Exercises

- 1.1(a) (a) Could 131 g of xenon gas in a vessel of volume 1.0 dm³ exert a pressure of 20 atm at 25°C if it behaved as a perfect gas? If not, what pressure would it exert? (b) What pressure would it exert if it behaved as a van der Waals gas?
- **1.1(b)** (a) Could 25 g of argon gas in a vessel of volume 1.5 dm³ exert a pressure of 2.0 bar at 30°C if it behaved as a perfect gas? If not, what pressure would it exert? (b) What pressure would it exert if it behaved as a van der Waals gas?
- **1.2(a)** A perfect gas undergoes isothermal compression, which reduces its volume by $2.20~\mathrm{dm^3}$. The final pressure and volume of the gas are $5.04~\mathrm{bar}$ and $4.65~\mathrm{dm^3}$, respectively. Calculate the original pressure of the gas in (a) bar, (b) atm.
- **1.2(b)** A perfect gas undergoes isothermal compression, which reduces its volume by 1.80 dm³. The final pressure and volume of the gas are 1.97 bar and 2.14 dm³, respectively. Calculate the original pressure of the gas in (a) bar, (b) Torr.
- **1.3(a)** A car tyre (i.e. an automobile tire) was inflated to a pressure of 24 lb in⁻² (1.00 atm = 14.7 lb in⁻²) on a winter's day when the temperature was -5° C. What pressure will be found, assuming no leaks have occurred and that the volume is constant, on a subsequent summer's day when the temperature is 35°C? What complications should be taken into account in practice?
- **1.3(b)** A sample of hydrogen gas was found to have a pressure of 125 kPa when the temperature was 23°C. What can its pressure be expected to be when the temperature is 11°C ?
- **1.4(a)** A sample of 255 mg of neon occupies 3.00 dm³ at 122 K. Use the perfect gas law to calculate the pressure of the gas.
- **1.4(b)** A homeowner uses 4.00×10^3 m³ of natural gas in a year to heat a home. Assume that natural gas is all methane, CH₄, and that methane is a perfect gas for the conditions of this problem, which are 1.00 atm and 20°C. What is the mass of gas used?
- **1.5(a)** A diving bell has an air space of 3.0 m³ when on the deck of a boat. What is the volume of the air space when the bell has been lowered to a depth of 50 m? Take the mean density of sea water to be 1.025 g cm⁻³ and assume that the temperature is the same as on the surface.
- **1.5(b)** What pressure difference must be generated across the length of a 15 cm vertical drinking straw in order to drink a water-like liquid of density 1.0 g cm⁻³?
- **1.6(a)** A manometer consists of a U-shaped tube containing a liquid. One side is connected to the apparatus and the other is open to the atmosphere. The pressure inside the apparatus is then determined from the difference in heights of the liquid. Suppose the liquid is water, the external pressure is 770 Torr, and the open side is 10.0 cm lower than the side connected to the apparatus. What is the pressure in the apparatus? (The density of water at 25°C is 0.997 07 g cm⁻³.)
- **1.6(b)** A manometer like that described in Exercise 1.6a contained mercury in place of water. Suppose the external pressure is 760 Torr, and the open side is 10.0 cm higher than the side connected to the apparatus. What is the pressure in the apparatus? (The density of mercury at 25°C is 13.55 g cm⁻³.)
- **1.7(a)** In an attempt to determine an accurate value of the gas constant, R, a student heated a container of volume 20.000 dm³ filled with 0.251 32 g of helium gas to 500°C and measured the pressure as 206.402 cm of water in a manometer at 25°C. Calculate the value of R from these data. (The density of water at 25°C is 0.997 07 g cm⁻³; the construction of a manometer is described in Exercise 1.6a.)

1.7(b) The following data have been obtained for oxygen gas at 273.15 K. Calculate the best value of the gas constant R from them and the best value of the molar mass of O_2 .

p/atm	0.750 000	0.500 000	0.250 000	
$V_{\rm m}/({\rm dm^3~mol^{-1}})$	29.9649	44.8090	89.6384	
$\rho/(g dm^{-3})$	1.07144	0.714110	0.356975	

- **1.8(a)** At 500° C and 93.2 kPa, the mass density of sulfur vapour is 3.710 kg m⁻³. What is the molecular formula of sulfur under these conditions?
- **1.8(b)** At 100° C and 1.60 kPa, the mass density of phosphorus vapour is 0.6388 kg m⁻³. What is the molecular formula of phosphorus under these conditions?
- **1.9(a)** Calculate the mass of water vapour present in a room of volume 400 m³ that contains air at 27°C on a day when the relative humidity is 60 per cent.
- **1.9(b)** Calculate the mass of water vapour present in a room of volume 250 m³ that contains air at 23°C on a day when the relative humidity is 53 per cent.
- **1.10(a)** Given that the density of air at 0.987 bar and 27° C is 1.146 kg m⁻³, calculate the mole fraction and partial pressure of nitrogen and oxygen assuming that (a) air consists only of these two gases, (b) air also contains 1.0 mole per cent Ar.
- **1.10(b)** A gas mixture consists of 320 mg of methane, 175 mg of argon, and 225 mg of neon. The partial pressure of neon at 300 K is 8.87 kPa. Calculate (a) the volume and (b) the total pressure of the mixture.
- **1.11(a)** The density of a gaseous compound was found to be $1.23~{\rm kg}~{\rm m}^{-3}$ at 330 K and 20 kPa. What is the molar mass of the compound?
- **1.11(b)** In an experiment to measure the molar mass of a gas, 250 cm³ of the gas was confined in a glass vessel. The pressure was 152 Torr at 298 K and, after correcting for buoyancy effects, the mass of the gas was 33.5 mg. What is the molar mass of the gas?
- **1.12(a)** The densities of air at -85°C, 0°C, and 100°C are 1.877 g dm⁻³, 1.294 g dm⁻³, and 0.946 g dm⁻³, respectively. From these data, and assuming that air obeys Charles's law, determine a value for the absolute zero of temperature in degrees Celsius.
- **1.12(b)** A certain sample of a gas has a volume of 20.00 dm³ at 0°C and 1.000 atm. A plot of the experimental data of its volume against the Celsius temperature, θ , at constant p, gives a straight line of slope 0.0741 dm³ (°C)⁻¹. From these data alone (without making use of the perfect gas law), determine the absolute zero of temperature in degrees Celsius.
- **1.13(a)** Calculate the pressure exerted by 1.0 mol C_2H_6 behaving as (a) a perfect gas, (b) a van der Waals gas when it is confined under the following conditions: (i) at 273.15 K in 22.414 dm³, (ii) at 1000 K in 100 cm³. Use the data in Table 1.6.
- **1.13(b)** Calculate the pressure exerted by 1.0 mol $\rm H_2S$ behaving as (a) a perfect gas, (b) a van der Waals gas when it is confined under the following conditions: (i) at 273.15 K in 22.414 dm³, (ii) at 500 K in 150 cm³. Use the data in Table 1.6.
- **1.14(a)** Express the van der Waals parameters a = 0.751 atm dm⁶ mol⁻² and b = 0.0226 dm³ mol⁻¹ in SI base units.
- **1.14(b)** Express the van der Waals parameters a = 1.32 atm dm⁶ mol⁻² and b = 0.0436 dm³ mol⁻¹ in SI base units.
- **1.15(a)** A gas at 250 K and 15 atm has a molar volume 12 per cent smaller than that calculated from the perfect gas law. Calculate (a) the compression factor under these conditions and (b) the molar volume of the gas. Which are dominating in the sample, the attractive or the repulsive forces?

- **1.15(b)** A gas at 350 K and 12 atm has a molar volume 12 per cent larger than that calculated from the perfect gas law. Calculate (a) the compression factor under these conditions and (b) the molar volume of the gas. Which are dominating in the sample, the attractive or the repulsive forces?
- **1.16(a)** In an industrial process, nitrogen is heated to 500 K at a constant volume of 1.000 m³. The gas enters the container at 300 K and 100 atm. The mass of the gas is 92.4 kg. Use the van der Waals equation to determine the approximate pressure of the gas at its working temperature of 500 K. For nitrogen, $a = 1.352 \text{ dm}^6$ atm mol⁻², $b = 0.0387 \text{ dm}^3$ mol⁻¹.
- **1.16(b)** Cylinders of compressed gas are typically filled to a pressure of 200 bar. For oxygen, what would be the molar volume at this pressure and 25°C based on (a) the perfect gas equation, (b) the van der Waals equation. For oxygen, $a = 1.364 \, \mathrm{dm^6}$ atm $\mathrm{mol^{-2}}$, $b = 3.19 \times 10^{-2} \, \mathrm{dm^3}$ $\mathrm{mol^{-1}}$.
- **1.17(a)** Suppose that 10.0 mol $C_2H_6(g)$ is confined to 4.860 dm³ at 27°C. Predict the pressure exerted by the ethane from (a) the perfect gas and (b) the van der Waals equations of state. Calculate the compression factor based on these calculations. For ethane, a = 5.507 dm⁶ atm mol⁻², b = 0.0651 dm³ mol⁻¹.
- **1.17(b)** At 300 K and 20 atm, the compression factor of a gas is 0.86. Calculate (a) the volume occupied by 8.2 mmol of the gas under these conditions and (b) an approximate value of the second virial coefficient *B* at 300 K.
- **1.18(a)** A vessel of volume 22.4 dm 3 contains 2.0 mol H $_2$ and 1.0 mol N $_2$ at 273.15 K. Calculate (a) the mole fractions of each component, (b) their partial pressures, and (c) their total pressure.
- **1.18(b)** A vessel of volume 22.4 dm 3 contains 1.5 mol H $_2$ and 2.5 mol N $_2$ at 273.15 K. Calculate (a) the mole fractions of each component, (b) their partial pressures, and (c) their total pressure.

- **1.19(a)** The critical constants of methane are p_c = 45.6 atm, V_c = 98.7 cm³ mol⁻¹, and T_c = 190.6 K. Calculate the van der Waals parameters of the gas and estimate the radius of the molecules.
- **1.19(b)** The critical constants of ethane are $p_c = 48.20$ atm, $V_c = 148 \text{ cm}^3 \text{ mol}^{-1}$, and $T_c = 305.4 \text{ K}$. Calculate the van der Waals parameters of the gas and estimate the radius of the molecules.
- **1.20(a)** Use the van der Waals parameters for chlorine to calculate approximate values of (a) the Boyle temperature of chlorine and (b) the radius of a Cl_2 molecule regarded as a sphere.
- **1.20(b)** Use the van der Waals parameters for hydrogen sulfide to calculate approximate values of (a) the Boyle temperature of the gas and (b) the radius of a H_2S molecule regarded as a sphere ($a = 4.484 \text{ dm}^6 \text{ atm mol}^{-2}$, $b = 0.0434 \text{ dm}^3 \text{ mol}^{-1}$).
- **1.21(a)** Suggest the pressure and temperature at which 1.0 mol of (a) NH₃, (b) Xe, (c) He will be in states that correspond to 1.0 mol H_2 at 1.0 atm and 25°C .
- **1.21(b)** Suggest the pressure and temperature at which 1.0 mol of (a) H_2S , (b) CO_2 , (c) Ar will be in states that correspond to 1.0 mol N_2 at 1.0 atm and 25°C.
- **1.22(a)** A certain gas obeys the van der Waals equation with $a = 0.50 \text{ m}^6 \text{ Pa mol}^{-2}$. Its volume is found to be $5.00 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}$ at 273 K and 3.0 MPa. From this information calculate the van der Waals constant b. What is the compression factor for this gas at the prevailing temperature and pressure?
- **1.22(b)** A certain gas obeys the van der Waals equation with $a = 0.76 \text{ m}^6 \text{ Pa mol}^{-2}$. Its volume is found to be $4.00 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1}$ at 288 K and 4.0 MPa. From this information calculate the van der Waals constant b. What is the compression factor for this gas at the prevailing temperature and pressure?

Problems*

Numerical problems

- 1.1 Recent communication with the inhabitants of Neptune have revealed that they have a Celsius-type temperature scale, but based on the melting point $(0^{\circ}N)$ and boiling point $(100^{\circ}N)$ of their most common substance, hydrogen. Further communications have revealed that the Neptunians know about perfect gas behaviour and they find that, in the limit of zero pressure, the value of pV is 28 dm³ atm at $0^{\circ}N$ and 40 dm³ atm at $100^{\circ}N$. What is the value of the absolute zero of temperature on their temperature scale?
- **1.2** Deduce the relation between the pressure and mass density, ρ , of a perfect gas of molar mass M. Confirm graphically, using the following data on dimethyl ether at 25°C, that perfect behaviour is reached at low pressures and find the molar mass of the gas.

p/kPa 12.223 25.20 36.97 60.37 85.23 101.3 $\rho/(kg \text{ m}^{-3})$ 0.225 0.456 0.664 1.062 1.468 1.734

1.3 Charles's law is sometimes expressed in the form $V = V_0(1 + \alpha\theta)$, where θ is the Celsius temperature, α is a constant, and V_0 is the volume of the sample at 0°C. The following values for α have been reported for nitrogen at 0°C:

p/Torr 749.7 599.6 333.1 98.6 $10^{3}\alpha/(^{\circ}\text{C})^{-1}$ 3.6717 3.6697 3.6665 3.6643

For these data calculate the best value for the absolute zero of temperature on the Celsius scale.

- **1.4** The molar mass of a newly synthesized fluorocarbon was measured in a gas microbalance. This device consists of a glass bulb forming one end of a beam, the whole surrounded by a closed container. The beam is pivoted, and the balance point is attained by raising the pressure of gas in the container, so increasing the buoyancy of the enclosed bulb. In one experiment, the balance point was reached when the fluorocarbon pressure was 327.10 Torr; for the same setting of the pivot, a balance was reached when CHF $_3$ ($M=70.014~{\rm g~mol^{-1}}$) was introduced at 423.22 Torr. A repeat of the experiment with a different setting of the pivot required a pressure of 293.22 Torr of the fluorocarbon and 427.22 Torr of the CHF $_3$. What is the molar mass of the fluorocarbon? Suggest a molecular formula.
- **1.5** A constant-volume perfect gas thermometer indicates a pressure of 6.69 kPa at the triple point temperature of water (273.16 K). (a) What change of pressure indicates a change of 1.00 K at this temperature? (b) What pressure indicates a temperature of 100.00°C? (c) What change of pressure indicates a change of 1.00 K at the latter temperature?
- **1.6** A vessel of volume 22.4 dm³ contains 2.0 mol H_2 and 1.0 mol N_2 at 273.15 K initially. All the H_2 reacted with sufficient N_2 to form NH_3 . Calculate the partial pressures and the total pressure of the final mixture.
- **1.7** Calculate the molar volume of chlorine gas at 350 K and 2.30 atm using (a) the perfect gas law and (b) the van der Waals equation. Use the answer to (a) to calculate a first approximation to the correction term for attraction and then use successive approximations to obtain a numerical answer for part (b).
- * Problems denoted with the symbol ‡ were supplied by Charles Trapp, Carmen Giunta, and Marshall Cady.

1.8 At 273 K measurements on argon gave $B=-21.7~{\rm cm^3~mol^{-1}}$ and $C=1200~{\rm cm^6~mol^{-2}}$, where B and C are the second and third virial coefficients in the expansion of Z in powers of $1/V_{\rm m}$. Assuming that the perfect gas law holds sufficiently well for the estimation of the second and third terms of the expansion, calculate the compression factor of argon at 100 atm and 273 K. From your result, estimate the molar volume of argon under these conditions.

1.9 Calculate the volume occupied by 1.00 mol N_2 using the van der Waals equation in the form of a virial expansion at (a) its critical temperature, (b) its Boyle temperature, and (c) its inversion temperature. Assume that the pressure is 10 atm throughout. At what temperature is the gas most perfect? Use the following data: $T_c = 126.3$ K, a = 1.352 dm⁶ atm mol⁻², b = 0.0387 dm³ mol⁻¹.

1.10‡ The second virial coefficient of methane can be approximated by the empirical equation $B'(T) = a + be^{-c/T^2}$, where a = -0.1993 bar⁻¹, b = 0.2002 bar⁻¹, and c = 1131 K² with 300 K < T < 600 K. What is the Boyle temperature of methane?

1.11 The mass density of water vapour at 327.6 atm and 776.4 K is 133.2 kg m⁻³. Given that for water $T_c = 647.4$ K, $p_c = 218.3$ atm, a = 5.464 dm⁶ atm mol⁻², b = 0.03049 dm³ mol⁻¹, and M = 18.02 g mol⁻¹, calculate (a) the molar volume. Then calculate the compression factor (b) from the data, (c) from the virial expansion of the van der Waals equation.

1.12 The critical volume and critical pressure of a certain gas are $160 \text{ cm}^3 \text{ mol}^{-1}$ and 40 atm, respectively. Estimate the critical temperature by assuming that the gas obeys the Berthelot equation of state. Estimate the radii of the gas molecules on the assumption that they are spheres.

1.13 Estimate the coefficients a and b in the Dieterici equation of state from the critical constants of xenon. Calculate the pressure exerted by 1.0 mol Xe when it is confined to 1.0 dm³ at 25°C.

Theoretical problems

1.14 Show that the van der Waals equation leads to values of Z < 1 and Z > 1, and identify the conditions for which these values are obtained.

1.15 Express the van der Waals equation of state as a virial expansion in powers of $1/V_{\rm m}$ and obtain expressions for B and C in terms of the parameters a and b. The expansion you will need is $(1-x)^{-1}=1+x+x^2+\cdots$. Measurements on argon gave B=-21.7 cm³ mol $^{-1}$ and C=1200 cm 6 mol $^{-2}$ for the virial coefficients at 273 K. What are the values of a and b in the corresponding van der Waals equation of state?

1.16‡ Derive the relation between the critical constants and the Dieterici equation parameters. Show that $Z_{\rm c} = 2{\rm e}^{-2}$ and derive the reduced form of the Dieterici equation of state. Compare the van der Waals and Dieterici predictions of the critical compression factor. Which is closer to typical experimental values?

1.17 A scientist proposed the following equation of state:

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

Show that the equation leads to critical behaviour. Find the critical constants of the gas in terms of *B* and *C* and an expression for the critical compression factor.

1.18 Equations 1.18 and 1.19 are expansions in p and $1/V_{\rm m}$, respectively. Find the relation between B, C and B', C'.

1.19 The second virial coefficient B' can be obtained from measurements of the density ρ of a gas at a series of pressures. Show that the graph of p/ρ against p should be a straight line with slope proportional to B'. Use the data on dimethyl ether in Problem 1.2 to find the values of B' and B at 25°C.

1.20 The equation of state of a certain gas is given by $p = RT/V_{\rm m} + (a + bT)/V_{\rm m}^2$, where a and b are constants. Find $(\partial V/\partial T)_p$.

1.21 The following equations of state are occasionally used for approximate calculations on gases: (gas A) $pV_{\rm m} = RT(1 + b/V_{\rm m})$, (gas B) $p(V_{\rm m} - b) = RT$. Assuming that there were gases that actually obeyed these equations of state, would it be possible to liquefy either gas A or B? Would they have a critical temperature? Explain your answer.

1.22 Derive an expression for the compression factor of a gas that obeys the equation of state p(V-nb)=nRT, where b and R are constants. If the pressure and temperature are such that $V_{\rm m}=10b$, what is the numerical value of the compression factor?

1.23‡ The discovery of the element argon by Lord Rayleigh and Sir William Ramsay had its origins in Rayleigh's measurements of the density of nitrogen with an eye toward accurate determination of its molar mass. Rayleigh prepared some samples of nitrogen by chemical reaction of nitrogencontaining compounds; under his standard conditions, a glass globe filled with this 'chemical nitrogen' had a mass of 2.2990 g. He prepared other samples by removing oxygen, carbon dioxide, and water vapour from atmospheric air; under the same conditions, this 'atmospheric nitrogen' had a mass of 2.3102 g (Lord Rayleigh, *Royal Institution Proceedings* **14**, 524 (1895)). With the hindsight of knowing accurate values for the molar masses of nitrogen and argon, compute the mole fraction of argon in the latter sample on the assumption that the former was pure nitrogen and the latter a mixture of nitrogen and argon.

1.24‡ A substance as elementary and well known as argon still receives research attention. Stewart and Jacobsen have published a review of thermodynamic properties of argon (R.B. Stewart and R.T. Jacobsen, *J. Phys. Chem. Ref. Data* **18**, 639 (1989)) that included the following 300 K isotherm.

p/MPa	0.4000	0.5000	0.6000	0.8000	1.000
$V_{\rm m}/({\rm dm^3~mol^{-1}})$	6.2208	4.9736	4.1423	3.1031	2.4795
p/MPa	1.500	2.000	2.500	3.000	4.000
$V_{}/(dm^3 \text{ mol}^{-1})$	1.6483	1.2328	0.98357	0.81746	0.60998

(a) Compute the second virial coefficient, *B*, at this temperature. (b) Use non-linear curve-fitting software to compute the third virial coefficient, *C*, at this temperature.

Applications: to environmental science

1.25 Atmospheric pollution is a problem that has received much attention. Not all pollution, however, is from industrial sources. Volcanic eruptions can be a significant source of air pollution. The Kilauea volcano in Hawaii emits 200–300 t of SO_2 per day. If this gas is emitted at 800°C and 1.0 atm, what volume of gas is emitted?

1.26 Ozone is a trace atmospheric gas that plays an important role in screening the Earth from harmful ultraviolet radiation, and the abundance of ozone is commonly reported in *Dobson units*. One Dobson unit is the thickness, in thousandths of a centimetre, of a column of gas if it were collected as a pure gas at 1.00 atm and 0°C. What amount of O₃ (in moles) is found in a column of atmosphere with a cross-sectional area of 1.00 dm² if the abundance is 250 Dobson units (a typical mid-latitude value)? In the seasonal Antarctic ozone hole, the column abundance drops below 100 Dobson units; how many moles of ozone are found in such a column of air above a 1.00 dm² area? Most atmospheric ozone is found between 10 and 50 km above the surface of the earth. If that ozone is spread uniformly through this portion of the atmosphere, what is the average molar concentration corresponding to (a) 250 Dobson units, (b) 100 Dobson units?

1.27 The barometric formula relates the pressure of a gas of molar mass M at an altitude h to its pressure p_0 at sea level. Derive this relation by showing that