22 Dimensions, units and some key mathematical ideas

Physical constants: $R = 8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}$, $h = 6.626 \times 10^{-34}\ \mathrm{J\,s}$, $k_B = 1.381 \times 10^{-23}\ \mathrm{J\,K^{-1}}$, $N_A = 6.022 \times 10^{23}\ \mathrm{mol^{-1}}$, $F = 96{,}485\ \mathrm{C\,mol^{-1}}$, $c = 2.998 \times 10^{8}\ \mathrm{m\,s^{-1}}$.

22.1 The so-called 'SUVAT' equations apply to an object experiencing a constant acceleration a and give various relationships between the distance travelled s, the initial velocity u, the final velocity v, and the time t. Determine the dimensions of each term in these equations, and hence show that they are dimensionally consistent.

$$v = u + at \quad s = ut + \tfrac{1}{2}at^2 \quad s = vt - \tfrac{1}{2}at^2 \quad v^2 = u^2 + 2as \quad s = \tfrac{1}{2}(u + v)t$$

22.2 A spherical particle of radius r moving with velocity v through a viscous medium (e.g. a liquid) experiences a retarding force F which can, under some circumstances, be approximated by the Stokes' Law

$$F = 6\pi\eta r v,$$

where η is the viscosity of the medium. Determine the dimensions of η, and hence its SI unit. [Hint: rearrange the expression to give $\eta = \ldots$, and then use the known dimensions of all the quantities then on the right.]

22.3 A first-order reaction has the rate law

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_{1\mathrm{st}}[\mathrm{A}],$$

where [A] is the concentration of a reactant, t is time and $k_{1\mathrm{st}}$ is the rate constant. Assuming that [A] is given in amount of substance per unit volume, determine the dimensions of $k_{1\mathrm{st}}$. Hence, state the SI unit of $k_{1\mathrm{st}}$.

22.4 A second-order reaction has the rate law

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -k_{2\mathrm{nd}}[\mathrm{A}]^2,$$

where [A] is the concentration of a reactant, t is time and $k_{2\mathrm{nd}}$ is the rate constant. Assuming that [A] is given in amount of substance per unit volume, determine the dimensions of $k_{2\mathrm{nd}}$. If the concentration is expressed in $\mathrm{mol\,dm^{-3}}$, what will be the units of $k_{2\mathrm{nd}}$?

22.5 The work done when a force F moves a distance x is $F \times x$. The work done when a charge q moves through a potential (voltage) V is $q \times V$. The work done when a surface is increased in area by A is given by $A \times \gamma$, where γ is the surface tension (SI unit $\mathrm{N\,m^{-1}}$).

Show that each of these work terms has the dimensions of energy.

22.6 (a) The rotational kinetic energy of an object with *moment of inertia* I rotating at angular frequency ω is given by $\frac{1}{2}I\omega^2$. Given that I has dimensions ML^2, confirm that $\frac{1}{2}I\omega^2$ has the dimensions of energy. [Hint: ω could be given in rad s^{-1}; recall that radians are dimensionless.]

(b) For a diatomic molecule, I is given by

$$I = \frac{m_1 m_2}{m_1 + m_2} R^2,$$

where m_1 and m_2 are the masses of the two atoms and R is the bond length. In quantum mechanics the energy E_J of a rotating diatomic is given by

$$E_J = BJ(J+1) \qquad \text{where } B = \frac{\hbar^2}{2I};$$

in this expression J is a dimensionless quantum number which takes integer values, and $\hbar$ is Planck's constant divided by 2π: $\hbar = h/2\pi$.

Determine the dimensions of I and B; hence show that E_J has the dimensions of energy.

22.7 In quantum mechanics, a simple model for the energy of a vibrating bond is

$$E_v = (v + \tfrac{1}{2})\hbar\omega \qquad \text{where } \omega = \sqrt{\frac{k_f}{m}};$$

in this expression v is a dimensionless quantum number which takes integer values, k_f is the force constant (SI unit N m^{-1}), m is the mass, and $\hbar$ is Planck's constant divided by 2π: $\hbar = h/2\pi$.

Determine the dimensions of k_f and ω; hence show that E_v has the dimensions of energy.

22.8 Convert the following to SI, using an prefix in your answer, where appropriate.

(a) The collision cross-section of O_2, 40 $Å^2$.

(b) The entropy change when one mole of liquid water is vaporized at 373 K, 26.05 e.u.

(c) The vapour pressure of water at its triple point, 4.58 τ.

(d) The vibrational frequency of the bond in H_2, 4401 cm^{-1}.

(e) The orbital energy of a 1*s* electron in He, −25 eV.

(f) The mass of one molecule of $^{19}F_2$, given that the mass of ^{19}F is 18.998 u.

22.9 (a) What volume, in cm^3, of a solution of concentration 0.15 mol dm^{-3} contains the same amount in moles as 13.5 cm^3 of a solution of concentration 1.2 mol dm^{-3}?

(b) 1.50 g of NaCl is dissolved in water and the solution made up to a total volume of 50 cm^3. What is the concentration, in mol dm^{-3} and in mol m^{-3}, of the resulting solution. [RFM for NaCl is 58.35 g mol^{-1}.]

(c) How much water needs to be added to 10 cm^3 of a solution of concentration 1.00 mol dm^{-3} to give a solution of concentration 0.15 mol dm^{-3}?

22.10 In quantum mechanics, the energy of a rotating diatomic is given by

$$E_J = BJ(J+1) \qquad \text{where } B = \frac{\hbar^2}{2I},$$

where all of the symbols are defined in question 22.7. If SI units are used for $\hbar$ and I, then the energy E_J will of course be in joules.

(a) Explain why the energy expressed in cm^{-1}, $\tilde{E}$ and the energy expressed in joules, E, are related by

$$E = h \times \tilde{c} \times \tilde{E},$$

where $\tilde{c}$ is the speed on light in cm s^{-1}.

(b) Hence show that the rotational energy, expressed in cm^{-1}, is given by

$$\tilde{E}_J = \frac{B}{h\tilde{c}} J(J+1).$$

(c) By substituting in $\hbar^2/2I$ for B, go on to show that the rotation energy in cm^{-1} can be written

$$\tilde{E}_J = \frac{h}{8\pi^2\tilde{c}I} J(J+1).$$

22.11 Sketch $\cos(3\alpha)$ in the range $\alpha = 0$ to 2π. What is the period of this function? At what values of α (expressed in terms of π) does the function go to zero? Classify the function as even or odd about the value $\alpha = \pi$.

22.12 (a) Given that

$$\sin(A+B) \equiv \sin A \cos B + \cos A \sin B \qquad \cos(A+B) \equiv \cos A \cos B - \sin A \sin B.$$

show that

$$\sin(2A) \equiv 2 \sin A \cos B \qquad \cos(2A) \equiv \cos^2 A - \sin^2 A.$$

(b) Using $\cos^2 A + \sin^2 A = 1$, show that $\cos(2A) \equiv \cos^2 A - \sin^2 A$ can be rewritten in two different ways

$$\cos(2A) \equiv 2\cos^2 A - 1 \quad \text{or} \quad \cos(2A) \equiv 1 - 2\sin^2 A.$$

(c) Show that these last two identities can be rearranged to give

$$\cos^2 A \equiv \tfrac{1}{2}[1 + \cos(2A)] \quad \text{and} \quad \sin^2 A \equiv \tfrac{1}{2}[1 - \cos(2A)].$$

22.13 The concentration of a reactant A in a first-order reaction varies with times as follows

$$[\text{A}](t) = [\text{A}]_0 \exp(-k_{1\text{st}}t),$$

where $[\text{A}](t)$ is the concentration at time t, $[\text{A}]_0$ is the concentration at time zero, and $k_{1\text{st}}$ is the rate constant. Show that the half life t_{half}, which is the time taken for the concentration to fall to half its initial value, is given by $t_{\text{half}} = \ln(2)/k_{1\text{st}}$.

22.14 (a) The Boltzmann distribution gives the population of energy level i, n_i, in terms of its energy ε_i and the population n_0 of the lowest level

$$n_i = n_0 \exp\left(\frac{-\varepsilon_i}{k_B T}\right).$$

Rearrange this to find expressions for $\ln(n_i)$ and $\ln(n_i/n_0)$.

(b) The standard Gibbs energy change $\Delta_r G^\circ$ and the equilibrium constant K are related by $\Delta_r G^\circ = -RT \ln K$. Rearrange this to find expressions for $\ln K$ and for K.

22.15 Compute the first and second derivatives of $f(t) = A \exp(-Bt^2)$ with respect to t (A and B are constants). Sketch a graph of $f(t)$ against t and, by interpreting the first derivative as the slope, explain how your expression for $\mathrm{d}f(t)/\mathrm{d}t$ is consistent with the plot.

22.16 Differentiate the function $f(r) = r^4 \exp(-r)$ with respect to r and hence show that there are extrema at $r = 0$, $r = 4$ and $r = +\infty$. Explain why $r = 4$ must correspond to a maximum.

22.17 (a) Using the identity $\sin^2\theta \equiv \frac{1}{2}[1 - \cos(2\theta)]$, show that

$$\int_0^A \sin^2\left(\frac{\pi x}{A}\right) \mathrm{d}x$$

can be written

$$\frac{1}{2}\int_0^A \mathrm{d}x - \frac{1}{2}\int_0^A \cos\left(\frac{2\pi x}{A}\right) \mathrm{d}x.$$

(b) Evaluate both integrals and show that together they come to $A/2$.

22.18 A second-order reaction has the following rate equation

$$\frac{\mathrm{d}[\mathrm{A}](t)}{\mathrm{d}t} = -k_{2\mathrm{nd}}[\mathrm{A}]^2(t),$$

where $[\mathrm{A}](t)$ is the concentration of reactant A at time t, and $k_{2\mathrm{nd}}$ is the second-order rate constant.

(a) Separate the variables, taking the terms in $[\mathrm{A}](t)$ to the left, and those in t to the right.

(b) Integrate both sides of the resulting equation.

(c) Use the fact that at time $t = 0$ the concentration of A is $[\mathrm{A}]_0$ to determine the constant of integration.