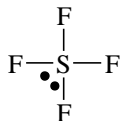


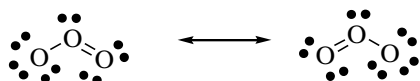
CHAPTER 5

Practice Questions

5.1



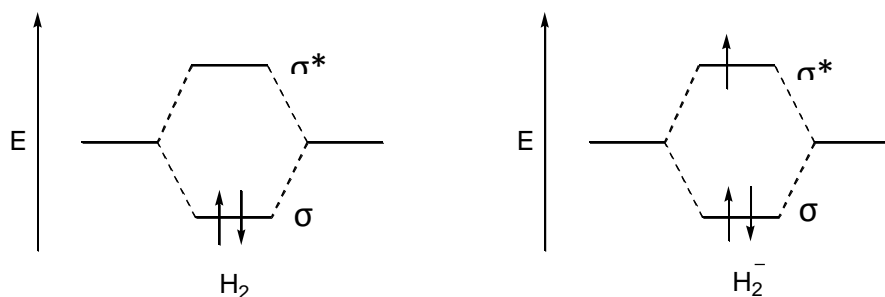
5.3



5.5 Ethane is symmetrical, so does not have a dipole moment. However, ethanol has a polar —O—H group at one end and so has a dipole moment.

5.7 Oxygen has the valence electron configuration $2s^2 2p^4$, so it uses four sp^3 hybridised orbitals. Two of these overlap with $1s$ orbitals from the hydrogen atoms to form σ bonds and the other two sp^3 hybrid orbitals contain lone pairs.

5.9 H_2 has two electrons which occupy a bonding orbital, but H_2^- has a third electron which must occupy an antibonding orbital, hence H_2 has the stronger bond.



5.11

$$CN^- : \sigma_{2s}^2 \quad \sigma_{2s}^{*2} \quad \sigma_{2p}^2 \quad \pi_{2p_x}^2 \quad \pi_{2p_y}^2 : \text{Bond Order} = \frac{8-2}{2} = 3$$

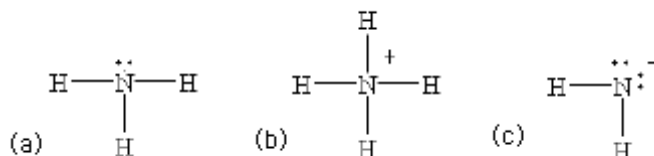
$$CN : \sigma_{2s}^2 \quad \sigma_{2s}^{*2} \quad \sigma_{2p}^2 \quad \pi_{2p_x}^2 \quad \pi_{2p_y}^1 : \text{Bond Order} = \frac{7-2}{2} = 2.5$$

$$CN^+ : \sigma_{2s}^2 \quad \sigma_{2s}^{*2} \quad \sigma_{2p}^2 \quad \pi_{2p_x}^1 \quad \pi_{2p_y}^1 : \text{Bond Order} = \frac{6-2}{2} = 1.5$$

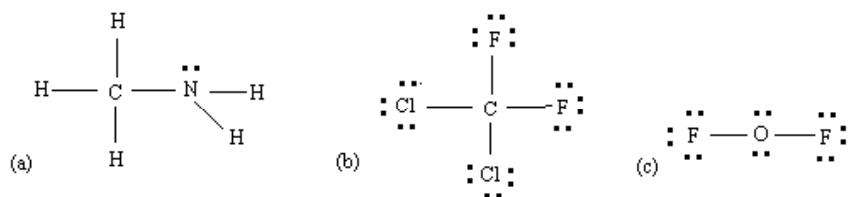
Stability order is : $CN^- > CN > CN^+$

Review Questions

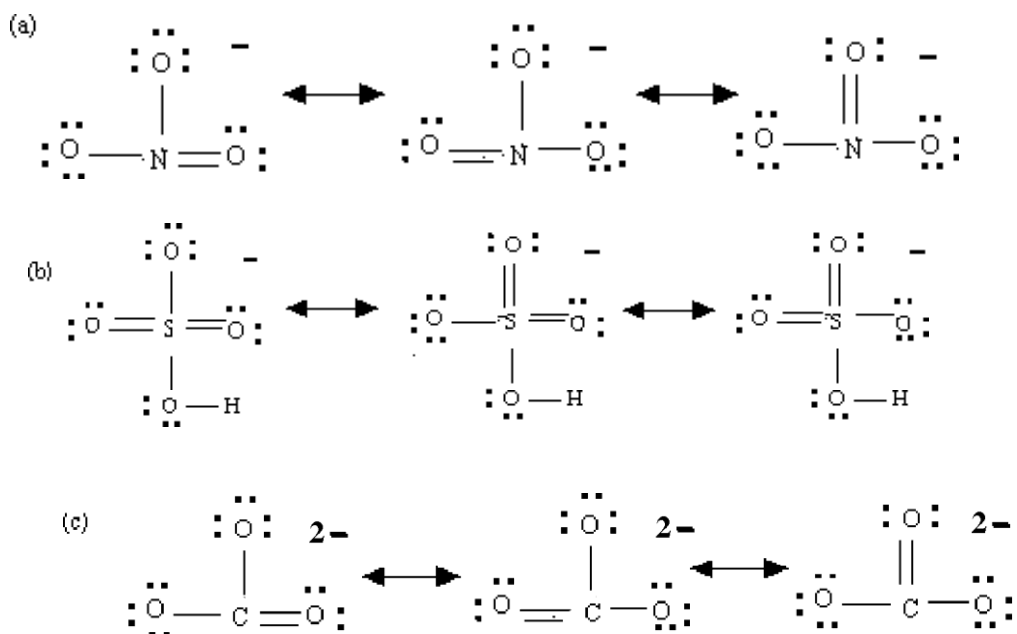
- 5.1 (a) O: $1s^2 2s^2 2p^4$; its six $n = 2$ electrons are involved in bond formation.
 (b) P: $1s^2 2s^2 2p^6 3s^2 3p^3$; its five $n = 3$ electrons are involved in bond formation.
 (c) B: $1s^2 2s^2 2p^2$; its three $n = 2$ electrons are involved in bond formation.
 (d) Br: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$; its seven $n = 4$ electrons are involved in bond formation.
- 5.3 (a) Al, group 13, $13 - 10 = 3$ valence electrons
 (b) As, group 15, $15 - 10 = 5$ valence electrons
 (c) F, group 17, $17 - 10 = 7$ valence electrons
 (d) Sn, group 14, $14 - 10 = 4$ valence electrons
- 5.5 (a) N (3.0) attracts electrons more than C (2.5)
 (b) S (2.5) attracts electrons more than H (2.1)
 (c) I (2.5) attracts electrons more than Zn (1.6)
 (d) S (2.5) attracts electrons more than As (2.0)
- 5.7 Bond polarity increases with the difference in electronegativity of the bond-forming elements. In these compounds, H is the less electronegative element, so bond polarity increases with the electronegativity of the other element. The electronegativity order is: $P < S < N < O$, so the order of bond polarity is $PH_3 < H_2S < NH_3 < H_2O$.
- 5.9 Stable anions form from elements in groups 16 (dianions) and 17 (monoanions). Stable cations form from metals:
 Ba, Be, and Bi, all metals, are found in ionic compounds as cations.
 Br is found in ionic compounds as a -1 anion.
 B is not found as an atomic ion.
- 5.11 (a) H_3PO_4 : each H has one valence electron, P (group 15) has five and each O (group 16) has six, giving a total of 32 valence electrons.
 (b) $(C_6H_5)_3C^+$: each H has one valence electron and each C (group 14) has four: subtract one for the positive charge, giving a total of 90 valence electrons.
 (c) $(NH_2)_2CO$: each H has one valence electron, each N (group 15) has five, C (group 14) has four and O has six, giving a total of 24 valence electrons.
 (d) SO_4^{2-} : S and O (group 16) have six valence electrons: add two for the two negative charges, giving a total of 32 valence electrons.
- 5.13



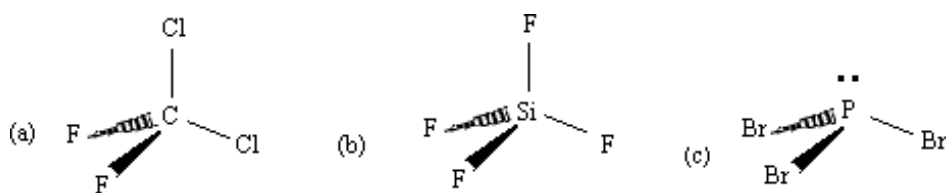
5.15



5.17

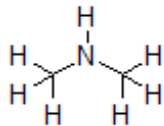


5.19

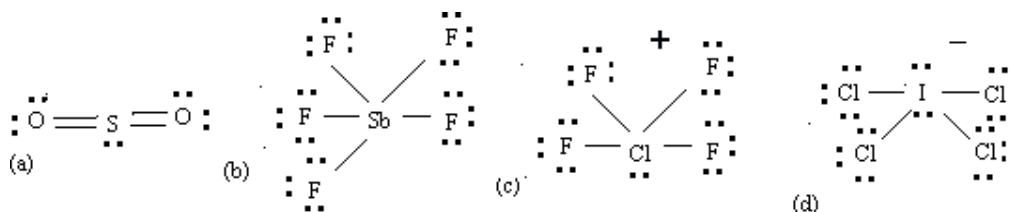


- (a) CF_2Cl_2 has tetrahedral shape, with F atoms at two apices and Cl atoms at the other two.
 (b) SiF_4 has tetrahedral shape.
 (c) PBr_3 , with a lone pair of electrons on the inner atom, has trigonal pyramidal shape.

5.21



5.23



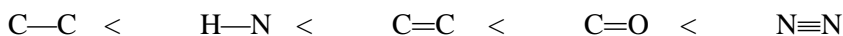
- (a) Three sets of electron pairs around the central atom, giving trigonal planar electron group geometry. One lone pair gives a bent shape, with ideal angle of 120° .
- (b) There are five sets of electron pairs around the central atom, giving trigonal bipyramidal shape and ideal angles of 90° and 120° .
- (c) A total of five sets of electron pairs, giving trigonal bipyramidal electron group geometry. One lone pair gives a seesaw shape, with ideal angles of 90° and 120° .
- (d) There are six sets of electron pairs around the central atom giving octahedral electron group geometry. Two lone pairs result in a square planar shape, with ideal bond angles of 90° .

5.25

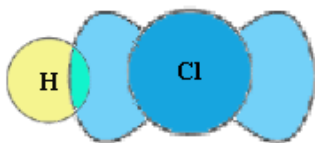


5.27

Bond



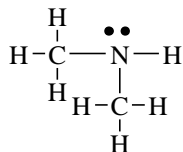
- 5.29 Hydrogen always uses its $1s$ orbital to form bonds. Chlorine, the halogen in the third row, has seven electrons in its $n = 3$ valence orbitals. Just as in Cl_2 , chlorine uses the $3p$ orbital pointing along the bond axis, which overlaps with the $1s$ orbital of the hydrogen atom:



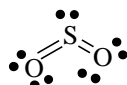
- 5.31 (a) This atom must have four sets of electron pairs, requiring sp^3 hybridisation.
- (b) Four sets of electron pairs, requiring sp^3 hybridisation.

5.33 (c) Three sets of electron pairs, requiring sp^3 hybridisation.

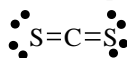
(a) Four sets of electron pairs around N, sp^3 hybrids.



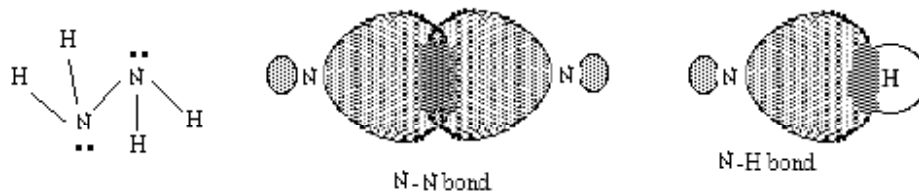
(b) Three sets of electron pairs around S, sp^2 hybrids.



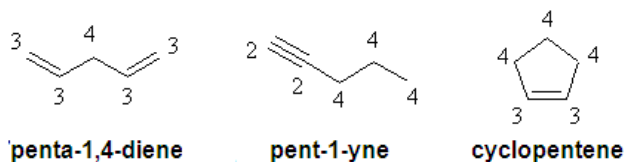
(c) $SN = 2$, sp hybrids.



5.35 A description of bonding begins with the Lewis structure of the molecule, from which steric numbers of inner atoms translate into hybridisation. Outer atoms use atomic orbitals for bond formation. The N atoms in hydrazine have $SN = 4$, use sp^3 hybrids and have tetrahedral geometry: $4 sp^3 (N) - 1s (H) \sigma$ bonds, $1 sp^3 (N) - sp^3 (N) \sigma$ bond, 2 lone pairs in sp^3 hybrids. The Lewis structure of hydrazine (showing the approximate geometry) and orbital overlap diagrams are:

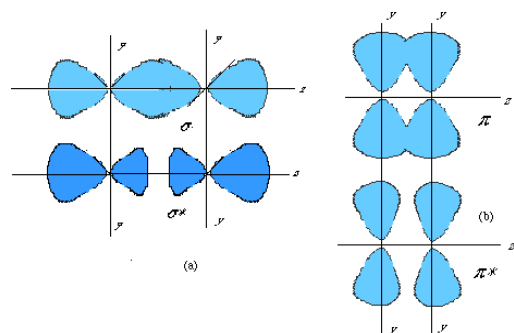


5.37



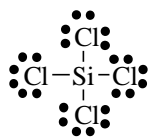
5.39 From weakest to strongest bond, the order is $H_2^{2-} < H_2^- < H_2$.

5.41

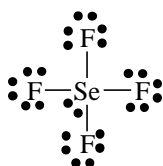


Review Problems

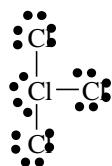
5.43 (a)



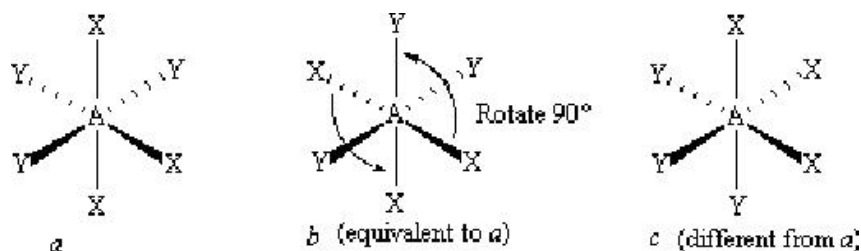
(b)



(c)



5.45



5.47 Determine Lewis structures using the standard procedure. Both ions have the same number of valence electrons, $5 + 4 + 6 + 1 = 16$. Two pairs are required to complete the bonding framework and the remaining six pairs are placed on the two outer atoms:



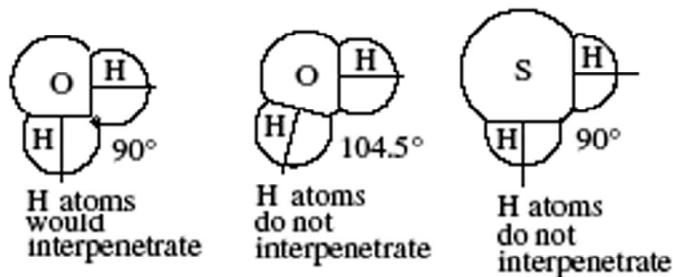
Shift electron pairs to make two additional bonds to the central atom, completing its octet. The cyanate ion has two near-equivalent structures, each of which has one atom with formal charge -1 :



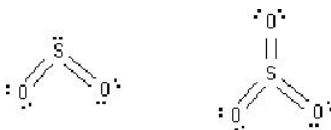
The isocyanate ion also has two near-equivalent structures, but the formal charge on the nitrogen atom cannot be reduced to zero:



- 5.49 (a) This is the trigonal pyramid, derived from the tetrahedron when there is one lone pair. The ideal bond angles are 109.5° and an example is NH_3 .
- (b) This is the trigonal planar shape associated with $\text{SN} = 3$ and no lone pairs. The ideal bond angles are 120° and an example is the nitrate anion, NO_3^- .
- (c) This is the T-shape, the shape associated with with five sets of electrons pairs around the central atom and two lone pairs. The ideal bond angles are 90° and 120° and an example is BrF_3 .
- 5.51 VSEPR theory predicts tetrahedral bond angles (109.5°) for both these molecules. A bond angle of 104.5° is smaller than this, because of the larger repulsion of lone pairs. An angle of 92.2° indicates that the bonding is described using p orbitals rather than spacing the electron pairs as far apart as possible. Space-filling models of the two molecules show that the smaller oxygen atom cannot accommodate two H atoms at right angles, but the larger S atom can.

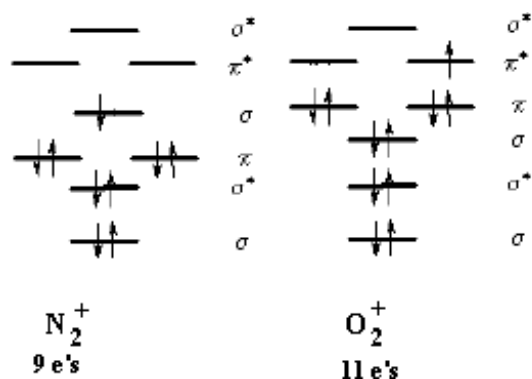


- 5.53 The provisional structure of each compound has a positive formal charge on the row 3 sulfur atom, which is reduced to zero by making double bonds to each oxygen atom:



The sulfur atom in each compound has three sets of electron pairs around the central atom, so sp^2 hybrids overlapping with oxygen $2p$ orbitals describe the σ bonds: two in SO_2 and three in SO_3 . SO_2 is bent, like O_3 and SO_3 is trigonal planar, like NO_3^- . The Lewis structures indicate the presence of two π bonds in SO_2 and three π bonds in SO_3 . All the π orbitals extend over the entire molecule. Because sulfur is a third-row element, its $3d$ orbitals contribute to the extended π bonding orbitals, which form from side-by-side overlap of oxygen $2p$ orbitals with sulfur $3p$ and $3d$ orbitals.

5.55



- (a) paramagnetic
 (b) paramagnetic

Additional Exercises

5.57 Determine the Lewis structures using the standard procedure. Both molecules have

$2(5) + 6 = 16$ valence electrons. Two pairs are required for the bonding framework and each outer atom has three pairs:



Because these molecules contain only row two atoms, the octets must be completed by shifting two electron pairs to make double bonds:



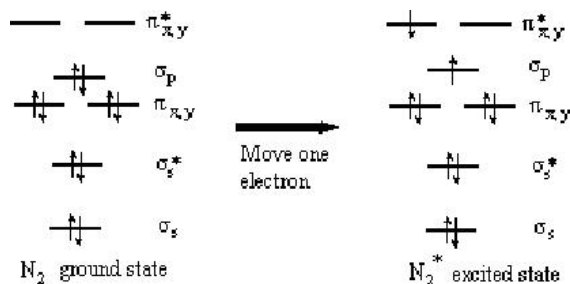
Molecules have dipole moments only if they are unsymmetric. A linear N—O—N structure does not have a dipole moment, because the N—O dipole exactly cancels the O—N dipole. Thus N_2O must have the structure N—N—O to have a dipole moment.

5.59 The Lewis structures of molecules with formula XF_3 show octets around the inner atom and $\text{FC}_x = 0$, making them stable. Compounds with formula XF_5 also have

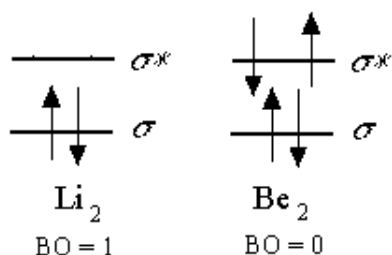
$\text{FC}_x = 0$ but have five electron pairs associated with the inner atom. This is possible for phosphorus, a third row element that has d orbitals available for bonding. It is not possible for nitrogen, a second row element that lacks valence d orbitals.

5.61 To generate the configuration of an excited state, move an electron from an occupied orbital to an unoccupied orbital. The most stable excited state results from moving an electron from the least stable occupied orbital to the most stable unoccupied orbital. The excited state has one more

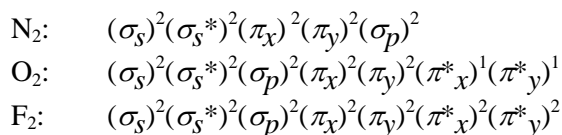
antibonding electron and one less bonding electron than the ground state, so the excited state has a weaker N—N bond than the ground state.



- 5.63 The MO diagrams for dilithium and diberyllium are shown below and reveal the instability of diberyllium. Dilithium resembles dihydrogen except that it uses $2s$ rather than $1s$ valence orbitals to form a covalent bond. Diberyllium is like dihelium and has no valence orbitals available for bonding and thus does not exist.



- 5.65 The MO configurations are:



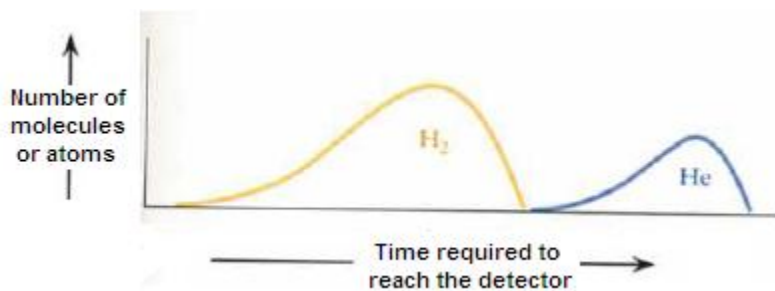
Each molecule has eight bonding electrons. N_2 has two antibonding electrons, for a net bond order of three, O_2 has four antibonding electrons, for a net bond order of two, F_2 has six antibonding electrons, for a net bond order of one. The bond lengths, which increase in the order $N_2 < O_2 < F_2$, reflect this trend in bond order.

CHAPTER 6

Practice Exercises

6.1 $1.446 \times 10^7 \text{ Pa}$

6.3



6.5
$$n_{\text{O}_2} = \frac{(7.50 \text{ g})}{(32.00 \text{ g mol}^{-1})} = 0.234 \text{ mol}$$

$$n_{\text{He}} = \frac{(2.50 \text{ g})}{(4.003 \text{ g mol}^{-1})} = 0.624 \text{ mol}$$

$$X_{\text{O}_2} = \frac{(0.234 \text{ mol})}{(0.234 \text{ mol} + 0.624 \text{ mol})} = 0.273$$

$$X_{\text{He}} = \frac{(0.624 \text{ mol})}{(0.234 \text{ mol} + 0.624 \text{ mol})} = 0.727$$

$$p_{\text{O}_2} = \frac{(0.234 \text{ mol})(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{5 \times 10^{-3} \text{ m}^3} = 1.16 \times 10^5 \text{ Pa}$$

$$p_{\text{He}} = \frac{(0.624 \text{ mol})(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{5 \times 10^{-3} \text{ m}^3} = 3.09 \times 10^5 \text{ Pa}$$

6.7
$$n = \frac{(1.03 \times 10^5 \text{ Pa})(5 \times 10^{-3} \text{ L})}{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(297.5 \text{ K})} = 0.208 \text{ mol}$$

$$M = \frac{(1260.33 \text{ g} - 1254.49 \text{ g})}{0.208 \text{ mol}} = 28.1 \text{ g mol}^{-1}$$

6.9 $1.54 \times 10^{-3} \text{ m}^3$ or 1.54 L

6.11
$$n_{\text{Mg}} = \frac{(14.0 \text{ g})}{(24.31 \text{ g mol}^{-1})} = 0.576 \text{ mol}$$

$n_{\text{HCl}} = 0.900 \text{ mol}$

Using reaction ratios, HCl is the limiting reagent. Therefore, there is 0.450 mole Mg^{2+} in the final solution and 0.450 mole of H_2 is produced.

$$[\text{Mg}^{2+}] = \frac{(0.450 \text{ mol})}{(0.15 \text{ L})} = 3 \text{ mol L}^{-1}$$

$$p_{\text{H}_2} = \frac{(0.450 \text{ mol})(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})}{4.85 \times 10^{-3} \text{ m}^3} = 2.30 \times 10^5 \text{ Pa}$$

$$p_{\text{total}} = (2.3 \times 10^5 \text{ Pa} + 1 \times 10^5 \text{ Pa}) = 3.30 \times 10^5 \text{ Pa}$$

- 6.13 Acetaldehyde is more compact than acetone and has fewer electrons, so its intermolecular forces are weaker and therefore it boils at a lower temperature than acetone. However, like acetone, acetaldehyde contains a polar C=O group, so it has stronger intermolecular dipole-dipole forces and a higher boiling point than either non-polar butane or the more weakly polar methoxyethane.

Review Questions

- 6.1 A pinhole in the top of the tube lets air leak into the space until the internal pressure matches the external atmospheric pressure. The barometer then indicates zero pressure because the height of the mercury column is determined by the pressure *difference* between inside and outside and this difference is zero in the presence of a pinhole.

6.3
$$455 \text{ torr} \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) \left(\frac{1.01325 \times 10^5 \text{ Pa}}{1 \text{ atm}} \right) = 6.07 \times 10^4 \text{ Pa}$$

(b)
$$2.45 \text{ atm} \left(\frac{1.01325 \times 10^5 \text{ Pa}}{1 \text{ atm}} \right) = 2.48 \times 10^5 \text{ Pa}$$

(c)
$$0.46 \text{ torr} \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) \left(\frac{1.01325 \times 10^5 \text{ Pa}}{1 \text{ atm}} \right) = 61 \text{ Pa}$$

$$(d) \quad 1.33 \times 10^{-3} \text{ atm} \left(\frac{1.01325 \times 10^5 \text{ Pa}}{1 \text{ atm}} \right) = 1.35 \times 10^2 \text{ Pa}$$

6.5 (a) n, R, V are constant: $\frac{p}{T} = \frac{nR}{V} = \text{constant}; \frac{p_i}{T_i} = \frac{p_f}{T_f}$

(b) $V = \frac{nRT}{p}$

(c) n, R, T are constant: $pV = nRT = \text{constant}; p_i V_i = p_f V_f$

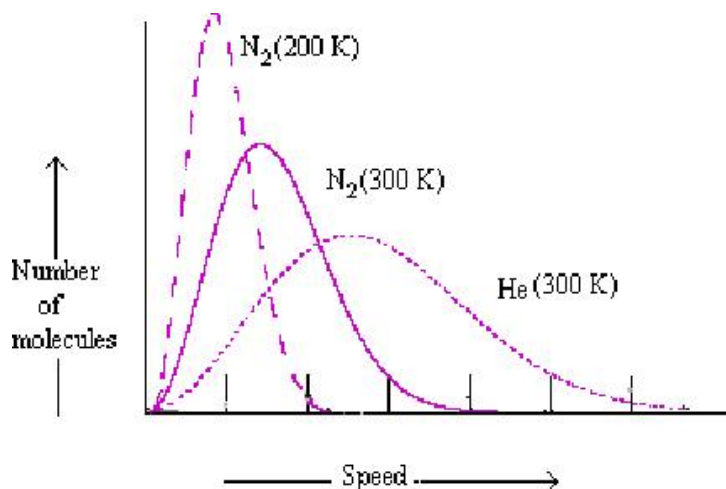
6.7 (a) n and T are fixed, so the equation is valid.

(b) n can change, so the equation is not valid.

(c) T changes, so the equation is not valid.

(d) The equation is not valid for liquids.

6.9



6.11 (a) At very high pressure, molecules are very close together, so their volumes are significant compared to the volume of their container. Because the first condition is not met, the gas is not ideal.

(b) At very low temperature, molecules move very slowly, so the forces between molecules, even though small, are sufficient to influence molecular motion. Because the second condition is not met, the gas is not ideal.

6.13 As a gas cools, its molecules move more slowly, so they impart smaller impulses on the walls of their container. This reduces the internal pressure, so the balloon collapses until the increase in gas density inside the balloon brings the internal pressure back up to the external pressure of $1 \times 10^5 \text{ Pa}$.

6.15 For two gases at the same temperature, the one with the smaller molar mass has the faster molecular speed and effuses faster. The molar masses of CO and N₂ are the same ($M = 28 \text{ g mol}^{-1}$).

¹⁾ so the average molecular speeds of these two gases are the same and are not separated by effusion.

$$6.17 \quad p_{\text{N}_2} = (1.0 \times 10^5 \text{ Pa})(0.7808) = 7.81 \times 10^4 \text{ Pa}$$

$$p_{\text{O}_2} = (1.0 \times 10^5 \text{ Pa})(0.2095) = 2.10 \times 10^4 \text{ Pa}$$

$$p_{\text{Ar}} = (1.0 \times 10^5 \text{ Pa})(9.34 \times 10^{-3}) = 934 \text{ Pa}$$

$$p_{\text{CO}_2} = (1.0 \times 10^5 \text{ Pa})(3.25 \times 10^{-4}) = 32.5 \text{ Pa}$$

$$6.19 \quad p_{\text{CO}_2} = 113.1 \times 10^3 \text{ Pa} \left(\frac{487.4 \text{ molecules CO}_2}{10^6 \text{ molecules of air}} \right) = 55.12 \text{ Pa}$$

$$p_{\text{NO}} = 113.1 \times 10^3 \text{ Pa} \left(\frac{10.3 \text{ molecules NO}}{10^9 \text{ molecules of air}} \right) = 1.16 \times 10^{-3} \text{ Pa}$$

$$p_{\text{CO}} = 113.1 \times 10^3 \text{ Pa} \left(\frac{4.2 \text{ molecules CO}}{10^9 \text{ molecules of air}} \right) = 4.8 \times 10^{-4} \text{ Pa}$$

$$6.21 \quad 3.94 \times 10^3 \text{ m}^3 \text{ or } 3.94 \text{ L}$$

$$6.23 \quad m_{\text{NH}_3} = nM = (1.34 \times 10^4 \text{ mol})(17.04 \text{ g mol}^{-1}) = 2.28 \times 10^5 \text{ g}$$

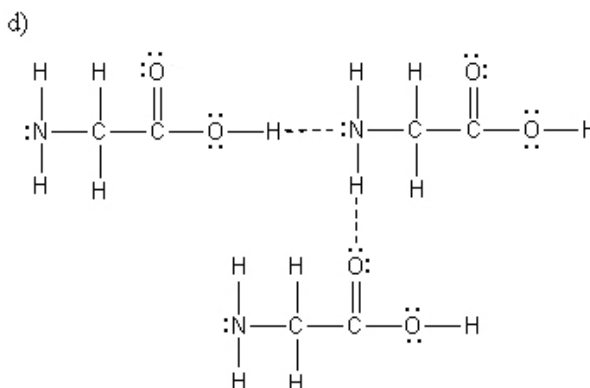
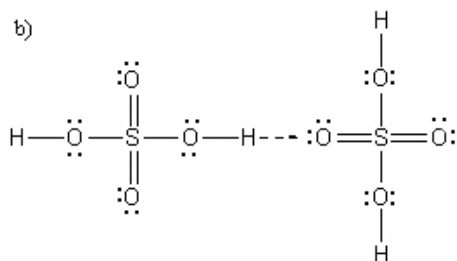
- 6.25 (a) Molecules are farther apart, making intermolecular attractions less significant and molecular size is less significant.
- (b) Molecules are closer together, so intermolecular attractions and molecular sizes are more significant.
- (c) Increasing the temperature at constant pressure leads to a volume increase, so molecules are farther apart, making intermolecular attractions and molecular size less significant.

$$6.27 \quad 2.88 \times 10^6 \text{ Pa}$$

6.29 Boiling point depends on the magnitude of intermolecular attractions, the larger the attractions, the higher the boiling point. All these substances are symmetrical (atomic), so the ranking depends entirely on dispersion forces. Boiling point increases with the total number of electrons (atomic number): He (lowest bp) < Ne < Ar < Xe (highest bp).

- 6.31 (a) no hydrogen bonding

- (b) hydrogen bonding
- (c) no hydrogen bonding
- (d) hydrogen bonding



Review Problems

$$6.33 \quad n = \frac{pV}{RT} = \frac{(145 \times 10^5 \text{ Pa})(9.50 \times 10^{-3} \text{ m}^3)}{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})} = 55.6 \text{ mol}$$

$$m = nM = (55.6 \text{ mol})(28.02 \text{ g mol}^{-1}) = 1.56 \times 10^3 \text{ g}$$

$$6.35 \quad 359 \text{ m s}^{-1}$$

6.37 The molar mass of gaseous oxygen is determined using the ideal gas law:

$$M = \frac{mRT}{PV}$$

Pump out a bulb of known volume, weigh the empty bulb, fill the bulb with oxygen at a measured pressure and weigh again. For monatomic oxygen, this experiment gives $M = 16.00 \text{ g mol}^{-1}$, whereas it gives $M = 32.00 \text{ g mol}^{-1}$ for the diatomic gas.

- 6.39
- (a) The bulb of hydrogen contains more molecules.
 - (b) The bulb of oxygen contains more mass.
 - (c) The average kinetic energy of molecules depends only on the temperature of the gas, so the oxygen molecules, being at higher temperature, have greater average kinetic energy.
 - (d) The hydrogen molecules have greater average speed by this factor.
- 6.41
- (a) $2.08 \times 10^{-3} \text{ m}^3$ or 2.08 L
 - (b) $1.05 \times 10^5 \text{ Pa}$

(c) $8.28 \times 10^4 \text{ Pa}$

6.43 $9.11 \times 10^{-4} \text{ m}^3$ or 0.911 L

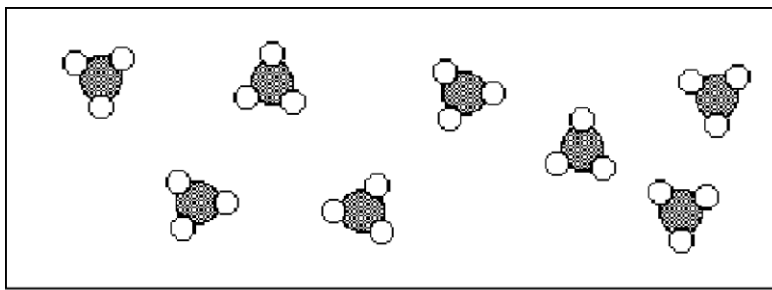
- 6.45 (a) NH_3 is polar and forms hydrogen bonds in addition to dispersion interactions
(b) CHCl_3 is a polar molecule in addition to dispersion interactions
(c) CCl_4 is symmetrical (tetrahedral), so it has only dispersion interactions
(d) CO_2 is symmetrical (linear) so it has only dispersion interactions

6.47 Deviations from ideal gas behaviour can be predicted based on the strengths of intermolecular interactions. The larger the intermolecular interactions, the greater the deviations are from the ideal behaviour. Both pairs of substances are non-polar, so dispersion interactions dominate the intermolecular forces. The substance with more electrons (Cl_2) has larger dispersion forces and therefore deviates more from ideal behaviour.

Additional Exercises

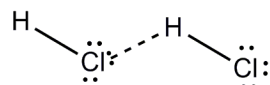
6.49 632 m^3

6.51



- 6.53 (a) Each container contains the same number of gas molecules. Because Container A has half the volume of container B, it has twice the pressure.
(b) Container A has the higher partial pressure of molecular hydrogen. Container A has 5 molecules of H_2 and container B has 8 molecules of H_2 but twice the volume. Thus, container A has a higher number of molecules per unit volume, producing a higher partial pressure of H_2 .
(c) The graph shows one large peak and one small peak, indicating an unequal amount of two different species. The lighter gas, molecular hydrogen, takes less time to reach the detector. The first peak is the larger peak, indicating that the container with a greater proportion of molecular hydrogen, Container B, is the one used in the experiment.

- 6.55 The boiling point of HCl is higher than that expected using the periodic trends (it should have a boiling point between PH_3 and SiH_4). This suggests that hydrogen-bonding occurs. Hydrogen bonding occurs between the H atom of one HCl molecule and the electronegative Cl atom of another HCl molecule:



- 6.57 A gas molecule approaching the wall of a container is subject to intermolecular attractions from its neighbouring molecules, which tend to pull it back into the gas volume. This slows the molecule so it exerts a lower force when it hits the wall. All other factors being the same, the more molecules that surround a gas molecule, the greater is this effect. Thus, the molecule in figure A, which has fewer other molecules around it, will strike the wall with greater force than the molecule in figure B.

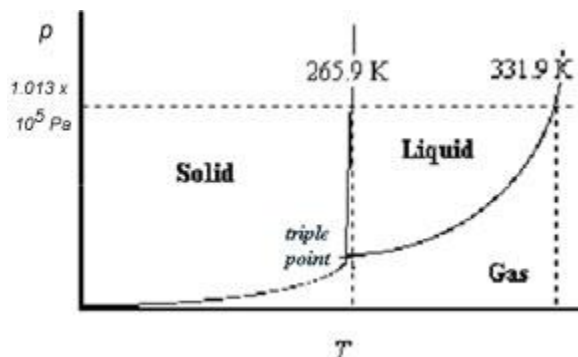
CHAPTER 7

Practice Exercises

- 7.1 Moles of water is $\frac{125}{18} = 6.9$, so heat involved is $6.9 \times 6.01 = 41.5$ kJ, which flows from the tray to the freezer compartment.
- 7.3 The gas liquefies at $p = 1.26 \times 10^4$ Pa and the liquid freezes when the pressure is approximately 0.5×10^5 Pa. At 1.013×10^5 Pa, 63.1 K, N_2 is a solid.

Review Questions

- 7.1 The viscosities of a set of similar substances increase with increasing chain length because of increased dispersion forces (stronger intermolecular attractions make it harder for molecules to slide by one another) and increased ‘tangling’ (longer chains are more entangled). Thus, the order of increasing viscosity is:
pentane (C_5) < gasoline (C_8) < fuel oil (C_{12})
- 7.3 Wax contains hydrocarbon molecules that cannot form hydrogen bonds to water molecules, so water forms beads on a freshly waxed surface. Windshield glass is a silicate structure with many —OH and =O groups that can form hydrogen bonds with water molecules, so water spreads out as a film on a clean windshield.
- 7.5 The position of an element in the periodic table, the chemical formula, and knowledge of polyatomic ions all help in identifying types of solids:
Sn, a metal, is a metallic solid; S_8 has a specific molecular formula, so it is a molecular solid; Se is not a metal, so it is a network solid; SiO_2 is a network solid; and Na_2SO_4 contains Na^+ cations and SO_4^{2-} anions, so it is an ionic solid.
- 7.7 (a) Br_2 is a discrete neutral molecule. It forms a molecular solid.
(b) KBr contains cations and anions. It forms an ionic solid.
(c) Ba is an alkaline earth metal. It forms a metallic solid.
(d) SiO_2 is a network solid.
(e) CO_2 is a covalent molecule. It forms a molecular solid.
- 7.9



- 7.11 The chemical formula is CaTiO_3 .
- 7.13 To determine the number of calcium ions in the unit cell, first determine the number of oxygen anions in the unit cell. An ionic face centred cube has six face ions and eight corner ions, giving $\frac{1}{2}(6) + \frac{1}{8}(8) = 4$ oxygen anions. The calcium cation has a charge of +2 and the oxide anion has a charge of -2, so we need the same number of oxide anions as calcium atoms in the unit cell. There are four calcium anions in the interior of the unit cell.
- 7.15 By measuring the various angles θ , the d-spacings between planes of atoms in the crystal lattice can be determined. This, plus the intensities of the diffracted X-rays, is used to deduce the locations of the atoms in the unit cell. Some chemical intuition is then needed in order to decide which atoms are bonded together.
- 7.17 An amorphous solid is a noncrystalline solid, which lacks the long-range order that characterises a crystalline substance. When crystalline solids are broken down, the angles are regular and the faces are flat. When amorphous solids are broken down, the faces are smooth and flat.
- 7.19 Substitutional impurities replace one atom (or ion) with another. For example, substitution of some Al^{3+} by Cr^{3+} in the Al_2O_3 crystal lattice makes rubies red.
- 7.21 Ceramics are inorganic materials that been heat-treated. Examples include: pottery, porcelain, floor/wall tiles and glass.
- 7.23 A refractory is a heat-resistant material. Refractories are used to line furnaces and rocket engine exhausts.

Review Problems

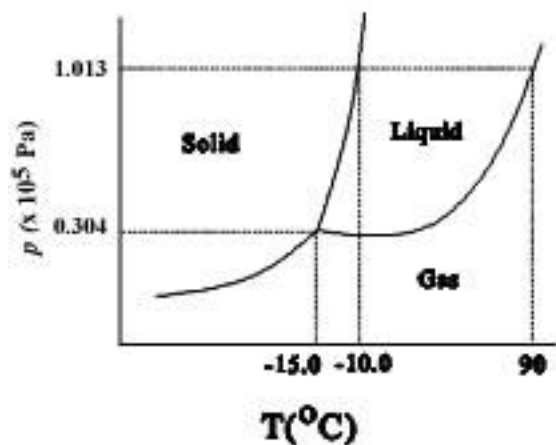
- 7.25 (a) NH_3 is polar and forms hydrogen bonds in addition to its dispersion interactions.
 (b) CHCl_3 is a polar molecule in addition to having dispersion interactions.
 (c) CCl_4 is symmetrical (tetrahedral), so it has only dispersion interactions.
 (d) CO_2 is symmetrical (linear) so it has only dispersion interactions.
- 7.27 Face-centred cubic crystals are close-packed, each atom having 12 nearest neighbours. Body-centred cubic crystals are not as closely packed, as each atom has 8 nearest neighbours. Thus, the face-centred cubic structure contains more atoms in a given volume and is denser.
- 7.29 (a) CH_3OH can form hydrogen bonds, so it boils at a higher temperature than CH_3OCH_3 .
 (b) SiO_2 is a network solid with covalent bonds that must break for it to boil, so it has a higher boiling point than SO_2 .
 (c) HF forms strong hydrogen bonds, so it boils at a higher temperature than HCl .
 (d) I_2 has larger orbitals, giving it higher polarisability, larger dispersion forces, and a higher boiling point than Br_2 .
- 7.31 When two substances of similar structures have different boiling points, differences in polarity and/or hydrogen-bonding behaviour apply. Melting requires that intermolecular hydrogen bonds

be overcome, but not intramolecular hydrogen bonds. Examination of the two structures reveals that oil of wintergreen has a polar O atom and polar OH bond positioned close together, which allows formation of intramolecular hydrogen bonds. The polar O atom in methyl-4-hydroxybenzoate is on the opposite side of the ring to the polar OH bond. Consequently, no intramolecular hydrogen bonds can form, but this structure forms strong intermolecular hydrogen bonds. Thus, stronger intermolecular forces must be overcome to melt methyl-4-hydroxybenzoate, accounting for its higher melting point.

7.33 A triple point is the intersection of two phase transition lines. Three triple points are shown on the phase diagram in figure 7.22: One is at 1300 °C (33.9×10^5 kPa), at which coesite, \square and \square quartz coexist. The second is at 1190 °C (1.41×10^5 kPa) at which \square quartz, tridymite, and cristobalite coexist. The third is at 1750 °C (4×10^5 kPa), at which cristobalite, \square quartz, and liquid silica coexist.

- 7.35 (a) For rhombic sulfur to melt, it must be heated above 153 °C and at a pressure greater than 1.438×10^8 Pa.
- (b) For rhombic sulfur to change to monoclinic sulfur, it must be heated to a temperature that depends on the pressure, ranging from 95.3 °C at 0.517 Pa to 153 °C at 1.438×10^8 Pa.
- (c) Rhombic sulfur only sublimes when the pressure is less than 0.517 Pa.

7.37



- 7.39 (a) There is a rhenium atom at each corner of the unit cell cube but nowhere else, so the rhenium lattice is simple cubic.
- (b) Each corner of a cube is shared by eight cubes and there are eight corners, so there are $8(\frac{1}{8}) = 1$ Re atom per unit cell. Each edge of a cube is shared by four cubes and there are 12 edges, so there are $12(\frac{1}{4}) = 3$ O atoms per unit cell. The chemical formula is ReO_3 .

7.41 The melting point of a metal is determined by the strength of interatomic forces: the larger these forces, the higher the melting point of the metal. The very high melting point of tungsten indicates that this metal has large interatomic forces compared to typical metals.

7.43 351 pm.

7.45 $d_{\text{Cl}} = 374.0 \text{ pm}$

7.47 Tin(IV) chloride must be a molecular solid, because if it were ionic it would be high-melting and the melt would conduct.

7.49 Gallium is a metallic solid.

7.51 Niobium is a metallic solid.

- 7.53
- (a) molecular
 - (b) ionic
 - (c) ionic
 - (d) metallic
 - (e) covalent
 - (f) molecular
 - (g) ionic

Additional Exercises

7.55 The magnitudes of dispersion forces depend on how extended the valence electrons are. In a molecule, valence electrons are spread over a larger volume because they are shared between atoms. Sketches of the electron clouds of H_2 and He illustrate this feature:

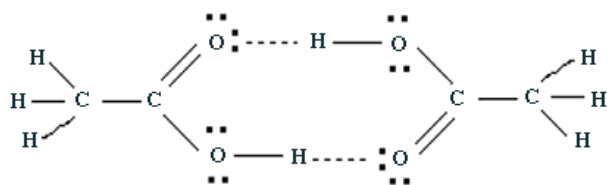


The more extended valence electron cloud of H_2 leads to stronger dispersion forces than for He, giving H_2 the higher boiling point.

7.57 The 'unit cell' corresponds to the 'pattern repeat unit' which is:



7.59 (a)



- (b) The fraction of paired molecules decreases as temperature rises because energy added to the system breaks some of the hydrogen bonds.

7.61 (a) 7.49 g cm^{-3}

(b) 9.70 g cm^{-3}

(c) 10.6 g cm^{-3}

Silver has a face-centred cubic lattice.