1 The properties of gases

1A The perfect gas

Answers to discussion questions

1A.2 The partial pressure of a gas in a mixture of gases is the pressure the gas would exert if it occupied alone the same container as the mixture at the same temperature. Dalton's law is a limiting law because it holds exactly only under conditions where the gases have no effect upon each other. This can only be true in the limit of zero pressure where the molecules of the gas are very far apart. Hence, Dalton's law holds exactly only for a mixture of perfect gases; for real gases, the law is only an approximation.

Solutions to exercises

1A.1(b) The perfect gas law [1A.5] is $pV = nRT$, implying that the pressure would be

$$p = \frac{nRT}{V}$$

All quantities on the right are given to us except n, which can be computed from the given mass of Ar.

$$n = \frac{25 \text{ g}}{39.95 \text{ g mol}^{-1}} = 0.62\bar{6} \text{ mol}$$

so
$$p = \frac{(0.62\bar{6} \text{ mol}) \times (8.31 \times 10^{-2} \text{dm}^3 \text{ bar K}^{-1} \text{ mol}^{-1}) \times (30 + 273) \text{ K}}{1.5 \text{ dm}^3} = \boxed{10.\bar{5} \text{bar}}$$

So $\boxed{\text{no}}$, the sample would not exert a pressure of 2.0 bar.

1A.2(b) Boyle's law [1A.4a] applies.
$$pV = \text{constant} \qquad \text{so} \qquad p_f V_f = p_i V_i$$
Solve for the initial pressure:

(i) $\quad p_i = \dfrac{p_f V_f}{V_i} = \dfrac{(1.97 \text{ bar}) \times (2.14 \text{dm}^3)}{(2.14 + 1.80) \text{dm}^3} = \boxed{1.07 \text{ bar}}$

(ii) The original pressure in Torr is

$$p_i = (1.07 \text{ bar}) \times \left(\frac{1 \text{ atm}}{1.013 \text{ bar}}\right) \times \left(\frac{760 \text{ Torr}}{1 \text{ atm}}\right) = \boxed{803 \text{ Torr}}$$

1A.3(b) The relation between pressure and temperature at constant volume can be derived from the perfect gas law, $pV = nRT$ [1A.5]

so $\quad p \propto T \quad$ and $\quad \dfrac{p_i}{T_i} = \dfrac{p_f}{T_f}$

The final pressure, then, ought to be

$$p_f = \frac{p_i T_f}{T_i} = \frac{(125 \text{ kPa}) \times (11 + 273)\text{K}}{(23 + 273)\text{K}} = \boxed{120 \text{ kPa}}$$

1A.4(b) According to the perfect gas law [1.8], one can compute the amount of gas from pressure, temperature, and volume.
$$pV = nRT$$

so $\quad n = \dfrac{pV}{RT} = \dfrac{(1.00 \text{ atm}) \times (1.013 \times 10^5 \text{Pa atm}^{-1}) \times (4.00 \times 10^3 \text{m}^3)}{(8.3145 \text{ J K}^{-1}\text{mol}^{-1}) \times (20 + 273)\text{K}} = 1.66 \times 10^5 \text{mol}$

Once this is done, the mass of the gas can be computed from the amount and the molar mass:

$$m = (1.66 \times 10^5 \text{mol}) \times (16.04 \text{ g mol}^{-1}) = 2.67 \times 10^6 \text{g} = \boxed{2.67 \times 10^3 \text{ kg}}$$

1A.5(b) The total pressure is the external pressure plus the hydrostatic pressure [1A.1], making the total pressure

1

$$p = \frac{kT}{\sigma\lambda} = \frac{(1.381\times10^{-23}\ \text{J K}^{-1})(293\ \text{K})}{0.36\times(10^{-9}\ \text{m})^2(10\times0.34\times10^{-9}\ \text{m})} = 3.3\times10^6\ \text{J m}^{-3} = \boxed{3.3\ \text{MPa}}$$

Comment. This pressure works out to 33 bar (about 33 atm), conditions under which the assumption of perfect gas behavior and kinetic model applicability at least begins to come into question.

1B.7(b) The mean free path [1B.13] is

$$\lambda = \frac{kT}{\sigma p} = \frac{(1.381\times10^{-23}\ \text{J K}^{-1})(217\ \text{K})}{0.43\times(10^{-9}\ \text{m})^2(12.1\times10^3\ \text{Pa atm}^{-1})} = \boxed{5.8\times10^{-7}\ \text{m}}$$

Solutions to problems

1B.2 The number of molecules that escape in unit time is the number per unit time that would have collided with a wall section of area A equal to the area of the small hole. This quantity is readily expressed in terms of Z_W, the collision flux (collisions per unit time with a unit area), given in eqn 19A.6. That is,

$$\frac{dN}{dt} = -Z_W A = \frac{-Ap}{(2\pi mkT)^{1/2}}$$

where p is the (constant) vapour pressure of the solid. The change in the number of molecules inside the cell in an interval Δt is therefore $\Delta N = -Z_W A\Delta t$, and so the mass loss is

$$\Delta w = m\Delta N = -Ap\left(\frac{m}{2\pi kT}\right)^{1/2}\Delta t = -Ap\left(\frac{M}{2\pi RT}\right)^{1/2}\Delta t$$

Therefore, the vapour pressure of the substance in the cell is

$$p = \left(\frac{-\Delta w}{A\Delta t}\right)\times\left(\frac{2\pi RT}{M}\right)^{1/2}$$

For the vapour pressure of germanium

$$p = \left(\frac{43\times10^{-9}\ \text{kg}}{\pi(0.50\times10^{-3}\ \text{m})(7200\ \text{s})}\right)\times\left(\frac{2\pi(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(1273\ \text{K})}{72.64\times10^{-3}\ \text{kg mol}^{-1}}\right)^{1/2}$$

$$= 7.3\times10^{-3}\ \text{Pa} = \boxed{7.3\ \text{mPa}}$$

1B.4 We proceed as in Justification 1B.2 except that, instead of taking a product of three one-dimensional distributions in order to get the three-dimensional distribution, we make a product of two one-dimensional distributions.

$$f(v_x,v_y)dv_xdv_y = f(v_x^2)f(v_y^2)dv_xdv_y = \left(\frac{m}{2\pi kT}\right)e^{-mv^2/2kT}dv_xdv_y$$

where $v^2 = v_x^2 + v_y^2$. The probability $f(v)dv$ that the molecules have a two-dimensional speed, v, in the range v to $v + dv$ is the sum of the probabilities that it is in any of the area elements dv_xdv_y in the circular shell of radius v. The sum of the area elements is the area of the circular shell of radius v and thickness dv which is $\pi(v+dv)^2 - \pi v^2 = 2\pi vdv$. Therefore,

$$f(v) = \boxed{\left(\frac{m}{kT}\right)ve^{-mv^2/2kT}} = \boxed{\left(\frac{M}{RT}\right)ve^{-Mv^2/2RT}}\quad\left[\frac{M}{R} = \frac{m}{k}\right]$$

The mean speed is determined as

$$v_{mean} = \int_0^\infty vf(v)\,dv = \left(\frac{m}{kT}\right)\int_0^\infty v^2 e^{-mv^2/2kT}\,dv$$

Using integral G.3 from the Resource Section yields

$$v_{mean} = \left(\frac{m}{kT}\right)\times\left(\frac{\pi^{1/2}}{4}\right)\times\left(\frac{2kT}{m}\right)^{3/2} = \boxed{\left(\frac{\pi kT}{2m}\right)^{1/2}} = \boxed{\left(\frac{\pi RT}{2M}\right)^{1/2}}$$

1B.6 The distribution [1B.4] is

$$n = \frac{pV}{RT} = \frac{(130\,\text{Torr}) \times \left(\dfrac{1\,\text{atm}}{760\,\text{Torr}}\right) \times (30.6\,\text{dm}^3)}{(0.08206\,\text{dm}^3\,\text{atm}\,\text{K}^{-1}\,\text{mol}^{-1}) \times (330.2\,\text{K})} = 0.193\,\text{mol}$$

This is a substantial fraction of the original amount of water and cannot be ignored. Consequently the calculation needs to be redone taking into account the fact that only a part, n_l, of the vapor condenses into a liquid while the remainder ($1.00\,\text{mol} - n_l$) remains gaseous. The heat flow involving water, then, becomes

$$q(\text{H}_2\text{O}) = -n_l \Delta_{\text{vap}} H + n_l C_{p,m}(\text{H}_2\text{O},l)\Delta T(\text{H}_2\text{O})$$
$$+ (1.00\,\text{mol} - n_l)C_{p,m}(\text{H}_2\text{O},g)\Delta T(\text{H}_2\text{O})$$

Because n_l depends on the equilibrium temperature through

$n_l = 1.00\,\text{mol} - \dfrac{pV}{RT}$, where p is the vapor pressure of water, we will have two unknowns (p and T) in

the equation $-q(\text{H}_2\text{O}) = q(\text{Cu})$. There are two ways out of this dilemma: (1) p may be expressed as a function of T by use of the Clapeyron equation, or (2) by use of successive approximations. Redoing the calculation yields:

$$\theta = \frac{n_l \Delta_{\text{vap}} H + n_l C_{p,m}(\text{H}_2\text{O},l) \times 100°\text{C} + (1.00 - n_l)C_{p,m}(\text{H}_2\text{O},g) \times 100°\text{C}}{mC_s + nC_{p,m}(\text{H}_2\text{O},l) + (1.00 - n_l)C_{p,m}(\text{H}_2\text{O},g)}$$

With

$$n_l = (1.00\,\text{mol}) - (0.193\,\text{mol}) = 0.80\overline{7}\,\text{mol}$$

(noting that $C_{p,m}(\text{H}_2\text{O},g) = 33.6\,\text{J}\,\text{mol}^{-1}\,\text{K}^{-1}$ [Table 2C.2]) $\theta = 47.2°\text{C}$. At this temperature, the vapor pressure of water is 80.41 Torr, corresponding to

$$n_l = (1.00\,\text{mol}) - (0.123\,\text{mol}) = 0.87\overline{7}\,\text{mol}$$

This leads to $\theta = 50.8°\text{C}$. The successive approximations eventually converge to yield a value of $\theta = \boxed{49.9°\text{C} = 323.1\,\text{K}}$ for the final temperature. (At this temperature, the vapor pressure is 0.123 bar.)
Using this value of the final temperature, the heat transferred and the various entropies are calculated as in part (a).

$$q(\text{Cu}) = (2.00 \times 10^3\,\text{g}) \times (0.385\,\text{J}\,\text{K}^{-1}\,\text{g}^{-1}) \times (49.9\,\text{K}) = \boxed{38.4\,\text{kJ}} = -q(\text{H}_2\text{O})$$

$$\Delta S(\text{H}_2\text{O}) = \frac{-n\Delta_{\text{vap}} H}{T_b} + nC_{p,m}\ln\left(\frac{T_f}{T_i}\right) = \boxed{-119.\overline{8}\,\text{J}\,\text{K}^{-1}}$$

$$\Delta S(\text{Cu}) = mC_s \ln\frac{T_f}{T_i} = \boxed{129.\overline{2}\,\text{J}\,\text{K}^{-1}}$$

$$\Delta S(\text{total}) = -119.\overline{8}\,\text{J}\,\text{K}^{-1} + 129.\overline{2}\,\text{J}\,\text{K}^{-1} = \boxed{9\,\text{J}\,\text{K}^{-1}}$$

3A.10 ΔS depends on only the initial and final states, so we can use $\Delta S = nC_{p,m}\ln\dfrac{T_f}{T_i}$ [3A.20]
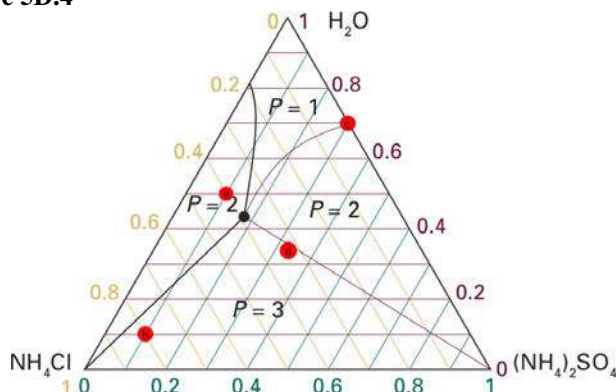
Since $q = nC_{p,m}(T_f - T_i),\ T_f = T_i + \dfrac{q}{nC_{p,m}} = T_i + \dfrac{I^2 Rt}{nC_{p,m}}$ [$q = ItV = I^2 Rt$]

That is, $\Delta S = nC_{p,m}\ln\left(1 + \dfrac{I^2 Rt}{nC_{p,m}T_i}\right)$

Since $n = \dfrac{500\,\text{g}}{63.5\,\text{g}\,\text{mol}^{-1}} = 7.87\,\text{mol}$

$$\Delta S = (7.87\,\text{mol}) \times (24.4\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}) \times \ln\left(1 + \frac{(1.00\,\text{A})^2 \times (1000\,\Omega) \times (15.0\,\text{s})}{(7.87) \times (24.4\,\text{J}\,\text{K}^{-1}) \times (293\,\text{K})}\right)$$

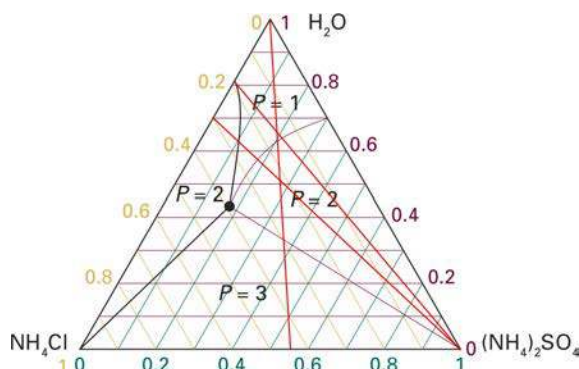$$= (192\,\text{J}\,\text{K}^{-1}) \times (\ln 1.27) = \boxed{+45.4\,\text{J}\,\text{K}^{-1}}$$

Figure 5D.4

Point (a) is in a two-phase region and point (b) in a three-phase region. Point (c) is practically in a single-phase region; that is, it is on the border between a single-phase and a two-phase region, so there would be a vanishingly small amount of a second phase present. Finally, point (d), for which all three components are present in nearly equal amounts, is in a three-phase region (although very near the border with a two-phase region).

5D.5(b) **(i)** Note the line in Figure 5D. 5 that runs from the water-NH_4Cl edge near $x(NH_4Cl) = 0.2$ (the point that represents a saturated aqueous solution of NH_4Cl) to the $(NH_4)_2SO_4$ vertex. Traveling along that line from the edge to the vertex represents adding $(NH_4)_2SO_4$ to a saturated aqueous solution of NH_4Cl. Note that it traverses the single-phase region at first. That is, the added $(NH_4)_2SO_4$ dissolves and does not cause NH_4Cl to precipitate out. If one starts with saturated aqueous NH_4Cl with solid NH_4Cl in excess, then the starting point is a bit further down on the water-NH_4Cl edge, for example at $x(NH_4Cl) = 0.3$. Adding $(NH_4)_2SO_4$ to such a solution would take one from that point to the $(NH_4)_2SO_4$ vertex. Initially, the system remains in the two-phase region, but eventually a single-phase region is reached. Note that the line intersects the single-phase region at a higher NH_4Cl-water ratio and even a higher overall $x(NH_4Cl)$ than that of saturated aqueous NH_4Cl. (That is, there is not only more NH_4Cl relative to water at that intersection point, but NH_4Cl is a larger fraction of the saturated **three**-component solution than it was in the saturated **two**-component system of water and NH_4Cl.) So here too, the effect of adding $(NH_4)_2SO_4$ is to make additional NH_4Cl dissolve, at least at first.

Figure 5D.5

(ii) First convert to moles for a convenient sample size, such as 100 g, and find composition by mole fraction.

NH_4Cl: $25 \text{ g} \times \dfrac{1 \text{ mol}}{53.49 \text{ g}} = 0.46\overline{7} \text{ mol}$

$(NH_4)_2SO_4$: $75 \text{ g} \times \dfrac{1 \text{ mol}}{132.15 \text{ g}} = 0.56\overline{8} \text{ mol}$

To get mole fractions, divide these amounts by the total amount of 1.03 mol:

$$x(NH_4Cl) = \frac{0.46\overline{7} \text{ mol}}{1.03 \text{ mol}} = 0.45 \qquad x((NH_4)_2SO_4) = 0.55$$

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$$\hat{p}_x e^{+ikx} = \frac{\hbar}{i}\frac{d}{dx}e^{+ikx} = \left(\frac{\hbar}{i}\right) \times (ik)e^{+ikx} = +k\hbar e^{+ikx}$$

$$\hat{p}_x e^{-ikx} = \frac{\hbar}{i}\frac{d}{dx}e^{-ikx} = \left(\frac{\hbar}{i}\right) \times (-ik)e^{-ikx} = -k\hbar e^{-ikx}$$

Because these functions are eigenfunctions of the momentum operator and the system wavefunction is a superposition of them, by the principle of linear superposition of eigenfunctions the probability of measuring a particular momentum eigenvalue in a series of observations is proportional to the square modulus $(|c_k|^2)$ of the corresponding coefficient in the superposition expression of ψ (see text Section 7C.2).

(a) The probability of observing the linear momentum $+k\hbar$ is $|c_1|^2 = \boxed{\cos^2 \chi}$.

(b) The probability of observing the linear momentum $-k\hbar$ is $|c_2|^2 = \boxed{\sin^2 \chi}$.

(c) $|c_1|^2 = 0.90$ and, taking c_1 to be positive, $c_1 = 0.95$.

Since the sum of the probabilities must equal 1, $|c_2|^2 = 1 - |c_1|^2 = 0.10$ and, therefore, $c_2 = \pm 0.32$.

Hence, the wavefunction is $\boxed{\psi = 0.95\, e^{ikx} \pm 0.32\, e^{-ikx}}$.

(d) $\qquad \psi = (\cos \chi)e^{+ikx} + (\sin \chi)e^{-ikx} = c_1 e^{+ikx} + c_2 e^{-ikx}$

The expectation value for kinetic energy depends upon the curvature of the wavefunction so we begin by finding the expression for $d^2\psi/dx^2$.

$$\frac{d\psi}{dx} = ikc_1 e^{+ikx} - ikc_2 e^{-ikx}$$

$$\frac{d^2\psi}{dx^2} = -k^2 c_1 e^{+ikx} - k^2 c_2 e^{-ikx} = -k^2\psi$$

Thus, ψ is an eigenfunction of the $d^2\psi/dx^2$ operator and it must also be an eigenfunction of the kinetic energy operator.

$$\hat{E}_k \psi = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi \ [7C.5] = \frac{(\hbar k)^2}{2m}\psi$$

The kinetic energy of the particle is the eigenvalue $\boxed{\dfrac{(\hbar k)^2}{2m}}$.

7C.12 The ground-state wavefunction of a hydrogen atom is $\psi = (1/\pi a_0^3)^{1/2}e^{-r/a_0}$. Calculate (a) the mean potential energy and (b) the mean kinetic energy of an electron in the ground state of a hydrogenic atom.

The normalized wavefunction is $\psi = \left(\dfrac{1}{\pi a_0^3}\right)^{1/2} e^{-r/a_0}$.

(a) $\qquad \langle V \rangle = \int \psi^* \hat{V} \psi\, d\tau \quad \left[\hat{V} = -\dfrac{e^2}{4\pi\varepsilon_0 r}\right]$

$$= \int \psi^* \left(\frac{-e^2}{4\pi\varepsilon_0} \cdot \frac{1}{r}\right)\psi\, d\tau = \frac{1}{\pi a_0^3}\left(\frac{-e^2}{4\pi\varepsilon_0}\right)\int_0^\infty r\, e^{-2r/a_0}dr \times 4\pi$$

$$= \frac{1}{\pi a_0^3}\left(\frac{-e^2}{4\pi\varepsilon_0}\right) \times \left(\frac{a_0}{2}\right)^2 \times 4\pi = \boxed{\frac{-e^2}{4\pi\varepsilon_0 a_0}}$$

(b) In one-dimension: $\hat{E}_k = \dfrac{\hat{p}_x^{\,2}}{2m} = \dfrac{1}{2m}\left(\dfrac{\hbar}{i}\dfrac{d}{dx}\right)\left(\dfrac{\hbar}{i}\dfrac{d}{dx}\right) = \boxed{-\dfrac{\hbar^2}{2m}\dfrac{d^2}{dx^2}}$ [7C.5]. For three-dimensional systems

such as the hydrogen atom the kinetic energy operator is

$$\hat{E}_k = \frac{\hat{p}_x^{\,2}}{2m} + \frac{\hat{p}_y^{\,2}}{2m} + \frac{\hat{p}_z^{\,2}}{2m} = -\frac{\hbar^2}{2m}\left\{\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right\} = \boxed{-\frac{\hbar^2}{2m}\nabla^2}$$

where $\dfrac{\partial^2}{\partial x^2} = \left(\dfrac{\partial^2}{\partial x^2}\right)_{y,z}$, $\dfrac{\partial^2}{\partial y^2} = \left(\dfrac{\partial^2}{\partial y^2}\right)_{x,z}$, $\dfrac{\partial^2}{\partial z^2} = \left(\dfrac{\partial^2}{\partial z^2}\right)_{x,y}$, and $\nabla^2 = \dfrac{\partial^2}{\partial x^2} + \dfrac{\partial^2}{\partial y^2} + \dfrac{\partial^2}{\partial z^2}$

The ∇^2 operator, called the laplacian operator or the del-squared operator, is advantageously written in spherical coordinates because the wavefunction has its simplest form in spherical coordinates. Mathematical

so $\quad \dfrac{1}{N_1^{\,2}} = \sin^2\zeta \int |s|^2\, d\tau + \cos^2\zeta \int |p|^2\, d\tau + \sin\zeta\cos\zeta \int (s*p + p*s)d\tau$

$\qquad\qquad = \sin^2\zeta + \cos^2\zeta = 1.$

In the last step, we used the fact that the s and p orbitals are orthogonal and normalized.
Thus

$\boxed{N_1 = 1}$ and $\boxed{\psi = (\sin\ \zeta)s + (\cos\ \zeta)p}$

Let $\quad \psi_2 = N_2 h_2 = N_2\{(\cos\ \zeta)s - (\sin\ \zeta)p\}$

Solve for the normalization constant N_2:

$$1 = N_2^{\,2} \int \{(\cos\zeta)s - (\sin\zeta)p\}*\{(\cos\zeta)s - (\sin\zeta)p\}d\tau$$

so $\quad \dfrac{1}{N_2^{\,2}} = \cos^2\zeta \int |s|^2\, d\tau + \sin^2\zeta \int |p|^2\, d\tau - \sin\zeta\cos\zeta \int (p*s + s*p)d\tau$

$\qquad\qquad = \cos^2\zeta + \sin^2\zeta = 1$

Thus

$\boxed{N_2 = 1}$ and $\boxed{\psi = (\cos\ \zeta)s - (\sin\ \zeta)p}$

In other words, the functions were already normalized.

Solutions to problem

10A.2   One approach is to construct the explicit forms of the orbitals and find the values of ϕ that maximize the squares of their magnitudes. We need the component unhybridized orbitals, put together from the radial and angular functions listed in Tables 9A.1 and 8C.1:

$$2s = R_{20}Y_{00} = \frac{1}{8^{1/2}}\left(\frac{Z}{a}\right)^{3/2} \times (2-\rho)e^{-\rho/2} \times \left(\frac{1}{4\pi}\right)^{1/2} = \left(\frac{1}{32\pi}\right)^{1/2}\left(\frac{Z}{a}\right)^{3/2}(2-\rho)e^{-\rho/2}$$

Use eqns. 9A.22 to write the p_x and p_y orbitals in terms of the complex hydrogenic orbitals defined in eqn. 9A.21:

$$2p_x = -\frac{1}{2^{1/2}}R_{21}(Y_{1,+1} - Y_{1,-1})$$

$$= -\frac{1}{2^{1/2}} \times \frac{1}{24^{1/2}}\left(\frac{Z}{a}\right)^{3/2}\rho e^{-\rho/2} \times \left(\frac{3}{8\pi}\right)^{1/2}\sin\theta(-e^{+i\phi} - e^{-i\phi})$$

$$= \left(\frac{1}{32\pi}\right)^{1/2}\left(\frac{Z}{a}\right)^{3/2}\rho e^{-\rho/2}\sin\theta\cos\phi$$

$$2p_y = \frac{i}{2^{1/2}}R_{21}(Y_{1,+1} + Y_{1,-1})$$

$$= \frac{i}{2^{1/2}} \times \frac{1}{24^{1/2}}\left(\frac{Z}{a}\right)^{3/2}\rho e^{-\rho/2} \times \left(\frac{3}{8\pi}\right)^{1/2}\sin\theta(-e^{+i\phi} + e^{-i\phi})$$
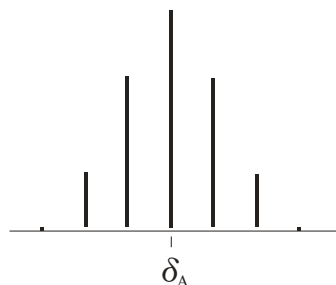
$$= \left(\frac{1}{32\pi}\right)^{1/2}\left(\frac{Z}{a}\right)^{3/2}\rho e^{-\rho/2}\sin\theta\sin\phi$$

where $\quad \rho = \dfrac{2Zr}{2a} = \dfrac{Zr}{a}$ [9A.11a]

In forming each hybrid, we neglect the factor $\left(\dfrac{1}{32\pi}\right)^{1/2}\left(\dfrac{Z}{a}\right)^{3/2}e^{-\rho/2}$ common to each

component; an angle-independent multiplicative term cannot influence the angle at which the hybrid is maximal.

Next, form the hybrids, using eqn. 10A.7:

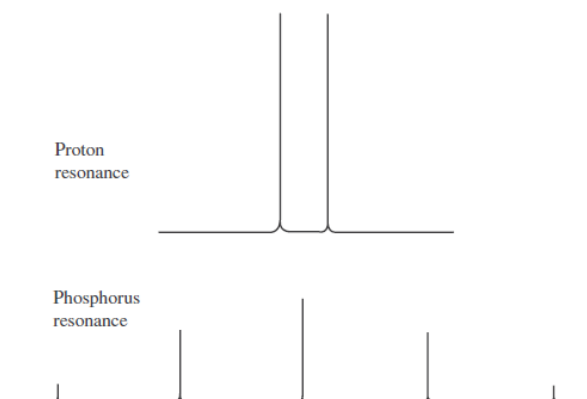$h_1 = s + 2^{1/2}p_y = (2-\rho) + 2^{1/2}(\rho\sin\theta\sin\phi) = 2 + \rho(2^{1/2}\sin\theta\sin\phi - 1)$

3

Figure 14B.2

$$\delta_A$$

E14B.5(b) $\quad v = \dfrac{g_I \mu_N \mathcal{B}_0}{h}$ [Solution to exercises 14A.3(a) & (b)]

Hence, $\dfrac{v(^{31}\mathbf{P})}{v(^{1}\mathbf{H})} = \dfrac{g(^{31}\mathbf{P})}{g(^{1}\mathbf{H})}$

or $v(^{31}\mathrm{P}) = \dfrac{2.2634}{5.5857} \times 500\,\mathrm{MHz} = \boxed{203\mathrm{MHz}}$

The proton resonance consists of 2 lines $(2 \times \frac{1}{2} + 1)$ and the ^{31}P resonance of 5 lines $[2 \times (4 \times \frac{1}{2}) + 1]$. The intensities are in the ratio 1:4:6:4:1 (Pascal's triangle for four equivalent spin $\frac{1}{2}$ nuclei, Section 48.3). The lines are spaced $\dfrac{5.5857}{2.2634} = 2.47$ times greater in the phosphorus region than the proton region. The spectrum is sketched in Fig. 14B.3.

Figure 14B.3

Proton resonance

Phosphorus resonance

E14B.6(b) See Section 14B.3(a), Example 14B.3 and Figs. 14B.12 and 14B.13 for the approach to the solution to this exercise. Also see Example 14D.1 and Figs. 14D.4 and 14D.5. That latter example and those figures are applied specifically to EPR spectra, but the process of determining the intensity pattern in the fine structure of an NMR spectrum is the same. See the table below for the version of Pascal's triangle for up to 3 spin-5/2 nuclei. Each number in the table is the sum of the six ($I = 5/2$, $2I + 1 = 6$) numbers above it (3 to the right and 3 to the left).

14:6

conclude that the largest stable clump of this two-dimensional lattice of ions consists of 7 rings around the central cation.

18C Mechanical, electrical, and magnetic properties of solids

Answers to discussion questions

18C.2 The most obvious difference is that there is no magnetic analog of electric charge; hence, there are no magnetic 'ions.' Both electric and magnetic moments exist and these can be either permanent or induced. Induced magnetic moments in the entire sample can be either parallel or antiparallel to the applied field producing them (paramagnetic or diamagnetic moments), whereas in the electric case they are always parallel. Magnetization, $\mathcal{M}$, is the analog of polarization, $\mathcal{P}$. Although both magnetization and induced dipole moment are proportional to the fields producing them, they are not analogous quantities, neither are volume magnetic susceptibility, χ, and electric polarizability, α. The magnetic quantities refer to the sample as a whole, the electric quantities to the molecules. Molar magnetic susceptibility is analogous to molar polarization as can be seen by comparing equations 18C.7 and 16A.5a and magnetizability is analogous to electric polarizability.

Solutions to exercises

18C.1(b) Poisson's ratio: $\nu_p = \dfrac{\text{transverse strain}}{\text{normal strain}}$ [18C.2] $= 0.41$

We note that the transverse strain is usually a contraction and that it is usually evenly distributed in both transverse directions. That is, if $(\Delta L/L)_z$ is the normal strain, then the transverse strains, $(\Delta L/L)_x$ and $(\Delta L/L)_y$, are equal. In this case of a 2.0% uniaxial stress:

$$\left(\frac{\Delta L}{L}\right)_z = +0.020, \qquad \left(\frac{\Delta L}{L}\right)_x = \left(\frac{\Delta L}{L}\right)_y = -0.020 \times 0.41 = -0.0082 \ \text{[a contraction of widths]}$$

Application of the stress to 1 dm^3 cube of lead results in a volume equal to

$$(1 - 0.0082)^2 \times (1 + 0.020) \times 1 \ \text{dm}^3 = 1.0033 \ \text{dm}^3$$

The change in volume is $\boxed{3.3 \times 10^{-3} \ \text{dm}^3}$.

18C.2(b) Is gallium-doped germanium a p-type or n-type semiconductors?
p-type; the dopant, gallium, belongs to Group 13 whereas germanium belongs to Group 14.

18C.3(b) $m = g_e \{S(S+1)\}^{1/2} \mu_B$ [18C.9, with S in place of s]

Therefore, since $m = 5.3 \ \mu_B$ and $g_e \approx 2$,

$$S(S+1) = \left(\tfrac{1}{4}\right) \times (5.3)^2 = 7.0, \quad \text{implying that} \quad S = 2.2$$

Because $S \approx \tfrac{4.4}{2}$, the Mn^{2+} ions typically have $\boxed{\text{4-5 unpaired spins}}$.

In actuality most Mn^{2+} compounds have 5 unpaired spins.

18C.4(b) $\chi_m = \chi V_m$ [18C.8] $= \chi M / \rho = (-7.9 \times 10^{-6}) \times (84.15 \ \text{g mol}^{-1}) / (0.811 \ \text{g cm}^{-3})$

$$= \boxed{-8.2 \times 10^{-4} \ \text{cm}^3 \ \text{mol}^{-1}} = \boxed{-8.2 \times 10^{-10} \ \text{m}^3 \ \text{mol}^{-1}}$$

18C.5(b) The molar susceptibility is given by

$$\chi_m = \frac{N_A g_e^2 \mu_0 \mu_B^2 S(S+1)}{3kT} \ \text{[18C.10a]} \quad \text{so} \quad S(S+1) = \frac{3kT \chi_m}{N_A g_e^2 \mu_0 \mu_B^2}$$

EA.17(a) $\theta / °C = \frac{5}{9} \times (\theta_F / °F - 32)$ or $\theta_F / °F = \frac{9}{5} \times \theta / °C + 32$, $\theta_F = 173 °F$

EA.18(a)   105 kPa

EA.19(a) S_8

EA.20(a)   1.8 MPa

EA.21(a) 4.6×10^5 Pa , 6.9×10^5 Pa

Topic B

EB.1(a)   (i) 9.81 m s^{-1}, 48 mJ   (ii) 29.4 m s^{-1}, 0.43 J

EB.2(a) $s_{\text{terminal}} = \dfrac{zeE}{6\pi\eta R}$

EB.4(a)   (i) 2.25×10^{-20} J   (ii) 9.00×10^{-20} J

EB.5(a)   (i) 1.88×10^8 m s^{-1}, 100 keV

EB.6(a) 1.15×10^{-18} J , 1.48×10^{-20} J

EB.7(a) -2.40 V

EB.8(a)   24.1 kJ , 28.8 °C

EB.9(a)   27.2 K or 27.2 °C

EB.10(a)   128 J

EB.11(a)   2.4194 J K^{-1} g^{-1}

EB.12(a)   75.3 J K^{-1} mol^{-1}

EB.13(a)   8.3145 kJ mol^{-1}

EB.14(a) $S_{H_2O(g)} > S_{H_2O(l)}$

EB.15(a) $S_{Fe(3000\ K)} > S_{Fe(300\ K)}$

EB.17(a)   (i) 1.6×10^{-17} (ii) 0.021

EB.19(a) 4.631×10^{-6}

EB.21(a)   1.07

EB.22(a)   1.25

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