Problems*

Numerical problems

20.1 The speed of molecules can be measured with a rotating slotted-disc apparatus, which consists of five coaxial 5.0 cm diameter discs 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.

20.2 Cars were timed by police radar as they passed in both directions below a bridge. Their velocities (kilometres per hour, numbers of cars in parentheses) to the east and west were as follows: 80 E (40), 85 E (62), 90 E (53), 95 E (12), 100 E (2); 80 W (38), 85 W (59), 90 W (50), 95 W (10), 100 W (2). What are (a) the mean velocity, (b) the mean speed, (c) the root mean square speed?

20.3 A population consists of people of the following heights (in metres, numbers of individuals in brackets): 1.80 (1), 1.82 (2), 1.84 (4), 1.86 (7), 1.88 (10), 1.90 (15), 1.92 (9), 1.94 (4), 1.96 (0), 1.98 (1). What are (a) the mean height, (b) the root mean square height of the population?

20.4 Calculate the ratio of the thermal conductivities of gaseous hydrogen at 300 K to gaseous hydrogen at 10 K. Be circumspect, and think about the modes of motion that are thermally active at the two temperatures.

20.5 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.

20.6 An atomic beam is designed to function with (a) cadmium, (b) mercury. The source is an oven maintained at 380 K, there being a small slit of dimensions 1.0 cm × 1.0 × 10^{-3} cm. The vapour pressure of cadmium is 0.13 Pa and that of mercury is 12 Pa at this temperature. What is the atomic current (the number of atoms per second) in the beams?

20.7 Conductivities are often measured by comparing the resistance of a cell filled with the sample to its resistance when filled with some standard solution, such as aqueous potassium chloride. The conductivity of water is 76 mS m^{-1} at 25°C and the conductivity of 0.100 mol dm^{-3} KCl(aq) is 1.1639 S m^{-1}. A cell had a resistance of 33.21 Ω when filled with 0.100 mol dm^{-3} KCl(aq) and 300.0 Ω when filled with 0.100 mol dm^{-3} CH_3COOH(aq). What is the molar conductivity of acetic acid at that concentration and temperature?

20.8 The resistances of a series of aqueous NaCl solutions, formed by successive dilution of a sample, were measured in a cell with cell constant (the constant C in the relation $\kappa = C/R$) equal to 0.2063 cm^{-1}. The following values were found:

c/(mol dm^{-3})	0.00050	0.0010	0.0050	0.010	0.020	0.050
R/Ω	3314	1669	342.1	174.1	89.08	37.14

Verify that the molar conductivity follows the Kohlrausch law and find the limiting molar conductivity. Determine the coefficient $\mathcal{K}$. Use the value of $\mathcal{K}$ (which should depend only on the nature, not the identity of the ions) and the information that $\lambda(Na^+) = 5.01$ mS m^2 mol^{-1} and $\lambda(I^-) = 7.68$ mS m^2 mol^{-1} to predict (a) the molar conductivity, (b) the conductivity, (c) the resistance it would show in the cell, of 0.010 mol dm^{-3} NaI(aq) at 25°C.

20.9 After correction for the water conductivity, the conductivity of a saturated aqueous solution of AgCl at 25°C was found to be 0.1887 mS m^{-1}. What is the solubility of silver chloride at this temperature?

20.10 What are the drift speeds of Li^+, Na^+, and K^+ in water when a potential difference of 10 V is applied across a 1.00-cm conductivity cell? How long would it take an ion to move from one electrode to the other? In conductivity measurements it is normal to use alternating current: what are the displacements of the ions in (a) centimetres, (b) solvent diameters, about 300 pm, during a half cycle of 1.0 kHz applied potential?

20.11 The mobilities of H^+ and Cl^- at 25°C in water are 3.623 × 10^{-7} m^2 s^{-1} V^{-1} and 7.91 × 10^{-8} m^2 s^{-1} V^{-1}, respectively. What proportion of the current is carried by the protons in 10^{-3} M HCl(aq)? What fraction do they carry when the NaCl is added to the acid so that the solution is 1.0 mol dm^{-3} in the salt? Note how concentration as well as mobility governs the transport of current.

20.12 A dilute solution of potassium permanganate in water at 25°C was prepared. The solution was in a horizontal tube of length 10 cm, and at first there was a linear gradation of intensity of the purple solution from the left (where the concentration was 0.100 mol dm^{-3}) to the right (where the concentration was 0.050 mol dm^{-3}). What are the magnitude and sign of the thermodynamic force acting on the solute (a) close to the left face of the container, (b) in the middle, (c) close to the right face? Give the force per mole and force per molecule in each case.

20.13 Estimate the diffusion coefficients and the effective hydrodynamic radii of the alkali metal cations in water from their mobilities at 25°C. Estimate the approximate number of water molecules that are dragged along by the cations. Ionic radii are given in Table 20.3.

20.14 Nuclear magnetic resonance can be used to determine the mobility of molecules in liquids. A set of measurements on methane in carbon tetrachloride showed that its diffusion coefficient is 2.05 × 10^{-9} m^2 s^{-1} at 0°C and 2.89 × 10^{-9} m^2 s^{-1} at 25°C. Deduce what information you can about the mobility of methane in carbon tetrachloride.

20.15 A concentrated sucrose solution is poured into a cylinder of diameter 5.0 cm. The solution consisted of 10 g of sugar in 5.0 cm^3 of water. A further 1.0 dm^3 of water is then poured very carefully on top of the layer, without disturbing the layer. Ignore gravitational effects, and pay attention only to diffusional processes. Find the concentration at 5.0 cm above the lower layer after a lapse of (a) 10 s, (b) 1.0 years.

20.16 In a series of observations on the displacement of rubber latex spheres of radius 0.212 μm, the mean square displacements after selected time intervals were on average as follows:

t/s	30	60	90	120
$10^{12}\langle x^2\rangle$/m^2	88.2	113.5	128	144

These results were originally used to find the value of Avogadro's constant, but there are now better ways of determining N_A, so the data can be used to find another quantity. Find the effective viscosity of water at the temperature of this experiment (25°C).

* Problems denoted with the symbol ‡ were supplied by Charles Trapp, Carmen Giunta, and Marshall Cady.

20.17‡ A.K. Srivastava *et al.* (*J. Chem. Eng. Data* **41**, 431 (1996)) measured the conductance of several salts in a binary solvent mixture of water and a dipolar aprotic solvent 1,3-dioxolan-2-one. They report the following conductances at 25°C in a solvent 80 per cent 1,3-dioxolan-2-one by mass:

NaI

$c/(\text{mmol dm}^{-3})$	32.02	20.28	12.06	8.64	2.85	1.24	0.83
$\Lambda_m/(\text{S cm}^2\text{ mol}^{-1})$	50.26	51.99	54.01	55.75	57.99	58.44	58.67

KI

$c/(\text{mmol dm}^{-3})$	17.68	10.8	87.19	2.67	1.28	0.83	0.19
$\Lambda_m/(\text{S cm}^2\text{ mol}^{-1})$	42.45	45.91	47.53	51.81	54.09	55.78	57.42

Calculate Λ_m° for NaI and KI in this solvent and $\lambda^\circ(\text{Na}) - \lambda^\circ(\text{K})$. Compare your results to the analogous quantities in aqueous solution using Table 20.5 in the *Data section*.

20.18‡ A. Fenghour *et al.* (*J. Phys. Chem. Ref. Data* **24**, 1649 (1995)) have compiled an extensive table of viscosity coefficients for ammonia in the liquid and vapour phases. Deduce the effective molecular diameter of NH_3 based on each of the following vapour-phase viscosity coefficients: (a) $\eta = 9.08 \times 10^{-6}$ kg m^{-1} s^{-1} at 270 K and 1.00 bar; (b) $\eta = 1.749 \times 10^{-5}$ kg m^{-1} s^{-1} at 490 K and 10.0 bar.

20.19‡ G. Bakale *et al.* (*J. Phys. Chem.* **100**, 12477 (1996)) measured the mobility of singly charged C_{60}^- ions in a variety of nonpolar solvents. In cyclohexane at 22°C, the mobility is 1.1 cm^2 V^{-1} s^{-1}. Estimate the effective radius of the C_{60}^- ion. The viscosity of the solvent is 0.93×10^{-3} kg m^{-1} s^{-1}. *Comment.* The researchers interpreted the substantial difference between this number and the van der Waals radius of neutral C_{60} in terms of a solvation layer around the ion.

Theoretical problems

20.20 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 $\frac{3}{2}kT$.

20.21 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.

20.22 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?

20.23 What 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?

20.24 Calculate the fractions of molecules in a gas that have a speed in a range Δv at the speed nc^* relative to those in the same range at c^* 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 $n = 4$.

20.25 Derive an expression that shows how the pressure of a gas inside an effusion oven (a heated chamber with a small hole in one wall) varies with time if the oven is not replenished as the gas escapes. Then show that $t_{1/2}$, the time required for the pressure to decrease to half its initial value, is independent of the initial pressure. *Hint.* Begin by setting up a differential equation relating dp/dt to $p = NkT/V$, and then integrating it.

20.26 Confirm that eqn 20.57 is a solution of the diffusion equation with the correct initial value.

20.27 Calculate the relation between $\langle x^2\rangle^{1/2}$ and $\langle x^4\rangle^{1/4}$ for diffusing particles at a time t if they have a diffusion constant D.

20.28 The diffusion equation is valid when many elementary steps are taken in the time interval of interest, but the random walk calculation lets us discuss distributions for short times as well as for long. Use eqn 20.61 to calculate the probability of being six paces from the origin (that is, at $x = 6\lambda$) after (a) four, (b) six, (c) twelve steps.

20.29‡ A dilute solution of a weak (1,1)-electrolyte contains both neutral ion pairs and ions in equilibrium ($AB \rightleftharpoons A^+ + B^-$). Prove that molar conductivities are related to the degree of ionization by the equations:

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m(\alpha)} + \frac{(1-\alpha)\Lambda_m^\circ}{\alpha^2\Lambda_m(\alpha)^2} \qquad \Lambda_m(\alpha) = \lambda_+ + \lambda_- = \Lambda_m^\circ - \mathcal{K}(\alpha c)^{1/2}$$

where Λ_m° is the molar conductivity at infinite dilution and $\mathcal{K}$ is the constant in Kohlrausch's law (eqn 20.28).

Applications: to astrophysics and biochemistry

20.30 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, $R = 6.37$ Mm, $g = 9.81$ m s^{-2}, (b) Mars, $R = 3.38$ Mm, $m_{\text{Mars}}/m_{\text{Earth}} = 0.108$. 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.

20.31‡ Interstellar space is a medium quite different from the gaseous environments we commonly encounter on Earth. For instance, a typical density of the medium is about 1 atom cm^{-3} and that atom is typically H; the effective temperature due to stellar background radiation is about 10 000 K. Estimate the diffusion coefficient and thermal conductivity of H under these conditions. *Comment.* Energy is in fact transferred much more effectively by radiation.

20.32 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?

20.33‡ In the *standard model* of stellar structure (I. Nicholson, *The sun*. Rand McNally, New York (1982)), the interior of the Sun is thought to consist of 36 per cent H and 64 per cent He by mass, at a density of 158 g cm^{-3}. Both atoms are completely ionized. The approximate dimensions of the nuclei can be calculated from the formula $r_{\text{nucleus}} = 1.4A^{1/3}$ fm, where A is the mass number. The size of the free electron, $r_e \approx 10^{-18}$ m, is negligible compared to the size of the nuclei. (a) Calculate the excluded volume in 1.0 cm^3 of the stellar interior and on that basis decide upon the applicability of the perfect gas law to this system. (b) The standard model suggests that the pressure in the stellar interior is 2.5×10^{11} atm. Calculate the temperature of the Sun's interior based on the perfect gas model. The generally accepted standard model value is 16 MK. (c) Would a van der Waals type of equation (with $a = 0$) give a better value for T?

20.34 Enrico Fermi, the great Italian scientist, was a master at making good approximate calculations based on little or no actual data. Hence, such calculations are often called 'Fermi calculations'. Do a Fermi calculation on how long it would take for a gaseous air-borne cold virus of molar mass 100 kg

mol^{-1} to travel the distance between two conversing people 1.0 m apart by diffusion in still air.

20.35 The diffusion coefficient of a particular kind of t-RNA molecule is $D = 1.0 \times 10^{-11}\ \mathrm{m^2\ s^{-1}}$ in the medium of a cell interior. How long does it take molecules produced in the cell nucleus to reach the walls of the cell at a distance 1.0 μm, corresponding to the radius of the cell?

20.36‡ In this problem, we examine a model for the transport of oxygen from air in the lungs to blood. First, show that, for the initial and boundary conditions $c(x,t) = c(x,0) = c_0$, $(0 < x < \infty)$ and $c(0,t) = c_s$, $(0 \le t \le \infty)$ where c_0 and c_s are constants, the concentration, $c(x,t)$, of a species is given by

$$c(x,t) = c_0 + (c_s - c_0)\{1 - \mathrm{erf}\,\xi\} \qquad \xi(x,t) = \frac{x}{(4Dt)^{1/2}}$$

where erf ξ is the error function and the concentration $c(x,t)$ evolves by diffusion from the *yz*-plane of constant concentration, such as might occur if a condensed phase is absorbing a species from a gas phase. Now draw graphs of concentration profiles at several different times of your choice for the diffusion of oxygen into water at 298 K (when $D = 2.10 \times 10^{-9}\ \mathrm{m^2\ s^{-1}}$) on a spatial scale comparable to passage of oxygen from lungs through alveoli into the blood. Use $c_0 = 0$ and set c_s equal to the solubility of oxygen in water. *Hint*. Use mathematical software.