$$
\begin{aligned}
V &= \frac{4}{3}\pi r^3 \\
&= \frac{4}{3}\pi\,(128\ \text{pm})^3 \\
&= 8.78 \times 10^6\ \text{pm}^3
\end{aligned}
$$

(c) The difference in these values illustrates that there is no easy definition for the boundaries of an atom. The van der Waals value obtained from the correction for molar volume is considerably larger than the atomic radius, owing perhaps to longer range and weak interactions between atoms. One should also bear in mind that the value for the van der Waals b is a parameter used to obtain a good fit to a curve, and its interpretation is more complicated than a simple molar volume.

3F.1 (a) London forces, dipole-dipole, hydrogen bonding; (b) London forces; (c) London forces, dipole-dipole, hydrogen bonding; (d) London forces, dipole-dipole

3F.3 Only (b) CH_3Cl, (c) CH_2Cl_2, and (d) $CHCl_3$ will have dipole-dipole interactions. The molecules CH_4 and CCl_4 do not have dipole moments.

3F.5 (a) NaCl (801°C vs −114.8°C) because it is an ionic compound as opposed to a molecular compound; (b) butanol (−90°C vs −116°C) due to hydrogen bonding in butanol that is not possible in diethyl ether; (c) triiodomethane because it will have much stronger London dispersion forces (−82.2°C for trifluoromethane vs. 219°C for triiodomethane); (d) Methanol (−94 °C vs −169 °C) because of the hydrogen bonding in methanol but not in ethylene.

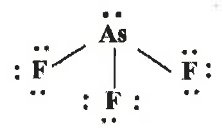
3F.7 (a) PBr_3 and PF_3 are both trigonal pyramidal and should have similar intermolecular forces, but PBr_3 has the greater number of electrons and should have the higher boiling point. The boiling point of PF_3 is −101.5°C and that of PBr_3 is 173.2 °C; (b) SO_2 and O_3 are both bent and have dipole moments. But SO_2 should have the higher boiling point due its greater number of electrons. SO_2 boils at −10°C, whereas O_3 boils at −112 °C. (c) BF_3 and BCl_3 are both trigonal planar, so the choice of higher boiling point depends on the difference in total number of electrons. BCl_3 should have the higher boiling point (12.5°C vs −99.9°C).

3F.9 The interaction energies can be ordered based on the relationship the energy has to the distance separating the interacting species. Thus ion-ion interactions are the strongest and are directly proportional to the distance separating the two interacting species. Ion-dipole energies are inversely proportional to d^2, whereas dipole-dipole for constrained molecules (i.e., solid state) is inversely proportional to d^3. Dipole-dipole interactions where the molecules are free to rotate become comparable with induced dipole-induced dipole interactions, which are both inversely related to d^6. The order thus derived is: (b) dipole-induced dipole ≅ (c) dipole-dipole in the gas phase < (e) dipole-dipole in the solid phase < (a) ion-dipole < (d) ion-ion.

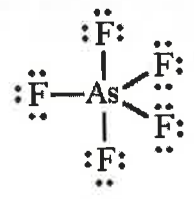
3F.11 Only molecules with H attached to the electronegative atoms F, N, and O can hydrogen bond. Additionally, there must be lone pairs available for the Hs to bond to. This is true only of (d) HNO_2.

3F.13 II because the dipoles are aligned with oppositely charged ends closest to each other thereby maximizing dipole-dipole attractions.

3F.15 The Lewis structures of AsF_3 and AsF_5 are as follows:



AsF_3



AsF_5

From the Lewis structures of these two molecules, it is clear that AsF_3 is a polar molecule while AsF_5 is not. So the dipole-dipole intermolecular forces in AsF_3 are stronger than the London (dispersion) forces in AsF_5, which results a higher boiling point of AsF_3.

3F.17 The ionic radius of Al^{3+} is 54 pm and that of Be^{2+} is 34 pm. The ratio of energies will be given by

$$E_p \propto \left(\frac{-|Z|\mu}{d^2}\right)$$

$$E_{pAl}{}^{3+} \propto \left(\frac{-|Z|\mu}{d^2}\right) = \left(\frac{-|3|\mu}{(54+100)^2}\right)$$

$$E_{pBe}{}^{2+} \propto \left(\frac{-|Z|\mu}{d^2}\right) = \left(\frac{-|2|\mu}{(34+100)^2}\right)$$

The electric dipole moment of the water molecule (μ) will cancel:

$$\text{Ratio}\left(\frac{E_{pAl^{2+}}}{E_{pBe^{2+}}}\right) = \left(\frac{-|3|\mu/(54+100)^2}{-|2|\mu/(34+100)^2}\right) = \left(\frac{3(134)^2}{2(154)^2}\right) = 1.14$$

The attraction of the Al^{3+} ion will be greater than that of the Be^{2+} ion. Even though the Al^{3+} ion has a larger radius, its charge is higher than that of Be^{2+}, making the attraction greater over all.

3F.19 (a) Xenon is larger, with more electrons, giving rise to larger London forces that increase the melting point. (b) Hydrogen bonding in water causes the molecules to be held together more tightly than in diethyl ether. (c) Both molecules have the same molar mass, but pentane is a linear molecule compared with dimethylpropane, which is a compact, spherical molecule. The compactness of the dimethylpropane gives it a lower surface area. That means that the intermolecular attractive forces, which are of the same type (London forces) for both molecules, will have a larger effect for pentane.

3F.21 $F = \frac{-\mathrm{d}E_P}{\mathrm{d}r} = \frac{-\mathrm{d}}{\mathrm{d}r}\left(\frac{1}{r^6}\right) = -\left(\frac{-6}{r^7}\right) \propto \frac{1}{r^7}$

3G.1 (a) As intermolecular forces increase, boiling point will increase because more thermal energy is required to separate molecules apart; (b) viscosity will increase with the increase of intermolecular forces because stronger intermolecular forces will make molecules less mobile (or do not let molecules move past one another easily); (c) surface tension also increases with the increase of intermolecular forces because stronger intermolecular forces tend to pull molecules together and inward.

3G.3 (a) *cis*-Dichloroethene is polar, whereas *trans*-dichloroethene, whose individual bond dipole moments cancel, is nonpolar. Therefore, *cis*-dichloroethene has the greater intermolecular forces and the greater surface tension. (b) Surface tension of liquids decreases with increasing temperature as a result of thermal motion as temperature rises. Increased thermal motion allows the molecules to more easily break away from each other, which manifests itself as decreased surface tension. Therefore, benzene at 20 degrees has a higher surface tension.

3G.5 At 50°C all three compounds are liquids. C_6H_6 (nonpolar) $<$ C_6H_5SH (polar, but no hydrogen bonding) $<$ C_6H_5OH (polar and with hydrogen bonding). The viscosity will show the same ordering as the boiling points, which are 80°C for C_6H_6, 169°C for C_6H_5SH, 182° for C_6H_5OH.

3G.7 CH_4, −162°C; CH_3CH_3, −88.5°C; $(CH_3)_2CHCH_2CH_3$, 28°C; $CH_3(CH_2)_3CH_3$, 36°C; CH_3OH, 64.5°C; CH_3CH_2OH, 78.3 °C; $CH_3CHOHCH_3$, 82.5°C; C_5H_9OH (cyclic, but not aromatic), 140°C; $C_6H_5CH_3OH$ (aromatic ring), 205°C; $OHCH_2CHOHCH_2OH$, 290°C

3G.9 Because of the silanol group (Si-OH) on the glass tube wall, water molecules that are close to the glass tube wall will strongly interact with the silanol group by forming H-bonding and climbing up to certain distance and forming a concave meniscus. Water molecules do not have such interactions with a plastic tube wall because of the hydrophobic character of the plastics, so water molecules will interact among one another through H-bonding and form a convex meniscus.

3G.11 Using $h = \dfrac{2\gamma}{gdr}$ we can calculate the height. For water:

$$r = \frac{1}{2}\,\text{diameter} = \frac{1}{2}(0.15\ \text{mm})\left(\frac{1\ \text{m}}{1000\ \text{mm}}\right) = 7.5\times10^{-5}\ \text{m}$$

$$d = 0.997\ \text{g}\cdot\text{cm}^{-3}\left(\frac{1\ \text{kg}}{1000\ \text{g}}\right)\left(\frac{10^{6}\ \text{cm}^{3}}{\text{m}^{3}}\right) = 9.97\times10^{2}\ \text{kg}\cdot\text{m}^{-3}$$

$$h = \frac{2(72.75\times10^{-3}\ \text{N}\cdot\text{m}^{-1})}{(9.81\ \text{m}\cdot\text{s}^{-1})(9.97\times10^{2}\ \text{kg}\cdot\text{m}^{-3})(7.5\times10^{-5}\ \text{m})} = 0.20\ \text{m or } 200\ \text{mm}$$

Remember that $1\ \text{N} = 1\ \text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-2}$

For ethanol:

$$d = 0.79\ \text{g}\cdot\text{cm}^{-3}\left(\frac{1\ \text{kg}}{1000\ \text{g}}\right)\left(\frac{10^{6}\ \text{cm}^{3}}{\text{m}^{3}}\right) = 7.9\times10^{2}\ \text{kg}\cdot\text{m}^{-3}$$

$$h = \frac{2(22.8\times10^{-3}\ \text{N}\cdot\text{m}^{-1})}{(9.81\ \text{m}\cdot\text{s}^{-1})(7.9\times10^{2}\ \text{kg}\cdot\text{m}^{-3})(7.5\times10^{-5}\ \text{m})} = 0.078\ \text{m or } 78\ \text{mm}$$

Water will rise to a higher level than ethanol. There are two opposing effects to consider. While the greater density of water than ethanol, acts against it rising as high, it has a much higher surface tension.

3G.13 There are too many ways that these molecules can rotate and twist so that they do not remain rodlike. The molecular backbone when the molecule is stretched out is rodlike, but the molecules tend to curl up on themselves, destroying any possibility of long range order with neighboring molecules. This is partly due to the fact that the molecules have only single bonds that allow rotation about the bonds, so that each molecule can adopt many configurations. If multiple bonds are present, the bonds are more rigid.

3G.15 Because benzene is isotropic solvent and its viscosity is the same in every direction. However, a liquid crystal solvent is anisotropic and its viscosity is smaller in the direction parallel to the long axis of the molecule than in the "sideway" direction. Since methylbenzene is a small sphere molecule and its diffusion movement does not affected greatly whether solvent is isotropic or anisotropic, it can move and rotate to the same extent in all directions.

3G.17 Substance (a), $C_5H_6N^+Cl^-$, would be a better choice as an ionic liquid solvent. The reason is that it has a larger organic cation with the same anion as that of (b), which has a larger nonpolar region to dissolve nonpolar organic compounds.

3H.1 (a) Glucose will be held in the solid by London forces, dipole-dipole interactions, and hydrogen bonds; benzophenone will be held in the solid by dipole-dipole interactions and London forces; (b) We would expect glucose to have a higher melting point because glucose can experience hydrogen bonding, which is a strong interaction and dominates intermolecular forces, but London forces are the strongest in benzophenone. The melting points for both compounds are: benzophenone (m.p. = 48 °C < glucose (m.p. = 148 – 155 °C)

3H.3 (a) Network; (b) ionic; (c) molecular; (d) molecular; (e) network

3H.5 Substance A: ionic; substance B: metallic; substance C: molecular solid

3H.7 (a) At center: 1 center × 1 atom · center^{-1} = 1 atom; at 8 corners, 8 corners × $\frac{1}{8}$ atom · corner^{-1} = 1 atom; total = 2 atoms; (b) There are eight nearest neighbors, hence a coordination number of 8; (c) The direction along which atoms touch each other is the body diagonal of the unit cell. This body diagonal will be composed of four times the radius of the atom. In terms of the unit cell edge length *a*, the body diagonal will be $\sqrt{3}\,a$. The unit cell edge length will, therefore, be given by

$$4r = \sqrt{3}\,a \text{ or } a = \frac{4r}{\sqrt{3}} = \frac{4 \cdot (124 \text{ pm})}{\sqrt{3}} = 286 \text{ pm}$$

3H.9 (a) a = length of side for a unit cell; for an fcc unit cell, $a = \sqrt{8}\,r$ or $2\sqrt{2}\,r = 404$ pm.

$V = a^3 = (404 \text{ pm} \times 10^{-12} \text{ m} \cdot \text{pm}^{-1})^3 = 6.59 \times 10^{-29} \text{ m}^3 = 6.59 \times 10^{-23} \text{cm}^3$.

Because for a fcc unit cell there are four atoms per unit cell, we have

$$\text{mass(g)} = 4 \text{ Al atoms} \times \frac{1 \text{ mol Al atoms}}{6.022 \times 10^{23} \text{ atoms} \cdot \text{mol}^{-1}} \times \frac{26.98 \text{ g}}{\text{mol Al atoms}}$$

$$= 1.79 \times 10^{-22} \text{ g}$$

$$d = \frac{1.79 \times 10^{-22} \text{ g}}{6.59 \times 10^{-23} \text{ cm}^3} = 2.72 \text{ g} \cdot \text{cm}^{-3}$$

(b) $a = \frac{4r}{\sqrt{3}} = \frac{4 \times 227 \text{ pm}}{\sqrt{3}} = 524 \text{ pm}$

$V = (524 \times 10^{-12} \text{ m})^3 = 1.44 \times 10^{-28} \text{ m}^3 = 1.44 \times 10^{-22} \text{ cm}^3$

There are two atoms per bcc unit cell:

$$\text{mass(g)} = 2 \text{ K atoms} \times \frac{1 \text{ mol K atoms}}{6.022 \times 10^{23} \text{ atoms} \cdot \text{mol}^{-1}} \times \frac{39.10 \text{ g}}{\text{mol K atoms}}$$

$$= 1.30 \times 10^{-22} \text{ g}$$

$$d = \frac{1.30 \times 10^{-22} \text{ g}}{1.60 \times 10^{-22} \text{ cm}^3} = 0.813 \text{ g} \cdot \text{cm}^{-3}$$

3H.11 a = length of unit cell edge

$$V = \frac{\text{mass of unit cell}}{d}$$

(a)

$$V = a^3 = \frac{(1 \text{ unit cell})\left(\dfrac{195.09 \text{ g Pt}}{\text{mol Pt}}\right)\left(\dfrac{1 \text{ mol Pt}}{6.022 \times 10^{23} \text{ atoms Pt}}\right)\left(\dfrac{4 \text{ atoms}}{1 \text{ unit cell}}\right)}{21.45 \text{ g} \cdot \text{cm}^3}$$

$$= 6.041 \times 10^{-23} \text{ cm}^3$$

$a = 3.924 \times 10^{-8}$ cm

Because for an fcc cell, $a = \sqrt{8}\,r, r = \frac{\sqrt{2}\,a}{4} = \frac{\sqrt{2}\,(3.92 \times 10^{-8} \text{ cm})}{4}$

$$= 1.387 \times 10^{-8} \text{ cm} = 138.7 \text{ pm}$$

(b) $V = a^3$

$$= \frac{(1 \text{ unit cell})\left(\dfrac{180.95 \text{ g Ta}}{1 \text{ mol Ta}}\right)\left(\dfrac{1 \text{ mol Ta}}{6.022 \times 10^{23} \text{ atoms Ta}}\right)\left(\dfrac{2 \text{ atoms}}{1 \text{ unit cell}}\right)}{16.65 \text{ g} \cdot \text{cm}^3}$$

$$= 3.609 \times 10^{-23} \text{ cm}^3$$

$a = 3.305 \times 10^{-8}$ cm

$$r = \frac{\sqrt{3}\,a}{4} = \frac{\sqrt{3}\left(3.305 \times 10^{-8} \text{ cm}\right)}{4} = 1.431 \times 10^{-8} \text{ cm} = 143.1 \text{ pm}$$

3H.13 Let's assume that rhodium metal structure is *ccp* (*fcc*). In *ccp* structure, there are four atoms in each unit cell. The atomic mass (M) of rhodium is 102.91 g/mol. Therefore, the density of rhodium is: $d = m/a^3$, m = mass of one unit cell = $4M/N_A$, a = the length of the side of a *fcc* unit cell = $8^{1/2}r$

$$d = \frac{4M/N_A}{(8^{1/2}r)^3} = \frac{4M}{N_A(8^{1/2}r)^3}$$

$$= \frac{4 \text{ atoms} \times (102.91 \text{g} \cdot \text{mol}^{-1})}{(6.022 \times 10^{23} \text{ atom} \cdot \text{mol}^{-1}) \times (8^{1/2} \times 1.34 \times 10^{-8} \text{cm})^3} = 12.55 \text{ g} \cdot \text{cm}^{-3}$$

Then we assume the rhodium metal structure is bcc. In bcc structure, there are two atoms in each unit cell, and a = the length of the side of a bcc unit cell $= 4r/3^{1/2}$. The density of rhodium is:

$$d = \frac{2M/N_A}{(4r/3^{1/2})^3} = \frac{2M}{N_A(4r/3^{1/2})^3}$$

$$= \frac{2\text{ atoms} \times (102.91\text{g} \cdot \text{mol}^{-1})}{(6.022 \times 10^{23}\text{ atom} \cdot \text{mol}^{-1}) \times (4 \times 1.34 \times 10^{-8}\text{cm}/3^{1/2})^3} = 11.53\text{ g} \cdot \text{cm}^{-3}$$

The density value for the ccp structure is closer to 12. 42 $\text{g} \cdot \text{cm}^{-3}$. Therefore, rhodium metal is close-packed structure.

3H.15 (a) The volume of the unit cell is

$$V_{\text{unit cell}} = \left(543\text{ pm} \times \frac{10^{-12}\text{ m}}{\text{pm}} \times \frac{100\text{ cm}}{\text{m}}\right)^3 = 1.601 \times 10^{-22}\text{ cm}^3$$

mass in unit cell $= (1.601 \times 10^{-22}\text{ cm}^3) \times (2.33\text{ g} \cdot \text{cm}^{-3}) = 3.73 \times 10^{-22}\text{ g}$

(b) The mass of a Si atom is

$28.09\text{ g} \cdot \text{mol}^{-1} \div (6.022 \times 10^{23})\text{ atoms} \cdot \text{mol}^{-1} = 4.665 \times 10^{-23}\text{ g} \cdot \text{atom}^{-1}$.

Therefore, there are $3.73 \times 10^{-22}\text{ g} \div 4.665 \times 10^{-23}\text{ g} \cdot \text{atom}^{-1} = 8$ atoms per unit cell.

3H.17 Volume of a cylinder = base area × length = $\pi r^2 l$;
Volume of a triangular prism = base area × length = $(bhl)/2 = \sqrt{3}r^2 l$ for a triangle inscribed in the centers of three touching cylinder bases; Each of the inscribed triangle's 60° angles accounts for 1/6 of the volume of each of the three touching cylinders, or a total cylinder volume of (3/6) $\pi r^2 l$. So the percent of the space occupied by the cylinders is $(0.5)\pi r^2 l * 100/\sqrt{3}r^2 l = 0.5\pi/\sqrt{3} = 90.7\%$.

3H.19 In diamond, carbon is sp^3 hybridized and forms a tetrahedral, three-dimensional network structure, which is extremely rigid. Graphite carbon is sp^2 hybridized and planar. Its application as a lubricant results from the fact that the two-dimensional sheets can "slide" across one another, thereby reducing friction. In graphite, the unhybridized p-electrons are free to move from one carbon atom to another, which results in its high electrical conductivity. In diamond, all electrons are localized in sp^3 hybridized C–C σ-bonds, so diamond is a poor conductor of electricity.

3H.21 (a) Carbon atomic radius is 77 pm. The number of carbon atom on the 2.0 cm × 1.0 cm tape is:

$$\frac{2.0\ cm \times 1.0\ cm}{\pi(77 \times 10^{-10}\ cm)^2} = 1.1 \times 10^{16}\text{ C atoms}$$

(b) $$\left(1.1 \times 10^{16} C\ \text{ atoms}\right)\left(\frac{1\text{ mol } \ \text{C } \ \text{atoms}}{6.022 \times 10^{23}\text{atoms} \cdot \text{mol}^{-1}}\right) = 1.8 \times 10^{-8}\text{mol}$$

$$\left(1.8 \times 10^{-8}\text{mol}\right)\left(\frac{1\text{ nmol}}{10^{-9}\text{mol}}\right) = 18\text{ nmol}$$

3H.23 (a) Indium arsenide has a (4,4)-coordination because each unit cell has four indium and four arsenic; (b) The formula of indium arsenide is InAs.

3H.25 (a) There are eight chloride ions at the eight corners, giving a total of

$8\text{ corners} \times \tfrac{1}{8}\text{ atom} \cdot \text{corner}^{-1} = 1\ \text{Cl}^-\text{ ion}$

There is one Cs^+ that lies at the center of the unit cell. All of this ion belongs to the unit cell. The ratio is thus 1 : 1 for an empirical formula of CsCl, with one formula unit per unit cell.

(b) The titanium atoms lie at the corners of the unit cell and at the body center: $8\text{ corners } \times \tfrac{1}{8}\text{ atom} \cdot \text{corner}^{-1} + 1\text{ at body center} = 2$ atoms per unit cell. Four Oxygen atoms lie on the faces of the unit cell and two lie completely within the unit cell, giving:

$4\text{ atoms in faces} \times \tfrac{1}{2}\text{ atom} \cdot \text{face}^{-1} + 2\text{ atoms wholly within cell} = 4\text{ atoms}$

The ratio is thus two Ti per four O, or an empirical formula of TiO_2 with two formula units per unit cell.

(c) The Ti atoms are 6-coordinate and the O atoms are 3-coordinate.

3H.27 (a) Each unit cell has one rhenium ($8\times\frac{1}{8}$) and three oxide ion ($12\times\frac{1}{4}$). Therefore, rhenium oxide has a (6,2)-coordination. (b) The formula of rhenium oxide is ReO_3.

3H.29 (a) $\text{Ratio}=\dfrac{133\text{ pm}}{152\text{ pm}}=0.875$, predict cesium-chloride structure with (8,8)-coordination; however, rubidium fluoride actually adopts the rock-salt structure

(b) $\text{Ratio}=\dfrac{72\text{ pm}}{140\text{ pm}}=0.51$, predict rock-salt structure with (6,6)-coordination

(c) $\text{Ratio}=\dfrac{102\text{ pm}}{196\text{ pm}}=0.520$, predict rock-salt structure with (6,6)-coordination

3H.31 (a) In the rock-salt structure, the unit cell edge length is equal to two times the radius of the cation plus two times the radius of the anion. Thus for CaO, $a=$ 2(100 pm) + 2(140 pm) = 480 pm. The volume of the unit cell will be given by (converting to cm^3 because density is normally given in terms of $\text{g}\cdot\text{cm}^{-3}$)

$$V=\left(480\text{ pm}\times\frac{10^{-12}\text{ m}}{\text{pm}}\times\frac{100\text{ cm}}{\text{m}}\right)^3=1.11\times10^{-22}\text{ cm}^3$$

There are four formula units in the unit cell, so the mass in the unit cell will be given by

$$\text{mass in unit cell}=\frac{\left(\dfrac{4\text{ formula units}}{1\text{ unit cell}}\right)\times\left(\dfrac{56.08\text{ g CaO}}{1\text{ mol CaO}}\right)}{6.022\times10^{23}\text{ molecules}\cdot\text{mol}^{-1}}=3.725\times10^{-22}\text{ g}$$

The density will be given by the mass in the unit cell divided by the volume of the unit cell:

$$d=\frac{3.725\times10^{-22}\text{ g}}{1.11\times10^{-22}\text{ cm}^3}=3.36\text{ g}\cdot\text{cm}^{-3}$$

(b) For a cesium chloridelike structure, it is the body diagonal that represents two times the radius of the cation and plus two times the radius of the anion. Thus the body diagonal for CsBr is equal to

2(167 pm) + 2(196) = 726 pm.

For a cubic cell, the body diagonal $=\sqrt{3}\,a=726\text{ pm}$

$a=419\text{ pm}$

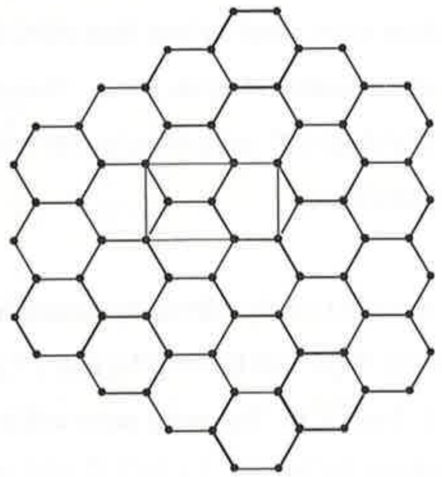
$$a^3=V=\left(419\text{ pm}\times\frac{10^{-12}\text{ m}}{\text{pm}}\times\frac{100\text{ cm}}{\text{m}}\right)^3=7.36\times10^{-23}\text{ cm}^3$$

There is one formula unit of CsBr in the unit cell, so the mass in the unit cell will be given by

$$\text{mass in unit cell}=\frac{\left(\dfrac{1\text{ formula units}}{1\text{ unit cell}}\right)\left(\dfrac{212.82\text{ g CsBr}}{1\text{ mol CsBr}}\right)}{6.022\times10^{23}\text{ molecules}\cdot\text{mol}^{-1}}=3.534\times10^{-22}\text{ g}$$

$$d=\frac{3.534\times10^{-22}\text{ g}}{7.36\times10^{-23}\text{ cm}^3}=4.80\text{ g}\cdot\text{cm}^3$$

3H.33 (a) The smallest possible rectangular unit cell is as follows:



(b) There are four of carbon atoms in each unit cell.

(c) The coordination number is three (C_3).

3H.35 Each unit cell contains four RbI; Total of unit cells = (6.022×10^{23} RbI molecules/mole)/(4 RbI molecules/unit cell) = 1.505×10^{23} unit cells/mole; The volume of one unit cell = $(732.6\ \text{pm})^3$.

Assume that the edge length of a cubic crystal of RbI that contains one mole RbI is X, then the volume of one mole RbI = X^3/mole =

$$\left(\frac{(732.6\,\text{pm})^3}{\text{unit cell}}\right) \times \left(\frac{1.505\times10^{23}\ \text{unit cell}}{\text{mole}}\right);$$

$$X = (732.6\ \text{pm}) \times \sqrt[3]{1.505\times10^{23}} = 3.897 \times 10^{10}\ \text{pm} = 3.897\ \text{cm}$$

3I.1 $$D_{\text{Al}} = \frac{m_1}{V} = \frac{26.98n}{V};$$

$$D_{\text{magnalium}} = \frac{m_2}{V} = \frac{(26.89 \times 70\%n + 24.31 \times 30\%n)}{V} = \frac{26.18n}{V}$$

$$D = \frac{D_{\text{magnalium}}}{D_{\text{Al}}} = 0.9703$$

3I.3 Alloys are usually (1) harder and more brittle, and (2) poorer conductors of electricity than the metals from which they are made.

3I.5 (a) The alloy is undoubtedly interstitial because the atomic radius of nitrogen is much smaller (74 pm vs 124 pm) than that of iron. The rule of thumb is that the solute atom must be less than 60% the solvent atom in radius in order for an interstitial alloy to form. That criterion is met here. (b) We expect that nitriding will make iron harder and stronger, with a lower electrical conductivity.

3I.7 (a) These problems are most easily solved by assuming 100 g of substance. In 100 g of Ni-Cu alloy there will be 25 g Ni and 75 g Cu, corresponding to 0.43 mol Ni and 1.2 mol Cu. The atom ratio will be the same as mole ratio:

$$\frac{1.2\ \text{mol Cu}}{0.43\ \text{mol Ni}} = 2.8\ \text{Cu per Ni}$$

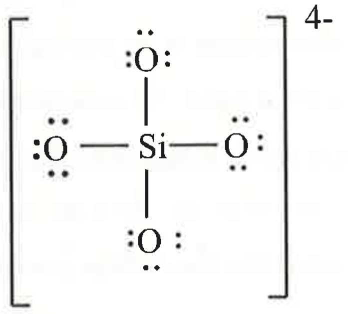
(b) Pewter, which is 7% Sb, 3% Cu, and 90% Sn, will contain 7 g Sb, 3 g Cu, and 90 g Sn per 100 g of alloy. This will correspond to 0.06 mol Sb, 0.05 mol Cu, and 0.76 mol Sn per 100 g alloy. The atom ratio will be 15 Sn: 1.2 Sb : 1 Cu.

3I.9 (a) By viewing the unit cell from different directions, it is clear that it belongs to a hexagonal crystal system. (b) There are eight carbonate ions on edges, giving ¼ × 8 = 2 carbonate ions, plus there are four carbonate ions completely within the unit cell. The total number of carbonate ions in the unit cell is six. Calcium ions lie at the corners of the unit cell ($\frac{1}{8} \times 8$ =1) as well as on the edges (¼ × 4) and within the cell (4). The total number of calcium ions in the cell is six, agreeing with the overall stoichiometry of calcite, $CaCO_3$.

3I.11 $D = \frac{m}{V}$, $m = DV$, $V = \frac{m}{D}$

$$V = \frac{m}{D} = \frac{19.28\ g \cdot \text{cm}^{-3} \times 4.0\ \text{cm}^3}{5.01\ g \cdot \text{cm}^{-3}} = 15.4\ \text{cm}^3$$

3I.13



Formal charge: Si = 0, O = –1; Oxidation number: Si = +4, O = –2; this is an AX_4 VSEPR structure; therefore, the shape is tetrahedral.

3I.15 The $Si_2O_7^{6-}$ ion is built from two SiO_4^{4-} tetrahedral ions in which the silicate tetrahedral share one O atom. This is the only case in which one O is shared. (b) The pyroxenes, for example, jade, $NaAl(SiO_3)_2$, consist of chains of SiO_4 units in which two O atoms are shared by neighboring units. The repeating unit has the formula SiO_3^{2-}.

3J.1 The conductivity of a semiconductor increases with temperature as increasing numbers of electrons are promoted into the conduction band, whereas the conductivity of a metal will decrease as the motion of atoms will slow down the migration of electrons.

3J.3 The diameter of silver is: 144 pm × 2 = 288 pm; for a 2.4-mm length of one-dimensional line, the total number of Ag atoms:

$$\frac{2.4\text{ mm}\times\dfrac{1.0\times10^{9}\text{ pm}}{1\text{ mm}}}{288\text{ pm}} = 8.3\times10^{6}\text{ Ag atoms}$$

Silver has two states since 5s is half filled. So, $n = 4.2 \times 10^6$

3J.5 (a) In and Ga; (b) P and Sb

3J.7 (a) In fluorescence, light absorbed by molecules is immediately emitted, whereas, in phosphorescence, molecules remain in an excited state for a length of time before emitting the absorbed light. So conservatively, emission of light in phosphorescence is much longer than that of fluorescence; (b) mechanistically, fluorescence involves the retention of the relative spin orientation of the excited electron where phosphorescence involves changes of electron spin state so relaxation is a slow process.

3J.9 Paramagnetic elements have at least one unpaired electron.

Sc = $3d^1 4s^2$ → Paramagnetic; Ti = $4s^2 3d^2$ → Paramagnetic
V = $3d^3 4s^2$ → Paramagnetic; Mn= $4s^2 3d^5$ → Paramagnetic

Fe = $3d^6 4s^2$ → Ferromagnetic; Co= $4s^2 3d^7$ → Ferromagnetic
Ni= $4s^2 3d^8$ → Ferromagnetic; Y = $4d^1 5s^2$ → Paramagnetic
Zr = $4d^2 5s^2$ → Paramagnetic; Nb = $4d^4 5s^1$ → Paramagnetic
Mo = $4d^5 5s^1$ → Paramagnetic; Tc = $4d^5 5s^2$ → Paramagnetic
Ru= $4d^7 5s^1$ → Paramagnetic; Rh= $4d^8 5s^1$ → Paramagnetic
Lu = $6s^2 4f^{14} 5d^1$ → Paramagnetic; Hf = $6s^2 4f^{14} 5d^2$ → Paramagnetic
Ta = $6s^2 4f^{14} 5d^3$ → Paramagnetic; W = $6s^2 4f^{14} 5d^4$ → Paramagnetic
Re = $6s^2 4f^{14} 5d^5$ → Paramagnetic; Os = $6s^2 4f^{14} 5d^6$ → Paramagnetic
Ir = $6s^2 4f^{14} 5d^7$ → Paramagnetic; Pt = $4f^{14} 5d^9 6s^1$ → Paramagnetic
Au = $4f^{14} 5d^{10} 6s^1$ → Paramagnetic; Zn = $3d^{10} 4s^2$ → Diamagnetic

More information can be found from:
http://www.periodictable.com/Properties/A/MagneticType.html

3J.11 The compound is ferromagnetic below T_c because the magnetization is higher. Above the Curie temperature, the compound is simple paramagnet with randomly oriented spins, but below that temperature, the spins align and the magnetization increases.

3J.13 The reaction is as following (1:1 for CaS):

$$CaCl_2(aq) + (NH_4)_2S(aq) \rightarrow CaS(s) + 2\,NH_4Cl(aq)$$

Assume 100% yield so the moles of CaS formed
$= (4.0 \times 10^{-3}\text{ L}) \times 0.0015\text{ mol/L} = 6.0 \times 10^{-6}$
Molarity of QDs $= (6.0 \times 10^{-6}\text{ mole}/168)/8.0 \times 10^{-3}\text{ L} = 4.5 \times 10^{-6}$ M

3J.15 Given the expression of the cubic box:

$$E_{xyz} = \frac{h^2}{8m_eL^2}(n_x^2+n_y^2+n_z^2)$$

Where E_{xyz} represents the energy of a given level having n values corresponding to x, y and z we can describe each new level by incrementing each n by one; any levels with the same energy will be degenerate. The three lowest energy levels will therefore be E_{111}, E_{211}, and E_{221}. From this we can arrive at expressions for the energy of each level:

$$E_{111} = \frac{h^2}{8m_eL^2}(1^2+1^2+1^2) = \frac{3h^2}{8m_eL^2}$$

Similarly, the other two energy levels are determined to be:

$$E_{211} = \frac{h^2}{8m_eL^2}(2^2+1^2+1^2) = \frac{3h^2}{4m_eL^2} \quad \text{and}$$

$$E_{221} = \frac{h^2}{8m_eL^2}(2^2+2^2+1^2) = \frac{9h^2}{8m_eL^2}$$

The 211, 121, and 112 levels are degenerate; that is $E_{211} = E_{121} = E_{112}$.

The 221, 122, and 212 levels are degenerate; that is $E_{221} = E_{122} = E_{212}$.

3.1 (a) $x_{\text{Ne}} = \left(\frac{6}{10}\right) = 0.6$; $x_{\text{Ar}} = \left(\frac{4}{10}\right) = 0.4$

At constant T and V, $\left(\frac{n_1}{P_1}\right) = \left(\frac{n_2}{P_2}\right) \rightarrow \left(\frac{x_{Ne}}{P_{Ne}}\right) = \left(\frac{x_{Ar}}{P_{Ar}}\right)$

$$P_{Ar} = \left(\frac{(0.4)(420\ \text{Torr})}{0.6}\right) = 280\ \text{Torr}$$

(b) $P_{\text{total}} = (280\ \text{Torr}) + (420\ \text{Torr}) = 700\ \text{Torr}$

3.3 The molar mass of glucose is $180.15\ \text{g}\cdot\text{mol}^{-1}$. From this, we can calculate the number of moles of glucose formed and, using the reaction stoichiometry, determine the number of moles of CO_2 needed. With that information and the other information provided in the problem, we can use the ideal gas law to calculate the volume of air that is needed:

$$PV = nRT$$

$$V = \frac{\left[\left(\frac{10.0\ \text{g glucose}}{180.15\ \text{g glucose}\cdot\text{mol}^{-1}\ \text{glucose}}\right)\left(\frac{6\ \text{mol CO}_2}{1\ \text{mol glucose}}\right)\right]}{\left(\frac{0.26\ \text{Torr}}{760\ \text{Torr}\cdot\text{atm}^{-1}}\right)}$$

$$\times (0.082\,06\ \text{L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(298\ \text{K})$$

$$= 2.4 \times 10^4\ \text{L}$$

3.5 Use the ideal gas law to calculate the number of moles of HCl.

$$n = \frac{PV}{RT} = \frac{(690\ \text{Torr})(200\ \text{mL})}{(0.08206\ \text{L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mL}^{-1})(293\ \text{K})}\cdot\frac{(1\ \text{atm})}{(760\ \text{Torr})}\cdot\frac{(1\ \text{L})}{(1000\ \text{mL})}$$

$$= 7.55\times10^{-3}\ \text{mol HCl}$$

Since the reaction between HCl and NaOH occurs in a 1:1 mole ratio, this number of moles of NaOH is also present in the volume of NaOH(aq) required to reach the stoichiometric point of the titration. Therefore, the molarity of the NaOH solution is

$$\frac{\text{moles NaOH}}{1\ \text{L of solution}} = \frac{(7.55\times10^{-3}\ \text{mol NaOH})}{(15.7\ \text{mL})}\cdot\frac{1000\ \text{mL}}{1\ \text{L}}$$

$$= 0.481\ \text{M}$$

3.7 (a) $N_2O_4(g) \rightarrow 2\ NO_2(g)$; (b) If all the gas were $N_2O_4(g)$, then the moles can be calculated from the ideal gas equation:

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

$$= \frac{\left(\frac{43.78\ \text{g}}{92.02\ \text{g}\cdot\text{mol}^{-1}}\right)(0.082\,06\ \text{L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(298\ \text{K})}{5.00\ \text{L}}$$

$$= 2.33\ \text{atm}$$

(c) The only difference in the calculation between part (b) and part (c) is that the molar mass of NO_2 is half that of N_2O_4.

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

$$= \frac{\left(\frac{43.78\ \text{g}}{46.01\ \text{g}\cdot\text{mol}^{-1}}\right)(0.082\,06\ \text{L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(298\ \text{K})}{5.00\ \text{L}}$$

$$= 4.65\ \text{atm}$$

(d) Because both N_2O_4 and NO_2 are present, we need to determine some way of calculating the relative amounts of each present. This can be done by taking advantage of the gas law relationships. The total pressure at the end of the reaction will give us the total number of moles present: