CHAPTER 1　The properties of gases

TOPIC 1A　The perfect gas

Discussion questions

1A.1 Explain how the perfect gas equation of state arises by combination of Boyle's law, Charles's law, and Avogadro's principle.

1A.2 Explain the term 'partial pressure' and explain why Dalton's law is a limiting law.

Exercises

1A.1(a) Could 131 g of xenon gas in a vessel of volume $1.0\,dm^3$ exert a pressure of 20 atm at 25 °C if it behaved as a perfect gas? If not, what pressure would it exert?

1A.1(b) Could 25 g of argon gas in a vessel of volume $1.5\,dm^3$ exert a pressure of 2.0 bar at 30 °C if it behaved as a perfect gas? If not, what pressure would it exert?

1A.2(a) A perfect gas undergoes isothermal compression, which reduces its volume by $2.20\,dm^3$. The final pressure and volume of the gas are 5.04 bar and $4.65\,dm^3$, respectively. Calculate the original pressure of the gas in (i) bar, (ii) atm.

1A.2(b) A perfect gas undergoes isothermal compression, which reduces its volume by $1.80\,dm^3$. The final pressure and volume of the gas are 1.97 bar and $2.14\,dm^3$, respectively. Calculate the original pressure of the gas in (i) bar, (ii) torr.

1A.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?

1A.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?

1A.4(a) A sample of 255 mg of neon occupies $3.00\,dm^3$ at 122 K. Use the perfect gas law to calculate the pressure of the gas.

1A.4(b) A homeowner uses $4.00 \times 10^3\,m^3$ of natural gas in a year to heat a home. Assume that natural gas is all methane, CH_4, 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?

1A.5(a) A diving bell has an air space of $3.0\,m^3$ 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.

1A.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 $1.0\,g\,cm^{-3}$?

1A.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 $0.99707\,g\,cm^{-3}$.)

1.A6(b) A manometer like that described in Exercise 1.6(a) 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 $13.55\,g\,cm^{-3}$.)

1A.7(a) In an attempt to determine an accurate value of the gas constant, R, a student heated a container of volume $20.000\,dm^3$ filled with $0.25132\,g$ 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 $0.99707\,g\,cm^{-3}$; the construction of a manometer is described in Exercise 1.6(a).)

1A.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
$V_m/(dm^3\,mol^{-1})$	29.9649	44.8090	89.6384

1A.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?

1A.8(b) At 100 °C and 16.0 kPa, the mass density of phosphorus vapour is $0.6388\,kg\,m^{-3}$. What is the molecular formula of phosphorus under these conditions?

1A.9(a) Calculate the mass of water vapour present in a room of volume $400\,m^3$ that contains air at 27 °C on a day when the relative humidity is 60 per cent.

1A.9(b) Calculate the mass of water vapour present in a room of volume $250\,m^3$ that contains air at 23 °C on a day when the relative humidity is 53 per cent.

1A.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 (i) air consists only of these two gases, (ii) air also contains 1.0 mole per cent Ar.

1A.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 (i) the volume and (ii) the total pressure of the mixture.

1A.11(a) The density of a gaseous compound was found to be $1.23\,kg\,m^{-3}$ at 330 K and 20 kPa. What is the molar mass of the compound?

1A.11(b) In an experiment to measure the molar mass of a gas, $250\,cm^3$ 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?

1A.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.

1A.12(b) A certain sample of a gas has a volume of $20.00\,dm^3$ 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 $0.0741\,dm^3\,°C^{-1}$. From these data determine the absolute zero of temperature in degrees Celsius.

1A.13(a) A vessel of volume 22.4 dm³ contains 2.0 mol H_2 and 1.0 mol N_2 at 273.15 K. Calculate (i) the mole fractions of each component, (ii) their partial pressures, and (iii) their total pressure.

1A.13(b) A vessel of volume 22.4 dm³ contains 1.5 mol H_2 and 2.5 mol N_2 at 273.15 K. Calculate (i) the mole fractions of each component, (ii) their partial pressures, and (iii) their total pressure.

Problems

1A.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 °N) and boiling point (100 °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 °N and 40 dm³ atm at 100 °N. What is the value of the absolute zero of temperature on their temperature scale?

1A.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
ρ/(kg m⁻³)	0.225	0.456	0.664	1.062	1.468	1.734

1A.3 Charles's law is sometimes expressed in the form $V = V_0(1 + \alpha\theta)$, where θ is the Celsius temperature, is a constant, and V_0 is the volume of the sample at 0 °C. The following values for have been reported for nitrogen at 0 °C:

p/Torr	749.7	599.6	333.1	98.6
$10^3\alpha$/°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.

1A.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 ($M = 70.014$ 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.

1A.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?

1A.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.

1A.7 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?

1A.8 Ozone is a trace atmospheric gas which 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 O_3 (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 O_3 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?

1A.9 The barometric formula (see *Impact* 1.1) 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 the change in pressure dp for an infinitesimal change in altitude dh where the density is ρ is $dp = -\rho g dh$. Remember that ρ depends on the pressure. Evaluate (a) the pressure difference between the top and bottom of a laboratory vessel of height 15 cm, and (b) the external atmospheric pressure at a typical cruising altitude of an aircraft (11 km) when the pressure at ground level is 1.0 atm.

1A.10 Balloons are still used to deploy sensors that monitor meteorological phenomena and the chemistry of the atmosphere. It is possible to investigate some of the technicalities of ballooning by using the perfect gas law. Suppose your balloon has a radius of 3.0 m and that it is spherical. (a) What amount of H_2 (in moles) is needed to inflate it to 1.0 atm in an ambient temperature of 25 °C at sea level? (b) What mass can the balloon lift at sea level, where the density of air is 1.22 kg m⁻³? (c) What would be the payload if He were used instead of H_2?

1A.11‡ The preceding problem is most readily solved with the use of Archimedes principle, which states that the lifting force is equal to the difference between the weight of the displaced air and the weight of the balloon. Prove Archimedes principle for the atmosphere from the barometric formula. *Hint*: Assume a simple shape for the balloon, perhaps a right circular cylinder of cross-sectional area A and height h.

1A.12‡ Chlorofluorocarbons such as CCl_3F and CCl_2F_2 have been linked to ozone depletion in Antarctica. As of 1994, these gases were found in quantities of 261 and 509 parts per trillion (10^{12}) by volume (World Resources Institute, *World resources 1996–97*). Compute the molar concentration of these gases under conditions typical of (a) the mid-latitude troposphere (10 °C and 1.0 atm) and (b) the Antarctic stratosphere (200 K and 0.050 atm).

1A.13‡ The composition of the atmosphere is approximately 80 per cent nitrogen and 20 per cent oxygen by mass. At what height above the surface of the Earth would the atmosphere become 90 per cent nitrogen and 10 per cent oxygen by mass? Assume that the temperature of the atmosphere is constant at 25 °C. What is the pressure of the atmosphere at that height?

‡ These problems were supplied by Charles Trapp and Carmen Giunta.

TOPIC 1B The kinetic model

Discussion questions

1B.1 Specify and analyse critically the assumptions that underlie the kinetic model of gases.

1B.2 Provide molecular interpretations for the dependencies of the mean free path on the temperature, pressure, and size of gas molecules.

Exercises

1B.1(a) Determine the ratios of (i) the mean speeds, (ii) the mean translational kinetic energies of H_2 molecules and Hg atoms at 20 °C.
1B.1(b) Determine the ratios of (i) the mean speeds, (ii) the mean kinetic energies of He atoms and Hg atoms at 25 °C.

1B.2(a) Calculate the root mean square speeds of H_2 and O_2 molecules at 20 °C.
1B.2(b) Calculate the root mean square speeds of CO_2 molecules and He atoms at 20 °C.

1B.3(a) Use the Maxwell–Boltzmann distribution of speeds to estimate the fraction of N_2 molecules at 400 K that have speeds in the range 200 to 210 m s^{-1}.
1B.3(b) Use the Maxwell–Boltzmann distribution of speeds to estimate the fraction of CO_2 molecules at 400 K that have speeds in the range 400 to 405 m s^{-1}.

1B.4(a) Calculate the most probable speed, the mean speed, and the mean relative speed of CO_2 molecules in air at 20 °C.
1B.4(b) Calculate the most probable speed, the mean speed, and the mean relative speed of H_2 molecules in air at 20 °C.

1B.5(a) Assume that air consists of N_2 molecules with a collision diameter of 395 pm. Calculate (i) the mean speed of the molecules, (ii) the mean free path, (iii) the collision frequency in air at 1.0 atm and 25 °C.
1B.5(b) The best laboratory vacuum pump can generate a vacuum of about 1 nTorr. At 25 °C and assuming that air consists of N_2 molecules with a collision diameter of 395 pm, calculate (i) the mean speed of the molecules, (ii) the mean free path, (iii) the collision frequency in the gas.

1B.6(a) At what pressure does the mean free path of argon at 20 °C become comparable to the diameter of a 100 cm^3 vessel that contains it? Take $\sigma = 0.36$ nm^2.
1B.6(b) At what pressure does the mean free path of argon at 20 °C become comparable to 10 times the diameters of the atoms themselves?

1B.7(a) At an altitude of 20 km the temperature is 217 K and the pressure 0.050 atm. What is the mean free path of N_2 molecules? ($\sigma = 0.43$ nm^2).
1B.7(b) At an altitude of 15 km the temperature is 217 K and the pressure 12.1 kPa. What is the mean free path of N_2 molecules? ($\sigma = 0.43$ nm^2).

Problems

1B.1 A rotating slotted-disc apparatus like that in Fig. 1B.5 consists of five coaxial 5.0 cm diameter disks separated by 1.0 cm, the slots in their rims being displaced by 2.0° between neighbours. The relative intensities, I, of the detected beam of Kr atoms for two different temperatures and at a series of rotation rates were as follows:

ν/Hz	20	40	80	100	120
I (40 K)	0.846	0.513	0.069	0.015	0.002
I (100 K)	0.592	0.485	0.217	0.119	0.057

Find the distributions of molecular velocities, $f(v_x)$, at these temperatures, and check that they conform to the theoretical prediction for a one-dimensional system.

1B.2 A Knudsen cell was used to determine the vapour pressure of germanium at 1000 °C. During an interval of 7200 s the mass loss through a hole of radius 0.50 mm amounted to 43 μg. What is the vapour pressure of germanium at 1000 °C? Assume the gas to be monatomic.

1B.3 Start from the Maxwell–Boltzmann distribution and derive an expression for the most probable speed of a gas of molecules at a temperature T. Go on to demonstrate the validity of the equipartition conclusion that the average translational kinetic energy of molecules free to move in three dimensions is $\frac{3}{2}kT$.

1B.4 Consider molecules that are confined to move in a plane (a two-dimensional gas). Calculate the distribution of speeds and determine the mean speed of the molecules at a temperature T.

1B.5 A specially constructed velocity-selector accepts a beam of molecules from an oven at a temperature T but blocks the passage of molecules with a speed greater than the mean. What is the mean speed of the emerging beam, relative to the initial value, treated as a one-dimensional problem?

1B.6 What, according to the Maxwell–Boltzmann distribution, is the proportion of gas molecules having (a) more than, (b) less than the root mean square speed? (c) What are the proportions having speeds greater and smaller than the mean speed?

1B.7 Calculate the fractions of molecules in a gas that have a speed in a range Δv at the speed nv_{mp} relative to those in the same range at v_m itself? This calculation can be used to estimate the fraction of very energetic molecules (which is important for reactions). Evaluate the ratio for $n=3$ and $n=4$.

1B.8 Derive an expression for $\langle v^n \rangle^{1/n}$ from the Maxwell–Boltzmann distribution of speeds. You will need standard integrals given in the *Resource section*.

1B.9 Calculate the escape velocity (the minimum initial velocity that will take an object to infinity) from the surface of a planet of radius R. What is the value for (a) the Earth, $R=6.37 \times 10^6$ m, $g=9.81$ m s^{-2}, (b) Mars, $R=3.38 \times 10^6$ m, $m_{Mars}/m_{Earth}=0.108$. At what temperatures do H_2, He, and O_2 molecules have mean speeds equal to their escape speeds? What proportion of the molecules have enough speed to escape when the temperature is (a) 240 K, (b) 1500 K? Calculations of this kind are very important in considering the composition of planetary atmospheres.

1B.10 The principal components of the atmosphere of the Earth are diatomic molecules, which can rotate as well as translate. Given that the translational kinetic energy density of the atmosphere is 0.15 J cm^{-3}, what is the total kinetic energy density, including rotation? The average rotational energy of a linear molecule is kT.

1B.11 Plot different Maxwell–Boltzmann speed distributions by keeping the molar mass constant at 100 g mol^{-1} and varying the temperature of the sample between 200 K and 2000 K.

1B.12 Evaluate numerically the fraction of molecules with speeds in the range 100 m s^{-1} to 200 m s^{-1} at 300 K and 1000 K.

TOPIC 1C   Real gases

Discussion questions

1C.1 Explain how the compression factor varies with pressure and temperature and describe how it reveals information about intermolecular interactions in real gases.

1C.2 What is the significance of the critical constants?

1C.3 Describe the formulation of the van der Waals equation and suggest a rationale for one other equation of state in Table 1C.6.

1C.4 Explain how the van der Waals equation accounts for critical behaviour.

Exercises

1C.1(a) Calculate the pressure exerted by 1.0 mol C_2H_6 behaving as 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 1C.3.
1C.1(b) Calculate the pressure exerted by 1.0 mol H_2S behaving as 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 1C.3.

1C.2(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.
1C.2(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.

1C.3(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 (i) the compression factor under these conditions and (ii) the molar volume of the gas. Which are dominating in the sample, the attractive or the repulsive forces?
1C.3(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 (i) the compression factor under these conditions and (ii) the molar volume of the gas. Which are dominating in the sample, the attractive or the repulsive forces?

1C.4(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, $a=1.352$ dm⁶ atm mol⁻², $b=0.0387$ dm³ mol⁻¹.
1C.4(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 (i) the perfect gas equation, (ii) the van der Waals equation? For oxygen, $a=1.364$ dm⁶ atm mol⁻², $b=3.19\times10^{-2}$ dm³ mol⁻¹.

1C.5(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 (i) the perfect gas and (ii) 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.

1C.5(b) At 300 K and 20 atm, the compression factor of a gas is 0.86. Calculate (i) the volume occupied by 8.2 mmol of the gas under these conditions and (ii) an approximate value of the second virial coefficient B at 300 K.

1C.6(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.
1C.6(b) The critical constants of ethane are $p_c=48.20$ atm, $V_c=148$ cm³ mol⁻¹, and $T_c=305.4$ K. Calculate the van der Waals parameters of the gas and estimate the radius of the molecules.

1C.7(a) Use the van der Waals parameters for chlorine in Table 1C.3 of the *Resource section* to calculate approximate values of (i) the Boyle temperature of chlorine and (ii) the radius of a Cl_2 molecule regarded as a sphere.
1C.7(b) Use the van der Waals parameters for hydrogen sulfide in Table 1C.3 of the *Resource section* to calculate approximate values of (i) the Boyle temperature of the gas and (ii) the radius of a H_2S molecule regarded as a sphere.

1C.8(a) Suggest the pressure and temperature at which 1.0 mol of (i) NH_3, (ii) Xe, (iii) He will be in states that correspond to 1.0 mol H_2 at 1.0 atm and 25 °C.
1C.8(b) Suggest the pressure and temperature at which 1.0 mol of (i) H_2S, (ii) CO_2, (iii) Ar will be in states that correspond to 1.0 mol N_2 at 1.0 atm and 25 °C.

1C.9(a) A certain gas obeys the van der Waals equation with $a=0.50$ m⁶ Pa mol⁻². Its volume is found to be 5.00×10^{-4} m³ 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?
1C.9(b) A certain gas obeys the van der Waals equation with $a=0.76$ m⁶ Pa mol⁻². Its volume is found to be 4.00×10^{-4} m³ 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

1C.1 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).

1C.2 At 273 K measurements on argon gave $B=-21.7$ cm³ mol⁻¹ and $C=1200$ cm⁶ mol⁻², where B and C are the second and third virial coefficients in the expansion of Z in powers of $1/V_m$. 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.

1C.3 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.

1C.4‡ 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?

1C.5 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, $p_c=21.3$ 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.

1C.6 The critical volume and critical pressure of a certain gas are 160 cm³ 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.

1C.7 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.

1C.8 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.

1C.9 Express the van der Waals equation of state as a virial expansion in powers of $1/V_m$ and obtain expressions for B and C in terms of the parameters a and b. The expansion you will need is $(1-x)^{-1} = 1 + x + x^2 + \ldots$. Measurements on argon gave $B = -21.7$ cm³ mol⁻¹ and $C = 1200$ cm⁶ 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?

1C.10‡ Derive the relation between the critical constants and the Dieterici equation parameters. Show that $Z_c = 2e^{-2}$ 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?

1C.11 A scientist proposed the following equation of state:

$$p = \frac{RT}{V_m} - \frac{B}{V_m^2} + \frac{C}{V_m^3}$$

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.

1C.12 Equations 1C.3a and 1C.3b are expansions in p and $1/V_m$, respectively. Find the relation between B, C and B', C'.

1C.13 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 1A.2 to find the values of B' and B at 25 °C.

1C.14 The equation of state of a certain gas is given by $p = RT/V_m + (a + bT)/V_m^2$, where a and b are constants. Find $(\partial V/\partial T)_p$.

1C.15 The following equations of state are occasionally used for approximate calculations on gases: (gas A) $pV_m = RT(1 + b/V_m)$, (gas B) $p(V_m - b) = RT$. 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.

1C.16 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 $V_m = 10b$, what is the numerical value of the compression factor?

1C.17‡ 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 nitrogen-containing 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 vapor 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.

1C.18‡ 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)) which included the following 300 K isotherm.

p/MPa	0.4000	0.5000	0.6000	0.8000	1.000
V_m/(dm³ 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_m/(dm³ 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.

1C.19 Use mathematical software, a spreadsheet, or the *Living graphs* on the web site for this book to: (a) Explore how the pressure of 1.5 mol CO_2(g) varies with volume as it is compressed at (a) 273 K, (b) 373 K from 30 dm³ to 15 dm³. (c) Plot the data as p against $1/V$.

1C.20 Calculate the molar volume of chlorine gas on the basis of the van der Waals equation of state at 250 K and 150 kPa and calculate the percentage difference from the value predicted by the perfect gas equation.

1C.21 Is there a set of conditions at which the compression factor of a van der Waals gas passes through a minimum? If so, how does the location and value of the minimum value of Z depend on the coefficients a and b?