software that is now generally accessible to physical chemistry students, and this is particularly true for many of the new Problems that request the use of such software for their solutions. But almost all of the Exercises and many of the Problems can still be solved with a modern hand-held scientific calculator. When a quantum chemical calculation or molecular modelling process has been called for, we have usually provided the solution with PC Spartan Pro^{TM} because of its common availability.

In general, we have adhered rigorously to the rules for significant figures in displaying the final answers. However, when intermediate answers are shown, they are often given with one more figure than would be justified by the data. These excess digits are indicated with an overline.

We have carefully cross-checked the solutions for errors and expect that most have been eliminated. We would be grateful to any readers who bring any remaining errors to our attention.

We warmly thank our publishers for their patience in guiding this complex, detailed project to completion.

P. W. A.

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M. P. C.

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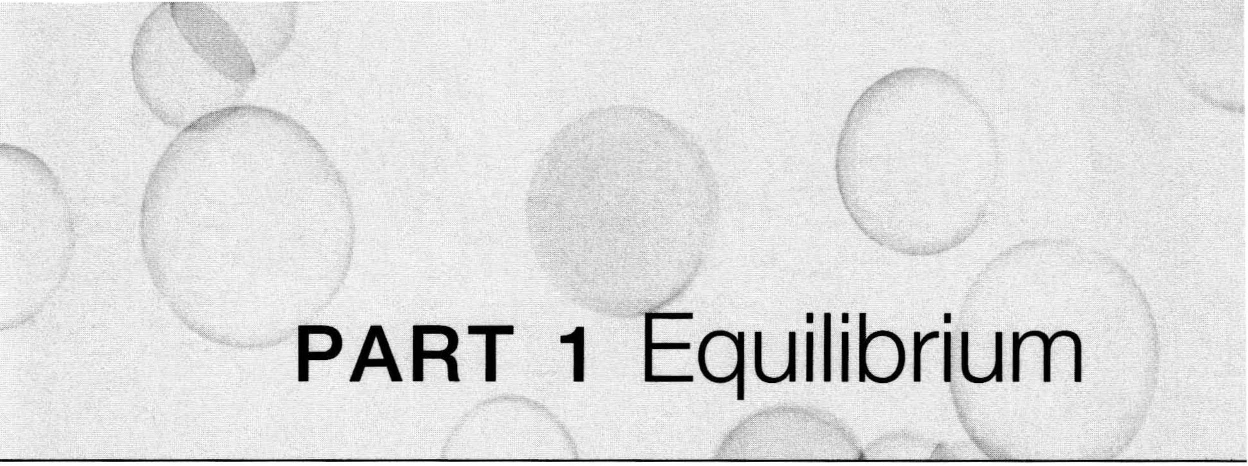
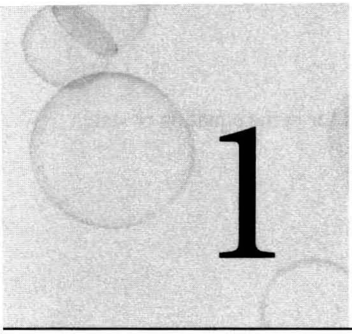


PART 1 Equilibrium



1 The properties of gases

Answers to discussion questions

D1.1 An equation of state is an equation that relates the variables that define the state of a system to each other. Boyle, Charles, and Avogadro established these relations for gases at low pressures (perfect gases) by appropriate experiments. Boyle determined how volume varies with pressure ($V \propto 1/p$), Charles how volume varies with temperature ($V \propto T$), and Avogadro how volume varies with amount of gas ($V \propto n$). Combining all of these proportionalities into one we find

$$V \propto \frac{nT}{p}.$$

Inserting the constant of proportionality, R, yields the perfect gas equation

$$V = \frac{RnT}{p} \quad \text{or} \quad pV = nRT.$$

D1.3 Consider three temperature regions:

(1) $T < T_{\mathrm{B}}$. At very low pressures, all gases show a compression factor, $Z \approx 1$. At high pressures, all gases have $Z > 1$, signifying that they have a molar volume greater than a perfect gas, which implies that repulsive forces are dominant. At intermediate pressures, most gases show $Z < 1$, indicating that attractive forces reducing the molar volume below the perfect value are dominant.

(2) $T \approx T_{\mathrm{B}}$. $Z \approx 1$ at low pressures, slightly greater than 1 at intermediate pressures, and significantly greater than 1 only at high pressures. There is a balance between the attractive and repulsive forces at low to intermediate pressures, but the repulsive forces predominate at high pressures where the molecules are very close to each other.

(3) $T > T_{\mathrm{B}}$. $Z > 1$ at all pressures because the frequency of collisions between molecules increases with temperature.

D1.5 The van der Waals equation 'corrects' the perfect gas equation for both attractive and repulsive interactions between the molecules in a real gas. See *Justification 1.1* for a fuller explanation.

The Bertholet equation accounts for the volume of the molecules in a manner similar to the van der Waals equation but the term representing molecular attractions is modified to account for the effect of temperature. Experimentally one finds that the van der Waals a decreases with increasing temperature. Theory (see Chapter 18) also suggests that intermolecular attractions can decrease with temperature.

This variation of the attractive interaction with temperature can be accounted for in the equation of state by replacing the van der Waals a with a/T.

Solutions to exercises

E1.1(b) **(a)** The perfect gas law is

$$pV = nRT$$

implying that the pressure would be

$$p = \frac{nRT}{V}$$

All quantities on the right are given to us except n, which can be computed from the given mass of Ar.

$$n = \frac{25\ \text{g}}{39.95\ \text{g mol}^{-1}} = 0.62\bar{6}\ \text{mol}$$

$$\text{so } p = \frac{(0.62\bar{6}\ \text{mol}) \times (8.31 \times 10^{-2}\ \text{dm}^3\ \text{bar K}^{-1}\text{mol}^{-1}) \times (30 + 273\ \text{K})}{1.5\ \text{dm}^3} = \boxed{10.\bar{5}\ \text{bar}}$$

not 2.0 bar.

(b) The van der Waals equation is

$$p = \frac{RT}{V_\text{m} - b} - \frac{a}{V_\text{m}^2}$$

$$\text{so } p = \frac{(8.31 \times 10^{-2}\ \text{dm}^3\ \text{bar K}^{-1}\text{mol}^{-1}) \times (30 + 273)\ \text{K}}{(1.53\ \text{dm}^3/0.62\bar{6}\ \text{mol}) - 3.20 \times 10^{-2}\ \text{dm}^3\ \text{mol}^{-1}}$$

$$- \frac{(1.337\ \text{dm}^6\text{atm mol}^{-2}) \times (1.013\ \text{bar atm}^{-1})}{(1.5\ \text{dm}^3/0.62\bar{6}\ \text{mol})^2} = \boxed{10.\bar{4}\ \text{bar}}$$

E1.2(b) **(a)** Boyle's law applies:

$$pV = \text{constant} \quad \text{so} \quad p_\text{f}V_\text{f} = p_\text{i}V_\text{i}$$

and

$$p_\text{i} = \frac{p_\text{f}V_\text{f}}{V_\text{i}} = \frac{(1.97\ \text{bar}) \times (2.14\ \text{dm}^3)}{(2.14 + 1.80)\ \text{dm}^3} = \boxed{1.07\ \text{bar}}$$

(b) The original pressure in bar is

$$p_\text{i} = (1.07\ \text{bar}) \times \left(\frac{1\ \text{atm}}{1.013\ \text{bar}}\right) \times \left(\frac{760\ \text{Torr}}{1\ \text{atm}}\right) = \boxed{803\ \text{Torr}}$$

E1.3(b) The relation between pressure and temperature at constant volume can be derived from the perfect gas law

$$pV = nRT \quad \text{so} \quad p \propto T \quad \text{and} \quad \frac{p_\text{i}}{T_\text{i}} = \frac{p_\text{f}}{T_\text{f}}$$

The final pressure, then, ought to be

$$p_\mathrm{f} = \frac{p_\mathrm{i}T_\mathrm{f}}{T_\mathrm{i}} = \frac{(125\ \mathrm{kPa}) \times (11 + 273)\ \mathrm{K}}{(23 + 273)\ \mathrm{K}} = \boxed{120\ \mathrm{kPa}}$$

E1.4(b) According to the perfect gas law, one can compute the amount of gas from pressure, temperature, and volume. Once this is done, the mass of the gas can be computed from the amount and the molar mass using

$$pV = nRT$$

$$\text{so } n = \frac{pV}{RT} = \frac{(1.00\ \mathrm{atm}) \times (1.013 \times 10^5\ \mathrm{Pa\ atm^{-1}}) \times (4.00 \times 10^3\ \mathrm{m^3})}{(8.3145\ \mathrm{J\ K^{-1}mol^{-1}}) \times (20 + 273)\ \mathrm{K}} = 1.66 \times 10^5\mathrm{mol}$$

$$\text{and } m = (1.66 \times 10^5\ \mathrm{mol}) \times (16.04\ \mathrm{g\ mol^{-1}}) = 2.67 \times 10^6\mathrm{g} = \boxed{2.67 \times 10^3\ \mathrm{kg}}$$

E1.5(b) Identifying p_ex in the equation $p = p_\mathrm{ex} + \rho gh$ [1.3] as the pressure at the top of the straw and p as the atmospheric pressure on the liquid, the pressure difference is

$$p - p_\mathrm{ex} = \rho gh = (1.0 \times 10^3\ \mathrm{kg\ m^{-3}}) \times (9.81\ \mathrm{m\ s^{-2}}) \times (0.15\ \mathrm{m})$$

$$= \boxed{1.5 \times 10^3\ \mathrm{Pa}}\ (= 1.5 \times 10^{-2}\ \mathrm{atm})$$

E1.6(b) The pressure in the apparatus is given by

$$p = p_\mathrm{atm} + \rho gh\ [1.3]$$

$$p_\mathrm{atm} = 760\ \mathrm{Torr} = 1\ \mathrm{atm} = 1.013 \times 10^5\ \mathrm{Pa}$$

$$\rho gh = 13.55\ \mathrm{g\ cm^{-3}} \times \left(\frac{1\ \mathrm{kg}}{10^3\ \mathrm{g}}\right) \times \left(\frac{10^6\ \mathrm{cm^3}}{\mathrm{m^3}}\right) \times 0.100\ \mathrm{m} \times 9.806\ \mathrm{m\ s^{-2}} = 1.33 \times 10^4\ \mathrm{Pa}$$

$$p = 1.013 \times 10^5\ \mathrm{Pa} + 1.33 \times 10^4\ \mathrm{Pa} = 1.146 \times 10^5\ \mathrm{Pa} = \boxed{115\ \mathrm{kPa}}$$

E1.7(b) All gases are perfect in the limit of zero pressure. Therefore the extrapolated value of pV_m/T will give the best value of R.

The molar mass is obtained from $pV = nRT = \dfrac{m}{M}RT$

which upon rearrangement gives $M = \dfrac{m}{V}\dfrac{RT}{p} = \rho\dfrac{RT}{p}$

The best value of M is obtained from an extrapolation of ρ/p versus p to $p = 0$; the intercept is M/RT.

Draw up the following table

p/atm	$(pV_\mathrm{m}/T)/(\mathrm{dm^3\ atm\ K^{-1}mol^{-1}})$	$(\rho/p)/(\mathrm{dm^{-3}atm^{-1}})$
0.750 000	0.082 0014	1.428 59
0.500 000	0.082 0227	1.428 22
0.250 000	0.082 0414	1.427 90

From Figure 1.1(a), $\left(\dfrac{pV_\mathrm{m}}{T}\right)_{p=0} = \boxed{0.082\,061\,5\ \mathrm{dm^3\ atm\ K^{-1}\ mol^{-1}}}$

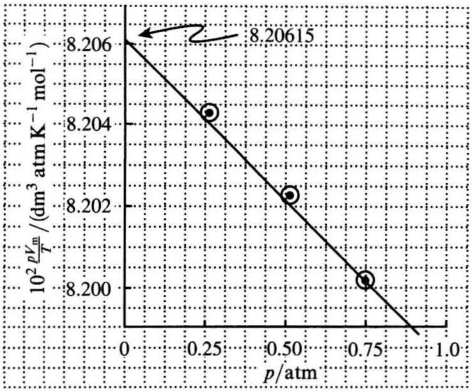


Figure 1.1(a)

From Figure 1.1(b), $\left(\dfrac{\rho}{p}\right)_{p=0} = 1.427\,55\ \mathrm{g\ dm^{-3}\ atm^{-1}}$

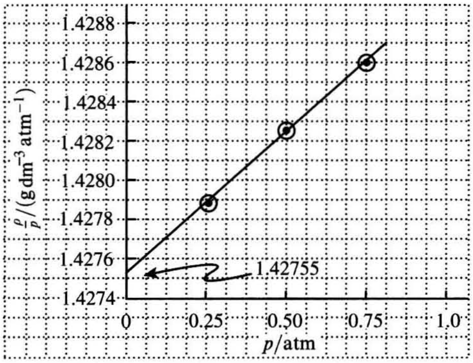


Figure 1.1(b)

$$M = RT\left(\frac{\rho}{p}\right)_{p=0} = (0.082\,061\,5\ \mathrm{dm^3\ atm\ mol^{-1}\ K^{-1}}) \times (273.15\ \mathrm{K}) \times (1.42755\ \mathrm{g\ dm^{-3} atm^{-1}})$$

$$= \boxed{31.9987\ \mathrm{g\ mol^{-1}}}$$

The value obtained for R deviates from the accepted value by 0.005 percent. The error results from the fact that only three data points are available and that a linear extrapolation was employed. The molar mass, however, agrees exactly with the accepted value, probably because of compensating plotting errors.

E1.8(b) The mass density ρ is related to the molar volume V_m by

$$V_m = \frac{M}{\rho}$$

where M is the molar mass. Putting this relation into the perfect gas law yields

$$pV_m = RT \quad \text{so} \quad \frac{pM}{\rho} = RT$$

Rearranging this result gives an expression for M; once we know the molar mass, we can divide by the molar mass of phosphorus atoms to determine the number of atoms per gas molecule

$$M = \frac{RT\rho}{p} = \frac{(8.314\ \mathrm{Pa\ m^3\ mol^{-1}}) \times [(100 + 273)\ \mathrm{K}] \times (0.6388\ \mathrm{kg\ m^{-3}})}{1.60 \times 10^4\ \mathrm{Pa}}$$

$$= 0.124\ \mathrm{kg\ mol^{-1}} = 124\ \mathrm{g\ mol^{-1}}$$

The number of atoms per molecule is

$$\frac{124\ \mathrm{g\ mol^{-1}}}{31.0\ \mathrm{g\ mol^{-1}}} = 4.00$$

suggesting a formula of $\boxed{\mathrm{P_4}}$

E1.9(b) Use the perfect gas equation to compute the amount; then convert to mass.

$$pV = nRT \quad \text{so} \quad n = \frac{pV}{RT}$$

We need the partial pressure of water, which is 53 percent of the equilibrium vapor pressure at the given temperature and standard pressure.

$$p = (0.53) \times (2.69 \times 10^3\ \mathrm{Pa}) = 1.4\bar{3} \times 10^3\ \mathrm{Pa}$$

$$\text{so } n = \frac{(1.4\bar{3} \times 10^3\ \mathrm{Pa}) \times (250\ \mathrm{m^3})}{(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (23 + 273)\ \mathrm{K}} = 1.4\bar{5} \times 10^2\ \mathrm{mol}$$

$$\text{or } m = (1.4\bar{5} \times 10^2\ \mathrm{mol}) \times (18.0\ \mathrm{g\ mol^{-1}}) = 2.6\bar{1} \times 10^3\ \mathrm{g} = \boxed{2.6\bar{1}\ \mathrm{kg}}$$

E1.10(b) **(a)** The volume occupied by each gas is the same, since each completely fills the container. Thus solving for V we have (assuming a perfect gas)

$$V = \frac{n_J RT}{p_J} \quad n_{\mathrm{Ne}} = \frac{0.225\ \mathrm{g}}{20.18\ \mathrm{g\ mol^{-1}}}$$

$$= 1.11\bar{5} \times 10^{-2}\ \mathrm{mol}, \quad p_{\mathrm{Ne}} = 8.87\ \mathrm{kPa}, \quad T = 300\ \mathrm{K}$$

$$V = \frac{(1.11\bar{5} \times 10^{-2}\ \mathrm{mol}) \times (8.314\ \mathrm{dm^3\ kPa\ K^{-1}\ mol^{-1}}) \times 300\ \mathrm{K})}{8.87\ \mathrm{kPa}} = 3.13\bar{7}\ \mathrm{dm^3}$$

$$= \boxed{3.14\ \mathrm{dm^3}}$$

(b) The total pressure is determined from the total amount of gas, $n = n_{\mathrm{CH_4}} + n_{\mathrm{Ar}} + n_{\mathrm{Ne}}$.

$$n_{\mathrm{CH_4}} = \frac{0.320\ \mathrm{g}}{16.04\ \mathrm{g\ mol^{-1}}} = 1.99\bar{5} \times 10^{-2}\mathrm{mol} \quad n_{\mathrm{Ar}} = \frac{0.175\ \mathrm{g}}{39.95\ \mathrm{g\ mol^{-1}}} = 4.38 \times 10^{-3}\mathrm{mol}$$

$$n = (1.99\bar{5} + 0.438 + 1.11\bar{5}) \times 10^{-2}\mathrm{mol} = 3.54\bar{8} \times 10^{-2}\mathrm{mol}$$

$$p = \frac{nRT}{V}[1.8] = \frac{(3.54\bar{8} \times 10^{-2}\ \mathrm{mol}) \times (8.314\ \mathrm{dm^3\ \ kPa\ K^{-1}\ mol^{-1}}) \times (300\ \ \mathrm{K})}{3.13\bar{7}\ \mathrm{dm^3}}$$

$$= \boxed{28.2\ \mathrm{kPa}}$$

E1.11(b) This is similar to Exercise 1.11(a) with the exception that the density is first calculated.

$$M = \rho\frac{RT}{p}\ \text{[Exercise 1.8(a)]}$$

$$\rho = \frac{33.5\,\text{mg}}{250\,\text{cm}^3} = 0.134\bar{0}\,\text{g dm}^{-3}, \quad p = 152\,\text{Torr}, \quad T = 298\,\text{K}$$

$$M = \frac{(0.134\bar{0}\,\text{g dm}^{-3}) \times (62.36\,\text{dm}^3\,\text{Torr K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K})}{152\,\text{Torr}} = \boxed{16.14\,\text{g mol}^{-1}}$$

E1.12(b) This exercise is similar to Exercise 1.12(a) in that it uses the definition of absolute zero as that temperature at which the volume of a sample of gas would become zero if the substance remained a gas at low temperatures. The solution uses the experimental fact that the volume is a linear function of the Celsius temperature.

Thus $V = V_0 + \alpha V_0\theta = V_0 + b\theta,\ b = \alpha V_0$

At absolute zero, $V = 0$, or $0 = 20.00\,\text{dm}^3 + 0.0741\,\text{dm}^3\,{}^\circ\text{C}^{-1} \times \theta(\text{abs. zero})$

$$\theta(\text{abs. zero}) = -\frac{20.00\,\text{dm}^3}{0.0741\,\text{dm}^3\,{}^\circ\text{C}^{-1}} = \boxed{-270\,{}^\circ\text{C}}$$

which is close to the accepted value of $-273\,{}^\circ\text{C}$.

E1.13(b) **(a)** $p = \dfrac{nRT}{V}$

$n = 1.0\,\text{mol}$

$T = \text{(i) } 273.15\,\text{K};\ \text{(ii) } 500\,\text{K}$

$V = \text{(i) } 22.414\,\text{dm}^3;\ \text{(ii) } 150\,\text{cm}^3$

(i)
$$p = \frac{(1.0\,\text{mol}) \times (8.206 \times 10^{-2}\,\text{dm}^3\,\text{atm K}^{-1}\,\text{mol}^{-1}) \times (273.15\,\text{K})}{22.414\,\text{dm}^3}$$

$$= \boxed{1.0\,\text{atm}}$$

(ii)
$$p = \frac{(1.0\,\text{mol}) \times (8.206 \times 10^{-2}\,\text{dm}^3\,\text{atm K}^{-1}\,\text{mol}^{-1}) \times (500\,\text{K})}{0.150\,\text{dm}^3}$$

$$= \boxed{270\,\text{atm}}\ \text{(2 significant figures)}$$

(b) From Table (1.6) for H_2S

$$a = 4.484\,\text{dm}^6\,\text{atm mol}^{-1} \qquad b = 4.34 \times 10^{-2}\,\text{dm}^3\,\text{mol}^{-1}$$

$$p = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

(i)
$$p = \frac{(1.0\,\text{mol}) \times (8.206 \times 10^{-2}\,\text{dm}^3\,\text{atm K}^{-1}\,\text{mol}^{-1}) \times (273.15\,\text{K})}{22.414\,\text{dm}^3 - (1.0\,\text{mol}) \times (4.34 \times 10^{-2}\,\text{dm}^3\,\text{mol}^{-1})}$$

$$- \frac{(4.484\,\text{dm}^6\,\text{atm mol}^{-1}) \times (1.0\,\text{mol})^2}{(22.414\,\text{dm}^3)^2}$$

$$= \boxed{0.99\,\text{atm}}$$

(ii)
$$p = \frac{(1.0\,\text{mol}) \times (8.206 \times 10^{-2}\,\text{dm}^3\,\text{atm K}^{-1}\,\text{mol}^{-1}) \times (500\,\text{K})}{0.150\,\text{dm}^3 - (1.0\,\text{mol}) \times (4.34 \times 10^{-2}\,\text{dm}^3\,\text{mol}^{-1})} - \frac{(4.484\,\text{dm}^6\text{atm mol}^{-1}) \times (1.0\,\text{mol})^2}{(0.150\,\text{dm}^3)^2}$$

$$= 18\overline{5.6}\,\text{atm} \approx \boxed{190\,\text{atm}}\ \text{(2 significant figures).}$$

E1.14(b) The conversions needed are as follows:

$1\,\text{atm} = 1.013 \times 10^5\,\text{Pa}$; $1\,\text{Pa} = 1\,\text{kg m}^{-1}\,\text{s}^{-2}$; $1\,\text{dm}^6 = 10^{-6}\,\text{m}^6$; $1\,\text{dm}^3 = 10^{-3}\,\text{m}^3$

Therefore,

$a = 1.32\,\text{atm dm}^6\,\text{mol}^{-2}$ becomes, after substitution of the conversions

$a = \boxed{1.34 \times 10^{-1}\,\text{kg m}^5\text{s}^{-2}\text{mol}^{-2}}$, and

$b = 0.0436\,\text{dm}^3\,\text{mol}^{-1}$ becomes

$b = \boxed{4.36 \times 10^{-5}\,\text{m}^3\text{mol}^{-1}}$

E1.15(b) The compression factor is

$$Z = \frac{pV_\text{m}}{RT} = \frac{V_\text{m}}{V_\text{m}^\text{o}}$$

(a) Because $V_\text{m} = V_\text{m}^\text{o} + 0.12\,V_\text{m}^\text{o} = (1.12)V_\text{m}^\text{o}$, we have $Z = \boxed{1.12}$ $\boxed{\text{Repulsive}}$ forces dominate.

(b) The molar volume is

$$V = (1.12)V_\text{m}^\text{o} = (1.12) \times \left(\frac{RT}{p}\right)$$

$$V = (1.12) \times \left(\frac{(0.08206\,\text{dm}^3\,\text{atm K}^{-1}\,\text{mol}^{-1}) \times (350\,\text{K})}{12\,\text{atm}}\right) = \boxed{2.7\,\text{dm}^3\,\text{mol}^{-1}}$$

E1.16(b) **(a)**
$$V_\text{m}^\text{o} = \frac{RT}{p} = \frac{(8.314\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (298.15\,\text{K})}{(200\,\text{bar}) \times (10^5\,\text{Pa bar}^{-1})}$$

$$= 1.24 \times 10^{-4}\,\text{m}^3\,\text{mol}^{-1} = \boxed{0.124\,\text{dm}^3\,\text{mol}^{-1}}$$

(b) The van der Waals equation is a cubic equation in V_m. The most direct way of obtaining the molar volume would be to solve the cubic analytically. However, this approach is cumbersome, so we proceed as in Example 1.4. The van der Waals equation is rearranged to the cubic form

$$V_\text{m}^3 - \left(b + \frac{RT}{p}\right)V_\text{m}^2 + \left(\frac{a}{p}\right)V_\text{m} - \frac{ab}{p} = 0 \text{ or } x^3 - \left(b + \frac{RT}{p}\right)x^2 + \left(\frac{a}{p}\right)x - \frac{ab}{p} = 0$$

with $x = V_\text{m}/(\text{dm}^3\,\text{mol}^{-1})$.

The coefficients in the equation are evaluated as

$$b+\frac{RT}{p}=(3.183\times10^{-2}\,\mathrm{dm^3\,mol^{-1}})+\frac{(8.206\times10^{-2}\,\mathrm{dm^3\,mol^{-1}})\times(298.15\,\mathrm{K})}{(200\,\mathrm{bar})\times(1.013\,\mathrm{atm\,bar^{-1}})}$$

$$=(3.183\times10^{-2}+0.120\overline{8})\,\mathrm{dm^3\,mol^{-1}}=0.152\overline{6}\,\mathrm{dm^3mol^{-1}}$$

$$\frac{a}{p}=\frac{1.360\,\mathrm{dm^6\,atm\,mol^{-2}}}{(200\,\mathrm{bar})\times(1.013\,\mathrm{atm\,bar^{-1}})}=6.71\times10^{-3}(\mathrm{dm^3\,mol^{-1}})^2$$

$$\frac{ab}{p}=\frac{(1.360\,\mathrm{dm^6\,atm\,mol^{-2}})\times(3.183\times10^{-2}\mathrm{dm^3\,mol^{-1}})}{(200\,\mathrm{bar})\times(1.013\,\mathrm{atm\,bar^{-1}})}=2.13\overline{7}\times10^{-4}(\mathrm{dm^3\,mol^{-1}})^3$$

Thus, the equation to be solved is $x^3-0.152\overline{6}x^2+(6.71\times10^{-3})x-(2.13\overline{7}\times10^{-4})=0$. Calculators and computer software for the solution of polynomials are readily available. In this case we find

$$x=0.112 \quad \text{or} \quad V_\mathrm{m}=\boxed{0.112\,\mathrm{dm^3\,mol^{-1}}}$$

The difference is about 15 percent.

E1.17(b) The molar volume is obtained by solving $Z=pV_\mathrm{m}/RT$ [1.17], for V_m, which yields

$$V_\mathrm{m}=\frac{ZRT}{p}=\frac{(0.86)\times(0.08206\,\mathrm{dm^3\,atm\,K^{-1}\,mol^{-1}})\times(300\,\mathrm{K})}{20\,\mathrm{atm}}=1.0\overline{59}\,\mathrm{dm^3\,mol^{-1}}$$

(a) Then, $V=nV_\mathrm{m}=(8.2\times10^{-3}\,\mathrm{mol})\times(1.0\overline{59}\,\mathrm{dm^3\,mol^{-1}})=8.7\times10^{-3}\,\mathrm{dm^3}=\boxed{8.7\,\mathrm{cm^3}}$

(b) An approximate value of B can be obtained from eqn 1.19 by truncation of the series expansion after the second term, B/V_m, in the series. Then,

$$B=V_\mathrm{m}\left(\frac{pV_\mathrm{m}}{RT}-1\right)=V_\mathrm{m}\times(Z-1)$$

$$=(1.0\overline{59}\,\mathrm{dm^3\,mol^{-1}})\times(0.86-1)=\boxed{-0.15\,\mathrm{dm^3mol^{-1}}}$$

E1.18(b) **(a)** Mole fractions are

$$x_\mathrm{N}=\frac{n_\mathrm{N}}{n_\mathrm{total}}=\frac{2.5\,\mathrm{mol}}{(2.5+1.5)\,\mathrm{mol}}=\boxed{0.63}$$

Similarly, $x_\mathrm{H}=\boxed{0.37}$

(c) According to the perfect gas law

$$p_\mathrm{total}V=n_\mathrm{total}RT$$

$$\text{so } p_\mathrm{total}=\frac{n_\mathrm{total}RT}{V}$$

$$=\frac{(4.0\,\mathrm{mol})\times(0.08206\,\mathrm{dm^3\,atm\,mol^{-1}\,K^{-1}})\times(273.15\,\mathrm{K})}{22.4\,\mathrm{dm^3}}=\boxed{4.0\,\mathrm{atm}}$$

(b) The partial pressures are

$$p_{\mathrm{N}} = x_{\mathrm{N}} p_{\mathrm{tot}} = (0.63) \times (4.0\,\mathrm{atm}) = \boxed{2.5\ \mathrm{atm}}$$

and $p_{\mathrm{H}} = (0.37) \times (4.0\,\mathrm{atm}) = \boxed{1.5\ \mathrm{atm}}$

E1.19(b) The critical volume of a van der Waals gas is

$$V_{\mathrm{c}} = 3b$$

so $b = \frac{1}{3}V_{\mathrm{c}} = \frac{1}{3}(148\,\mathrm{cm^3\,mol^{-1}}) = 49.3\,\mathrm{cm^3\,mol^{-1}} = \boxed{0.0493\ \mathrm{dm^3\,mol^{-1}}}$

By interpreting b as the excluded volume of a mole of spherical molecules, we can obtain an estimate of molecular size. The centers of spherical particles are excluded from a sphere whose radius is the diameter of those spherical particles (i.e. twice their radius); that volume times the Avogadro constant is the molar excluded volume b

$$b = N_{\mathrm{A}}\left(\frac{4\pi(2r)^3}{3}\right) \quad \text{so} \quad r = \frac{1}{2}\left(\frac{3b}{4\pi N_{\mathrm{A}}}\right)^{1/3}$$

$$r = \frac{1}{2}\left(\frac{3(49.3\,\mathrm{cm^3\,mol^{-1}})}{4\pi(6.022\times10^{23}\,\mathrm{mol^{-1}})}\right)^{1/3} = 1.94\times10^{-8}\,\mathrm{cm} = \boxed{1.94\times10^{-10}\,\mathrm{m}}$$

The critical pressure is

$$p_{\mathrm{c}} = \frac{a}{27b^2}$$

so $a = 27p_{\mathrm{c}}b^2 = 27(48.20\,\mathrm{atm}) \times (0.0493\,\mathrm{dm^3\,mol^{-1}})^2 = \boxed{3.16\ \mathrm{dm^6\,atm\,mol^{-2}}}$

But this problem is overdetermined. We have another piece of information

$$T_{\mathrm{c}} = \frac{8a}{27Rb}$$

According to the constants we have already determined, T_{c} should be

$$T_{\mathrm{c}} = \frac{8(3.16\,\mathrm{dm^6\,atm\,mol^{-2}})}{27(0.08206\,\mathrm{dm^3\,atm\,K^{-1}\,mol^{-1}}) \times (0.0493\,\mathrm{dm^3\,mol^{-1}})} = 231\ \mathrm{K}$$

However, the reported T_{c} is 305.4 K, suggesting our computed a/b is about 25 percent lower than it should be.

E1.20(b) **(a)** The Boyle temperature is the temperature at which $\lim_{V_{\mathrm{m}}\to\infty} \mathrm{d}Z/(\mathrm{d}(1/V_{\mathrm{m}}))$ vanishes. According to the van der Waals equation

$$Z = \frac{pV_{\mathrm{m}}}{RT} = \frac{\left(\dfrac{RT}{V_{\mathrm{m}}-b} - \dfrac{a}{V_{\mathrm{m}}^2}\right)V_{\mathrm{m}}}{RT} = \frac{V_{\mathrm{m}}}{V_{\mathrm{m}}-b} - \frac{a}{V_{\mathrm{m}}RT}$$

$$\text{so}\quad \frac{\mathrm{d}Z}{\mathrm{d}(1/V_\mathrm{m})} = \left(\frac{\mathrm{d}Z}{\mathrm{d}V_\mathrm{m}}\right) \times \left(\frac{\mathrm{d}V_\mathrm{m}}{\mathrm{d}(1/V_\mathrm{m})}\right)$$

$$= -V_\mathrm{m}^2\left(\frac{\mathrm{d}Z}{\mathrm{d}V_\mathrm{m}}\right) = -V_\mathrm{m}^2\left(\frac{-V_\mathrm{m}}{(V_\mathrm{m}-b)^2} + \frac{1}{V_\mathrm{m}-b} + \frac{a}{V_\mathrm{m}^2RT}\right)$$

$$= \frac{V_\mathrm{m}^2 b}{(V_\mathrm{m}-b)^2} - \frac{a}{RT}$$

In the limit of large molar volume, we have

$$\lim_{V_\mathrm{m}\to\infty} \frac{\mathrm{d}Z}{\mathrm{d}(1/V_\mathrm{m})} = b - \frac{a}{RT} = 0 \quad \text{so} \quad \frac{a}{RT} = b$$

$$\text{and } T = \frac{a}{Rb} = \frac{\left(4.484\,\mathrm{dm^6\,atm\,mol^{-2}}\right)}{\left(0.08206\,\mathrm{dm^3\,atm\,K^{-1}\,mol^{-1}}\right) \times \left(0.0434\,\mathrm{dm^3\,mol^{-1}}\right)} = \boxed{1259\,\mathrm{K}}$$

(b) By interpreting b as the excluded volume of a mole of spherical molecules, we can obtain an estimate of molecular size. The centres of spherical particles are excluded from a sphere whose radius is the diameter of those spherical particles (i.e. twice their radius); the Avogadro constant times the volume is the molar excluded volume b

$$b = N_\mathrm{A}\left(\frac{4\pi(2r)^3}{3}\right) \quad \text{so} \quad r = \frac{1}{2}\left(\frac{3b}{4\pi N_\mathrm{A}}\right)^{1/3}$$

$$r = \frac{1}{2}\left(\frac{3(0.0434\,\mathrm{dm^3\,mol^{-1}})}{4\pi(6.022\times10^{23}\,\mathrm{mol^{-1}})}\right)^{1/3} = 1.286\times10^{-9}\,\mathrm{dm} = 1.29\times10^{-10}\,\mathrm{m} = \boxed{0.129\,\mathrm{nm}}$$

E1.21(b) States that have the same reduced pressure, temperature, and volume are said to correspond. The reduced pressure and temperature for N_2 at 1.0 atm and 25 °C are

$$p_\mathrm{r} = \frac{p}{p_\mathrm{c}} = \frac{1.0\,\mathrm{atm}}{33.54\,\mathrm{atm}} = 0.030 \quad \text{and} \quad T_\mathrm{r} = \frac{T}{T_\mathrm{c}} = \frac{(25+273)\,\mathrm{K}}{126.3\,\mathrm{K}} = 2.36$$

The corresponding states are

(a) For H_2S

$$p = p_\mathrm{r}p_\mathrm{c} = (0.030) \times (88.3\,\mathrm{atm}) = \boxed{2.6\,\mathrm{atm}}$$

$$T = T_\mathrm{r}T_\mathrm{c} = (2.36) \times (373.2\,\mathrm{K}) = \boxed{881\,\mathrm{K}}$$

(Critical constants of H_2S obtained from *Handbook of Chemistry and Physics*.)

(b) For CO_2

$$p = p_\mathrm{r}p_\mathrm{c} = (0.030) \times (72.85\,\mathrm{atm}) = \boxed{2.2\,\mathrm{atm}}$$

$$T = T_\mathrm{r}T_\mathrm{c} = (2.36) \times (304.2\,\mathrm{K}) = \boxed{718\,\mathrm{K}}$$

(c) For Ar

$$p = p_\mathrm{r}p_\mathrm{c} = (0.030) \times (48.00\,\mathrm{atm}) = \boxed{1.4\,\mathrm{atm}}$$

$$T = T_\mathrm{r}T_\mathrm{c} = (2.36) \times (150.72\,\mathrm{K}) = \boxed{356\,\mathrm{K}}$$

E1.22(b) The van der Waals equation is

$$p = \frac{RT}{V_{\mathrm{m}} - b} - \frac{a}{V_{\mathrm{m}}^2}$$

which can be solved for b

$$b = V_{\mathrm{m}} - \frac{RT}{p + \dfrac{a}{V_{\mathrm{m}}^2}} = 4.00 \times 10^{-4}\,\mathrm{m^3\,mol^{-1}} - \frac{(8.3145\,\mathrm{J\,K^{-1}mol^{-1}}) \times (288\,\mathrm{K})}{4.0 \times 10^6\,\mathrm{Pa} + \left(\dfrac{0.76\,\mathrm{m^6\,Pa\,mol^{-2}}}{(4.00 \times 10^{-4}\,\mathrm{m^3\,mol^{-1}})^2}\right)}$$

$$= \boxed{1.3 \times 10^{-4}\,\mathrm{m^3\,mol^{-1}}}$$

The compression factor is

$$z = \frac{pV_{\mathrm{m}}}{RT} = \frac{(4.0 \times 10^6\,\mathrm{Pa}) \times (4.00 \times 10^{-4}\,\mathrm{m^3\,mol^{-1}})}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (288\,\mathrm{K})} = \boxed{0.67}$$

Solutions to problems

Solutions to numerical problems

P1.1 Since the Neptunians know about perfect gas behavior, we may assume that they will write $pV = nRT$ at both temperatures. We may also assume that they will establish the size of their absolute unit to be the same as the °N, just as we write $1\,\mathrm{K} = 1°\mathrm{C}$. Thus

$$pV(T_1) = 28.0\,\mathrm{dm^3\,atm} = nRT_1 = nR \times (T_1 + 0°\mathrm{N}),$$

$$pV(T_2) = 40.0\,\mathrm{dm^3\,atm} = nRT_2 = nR \times (T_1 + 100°\mathrm{N}),$$

$$\text{or } T_1 = \frac{28.0\,\mathrm{dm^3\,atm}}{nR}, \qquad T_1 + 100°\mathrm{N} = \frac{40.0\,\mathrm{dm^3\,atm}}{nR}.$$

Dividing, $\dfrac{T_1 + 100°\mathrm{N}}{T_1} = \dfrac{40.0\,\mathrm{dm^3\,atm}}{28.0\,\mathrm{dm^3\,atm}} = 1.42\overline{9}$ or $T_1 + 100°\mathrm{N} = 1.42\overline{9}T_1, T_1 = 233$ absolute units. As in the relationship between our Kelvin scale and Celsius scale $T = \theta -$ absolute zero(°N) so absolute zero (°N) = $\boxed{-233°\mathrm{N}}$.

COMMENT. To facilitate communication with Earth students we have converted the Neptunians' units of the pV product to units familiar to humans, which are dm^3 atm. However, we see from the solution that only the ratio of pV products is required, and that will be the same in any civilization.

Question. If the Neptunians' unit of volume is the lagoon (L), their unit of pressure is the poseidon (P), their unit of amount is the nereid (n), and their unit of absolute temperature is the titan (T), what is the value of the Neptunians' gas constant (R) in units of L, P, n, and T?

P1.3 The value of absolute zero can be expressed in terms of α by using the requirement that the volume of a perfect gas becomes zero at the absolute zero of temperature. Hence

$$0 = V_0[1 + \alpha\theta(\text{abs. zero})].$$

Then θ (abs. zero) $= -\dfrac{1}{\alpha}$.

All gases become perfect in the limit of zero pressure, so the best value of α and, hence, θ (abs. zero) is obtained by extrapolating α to zero pressure. This is done in Fig. 1.2. Using the extrapolated value, $\alpha = 3.6637 \times 10^{-3}\,{}^\circ\mathrm{C}^{-1}$, or

$$\theta(\text{abs. zero}) = -\frac{1}{3.6637 \times 10^{-3}\,{}^\circ\mathrm{C}^{-1}} = \boxed{-272.95^\circ\mathrm{C}},$$

which is close to the accepted value of −273.15°C.

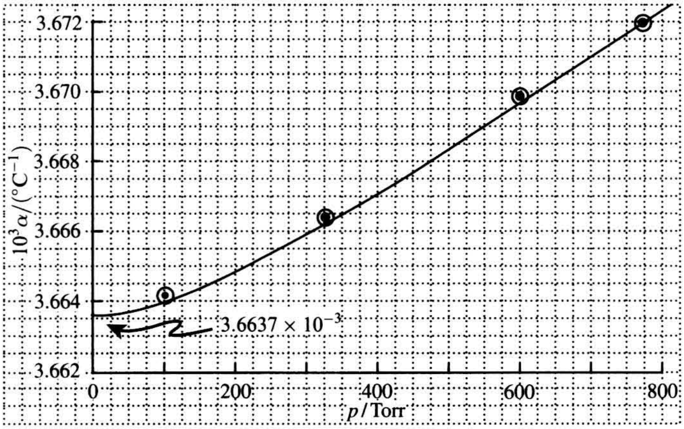


Figure 1.2

P1.5 $\dfrac{p}{T} = \dfrac{nR}{V}$ = constant, if n and V are constant. Hence, $\dfrac{p}{T} = \dfrac{p_3}{T_3}$, where p is the measured pressure at temperature, T, and p_3 and T_3 are the triple point pressure and temperature, respectively. Rearranging, $p = \left(\dfrac{p_3}{T_3}\right)T$.

The ratio $\dfrac{p_3}{T_3}$ is a constant $= \dfrac{6.69\,\mathrm{kPa}}{273.16\,\mathrm{K}} = 0.0245\,\mathrm{kPa\,K^{-1}}$. Thus the change in p, Δp, is proportional to the change in temperature, $\Delta T : \Delta p = (0.0245\,\mathrm{kPa\,K^{-1}}) \times (\Delta T)$.

(a) $\Delta p = (0.0245\,\mathrm{kPa\,K^{-1}}) \times (1.00\,\mathrm{K}) = \boxed{0.0245\,\mathrm{kPa}}$.

(b) Rearranging, $p = \left(\dfrac{T}{T_3}\right)p_3 = \left(\dfrac{373.16\,\mathrm{K}}{273.16\,\mathrm{K}}\right) \times (6.69\,\mathrm{kPa}) = \boxed{9.14\,\mathrm{kPa}}$.

(c) Since $\dfrac{p}{T}$ is a constant at constant n and V, it always has the value $0.0245\,\mathrm{kPa\,K^{-1}}$; hence

$$\Delta p = p_{374.15\,\mathrm{K}} - p_{373.15\,\mathrm{K}} = (0.0245\,\mathrm{kPa\,K^{-1}}) \times (1.00\,\mathrm{K}) = \boxed{0.0245\,\mathrm{kPa}}.$$

P1.7 **(a)** $V_\mathrm{m} = \dfrac{RT}{p} = \dfrac{(8.206 \times 10^{-2}\,\mathrm{dm^3\,atm\,K^{-1}\,mol^{-1}}) \times (350\,\mathrm{K})}{2.30\,\mathrm{atm}} = \boxed{12.5\,\mathrm{dm^3\,mol^{-1}}}$.

(b) From $p = \dfrac{RT}{V_\mathrm{m} - b} - \dfrac{a}{V_\mathrm{m}^2}$ [1.21b], we obtain $V_\mathrm{m} = \dfrac{RT}{\left(p + \dfrac{a}{V_\mathrm{m}^2}\right)} + b$ [rearrange1.21b].

Then, with a and b from Table 1.6,

$$V_\mathrm{m} \approx \frac{(8.206 \times 10^{-2}\,\mathrm{dm^3\,atm\,K^{-1}\,mol^{-1}}) \times (350\,\mathrm{K})}{(2.30\,\mathrm{atm}) + \left((6.260\,\mathrm{dm^6\,atm\,mol^{-2}})/\left(12.5\,\mathrm{dm^3\,mol^{-1}}\right)^2\right)} + (5.42 \times 10^{-2}\,\mathrm{dm^3\,mol^{-1}})$$

$$\approx \frac{28.7\bar{2}\,\mathrm{dm^3\,mol^{-1}}}{2.34} + \left(5.42 \times 10^{-2}\,\mathrm{dm^3\,mol^{-1}}\right) \approx \boxed{12.3\,\mathrm{dm^3\,mol^{-1}}}.$$

Substitution of $12.3\,\mathrm{dm^3\,mol^{-1}}$ into the denominator of the first expression again results in $V_\mathrm{m} = 12.3\,\mathrm{dm^3\,mol^{-1}}$, so the cycle of approximation may be terminated.

P1.9 As indicated by eqns 1.18 and 1.19 the compression factor of a gas may be expressed as either a virial expansion in p or in $\left(\frac{1}{V_\mathrm{m}}\right)$. The virial form of the van der Waals equation is derived in Exercise 1.20(a) and is $p = \frac{RT}{V_\mathrm{m}}\left\{1 + \left(b - \frac{a}{RT}\right) \times \left(\frac{1}{V_\mathrm{m}}\right) + \cdots\right\}$

Rearranging, $Z = \frac{pV_\mathrm{m}}{RT} = 1 + \left(b - \frac{a}{RT}\right) \times \left(\frac{1}{V_\mathrm{m}}\right) + \cdots$

On the assumption that the perfect gas expression for V_m is adequate for the second term in this expansion, we can readily obtain Z as a function of p.

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

(a) $T_\mathrm{c} = 126.3\,\mathrm{K}$.

$$V_\mathrm{m} = \left(\frac{RT}{p}\right) \times Z = \frac{RT}{p} + \left(b - \frac{a}{RT}\right) + \cdots$$

$$= \frac{(0.08206\,\mathrm{dm^3\,atm\,K^{-1}\,mol^{-1}}) \times (126.3\,\mathrm{K})}{10.0\,\mathrm{atm}} + \left\{(0.0387\,\mathrm{dm^3\,mol^{-1}}) - \left(\frac{1.352\,\mathrm{dm^6\,atm\,mol^{-2}}}{(0.08206\,\mathrm{dm^3\,atm\,K^{-1}mol^{-1}}) \times (126.3\,\mathrm{K})}\right)\right\}$$

$$= (1.036 - 0.092)\,\mathrm{dm^3\,mol^{-1}} = \boxed{0.944\,\mathrm{dm^3\,mol^{-1}}}.$$

$$Z = \left(\frac{p}{RT}\right) \times (V_\mathrm{m}) = \frac{(10.0\,\mathrm{atm}) \times (0.944\,\mathrm{dm^3\,mol^{-1}})}{(0.08206\,\mathrm{dm^3\,atm\,K^{-1}\,mol^{-1}}) \times (126.3\,\mathrm{K})} = 0.911.$$

(b) The Boyle temperature corresponds to the temperature at which the second virial coefficient is zero, hence correct to the first power in p, $Z = 1$, and the gas is close to perfect. However, if we assume that N_2 is a van der Waals gas, when the second virial coefficient is zero,

$$\left(b - \frac{a}{RT_\mathrm{B}}\right) = 0, \quad \text{or} \quad T_\mathrm{B} = \frac{a}{bR}.$$

$$T_\mathrm{B} = \frac{1.352\,\mathrm{dm^6\,atm\,mol^{-2}}}{(0.0387\,\mathrm{dm^3\,mol^{-1}}) \times (0.08206\,\mathrm{dm^3\,atm\,K^{-1}\,mol^{-1}})} = 426\,\mathrm{K}.$$

The experimental value (Table 1.5) is 327.2 K. The discrepancy may be explained by two considerations.

1. Terms beyond the first power in p should not be dropped in the expansion for Z.
2. Nitrogen is only approximately a van der Waals gas.

$$\text{When } Z = 1,\ V_m = \frac{RT}{p},\ \text{and using } T_B = 327.2\,\text{K}$$

$$= \frac{(0.08206\,\text{dm}^3\,\text{atm}\,\text{K}^{-1}\text{mol}^{-1}) \times 327.2\,\text{K}}{10.0\,\text{atm}}$$

$$= \boxed{2.69\,\text{dm}^3\,\text{mol}^{-1}}$$

and this is the ideal value of V_m. Using the experimental value of T_B and inserting this value into the expansion for V_m above, we have

$$V_m = \frac{0.08206\,\text{dm}^3\,\text{atm}\,\text{K}^{-1}\text{mol}^{-1} \times 327.2\,\text{K}}{10.0\,\text{atm}} + \left\{0.0387\,\text{dm}^3\text{mol}^{-1} - \left(\frac{1.352\,\text{dm}^6\text{atm}\,\text{mol}^{-2}}{0.08206\,\text{dm}^3\,\text{atm}\,\text{K}^{-1}\text{mol}^{-1} \times 327.2\,\text{K}}\right)\right\}$$

$$= (2.68\overline{5} - 0.012)\,\text{dm}^3\text{mol}^{-1} = \boxed{2.67\,\text{dm}^3\,\text{mol}^{-1}}$$

$$\text{and } Z = \frac{V_m}{V_m^\circ} = \frac{2.67\,\text{dm}^3\,\text{mol}^{-1}}{2.69\,\text{dm}^3\,\text{mol}^{-1}} = 0.992 \approx 1.$$

(c) $T_I = 621\,\text{K}$ [Table 2.9].

$$V_m = \frac{0.08206\,\text{dm}^3\text{atm}\,\text{K}^{-1}\text{mol}^{-1} \times 621\,\text{K}}{10.0\,\text{atm}} + \left\{0.0387\,\text{dm}^3\,\text{mol}^{-1} - \left(\frac{1.352\,\text{dm}^6\text{atm}\,\text{mol}^{-2}}{0.08206\,\text{dm}^3\,\text{atm}\,\text{K}^{-1}\text{mol}^{-1} \times 621\,\text{K}}\right)\right\}$$

$$= (5.09\overline{6} + 0.012)\,\text{dm}^3\,\text{mol}^{-1} = \boxed{5.11\,\text{dm}^3\,\text{mol}^{-1}}$$

$$\text{and } Z = \frac{5.11\,\text{dm}^3\text{mol}^{-1}}{5.10\,\text{dm}^3\,\text{mol}^{-1}} = 1.002 \approx 1.$$

Based on the values of T_B and T_I given in Tables 1.4 and 2.9 and assuming that N_2 is a van der Waals gas, the calculated value of Z is closest to 1 at $\boxed{T_I}$, but the difference from the value at T_B is less than the accuracy of the method.

P1.11 **(a)** $V_m = \dfrac{\text{molar mass}}{\text{density}} = \dfrac{M}{\rho} = \dfrac{18.02\,\text{g}\,\text{mol}^{-1}}{1.332 \times 10^2\,\text{g}\,\text{dm}^{-3}} = \boxed{0.1353\,\text{dm}^3\,\text{mol}^{-1}}.$

(b) $Z = \dfrac{pV_m}{RT}\ [1.17\text{b}] = \dfrac{(327.6\,\text{atm}) \times (0.1353\,\text{dm}^3\,\text{mol}^{-1})}{(0.08206\,\text{dm}^3\,\text{atm}\,\text{K}^{-1}\,\text{mol}^{-1}) \times (776.4\,\text{K})} = \boxed{0.6957}.$

(c) Two expansions for Z based on the van der Waals equation are given in Problem 1.9. They are

$$
\begin{aligned}
Z &= 1 + \left(b - \frac{a}{RT}\right) \times \left(\frac{1}{V_\mathrm{m}}\right) + \cdots \\
&= 1 + \left\{(0.0305\,\mathrm{dm^3\,mol^{-1}}) - \left(\frac{5.464\,\mathrm{dm^6\,atm\,mol^{-2}}}{(0.08206\,\mathrm{dm^3\,atm\,K^{-1}\,mol^{-1}}) \times (776.4\,\mathrm{K})}\right)\right\} \\
&\quad \times \frac{1}{0.1353\,\mathrm{dm^3\,mol^{-1}}} = 1 - 0.4084 = 0.5916 \approx 0.59. \\
Z &= 1 + \left(\frac{1}{RT}\right) \times \left(b - \frac{a}{RT}\right) \times (p) + \cdots \\
&= 1 + \frac{1}{(0.08206\,\mathrm{dm^3\,atm\,K^{-1}\,mol^{-1}}) \times (776.4\,\mathrm{K})} \\
&\quad \times \left\{(0.0305\,\mathrm{dm^3\,mol^{-1}}) - \left(\frac{5.464\,\mathrm{dm^6\,atm\,mol^{-2}}}{(0.08206\,\mathrm{dm^3\,atm\,K^{-1}\,mol^{-1}}) \times (776.4\,\mathrm{K})}\right)\right\} \times 327.6\,\mathrm{atm} \\
&= 1 - 0.2842 \approx \boxed{0.72}.
\end{aligned}
$$

In this case the expansion in p gives a value close to the experimental value; the expansion in $\dfrac{1}{V_\mathrm{m}}$ is not as good. However, when terms beyond the second are included the results from the two expansions for Z converge.

P1.13 $V_\mathrm{c} = 2b, \qquad T_\mathrm{c} = \dfrac{a}{4bR}$ [Table 1.7]

Hence, with V_c and T_c from Table 1.5, $b = \dfrac{1}{2}V_\mathrm{c} = \dfrac{1}{2} \times (118.8\,\mathrm{cm^3\,mol^{-1}}) = \boxed{59.4\,\mathrm{cm^3\,mol^{-1}}}$.

$$
\begin{aligned}
a &= 4bRT_\mathrm{c} = 2RT_\mathrm{c}V_\mathrm{c} \\
&= (2) \times (8.206 \times 10^{-2}\,\mathrm{dm^3\,atm\,K^{-1}\,mol^{-1}}) \times (289.75\,\mathrm{K}) \times (118.8 \times 10^{-3}\,\mathrm{dm^3\,mol^{-1}}) \\
&= \boxed{5.649\,\mathrm{dm^6\,atm\,mol^{-2}}}.
\end{aligned}
$$

Hence

$$
\begin{aligned}
p &= \frac{RT}{V_\mathrm{m} - b}\mathrm{e}^{-a/RTV_\mathrm{m}} = \frac{nRT}{V - nb}\mathrm{e}^{-na/RTV} \\
&= \frac{(1.0\,\mathrm{mol}) \times (8.206 \times 10^{-2}\,\mathrm{dm^3\,atm\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K})}{(1.0\,\mathrm{dm^3}) - (1.0\,\mathrm{mol}) \times (59.4 \times 10^{-3}\,\mathrm{dm^3\,mol^{-1}})} \\
&\quad \times \exp\left(\frac{-(1.0\,\mathrm{mol}) \times (5.649\,\mathrm{dm^6\,atm\,mol^{-2}})}{(8.206 \times 10^{-2}\,\mathrm{dm^3\,atm\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K}) \times (1.0\,\mathrm{dm^6\,atm\,mol^{-1}})}\right) \\
&= 26.\bar{0}\,\mathrm{atm} \times \mathrm{e}^{-0.23\bar{1}} = \boxed{21\,\mathrm{atm}}.
\end{aligned}
$$

Solutions to theoretical problems

P1.15 This expansion has already been given in the solutions to Exercise 1.20(a) and Problem 1.14; the result is

$$p = \frac{RT}{V_{\mathrm{m}}}\left(1 + \left[b - \frac{a}{RT}\right]\frac{1}{V_{\mathrm{m}}} + \frac{b^2}{V_{\mathrm{m}}^2} + \cdots\right).$$

Compare this expansion with $p = \frac{RT}{V_{\mathrm{m}}}\left(1 + \frac{B}{V_{\mathrm{m}}} + \frac{C}{V_{\mathrm{m}^2}} + \cdots\right)$ [1.19]

and hence find $\boxed{B = b - \frac{a}{RT}}$ and $\boxed{C = b^2}$.

Since $C = 1200\,\mathrm{cm^6\,mol^{-2}}$, $\quad b = C^{1/2} = \boxed{34.6\,\mathrm{cm^3\,mol^{-1}}}$

$$a = RT(b - B) = (8.206 \times 10^{-2}) \times (273\,\mathrm{dm^3\,atm\,mol^{-1}}) \times (34.6 + 21.7)\,\mathrm{cm^3\,mol^{-1}}$$

$$= (22.4\bar{0}\,\mathrm{dm^3\,atm\,mol^{-1}}) \times (56.3 \times 10^{-3}\,\mathrm{dm^3\,mol^{-1}}) = \boxed{1.26\,\mathrm{dm^6\,atm\,mol^{-2}}}.$$

P1.17 The critical point corresponds to a point of zero slope that is simultaneously a point of inflection in a plot of pressure versus molar volume. A critical point exists if there are values of p, V, and T that result in a point that satisfies these conditions.

$$p = \frac{RT}{V_{\mathrm{m}}} - \frac{B}{V_{\mathrm{m}}^2} + \frac{C}{V_{\mathrm{m}}^3}.$$

$$\left.\begin{aligned} \left(\frac{\partial p}{\partial V_{\mathrm{m}}}\right)_T &= -\frac{RT}{V_{\mathrm{m}}^2} + \frac{2B}{V_{\mathrm{m}}^3} - \frac{3C}{V_{\mathrm{m}}^4} = 0 \\ \left(\frac{\partial^2 p}{\partial V_{\mathrm{m}}^2}\right)_T &= \frac{2RT}{V_{\mathrm{m}}^3} - \frac{6B}{V_{\mathrm{m}}^4} + \frac{12C}{V_{\mathrm{m}}^5} = 0 \end{aligned}\right\} \text{ at the critical point.}$$

That is, $\left.\begin{aligned} -RT_{\mathrm{c}}V_{\mathrm{c}}^2 + 2BV_{\mathrm{c}} - 3C &= 0 \\ RT_{\mathrm{c}}V_{\mathrm{c}}^2 - 3BV_{\mathrm{c}} + 6C &= 0 \end{aligned}\right\}$

which solve to $V_{\mathrm{c}} = \boxed{\frac{3C}{B}}$, $\boxed{T_{\mathrm{c}} = \frac{B^2}{3RC}}$.

Now use the equation of state to find p_{c}

$$p_{\mathrm{c}} = \frac{RT_{\mathrm{c}}}{V_{\mathrm{c}}} - \frac{B}{V_{\mathrm{c}}^2} + \frac{C}{V_{\mathrm{c}}^3} = \left(\frac{RB^2}{3RC}\right) \times \left(\frac{B}{3C}\right) - B\left(\frac{B}{3C}\right)^2 + C\left(\frac{B}{3C}\right)^3 = \boxed{\frac{B^3}{27C^2}}.$$

It follows that $Z_{\mathrm{c}} = \frac{p_{\mathrm{c}}V_{\mathrm{c}}}{RT_{\mathrm{c}}} = \left(\frac{B^3}{27C^2}\right) \times \left(\frac{3C}{B}\right) \times \left(\frac{1}{R}\right) \times \left(\frac{3RC}{B^2}\right) = \boxed{\frac{1}{3}}$.

P1.19 For a real gas we may use the virial expansion in terms of p [1.18]

$$p = \frac{nRT}{V}(1 + B'p + \cdots) = \rho\frac{RT}{M}(1 + B'p + \cdots)$$

which rearranges to $\dfrac{p}{\rho} = \dfrac{RT}{M} + \dfrac{RT\,B'}{M}p + \cdots$.

Therefore, the limiting slope of a plot of $\dfrac{p}{\rho}$ against p is $\dfrac{B'RT}{M}$. From Fig. 1.3 the limiting slope is

$$\frac{B'RT}{M} = \frac{(5.84 - 5.44) \times 10^4\ \mathrm{m^2\,s^{-2}}}{(10.132 - 1.223) \times 10^4\ \mathrm{Pa}} = 4.4 \times 10^{-2}\ \mathrm{kg^{-1}\,m^3}.$$

From Fig. 1.3, $\dfrac{RT}{M} = 5.40 \times 10^4\ \mathrm{m^2\,s^{-2}}$; hence

$$B' = \frac{4.4 \times 10^{-2}\ \mathrm{kg^{-1}\,m^3}}{5.40 \times 10^4\ \mathrm{m^2\,s^{-2}}} = 0.81 \times 10^{-6}\ \mathrm{Pa^{-1}},$$

$$B' = (0.81 \times 10^{-6}\ \mathrm{Pa^{-1}}) \times (1.0133 \times 10^5\ \mathrm{Pa\,atm^{-1}}) = \boxed{0.082\ \mathrm{atm^{-1}}}.$$

$$\begin{aligned} B &= RTB' \text{ [Problem 1.18]} \\ &= (8.206 \times 10^{-2}\ \mathrm{dm^3\,atm\,K^{-1}\,mol^{-1}}) \times (298\ \mathrm{K}) \times (0.082\ \mathrm{atm^{-1}}) \\ &= \boxed{2.0\ \mathrm{dm^3\,mol^{-1}}}. \end{aligned}$$

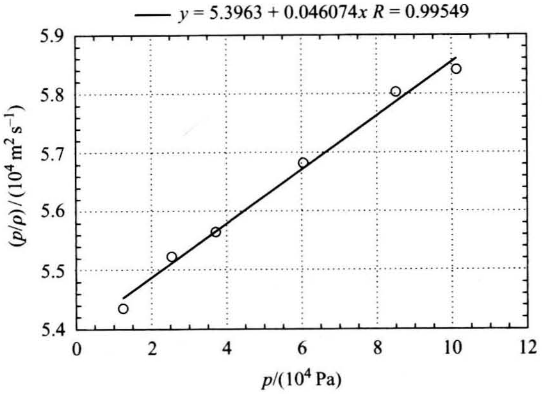


Figure 1.3

P1.21 The critical temperature is that temperature above which the gas cannot be liquefied by the application of pressure alone. Below the critical temperature two phases, liquid and gas, may coexist at equilibrium, and in the two-phase region there is more than one molar volume corresponding to the same conditions of temperature and pressure. Therefore, any equation of state that can even approximately describe this situation must allow for more than one real root for the molar volume at some values of T and p, but as the temperature is increased above T_c, allows only one real root. Thus, appropriate equations of state must be equations of odd degree in V_m.

The equation of state for gas A may be rewritten $V_m^2 - (RT/p)V_m - (RTb/p) = 0$, which is a quadratic and never has just one real root. Thus, this equation can never model critical behavior. It could possibly model in a very crude manner a two-phase situation, since there are some conditions under which a quadratic has two real positive roots, but not the process of liquefaction.

The equation of state of gas B is a first-degree equation in V_m and therefore can never model critical behavior, the process of liquefaction, or the existence of a two-phase region.

A cubic equation is the equation of lowest degree that can show a cross-over from more than one real root to just one real root as the temperature increases. The van der Waals equation is a cubic equation in V_m.

P1.23 The two masses represent the same volume of gas under identical conditions, and therefore, the same number of molecules (Avogadro's principle) and moles, n. Thus, the masses can be expressed as

$$nM_N = 2.2990\,\mathrm{g}$$

for 'chemical nitrogen' and

$$n_{Ar}M_{Ar} + n_N M_N = n[x_{Ar}M_{Ar} + (1 - x_{Ar})M_N] = 2.3102\,\mathrm{g}$$

for 'atmospheric nitrogen'. Dividing the latter expression by the former yields

$$\frac{x_{Ar}M_{Ar}}{M_N} + (1 - x_{Ar}) = \frac{2.3102}{2.2990} \quad \text{so} \quad x_{Ar}\left(\frac{M_{Ar}}{M_N} - 1\right) = \frac{2.3102}{2.2990} - 1$$

and $x_{Ar} = \dfrac{(2.3102/2.2990) - 1}{(M_{Ar}/M_N) - 1} = \dfrac{(2.3102/2.2990) - 1}{(39.95\,\mathrm{g\,mol^{-1}})/(28.013\,\mathrm{g\,mol^{-1}} - 1)} = \boxed{0.011}$.

COMMENT. This value for the mole fraction of argon in air is close to the modern value.

Solutions to applications

P1.25 1 t = 10^3 kg. Assume 300 t per day.

$$n(SO_2) = \frac{300 \times 10^3\,\mathrm{kg}}{64 \times 10^{-3}\,\mathrm{kg\,mol^{-1}}} = 4.7 \times 10^6\,\mathrm{mol}.$$

$$V = \frac{nRT}{p} = \frac{(4.7 \times 10^6\,\mathrm{mol}) \times (0.082\,\mathrm{dm^3 atm\,K^{-1}mol^{-1}}) \times 1073\,\mathrm{K}}{1.0\,\mathrm{atm}} = \boxed{4.1 \times 10^8\,\mathrm{dm^3}}.$$

P1.27 The pressure at the base of a column of height H is $p = \rho g H$ (Example 1.1). But the pressure at any altitude h within the atmospheric column of height H depends only on the air above it; therefore

$$p = \rho g(H - h) \text{ and } \mathrm{d}p = -\rho g\,\mathrm{d}h.$$

Since $\rho = \dfrac{pM}{RT}$ [Problem 1.2], $\mathrm{d}p = -\dfrac{pMg\mathrm{d}h}{RT}$, implying that $\dfrac{\mathrm{d}p}{p} = -\dfrac{Mg\,\mathrm{d}h}{RT}$

This relation integrates to $p = p_0 e^{-Mgh/RT}$

For air $M \approx 29\,\mathrm{g\,mol^{-1}}$ and at 298 K

$$\frac{Mg}{RT} \approx \frac{(29 \times 10^{-3}\,\mathrm{kg\,mol^{-1}}) \times (9.81\,\mathrm{m\,s^{-2}})}{2.48 \times 10^3\,\mathrm{J\,mol^{-1}}} = 1.1\bar{5} \times 10^{-4}\mathrm{m^{-1}}\ [1\,\mathrm{J} = 1\,\mathrm{kg\,m^2\,s^{-2}}].$$

(a) $h = 15\text{ cm}$.

$$p = p_0 \times e^{(-0.15\,\text{m})\times(1.1\bar{5}\times10^{-4}\,\text{m}^{-1})} = 0.99\overline{998}\,p_0; \quad \frac{p - p_0}{p_0} = \boxed{0.00}.$$

(b) $h = 11\text{ km} = 1.1 \times 10^4\text{ m}$.

$$p = p_0 \times e^{(-1.1\times10^{-4})\times(1.1\bar{5}\times10^{-4}\text{m}^{-1})} = 0.28\,p_0; \quad \frac{p - p_0}{p_0} = \boxed{-0.72}.$$

P1.29 Refer to Fig. 1.4.

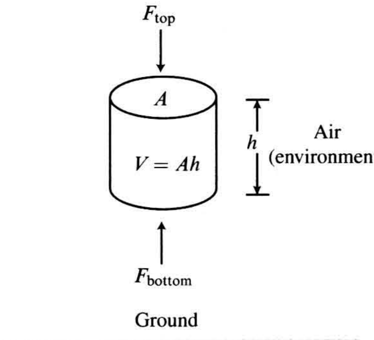


Figure 1.4

The buoyant force on the cylinder is

$$\begin{aligned} F_{\text{buoy}} &= F_{\text{bottom}} - F_{\text{top}} \\ &= A(p_{\text{bottom}} - p_{\text{top}}) \end{aligned}$$

according to the barometric formula.

$$p_{\text{top}} = p_{\text{bottom}}\text{e}^{-Mgh/RT}$$

where M is the molar mass of the environment (air). Since h is small, the exponential can be expanded in a Taylor series around $h = 0$ $\left(\text{e}^{-x} = 1 - x + \frac{1}{2!}x^2 + \cdots\right)$. Keeping the first-order term only yields

$$p_{\text{top}} = p_{\text{bottom}}\left(1 - \frac{Mgh}{RT}\right).$$

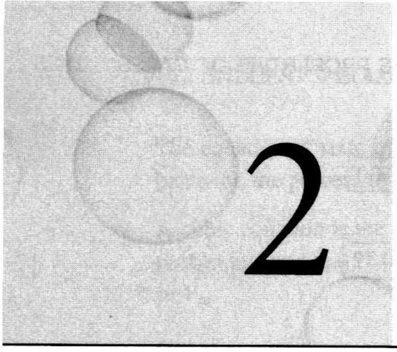
The buoyant force becomes

$$\begin{aligned} F_{\text{buoy}} &= Ap_{\text{bottom}}\left(1 - 1 + \frac{Mgh}{RT}\right) = Ah\left(\frac{p_{\text{bottom}}M}{RT}\right)g \\ &= \left(\frac{p_{\text{bottom}}VM}{RT}\right)g = nMg \quad \left[n = \frac{p_{\text{bottom}}V}{RT}\right] \end{aligned}$$

n is the number of moles of the environment (air) displaced by the balloon, and $nM = m$, the mass of the displaced environment. Thus $F_{\text{buoy}} = mg$. The net force is the difference between the buoyant force and the weight of the balloon. Thus

$$F_{\text{net}} = mg - m_{\text{balloon}} \quad g = (m - m_{\text{balloon}})g$$

This is Archimedes' principle.



2

The First Law

Answers to discussion questions

D2.1 Work is a precisely defined mechanical concept. It is produced from the application of a force through a distance. The technical definition is based on the realization that both force and displacement are vector quantities and it is the component of the force acting in the direction of the displacement that is used in the calculation of the amount of work, that is, work is the scalar product of the two vectors. In vector notation $w = -\boldsymbol{f} \cdot \boldsymbol{d} = -fd\cos\theta$, where θ is the angle between the force and the displacement. The negative sign is inserted to conform to the standard thermodynamic convention.

Heat is associated with a non-adiabatic process and is defined as the difference between the adiabatic work and the non-adiabatic work associated with the same change in state of the system. This is the formal (and best) definition of heat and is based on the definition of work. A less precise definition of heat is the statement that heat is the form of energy that is transferred between bodies in thermal contact with each other by virtue of a difference in temperature.

At the molecular level, work is a transfer of energy that results in orderly motion of the atoms and molecules in a system; heat is a transfer of energy that results in disorderly motion. See *Molecular interpretation* 2.1 for a more detailed discussion.

D2.3 The difference results from the definition $H = U + PV$; hence $\Delta H = \Delta U + \Delta(PV)$. As $\Delta(PV)$ is not usually zero, except for isothermal processes in a perfect gas, the difference between ΔH and ΔU is a non-zero quantity. As shown in Sections 2.4 and 2.5 of the text, ΔH can be interpreted as the heat associated with a process at constant pressure, and ΔU as the heat at constant volume.

D2.5 In the Joule experiment, the change in internal energy of a gas at low pressures (a perfect gas) is zero. Hence in the calculation of energy changes for processes in a perfect gas one can ignore any effect due to a change in volume. This greatly simplifies the calculations involved because one can drop the first term of eqn 2.40 and need work only with $\mathrm{d}U = C_V\,\mathrm{d}T$. In a more sensitive apparatus, Joule would have observed a small temperature change upon expansion of the 'real' gas. Joule's result holds exactly only in the limit of zero pressure where all gases can be considered perfect.

The solution to Problem 2.33 shows that the Joule–Thomson coefficient can be expressed in terms of the parameters representing the attractive and repulsive interactions in a real gas. If the attractive forces predominate, then expanding the gas will reduce its energy and hence its temperature. This reduction in temperature could continue until the temperature of the gas falls below its condensation point. This is the principle underlying the liquefaction of gases with the Linde refrigerator, which utilizes the Joule–Thomson effect. See Section 2.12 for a more complete discussion.

D2.7 The vertical axis of a thermogram represents C_p, and the baselines represent the heat capacity associated with simple heating in the absence of structural transformations or similar transitions. In the example shown in Fig. 2.16, the sample undergoes a structural change between T_1 and T_2, so there is no reason to expect C_p after the transition to return to its value before the transition. Just as diamond and graphite have different heat capacities because of their different structures, the structural changes that occur during the measurement of a thermogram can also give rise to a change in heat capacity.

Solutions to exercises

E2.1(b) The physical definition of work is $\mathrm{d}w = -F\,\mathrm{d}z$ [2.4]

In a gravitational field the force is the weight of the object, which is $F = mg$

If g is constant over the distance the mass moves, $\mathrm{d}w$ may be intergrated to give the total work

$$w = -\int_{z_\mathrm{i}}^{z_\mathrm{f}} F\,\mathrm{d}z = -\int_{z_\mathrm{i}}^{z_\mathrm{f}} mg\,\mathrm{d}z = -mg(z_\mathrm{f} - z_\mathrm{i}) = -mgh \quad \text{where} \quad h = (z_\mathrm{f} - z_\mathrm{i})$$

$$w = -(0.120\,\mathrm{kg}) \times (9.81\,\mathrm{m\,s^{-2}}) \times (50\,\mathrm{m}) = -59\,\mathrm{J} = \boxed{59\,\mathrm{J\ needed}}$$

E2.2(b) This is an expansion against a constant external pressure; hence $w = -p_\mathrm{ex}\Delta V$ [2.8]

The change in volume is the cross-sectional area times the linear displacement:

$$\Delta V = (50.0\,\mathrm{cm^2}) \times (15\,\mathrm{cm}) \times \left(\frac{1\,\mathrm{m}}{100\,\mathrm{cm}}\right)^3 = 7.5 \times 10^{-4}\,\mathrm{m^3},$$

so $w = -(121 \times 10^3\,\mathrm{Pa}) \times (7.5 \times 10^{-4}\,\mathrm{m^3}) = \boxed{-91\,\mathrm{J}}$ as $1\,\mathrm{Pa\,m^3} = 1\,\mathrm{J}$.

E2.3(b) For all cases $\Delta U = 0$, since the internal energy of a perfect gas depends only on temperature. (See *Molecular interpretation* 2.2 and Section 2.11(b) for a more complete discussion.) From the definition of enthalpy, $H = U + pV$, so $\Delta H = \Delta U + \Delta(pV) = \Delta U + \Delta(nRT)$ (perfect gas). Hence, $\Delta H = 0$ as well, at constant temperature for all processes in a perfect gas.

(a) $\boxed{\Delta U = \Delta H = 0}$

$$w = -nRT\ln\left(\frac{V_\mathrm{f}}{V_\mathrm{i}}\right) \text{ [2.11]}$$

$$= -(2.00\,\mathrm{mol}) \times (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (22 + 273)\,\mathrm{K} \times \ln\frac{31.7\,\mathrm{dm^3}}{22.8\,\mathrm{dm^3}} = \boxed{-1.62 \times 10^3\,\mathrm{J}}$$

$$q = -w = \boxed{1.62 \times 10^3\,\mathrm{J}}$$

(b) $\boxed{\Delta U = \Delta H = 0}$

$w = -p_\mathrm{ex}\Delta V$ [2.8]

where p_ex in this case can be computed from the perfect gas law

$pV = nRT$

$$\text{so } p = \frac{(2.00\,\text{mol}) \times (8.3145\,\text{J K}^{-1}\text{mol}^{-1}) \times (22 + 273)\,\text{K}}{31.7\,\text{dm}^3} \times (10\,\text{dm m}^{-1})^3 = 1.55 \times 10^5\,\text{Pa}$$

$$\text{and } w = \frac{-(1.55 \times 10^5\,\text{Pa}) \times (31.7 - 22.8)\,\text{dm}^3}{(10\,\text{dm m}^{-1})^3} = \boxed{-1.38 \times 10^3\,\text{J}}$$

$$q = -w = \boxed{1.38 \times 10^3\,\text{J}}$$

(c) $\boxed{\Delta U = \Delta H = 0}$

$\boxed{w = 0}$ [free expansion] $q = \Delta U - w = 0 - 0 = \boxed{0}$

COMMENT. An isothermal free expansion of a perfect gas is also adiabatic.

E2.4(b) The perfect gas law leads to

$$\frac{p_1 V}{p_2 V} = \frac{nRT_1}{nRT_2} \quad \text{or} \quad p_2 = \frac{p_1 T_2}{T_1} = \frac{(111\,\text{kPa}) \times (356\,\text{K})}{277\,\text{K}} = \boxed{143\,\text{kPa}}$$

There is no change in volume, so $\boxed{w = 0}$. The heat flow is

$$q = \int C_V\,\mathrm{d}T \approx C_V \Delta T = (2.5) \times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (2.00\,\text{mol}) \times (356 - 277)\,\text{K}$$

$$= \boxed{3.28 \times 10^3\,\text{J}}$$

$$\Delta U = q + w = \boxed{3.28 \times 10^3\,\text{J}}$$

E2.5(b) **(a)** $w = -p_{\text{ex}} \Delta V = \dfrac{-(7.7 \times 10^3\,\text{Pa}) \times (2.5\,\text{dm}^3)}{(10\,\text{dm m}^{-1})^3} = \boxed{-19\,\text{J}}$

(b) $w = -nRT \ln\left(\dfrac{V_\text{f}}{V_\text{i}}\right)$ [2.11]

$$w = -\left(\frac{6.56\,\text{g}}{39.95\,\text{g mol}^{-1}}\right) \times \left(8.3145\,\text{J K}^{-1}\text{mol}^{-1}\right) \times (305\text{K}) \times \ln \frac{(2.5 + 18.5)\,\text{dm}^3}{18.5\,\text{dm}^3}$$

$$= \boxed{-52.8\,\text{J}}$$

E2.6(b) $\Delta H = \Delta_{\text{cond}} H = -\Delta_{\text{vap}} H = -(2.00\,\text{mol}) \times (35.3\,\text{kJ mol}^{-1}) = \boxed{-70.6\,\text{kJ}}$

Since the condensation is done isothermally and reversibly, the external pressure is constant at 1.00 atm. Hence,

$$q = q_p = \Delta H = \boxed{-70.6\,\text{kJ}}$$

$$w = -p_{\text{ex}} \Delta V \;[2.8] \quad \text{where} \quad \Delta V = V_{\text{liq}} - V_{\text{vap}} \approx -V_{\text{vap}} \quad \text{because} \quad V_{\text{liq}} \ll V_{\text{vap}}$$

On the assumption that methanol vapor is a perfect gas, $V_{\text{vap}} = nRT/p$ and $p = p_{\text{ex}}$, since the condensation is done reversibly. Hence,

$$w \approx nRT = (2.00\,\text{mol}) \times (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (64 + 273)\,\text{K} = \boxed{5.60 \times 10^3\,\text{J}}$$

and $\Delta U = q + w = (-70.6 + 5.60)\,\text{kJ} = \boxed{-65.0\,\text{kJ}}$

E2.7(b) The reaction is

$$\mathrm{Zn} + 2\mathrm{H}^+ \rightarrow \mathrm{Zn}^{2+} + \mathrm{H}_2$$

so it liberates 1 mol of $H_2(g)$ for every 1 mol Zn used. Work at constant pressure is

$$w = -p_{\mathrm{ex}}\Delta V = -pV_{\mathrm{gas}} = -nRT$$

$$= -\left(\frac{5.0\,\mathrm{g}}{65.4\,\mathrm{g\,mol^{-1}}}\right) \times \left(8.3145\,\mathrm{J\,K^{-1}mol^{-1}}\right) \times (23 + 273)\ \mathrm{K} = \boxed{-188\ \mathrm{J}}$$

E2.8(b) **(a)** At constant pressure, $q = \Delta H$.

$$q = \int C_{\mathrm{p}}\mathrm{d}T = \int_{0+273\,\mathrm{K}}^{100+273\,\mathrm{K}} [20.17 + (0.4001)T/\mathrm{K}]\,\mathrm{d}T\ \mathrm{J\,K^{-1}}$$

$$= \left[(20.17)\,T + \frac{1}{2}(0.4001) \times \left(\frac{T^2}{\mathrm{K}}\right)\right]\Bigg|_{273\,\mathrm{K}}^{373\,\mathrm{K}}\ \mathrm{J\,K^{-1}}$$

$$= \left[(20.17) \times (373 - 273) + \frac{1}{2}(0.4001) \times (373^2 - 273^2)\right]\mathrm{J} = \boxed{14.9 \times 10^3\ \mathrm{J}} = \Delta H$$

$$w = -p\Delta V = -nR\Delta T = -\,(1.00\,\mathrm{mol}) \times \left(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}\right) \times (100\,\mathrm{K}) = \boxed{-831\ \mathrm{J}}$$

$$\Delta U = q + w = (14.9 - 0.831)\,\mathrm{kJ} = \boxed{14.1\ \mathrm{kJ}}$$

(b) The energy and enthalpy of a perfect gas depend on temperature alone. Thus, $\Delta H = \boxed{14.9\ \mathrm{kJ}}$ and $\Delta U = \boxed{14.1\ \mathrm{kJ}}$ as above. At constant volume, $w = \boxed{0}$ and $\Delta U = q$, so $q = \boxed{+14.1\ \mathrm{kJ}}$.

E2.9(b) For reversible adiabatic expansion

$$T_{\mathrm{f}} = T_{\mathrm{i}}\left(\frac{V_{\mathrm{i}}}{V_{\mathrm{f}}}\right)^{1/c} \quad [2.28\mathrm{a}]$$

where

$$c = \frac{C_{V,\mathrm{m}}}{R} = \frac{C_{p,\mathrm{m}} - R}{R} = \frac{(37.11 - 8.3145)\ \mathrm{J\,K^{-1}mol^{-1}}}{8.3145\,\mathrm{J\ K^{-1}mol^{-1}}} = 3.463,$$

so the final temperature is

$$T_{\mathrm{f}} = (298.15\,\mathrm{K}) \times \left(\frac{500 \times 10^{-3}\,\mathrm{dm^3}}{2.00\,\mathrm{dm^3}}\right)^{1/3.463} = \boxed{200\ \mathrm{K}}$$

E2.10(b) Reversible adiabatic work is

$$w = C_V\Delta T\ \ [2.27] = n(C_{p,\mathrm{m}} - R) \times (T_{\mathrm{f}} - T_{\mathrm{i}})$$

where the temperatures are related by [solution to Exercise 2.15(b)]

$$T_{\mathrm{f}} = T_{\mathrm{i}}\left(\frac{V_{\mathrm{i}}}{V_{\mathrm{f}}}\right)^{1/c}\ [2.28\mathrm{a}] \quad \text{where} \quad c = \frac{C_{V,\mathrm{m}}}{R} = \frac{C_{p,\mathrm{m}} - R}{R} = 2.503$$

$$\text{So } T_{\mathrm{f}} = [(23.0 + 273.15)\ \mathrm{K}] \times \left(\frac{400 \times 10^{-3}\mathrm{dm}^3}{2.00\,\mathrm{dm}^3}\right)^{1/2.503} = 156\ \mathrm{K}$$

$$\text{and } w = \left(\frac{3.12\ \mathrm{g}}{28.0\ \mathrm{g\,mol^{-1}}}\right) \times (29.125 - 8.3145)\ \mathrm{J\,K^{-1}\,mol^{-1}} \times (156 - 296)\ \mathrm{K} = \boxed{-325\ \mathrm{J}}$$

E2.11(b) For reversible adiabatic expansion

$$p_{\mathrm{f}}V_{\mathrm{f}}^{\gamma} = p_{\mathrm{i}}V_{\mathrm{i}}^{\gamma}\ [2.29] \quad \text{so} \quad p_{\mathrm{f}} = p_{\mathrm{i}}\left(\frac{V_{\mathrm{i}}}{V_{\mathrm{f}}}\right)^{\gamma} = (8.73\,\mathrm{Torr}) \times \left(\frac{500 \times 10^{-3}\,\mathrm{dm}^3}{3.0\,\mathrm{dm}^3}\right)^{1.3} = \boxed{8.5\ \mathrm{Torr}}$$

E2.12(b)

$$q_p = nC_{p,\mathrm{m}}\Delta T\ [2.24]$$

$$C_{p,\mathrm{m}} = \frac{q_p}{n\Delta T} = \frac{178\,\mathrm{J}}{1.9\,\mathrm{mol} \times 1.78\,\mathrm{K}} = \boxed{53\ \mathrm{J\,K^{-1}\ mol^{-1}}}$$

$$C_{V,\mathrm{m}} = C_{p,\mathrm{m}} - R = (53 - 8.3)\,\mathrm{J\,K^{-1}\ mol^{-1}} = \boxed{45\ \mathrm{J\,K^{-1}\ mol^{-1}}}$$

E2.13(b)

$$\Delta H = q_p = C_p\Delta T\ [2.23\mathrm{b}, 2.24] = nC_{p,\mathrm{m}}\Delta T$$

$$\Delta H = q_p = (2.0\,\mathrm{mol}) \times (37.11\,\mathrm{J\,K^{-1}\ mol^{-1}}) \times (277 - 250)\ \mathrm{K} = \boxed{2.0 \times 10^3\ \mathrm{J\ mol^{-1}}}$$

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + nR\Delta T \quad \text{so} \quad \Delta U = \Delta H - nR\Delta T$$

$$\Delta U = 2.0 \times 10^3\,\mathrm{J\,mol^{-1}} - (2.0\,\mathrm{mol}) \times (8.3145\,\mathrm{J\,K^{-1}\ mol^{-1}}) \times (277 - 250)\ \mathrm{K}$$

$$= \boxed{1.6 \times 10^3\ \mathrm{J\ mol^{-1}}}$$

E2.14(b) In an adiabatic process, $q = \boxed{0}$. Work against a constant external pressure is

$$w = -p_{\mathrm{ex}}\Delta V = \frac{-(78.5 \times 10^3\,\mathrm{Pa}) \times (4 \times 15 - 15)\,\mathrm{dm}^3}{(10\,\mathrm{dm\,m^{-1}})^3} = \boxed{-3.5 \times 10^3\ \mathrm{J}}$$

$$\Delta U = q + w = \boxed{-3.5 \times 10^3\ \mathrm{J}}$$

One can also relate adiabatic work to ΔT (eqn 2.27):

$$w = C_V\Delta T = n(C_{p,\mathrm{m}} - R)\Delta T \quad \text{so} \quad \Delta T = \frac{w}{n(C_{p,\mathrm{m}} - R)},$$

$$\Delta T = \frac{-3.5 \times 10^3\ \mathrm{J}}{(5.0\,\mathrm{mol}) \times (37.11 - 8.3145)\,\mathrm{J\,K^{-1}\ mol^{-1}}} = \boxed{-24\ \mathrm{K}}.$$

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + nR\Delta T,$$

$$= -3.5 \times 10^3\,\mathrm{J} + (5.0\,\mathrm{mol}) \times (8.3145\,\mathrm{J\,K^{-1}\ mol^{-1}}) \times (-24\,\mathrm{K}) = \boxed{-4.5 \times 10^3\ \mathrm{J}}$$

E2.15(b) In an adiabatic process, the initial and final pressures are related by (eqn 2.29)

$$p_{\mathrm{f}}V_{\mathrm{f}}^{\gamma} = p_{\mathrm{i}}V_{\mathrm{i}}^{\gamma} \quad \text{where} \quad \gamma = \frac{C_{p,\mathrm{m}}}{C_{V,\mathrm{m}}} = \frac{C_{p,\mathrm{m}}}{C_{p,\mathrm{m}} - R} = \frac{20.8\,\mathrm{J\,K^{-1}\ mol^{-1}}}{(20.8 - 8.31)\,\mathrm{J\,K^{-1}\ mol^{-1}}} = 1.67$$

Find V_{i} from the perfect gas law:

$$V_{\mathrm{i}} = \frac{nRT_{\mathrm{i}}}{p_{\mathrm{i}}} = \frac{(1.5\,\mathrm{mol})(8.31\,\mathrm{J\,K^{-1}\,mol^{-1}})(315\,\mathrm{K})}{230\times10^{3}\,\mathrm{Pa}} = 0.017\bar{1}\,\mathrm{m^3}$$

$$\text{so}\;\; V_{\mathrm{f}} = V_{\mathrm{i}}\left(\frac{p_{\mathrm{i}}}{p_{\mathrm{f}}}\right)^{1/\gamma} = (0.017\bar{1}\mathrm{m^3})\left(\frac{230\,\mathrm{kPa}}{170\,\mathrm{kPa}}\right)^{1/1.67} = \boxed{0.020\bar{5}\,\mathrm{m^3}}.$$

Find the final temperature from the perfect gas law:

$$T_{\mathrm{f}} = \frac{p_{\mathrm{f}}V_{\mathrm{f}}}{nR} = \frac{(170\times10^{3}\,\mathrm{Pa})\times(0.020\bar{5}\,\mathrm{m^3})}{(1.5\,\mathrm{mol})(8.31\,\mathrm{J\,K^{-1}\,mol^{-1}})} = \boxed{27\bar{9}\,\mathrm{K}}$$

Adiabatic work is (eqn 2.27)

$$w = C_V\Delta T = (20.8-8.31)\,\mathrm{J\,K^{-1}\,mol^{-1}}\times1.5\,\mathrm{mol}\times(27\bar{9}-315)\,\mathrm{K} = \boxed{-6.\bar{7}\times10^{2}\,\mathrm{J}}$$

E2.16(b) At constant pressure

$$q = \Delta H = n\Delta_{\mathrm{vap}}H^{\ominus} = (0.75\,\mathrm{mol})\times(32.0\,\mathrm{kJ\,mol^{-1}}) = \boxed{24.\bar{0}\,\mathrm{kJ}}$$

$$\text{and}\;\; w = -p\Delta V \approx -pV_{\mathrm{vapor}} = -nRT = -(0.75\,\mathrm{mol})\times(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\times(260\,\mathrm{K})$$

$$w = -1.6\times10^{3}\mathrm{J} = \boxed{-1.6\,\mathrm{kJ}}$$

$$\Delta U = w + q = 24.\bar{0} - 1.6\,\mathrm{kJ} = \boxed{22.\bar{4}\,\mathrm{kJ}}$$

COMMENT. Because the vapor is here treated as a perfect gas, the specific value of the external pressure provided in the statement of the exercise does not affect the numerical value of the answer.

E2.17(b) The reaction is

$$\mathrm{C_6H_5OH(l)} + 7\mathrm{O_2(g)} \rightarrow 6\mathrm{CO_2(g)} + 3\mathrm{H_2O(l)}$$

$$\Delta_{\mathrm{c}}H^{\ominus} = 6\Delta_{\mathrm{f}}H^{\ominus}(\mathrm{CO_2}) + 3\Delta_{\mathrm{f}}H^{\ominus}(\mathrm{H_2O}) - \Delta_{\mathrm{f}}H^{\ominus}(\mathrm{C_6H_5OH}) - 7\Delta_{\mathrm{f}}H^{\ominus}(\mathrm{O_2})$$

$$= [6(-393.15) + 3(-285.83) - (-165.0) - 7(0)]\,\mathrm{kJ\,mol^{-1}} = \boxed{-3053.6\ \mathrm{kJ\ mol^{-1}}}$$

E2.18(b) We need $\Delta_{\mathrm{f}}H^{\ominus}$ for the reaction

$$(4)\quad 2\mathrm{B(s)} + 3\mathrm{H_2(g)} \rightarrow \mathrm{B_2H_6(g)}$$

$$\text{reaction}(4) = \text{reaction}(2) + 3\times\text{reaction}(3) - \text{reaction}(1)$$

$$\text{Thus,}\quad \Delta_{\mathrm{f}}H^{\ominus} = \Delta_{\mathrm{r}}H^{\ominus}\{\text{reaction}(2)\} + 3\times\Delta_{\mathrm{r}}H^{\ominus}\{\text{reaction}(3)\} - \Delta_{\mathrm{r}}H^{\ominus}\{\text{reaction}(1)\}$$

$$= [-2368 + 3\times(-241.8) - (-1941)]\,\mathrm{kJ\,mol^{-1}} = \boxed{-1152\,\mathrm{kJ\,mol^{-1}}}$$

E2.19(b) For anthracene the reaction is

$$\mathrm{C_{14}H_{10}(s)} + \tfrac{33}{2}\mathrm{O_2(g)} \rightarrow 14\mathrm{CO_2(g)} + 5\mathrm{H_2O(l)}$$

$$\Delta_c U^\ominus = \Delta_c H^\ominus - \Delta n_g RT \text{ [2.21]}, \quad \Delta n_g = -\tfrac{5}{2}\,\mathrm{mol}$$

$$\begin{aligned}\Delta_c U^\ominus &= -7061\,\mathrm{kJ\,mol^{-1}} - \left(-\tfrac{5}{2} \times 8.3 \times 10^{-3}\,\mathrm{kJ\,K^{-1}mol^{-1}} \times 298\,\mathrm{K}\right)\\ &= -7055\,\mathrm{kJ\,mol^{-1}}\end{aligned}$$

$$|q| = |q_V| = \left|n\Delta_c U^\ominus\right| = \left(\frac{2.25 \times 10^{-3}\,\mathrm{g}}{172.23\,\mathrm{g\,mol^{-1}}}\right) \times \left(7055\,\mathrm{kJ\,mol^{-1}}\right) = 0.0922\,\mathrm{kJ}$$

$$C = \frac{|q|}{\Delta T} = \frac{0.0922\,\mathrm{kJ}}{1.35\,\mathrm{K}} = 0.0683\,\mathrm{kJ\,K^{-1}} = \boxed{68.3\,\mathrm{J\,K^{-1}}}$$

When phenol is used the reaction is

$$\mathrm{C_6H_5OH(s)} + \tfrac{15}{2}\mathrm{O_2(g)} \rightarrow 6\mathrm{CO_2(g)} + 3\mathrm{H_2O(l)}$$

$$\Delta_c H^\ominus = -3054\,\mathrm{kJ\,mol^{-1}} \text{ [Table 2.5]}$$

$$\begin{aligned}\Delta_c U &= \Delta_c H - \Delta n_g RT, \quad \Delta n_g = -\tfrac{3}{2}\\ &= (-3054\,\mathrm{kJ\,mol^{-1}}) + (\tfrac{3}{2}) \times (8.314 \times 10^{-3}\,\mathrm{kJ\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K})\\ &= -3050\,\mathrm{kJ\,mol^{-1}}\end{aligned}$$

$$|q| = \left(\frac{135 \times 10^{-3}\,\mathrm{g}}{94.12\,\mathrm{g\,mol^{-1}}}\right) \times \left(3050\,\mathrm{kJ\,mol^{-1}}\right) = 4.37\overline{5}\,\mathrm{kJ}$$

$$\Delta T = \frac{|q|}{C} = \frac{4.37\overline{5}\,\mathrm{kJ}}{0.0683\,\mathrm{kJ\,K^{-1}}} = \boxed{+64.1\,\mathrm{K}}$$

COMMENT. In this case $\Delta_c U^\ominus$ and $\Delta_c H^\ominus$ differed by about 0.1 percent. Thus, to within 3 significant figures, it would not have mattered if we had used $\Delta_c H^\ominus$ instead of $\Delta_c U^\ominus$, but for very precise work it would.

E2.20(b) The reaction is $\mathrm{AgBr(s)} \rightarrow \mathrm{Ag^+(aq)} + \mathrm{Br^-(aq)}$

$$\begin{aligned}\Delta_{\mathrm{sol}} H^\ominus &= \Delta_f H^\ominus(\mathrm{Ag^+, aq}) + \Delta_f H^\ominus(\mathrm{Br^-, aq}) - \Delta_f H^\ominus(\mathrm{AgBr, s})\\ &= [105.58 + (-121.55) - (-100.37)]\,\mathrm{kJ\,mol^{-1}} = \boxed{+84.40\,\mathrm{kJ\,mol^{-1}}}\end{aligned}$$

E2.21(b) The combustion products of graphite and diamond are the same, so the transition C(gr) → C(d) is equivalent to the combustion of graphite plus the reverse of the combustion of diamond, and

$$\Delta_{\mathrm{trans}} H^\ominus = [-393.51 - (395.41)]\,\mathrm{kJ\,mol^{-1}} = \boxed{+1.90\ \mathrm{kJ\,mol^{-1}}}$$

E2.22(b) **(a)** reaction(3) = (−2) × reaction(1) + reaction(2) and $\Delta n_{\mathrm{g}} = -1$

The enthalpies of reactions are combined in the same manner as the equations (Hess's law).

$$\begin{aligned}\Delta_{\mathrm{r}}H^{\ominus}(3) &= (-2)\times\Delta_{\mathrm{r}}H^{\ominus}(1)+\Delta_{\mathrm{r}}H^{\ominus}(2)\\ &= [(-2)\times(52.96)+(-483.64)]\,\mathrm{kJ\,mol^{-1}}\\ &= \boxed{-589.56\,\mathrm{kJ\,mol^{-1}}}\end{aligned}$$

$$\begin{aligned}\Delta_{\mathrm{r}}U^{\ominus} &= \Delta_{\mathrm{r}}H^{\ominus}-\Delta n_{\mathrm{g}}RT\\ &= -589.56\,\mathrm{kJ\,mol^{-1}}-(-3)\times(8.314\,\mathrm{J\,K^{-1}mol^{-1}})\times(298\,\mathrm{K})\\ &= -589.56\,\mathrm{kJ\,mol^{-1}}+7.43\,\mathrm{kJ\,mol^{-1}}=\boxed{-582.13\,\mathrm{kJ\,mol^{-1}}}\end{aligned}$$

(b) $\Delta_{\mathrm{f}}H^{\ominus}$ refers to the formation of one mole of the compound, so

$$\Delta_{\mathrm{f}}H^{\ominus}(\mathrm{HI})=\tfrac{1}{2}\left(52.96\,\mathrm{kJ\,mol^{-1}}\right)=\boxed{26.48\,\mathrm{kJ\,mol^{-1}}}$$

$$\Delta_{\mathrm{f}}H^{\ominus}(\mathrm{H_2O})=\tfrac{1}{2}\left(-483.64\,\mathrm{kJ\,mol^{-1}}\right)=\boxed{-241.82\,\mathrm{kJ\,mol^{-1}}}$$

E2.23(b)

$$\begin{aligned}\Delta_{\mathrm{r}}H^{\ominus} &= \Delta_{\mathrm{r}}U^{\ominus}+RT\Delta n_g\ [2.21]\\ &= -772.7\,\mathrm{kJ\,mol^{-1}}+(5)\times(8.3145\times10^{-3}\,\mathrm{kJ\,K^{-1}mol^{-1}})\times(298\,\mathrm{K})\\ &= \boxed{-760.3\,\mathrm{kJ\,mol^{-1}}}\end{aligned}$$

E2.24(b) Combine the reactions in such a way that the combination is the desired formation reaction. The enthalpies of the reactions are then combined in the same way as the equations to yield the enthalpy of formation.

	$\Delta_{\mathrm{r}}H^{\ominus}/(\mathrm{kJ\,mol^{-1}})$
$\tfrac{1}{2}\mathrm{N_2(g)}+\tfrac{1}{2}\mathrm{O_2(g)}\rightarrow\mathrm{NO(g)}$	$+\,90.25$
$\mathrm{NO(g)}+\tfrac{1}{2}\mathrm{Cl_2(g)}\rightarrow\mathrm{NOCl(g)}$	$-\tfrac{1}{2}(75.5)$
$\tfrac{1}{2}\mathrm{N_2(g)}+\tfrac{1}{2}\mathrm{O_2(g)}+\tfrac{1}{2}\mathrm{Cl_2(g)}\rightarrow\mathrm{NOCl(g)}$	$+\,52.5$

Hence, $\Delta_{\mathrm{f}}H^{\ominus}(\mathrm{NOCl,g})=\boxed{+52.5\,\mathrm{kJ\,mol^{-1}}}$

E2.25(b) According to Kirchhoff's law [2.36]

$$\Delta_{\mathrm{r}}H^{\ominus}(100^{\circ}\mathrm{C})=\Delta_{\mathrm{r}}H^{\ominus}(25\,^{\circ}\mathrm{C})+\int_{25^{\circ}\mathrm{C}}^{100^{\circ}\mathrm{C}}\Delta_{\mathrm{r}}C_p^{\ominus}\,\mathrm{d}T$$

where Δ_{r} as usual signifies a sum over product and reactant species weighted by stoichiometric coefficients. Because $C_{p,\mathrm{m}}$ can frequently be parametrized as

$$C_{p,\mathrm{m}}=a+bT+c/T^2$$

the indefinite integral of $C_{p,\mathrm{m}}$ has the form

$$\int C_{p,\mathrm{m}}\mathrm{d}T = aT + \tfrac{1}{2}bT^2 - c/T$$

Combining this expression with our original integral, we have

$$\Delta_\mathrm{r}H^\ominus(100\,^\circ\mathrm{C}) = \Delta_\mathrm{r}H^\ominus(25\,^\circ\mathrm{C}) + (T\Delta_\mathrm{r}a + \tfrac{1}{2}T^2\Delta_\mathrm{r}b - \Delta_\mathrm{r}c/T)\Big|_{298\,\mathrm{K}}^{373\,\mathrm{K}}$$

Now for the pieces

$$\Delta_\mathrm{r}H^\ominus(25\,^\circ\mathrm{C}) = 2(-285.83\,\mathrm{kJ\,mol^{-1}}) - 2(0) - 0 = -571.66\,\mathrm{kJ\,mol^{-1}}$$

$$\Delta_\mathrm{r}a = [2(75.29) - 2(27.28) - (29.96)]\,\mathrm{J\,K^{-1}\,mol^{-1}} = 0.06606\,\mathrm{kJ\,K^{-1}\,mol^{-1}}$$

$$\Delta_\mathrm{r}b = [2(0) - 2(3.29) - (4.18)] \times 10^{-3}\,\mathrm{J\,K^{-2}\,mol^{-1}} = -10.76 \times 10^{-6}\,\mathrm{kJ\,K^{-2}\,mol^{-1}}$$

$$\Delta_\mathrm{r}c = [2(0) - 2(0.50) - (-1.67)] \times 10^{5}\,\mathrm{J\,K\,mol^{-1}} = 67\,\mathrm{kJ\,K\,mol^{-1}}$$

$$\begin{aligned}\Delta_\mathrm{r}H^\ominus(100\,^\circ\mathrm{C}) &= \Big[-571.66 + (373-298)\times(0.06606) + \frac{1}{2}(373^2 - 298^2) \\ &\quad \times(-10.76\times10^{-6}) - (67)\times\left(\frac{1}{373} - \frac{1}{298}\right)\Big]\,\mathrm{kJ\,mol^{-1}} \\ &= \boxed{-566.93\,\mathrm{kJ\,mol^{-1}}}\end{aligned}$$

E2.26(b) The hydrogenation reaction is

(1) $C_2H_2(g) + H_2(g) \rightarrow C_2H_4(g) \quad \Delta_\mathrm{r}H^\ominus(T) = ?$

The reactions and accompanying data which are to be combined in order to yield reaction (1) and $\Delta_\mathrm{r}H^\ominus(T)$ are

(2) $H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l) \quad \Delta_\mathrm{c}H^\ominus(2) = -285.83\,\mathrm{kJ\,mol^{-1}}$

(3) $C_2H_4(g) + 3O_2(g) \rightarrow 2H_2O(l) + 2CO_2(g) \quad \Delta_\mathrm{c}H^\ominus(3) = -1411\,\mathrm{kJ\,mol^{-1}}$

(4) $C_2H_2(g) + \tfrac{5}{2}O_2(g) \rightarrow H_2O(l) + 2CO_2(g) \quad \Delta_\mathrm{c}H^\ominus(4) = -1300\,\mathrm{kJ\,mol^{-1}}$

reaction (1) = reaction (2) − reaction (3) + reaction (4)

(a) Hence, at 298 K:

$$\begin{aligned}\Delta_\mathrm{r}H^\ominus &= \Delta_\mathrm{c}H^\ominus(2) - \Delta_\mathrm{c}H^\ominus(3) + \Delta_\mathrm{c}H^\ominus(4) \\ &= [(-285.83) - (-1411) + (-1300)]\,\mathrm{kJ\,mol^{-1}} = \boxed{-175\,\mathrm{kJ\,mol^{-1}}}\end{aligned}$$

$$\begin{aligned}\Delta_\mathrm{r}U^\ominus &= \Delta_\mathrm{r}H^\ominus - \Delta n_\mathrm{g}RT \quad [2.21]; \quad \Delta n_\mathrm{g} = -1 \\ &= -175\,\mathrm{kJ\,mol^{-1}} - (-1)\times(2.48\,\mathrm{kJ\,mol^{-1}}) = \boxed{-173\,\mathrm{kJ\,mol^{-1}}}\end{aligned}$$

(b) At 348 K:

$$\Delta_r H^\ominus(348\,\mathrm{K}) = \Delta_r H^\ominus(298\,\mathrm{K}) + \Delta_r C_p^\ominus(348\,\mathrm{K} - 298\,\mathrm{K}) \quad \text{[Example 2.6]}$$

$$\Delta_r C_p = \sum_J \nu_J C_{p,\mathrm{m}}^\ominus(\mathrm{J})\ [2.37] = C_{p,\mathrm{m}}^\ominus(\mathrm{C_2H_4, g}) - C_{p,\mathrm{m}}^\ominus(\mathrm{C_2H_2, g}) - C_{p,\mathrm{m}}^\ominus(\mathrm{H_2, g})$$

$$= (43.56 - 43.93 - 28.82) \times 10^{-3}\,\mathrm{kJ\,K^{-1}\,mol^{-1}} = -29.19 \times 10^{-3}\,\mathrm{kJ\,K^{-1}\,mol^{-1}}$$

$$\Delta_r H^\ominus(348\,\mathrm{K}) = (-175\,\mathrm{kJ\,mol^{-1}}) - (29.19 \times 10^{-3}\,\mathrm{kJ\,K^{-1}\,mol^{-1}}) \times (50\,\mathrm{K})$$

$$= \boxed{-176\,\mathrm{kJ\,mol^{-1}}}$$

E2.27(b) NaCl, $AgNO_3$, and $NaNO_3$ are strong electrolytes; therefore the net ionic equation is

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

$$\Delta_r H^\ominus = \Delta_f H^\ominus(\mathrm{AgCl}) - \Delta_f H^\ominus(\mathrm{Ag^+}) - \Delta_f H^\ominus(\mathrm{Cl^-})$$

$$= [(-127.07) - (105.58) - (-167.16)]\,\mathrm{kJ\,mol^{-1}} = \boxed{-65.49\,\mathrm{kJ\,mol^{-1}}}$$

E2.28(b) The cycle is shown in Figure 2.1.

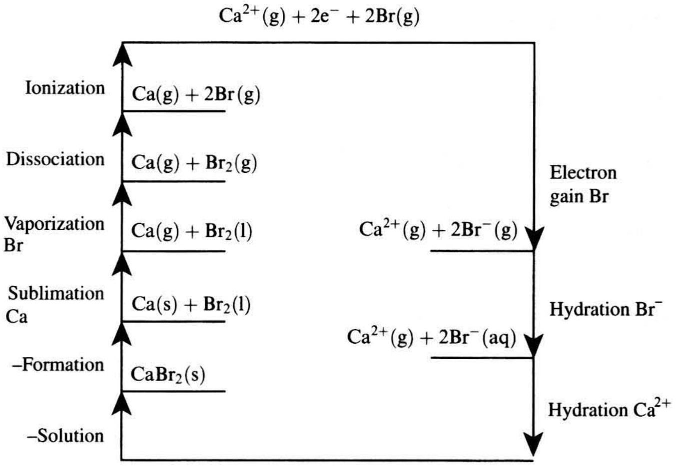


Figure 2.1

$$-\Delta_{\mathrm{hyd}} H^\ominus(\mathrm{Ca^{2+}}) = -\Delta_{\mathrm{soln}} H^\ominus(\mathrm{CaBr_2}) - \Delta_f H^\ominus(\mathrm{CaBr_2, s}) + \Delta_{\mathrm{sub}} H^\ominus(\mathrm{Ca})$$

$$+ \Delta_{\mathrm{vap}} H^\ominus(\mathrm{Br_2}) + \Delta_{\mathrm{diss}} H^\ominus(\mathrm{Br_2}) + \Delta_{\mathrm{ion}} H^\ominus(\mathrm{Ca})$$

$$+ \Delta_{\mathrm{ion}} H^\ominus(\mathrm{Ca^+}) + 2\Delta_{\mathrm{eg}} H^\ominus(\mathrm{Br}) + 2\Delta_{\mathrm{hyd}} H^\ominus(\mathrm{Br^-})$$

$$= [-(-103.1) - (-682.8) + 178.2 + 30.91 + 192.9$$

$$+ 589.7 + 1145 + 2(-331.0) + 2(-337)]\,\mathrm{kJ\,mol^{-1}}$$

$$= \boxed{1587\,\mathrm{kJ\,mol^{-1}}}$$

so $\Delta_{\mathrm{hyd}} H^\ominus(\mathrm{Ca^{2+}}) = \boxed{-1587\,\mathrm{kJ\,mol^{-1}}}$

E2.29(b) The Joule–Thomson coefficient μ is the ratio of temperature change to pressure change under conditions of isenthalpic expansion. So

$$\mu = \left(\frac{\partial T}{\partial p}\right)_H \approx \frac{\Delta T}{\Delta p} = \frac{-10\,\mathrm{K}}{(1.00 - 22)\,\mathrm{atm}} = \boxed{0.48\ \mathrm{K\,atm^{-1}}}$$

E2.30(b) The internal energy is a function of temperature and volume, $U_\mathrm{m} = U_\mathrm{m}(T, V_\mathrm{m})$, so

$$\mathrm{d}U_\mathrm{m} = \left(\frac{\partial U_\mathrm{m}}{\partial T}\right)_{V_\mathrm{m}} \mathrm{d}T + \left(\frac{\partial U_\mathrm{m}}{\partial V_\mathrm{m}}\right)_T \mathrm{d}V_\mathrm{m} \quad \left[\pi_T = \left(\frac{\partial U_\mathrm{m}}{\partial V}\right)_T\right]$$

For an isothermal expansion $\mathrm{d}T = 0$; hence

$$\mathrm{d}U_\mathrm{m} = \left(\frac{\partial U_\mathrm{m}}{\partial V_\mathrm{m}}\right)_T \mathrm{d}V_\mathrm{m} = \pi_T\,\mathrm{d}V_\mathrm{m} = \frac{a}{V_\mathrm{m}^2}\,\mathrm{d}V_\mathrm{m}$$

$$\Delta U_\mathrm{m} = \int_{V_\mathrm{m,1}}^{V_\mathrm{m,2}} \mathrm{d}U_\mathrm{m} = \int_{V_\mathrm{m,1}}^{V_\mathrm{m,2}} \frac{a}{V_\mathrm{m}^2}\,\mathrm{d}V_\mathrm{m} = a\int_{1.00\,\mathrm{dm^3\,mol^{-1}}}^{22.1\,\mathrm{dm^3\,mol^{-1}}} \frac{\mathrm{d}V_\mathrm{m}}{V_\mathrm{m}^2} = -\frac{a}{V_\mathrm{m}}\Bigg|_{1.00\,\mathrm{dm^3\,mol^{-1}}}^{22.1\,\mathrm{dm^3\,mol^{-1}}}$$

$$= -\frac{a}{22.1\,\mathrm{dm^3\,mol^{-1}}} + \frac{a}{1.00\,\mathrm{dm^3\,mol^{-1}}} = \frac{21.1a}{22.1\,\mathrm{dm^3\,mol^{-1}}} = 0.954\overline{75}a\,\mathrm{dm^{-3}\,mol}$$

From Table 1.6, $a = 1.337\ \mathrm{dm^6\ atm\ mol^{-1}}$

$$\Delta U_\mathrm{m} = (0.95475\,\mathrm{mol\,dm^3}) \times (1.337\,\mathrm{atm\,dm^6\,mol^{-2}})$$

$$= (1.27\overline{65}\,\mathrm{atm\,dm^3\,mol^{-1}}) \times (1.01325 \times 10^5\,\mathrm{Pa\,atm^{-1}}) \times \left(\frac{1\,\mathrm{m^3}}{10^3\,\mathrm{dm^3}}\right)$$

$$= 129\,\mathrm{Pa\,m^3\,mol^{-1}} = \boxed{129\,\mathrm{J\,mol^{-1}}}$$

$$w = -\textstyle\int p\,\mathrm{d}V_\mathrm{m} \quad \text{where} \quad p = \frac{RT}{V_\mathrm{m} - b} - \frac{a}{V_\mathrm{m}^2} \text{ for a van der Waals gas.}$$

Hence,

$$w = -\int \left(\frac{RT}{V_\mathrm{m} - b}\right)\mathrm{d}V_\mathrm{m} + \int \frac{a}{V_\mathrm{m}^2}\,\mathrm{d}V_\mathrm{m} = -q + \Delta U_\mathrm{m}$$

Thus

$$q = \int_{1.00\,\mathrm{dm^3\,mol^{-1}}}^{22.1\,\mathrm{dm^3\,mol^{-1}}} \left(\frac{RT}{V_\mathrm{m} - b}\right)\mathrm{d}V_\mathrm{m} = RT\ln(V_\mathrm{m} - b)\Big|_{1.00\,\mathrm{dm^3\,mol^{-1}}}^{22.1\,\mathrm{dm^3\,mol^{-1}}}$$

$$= (8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (298\,\mathrm{K}) \times \ln\left(\frac{22.1 - 3.20 \times 10^{-2}}{1.00 - 3.20 \times 10^{-2}}\right) = \boxed{+7.74\overline{65}\,\mathrm{kJ\,mol^{-1}}}$$

and $w = -q + \Delta U_\mathrm{m} = -(774\overline{7}\,\mathrm{J\,mol^{-1}}) + (129\,\mathrm{J\,mol^{-1}}) = \boxed{-761\overline{8}\,\mathrm{J\,mol^{-1}}} = \boxed{-7.62\,\mathrm{kJ\,mol^{-1}}}$

E2.31(b) The expansion coefficient is

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{V'(3.7\times 10^{-4}\,\mathrm{K}^{-1} + 2\times 1.52\times 10^{-6}\,T\,\mathrm{K}^{-2})}{V}$$

$$= \frac{V'[3.7\times 10^{-4} + 2\times 1.52\times 10^{-6}\,(T/\mathrm{K})]\,\mathrm{K}^{-1}}{V'[0.77 + 3.7\times 10^{-4}(T/\mathrm{K}) + 1.52\times 10^{-6}(T/\mathrm{K})^2]}$$

$$= \frac{[3.7\times 10^{-4} + 2\times 1.52\times 10^{-6}(310)]\,\mathrm{K}^{-1}}{0.77 + 3.7\times 10^{-4}(310) + 1.52\times 10^{-6}(310)^2} = \boxed{1.27\times 10^{-3}\,\mathrm{K}^{-1}}$$

E2.32(b) Isothermal compressibility is

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \approx -\frac{\Delta V}{V\Delta p} \qquad \text{so} \qquad \Delta p = -\frac{\Delta V}{V\kappa_T}$$

A density increase of 0.08 percent means $\Delta V/V = -0.0008$. So the additional pressure that must be applied is

$$\Delta p = \frac{0.0008}{2.21\times 10^{-6}\,\mathrm{atm}^{-1}} = \boxed{3.\bar{6}\times 10^{2}\,\mathrm{atm}}$$

E2.33(b) The isothermal Joule–Thomson coefficient is

$$\left(\frac{\partial H}{\partial p}\right)_T = -\mu C_p = -(1.11\,\mathrm{K\,atm}^{-1})\times(37.11\,\mathrm{J\,K}^{-1}\,\mathrm{mol}^{-1}) = \boxed{-41.2\,\mathrm{J\,atm}^{-1}\,\mathrm{mol}^{-1}}$$

If this coefficient is constant in an isothermal Joule–Thomson experiment, then the heat which must be supplied to maintain constant temperature is ΔH in the following relationship

$$\frac{\Delta H/n}{\Delta p} = -41.2\,\mathrm{J\,atm}^{-1}\,\mathrm{mol}^{-1} \quad \text{so} \quad \Delta H = -(41.2\,\mathrm{J\,atm}^{-1}\,\mathrm{mol}^{-1})n\Delta p$$

$$\Delta H = -(41.2\,\mathrm{J\,atm}^{-1}\,\mathrm{mol}^{-1})\times(12.0\,\mathrm{mol})\times(-55\,\mathrm{atm}) = \boxed{27.\bar{2}\times 10^{3}\,\mathrm{J}}$$

Solutions to problems

Assume all gases are perfect unless stated otherwise. Unless otherwise stated, thermochemical data are for 298 K.

Solutions to numerical problems

P2.1 The temperatures are readily obtained from the perfect gas equation, $T = \dfrac{pV}{nR}$,

$$T_1 = \frac{(1.00\,\mathrm{atm})\times(22.4\,\mathrm{dm}^3)}{(1.00\,\mathrm{mol})\times(0.0821\,\mathrm{dm}^3\,\mathrm{atm\,mol}^{-1}\,\mathrm{K}^{-1})} = \boxed{273\,\mathrm{K}} = T_3\ [\text{isotherm}].$$

Similarly, $T_2 = \boxed{546\,\mathrm{K}}$.