

UNITS

1. (a) The relevant base units are kg, m, s, A, K, mol.

force: $N = \text{kg m s}^{-2}$.

pressure: $\text{Pa} = \text{kg m}^{-1} \text{s}^{-2}$.

energy: $J = \text{kg m}^2 \text{s}^{-2}$.

power: $W = \text{kg m}^2 \text{s}^{-3}$.

charge: $C = \text{A s}$.

potential difference: $V = \text{kg m}^2 \text{s}^{-3} \text{A}^{-1}$.

- (b) (i) $h = 6.626 \times 10^{-34} \text{ J s} = 6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$.
(ii) $k = 1.381 \times 10^{-23} \text{ J K}^{-1} = 1.381 \times 10^{-23} \text{ kg m}^2 \text{ s}^{-2} \text{ K}^{-1}$.
(iii) $e = 1.602 \times 10^{-19} \text{ C} = 1.602 \times 10^{-19} \text{ A s}$.
(iv) $\epsilon_0 = 8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1} = 8.854 \times 10^{-12} \text{ kg}^{-1} \text{ m s}^2 \text{ A}^2$.

2. flux: units = $\text{mol s}^{-1} \text{ m}^{-2}$ (rate of change of amount per unit time per unit area)

concentration gradient = $\frac{dc}{dx}$, units = mol m^{-4} (concentration / distance)

$D = \text{flux}/\text{conc. grad.} : \text{units m}^2 \text{ s}^{-1}$.

3. $1 \text{ m}^3 = 1 \text{ m}^3 \times \left(\frac{10 \text{ dm}}{1 \text{ m}}\right)^3 = 10^3 \text{ dm}^3$

Calculations with quantities

4 (a) $R = \frac{pV}{nT} : \text{units} = \frac{\text{Pa m}^3}{\text{mol K}} = \text{kg m}^2 \text{ s}^{-2} \text{ mol}^{-1} \text{ K}^{-1} = \text{J mol}^{-1} \text{ K}^{-1}$

(b) $R = \frac{pV}{nT} = \frac{1.00 \times 10^{-3} \text{ bar} \left(\frac{10^5 \text{ Pa}}{1 \text{ bar}}\right) 24.8 \text{ m}^3}{1 \text{ mol} \times 298 \text{ K}} = 8.32 \text{ J mol}^{-1} \text{ K}^{-1}$

(c) $c = \frac{n}{V} = \frac{p}{RT} = 2.43 \times 10^{16} \text{ molec cm}^{-3}$

5. The cycle is $\text{I}_2(\text{s}) \rightarrow \text{I}_2(\text{g}) \rightarrow 2\text{I}(\text{g})$, hence

$$\Delta_f H(\text{I}(\text{g})) = \frac{1}{2} (\Delta_{\text{sub}} H(\text{I}_2(\text{g})) + \Delta_{\text{bond}} H(\text{I}_2(\text{g}))) = 104 \text{ kJ mol}^{-1}.$$

6. C is the correct statement, activities are defined with respect to a standard state with defined units, so that the activity is dimensionless.

A is common practice among students who want to fail exam.

B is a common error in school level text books.

D is not correct because it is strictly forbidden to log a quantity with units.

Unit conversion

9. $3.2 \times 10^{-26} \text{ m}^3 \times \left(\frac{10 \text{ cm}}{1 \text{ m}} \right)^3 \times \frac{1 \text{ minim}}{0.05919385 \text{ cm}^3} = 5.41 \times 10^{-19} \text{ minim}$
10. $135000 \frac{\text{furlong}}{\text{fortnight}} = 135000 \frac{\text{furlong}}{\text{fortnight}} \times \frac{1 \text{ mile}}{8 \text{ furlong}} \times \frac{1 \text{ fortnight}}{14 \text{ days}} \times \frac{1 \text{ day}}{24 \text{ hour}} = 50.2 \text{ mph}$
11. $3.01 \frac{\text{g}}{\text{cm}^3} = 3.01 \frac{\text{g}}{\text{cm}^3} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{1 \text{ slug}}{14.5939 \text{ kg}} \times \left(\frac{30.48 \text{ cm}}{1 \text{ foot}} \right)^3 = 5.84 \text{ slug ft}^{-3}$
12. To do this we need the conversion factors
 1 lb (pound) = 0.454 kg
 1 in = 2.54 cm
 and the acceleration due to gravity $g = 9.81 \text{ m s}^{-2}$.
 $22 \frac{\text{lbf}}{\text{in}^2} = 22 \frac{\text{lbf}}{\text{in}^2} \times \frac{0.454 \text{ kg}}{1 \text{ lb}} \times 9.81 \text{ m s}^{-2} \times \left(\frac{1 \text{ in}}{2.54 \times 10^{-2} \text{ m}} \right)^2 = 152 \text{ kPa}$
 The multiplication by g is necessary to convert the mass into a force.
13. $0.15 \frac{\text{mol}}{\text{dm}^3} = 0.0903 \text{ molec nm}^{-3}$
14. (a) a temperature difference of 1°F is equivalent to $1^\circ\text{F} \times \frac{100^\circ\text{C}}{180^\circ\text{F}} = 0.556^\circ\text{C}$
 (b) -459.67°F .
 (c) This follows from the calculation of (b), the freezing point of water is 491.67°R .
 (d) $8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times \frac{100 \text{ K}}{180^\circ\text{R}} = 4.619 \text{ J }^\circ\text{R}^{-1} \text{ mol}^{-1}$
15. Using the perfect gas law,
 $n = \frac{pV}{RT} = \frac{1 \text{ atm} \times 1 \text{ ft}^3}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 273.15 \text{ K}} \times \frac{101325 \text{ Pa}}{1 \text{ atm}} \times \left(\frac{0.3048 \text{ m}}{1 \text{ ft}} \right)^3 = 1.263 \text{ mol}$

Dimensional analysis

16. (a) **density:** kg m^{-3} .
pressure: $\text{Pa} = \text{kg m}^{-1} \text{ s}^{-2}$ (see Q 1).
- (b) (i) Use dimensional analysis to determine this dependence.
 In terms of dimensions (M = mass, L = length, T = time)
 $MT^{-1} = (ML^{-1}T^{-2})^x (ML^{-3})^y (L^2)^z$
 equating powers rate $\propto A\sqrt{\rho\rho}$

(ii) At a given pressure and temperature the number density of all perfect gases is the same and so the density of the gas is proportional to the molecular weight. The rate of loss of mass is therefore proportional to the square root of the molecular weight.

17. (a) $c \propto \sqrt{p/\rho}$

(b) If the gas is perfect $c \propto \sqrt{\frac{p}{\rho}} = \sqrt{\frac{pV}{nM}} = \sqrt{\frac{RT}{M}}$, where M is the molar mass.

(c) $\frac{c_{\text{He}}}{c_{\text{air}}} = \sqrt{\frac{M_{\text{air}}}{M_{\text{He}}}} = \sqrt{\frac{M_{\text{air}}}{M_{\text{He}}}} \Rightarrow c_{\text{He}} = 886 \text{ m s}^{-1}$, having taken the rmm of air to be 28.97 and the ram of He to be 4.02.

18. (a) The question states that the physics involves the gravitational force mg and so the powers of m and g are the same.

$$v_t \propto (mg)^x \eta^y a^z \Rightarrow LT^{-1} = (MLT^{-2})^x (ML^{-1}T^{-1})^y (L)^z$$

hence $v_t \propto \frac{mg}{\eta a}$.

(b) (i) the terminal velocity will halve.

(ii) assuming the drop to be spherical the mass will increase by a factor of $2^{1/3}$, and therefore the terminal velocity will be reduced by a factor $2^{2/3}$.

19. $E \propto r^{-2} \mu^{-1} h^2 = \frac{h^2}{\mu r^2}$.

20. $v \propto \frac{qE}{\eta a}$

21. (a) V and nb must have the same units, thus b has units $\text{m}^3 \text{mol}^{-1}$.
 p and $n^2 a/V^2$ must have the same units, thus a has units $\text{kg m}^5 \text{s}^{-2} \text{mol}^{-2}$.
 R has units of pV/nT , i.e. $\text{kg m}^2 \text{s}^{-2} \text{K}^{-1} \text{mol}^{-1}$.

(b) V_c has the same units as b , and so $V_c \propto b$, $p_c \propto ab^{-2}$ and $T_c \propto ab^{-1}R^{-1}$.

(c) From the results above, define $p = p^* \frac{a}{b^2}$, $V = V^* b$, $T = T^* \frac{a}{bR}$, hence

$$\left(p^* \frac{a}{b^2} + \frac{n^2 a}{V^{*2} n^2 b^2} \right) (V^* nb - nb) = nRT^* \frac{a}{bR}, \text{ and cancelling,}$$

$$\left(p^* + \frac{1}{V^{*2}} \right) (V^* - 1) = T^*$$

(d) This is called the principle of corresponding states, it means that all systems obeying the vdW equation can be represented on the same set of universal curves,

as can any model based on two constants plus the gas constant.

$$(e) V_c = 3b, T_c = \frac{8a}{27bR}, p_c = \frac{a}{27b^2}.$$

$$22. (a) \text{J m}^{-2}.$$

$$(b) h \propto \frac{\gamma}{\rho g}$$

$$23. \Delta T \propto mv^2 / k.$$

$$24. \text{velocity } v \text{ } LT^{-1}, \text{ gravity } g \text{ } LT^{-2}, \text{ radius } a \text{ } L, \text{ density } \rho - \rho_l \text{ } ML^{-3}, \text{ viscosity } \eta \text{ } ML^{-1}T^{-1}.$$

$$v \propto ga^2(\rho - \rho_l) / \eta$$

$$25. \eta \propto \frac{\sqrt{mkT}}{a^2}.$$

$$26. (a) \Lambda \propto \frac{h}{\sqrt{mk_B T}}.$$

$$(b) \Delta S \propto \Delta p^3 T^{-1} \beta.$$

$$27. (a) p: \text{kg m}^{-1} \text{ s}^{-2}, k: \text{kg m}^2 \text{ s}^{-2} \text{ K}^{-1}, T: \text{K}, \sigma: \text{m}^2, m: \text{kg}$$

$$(b) D \propto p^{-1} (kT)^{3/2} \sigma^{-1} m^{-1/2}$$

$$28. Z \propto (kT)^{1/2} d^2 m^{-1/2}$$

$$29. (a) r: \text{m}; \omega: \text{rad s}^{-1}; v: \text{m s}^{-1}. \text{ Hence the units of } s \text{ are s.}$$

$$(b) M^* \propto \frac{sRT}{D}$$

$$30. E \propto \frac{\mu e^4}{(h\epsilon_0)^2}$$

$$31. (a) E_{\min} \propto \frac{h^2}{mr^2}$$

$$(b) 1.5 \times 10^{-21} \text{ J.}$$

$$32. M \propto \frac{c^3}{\sqrt{\rho G^3}}$$

33. (i) $\text{J s}^{-1} \text{m}^{-2} \text{K}^{-4}$, hence $\text{kg s}^{-3} \text{K}^{-4}$

(ii) $\sigma \propto \frac{k^4}{h^3 c^2}$.