

Chapter 7

Chemical Bonding and Molecular Structure

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Lattice Energy

- The potential energy, V , for the ion pair can be calculated.

$$V = k \frac{q_1 q_2}{r}$$

- $k = 1.389 \times 10^5 \text{ kJ pm/mol}$
- The **lattice energy** is the overall result of the potential energy between the ions in a crystal.

Small ions with large charges form ionic compounds with large lattice energies.

Large ions with small charges form ionic compounds with small lattice energies.

Example Problem

Choose the compound below that should have the largest lattice energy.

- a) KF b) KCl c) KBr d) KI e) KAt

$$r = r_{\text{cation}} + r_{\text{anion}}$$

$$r_{\text{F}^-} < r_{\text{Cl}^-} < r_{\text{Br}^-} < r_{\text{I}^-} < r_{\text{At}^-}$$

$$r_{\text{KF}} < r_{\text{KCl}} < r_{\text{KBr}} < r_{\text{KI}} < r_{\text{KAt}}$$

$$V_{\text{KF}} > V_{\text{KCl}} > V_{\text{KBr}} > V_{\text{KI}} > V_{\text{KAt}}$$

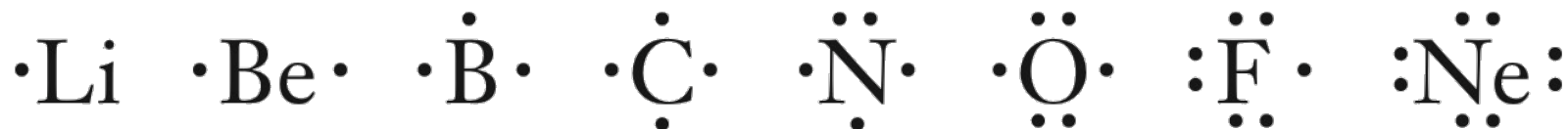
$$V = k \frac{q_1 q_2}{r}$$

Small ions with large charges form ionic compounds with large lattice energies.

Large ions with small charges form ionic compounds with small lattice energies.

Chemical Bonds and the Structure of Molecules

- **Octet rule** - an atom will form covalent bonds to achieve a complement of eight valence electrons.
 - The valence shell electronic configuration is ns^2np^6 for a total of eight electrons.
- **Lewis dot symbols** keep track of valence electrons, especially for main group elements, allowing prediction of bonding in molecules.
 - To draw a Lewis dot symbol, the valence electrons are represented by dots and are placed around the element symbol.
 - The first four dots are placed singly.
 - Starting with the fifth dot, they are paired.



Example Problem

In assembling a Lewis Dot diagram of PO_4^{3-} , there are _____ total electrons to use in the model.

a) 50

b) 48

c) 40

d) 32

e) 29

$$\text{P} \quad 1 \times 5 = 5$$

$$\text{O} \quad 4 \times 6 = 24$$

$$+ 3 \text{ extra } e^- = 3$$

$$\text{Total} = \underline{32}$$

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How about
 NO_3^- , CO_3^{2-}

- Lewis dot symbols keep track of valence electrons, especially for main group elements, allowing prediction of bonding in molecules.

Covalent Bonds

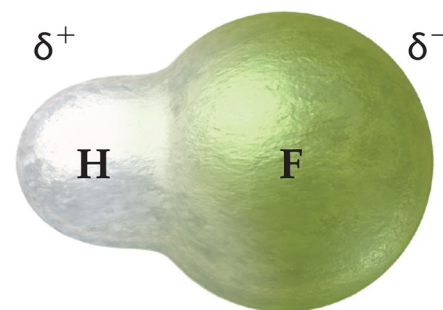
- Bonding atoms in molecules can share more than one bonding pair of electrons.
 - A **double bond** results when two bonding pairs are shared.
 - A **triple bond** results when three bonding pairs are shared.
- Strength of the covalent bond increases as the number of bonding pairs increases.

Type of Bond	Bond Energy (kJ/mol)
C—C	346
C=C	602
C≡C	835

Bond Polarity

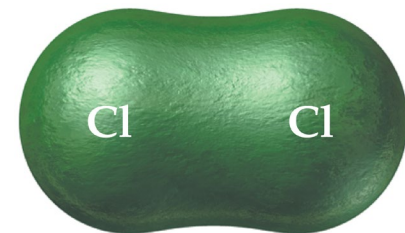
- A bond along which a dipole exists is a **polar bond**.
 - Also referred to as a **polar covalent bond** since electrons are still being shared.

- The greater the electronegativity difference, the more polar the bond.

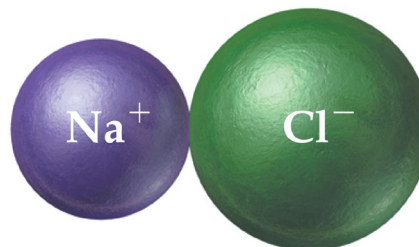


H-F > H-Cl


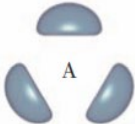


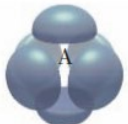
- When the electronegativity difference is zero, the bond is classified as **nonpolar covalent**.



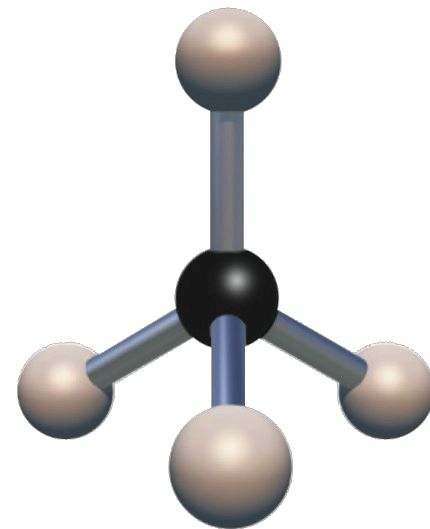
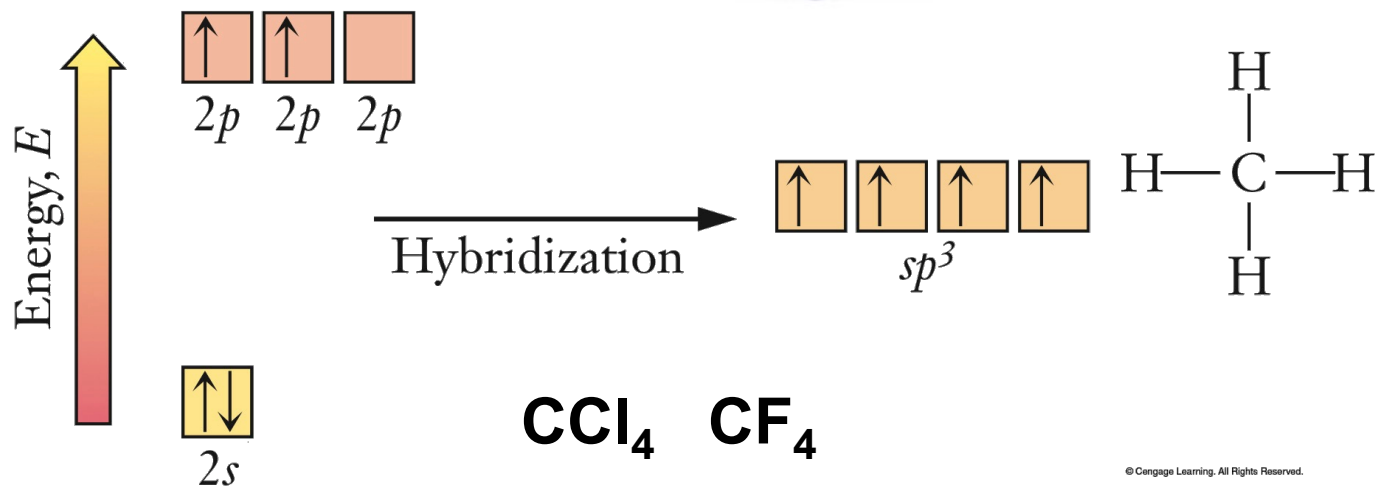
- When the electronegativity difference exceeds 2.0, the bond is classified as ionic.



Hybrid Orbitals

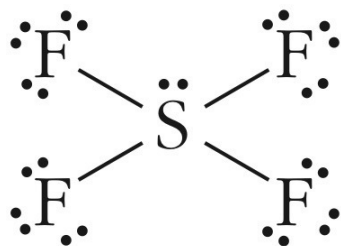
Orbitals Combined	Hybridization	Orbital Geometry
s, p	sp	
s, p, p	sp^2	
s, p, p, p	sp^3	
s, p, p, p, d	sp^3d	
s, p, p, p, d, d	sp^3d^2	

- Hybrid orbital name comes from the type and number of atomic orbitals combined (e.g., sp^3)
- The indicated orbital geometry gives rise to common molecular shapes.

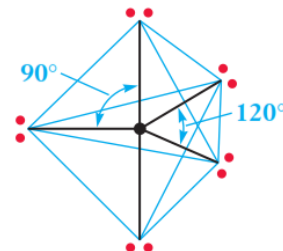


Example Problem

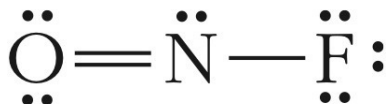
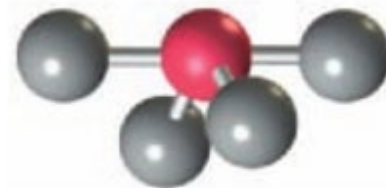
- Determine the shape of the following molecules using VSEPR theory:



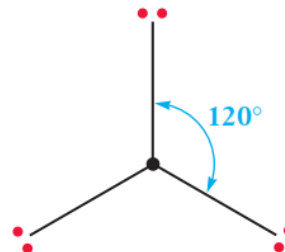
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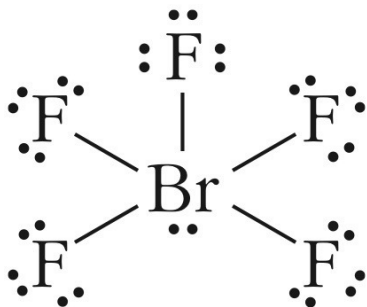
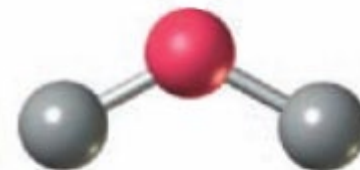
5: Trigonal bipyramidal



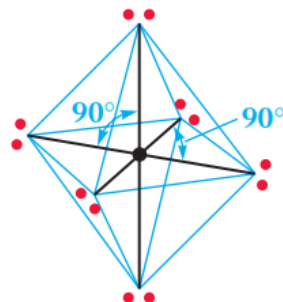
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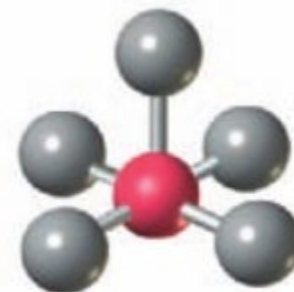
3: Trigonal planar



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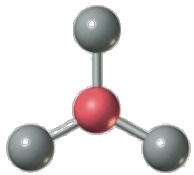
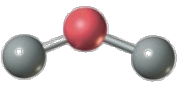
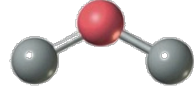
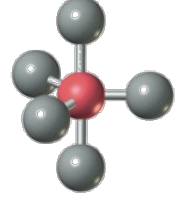
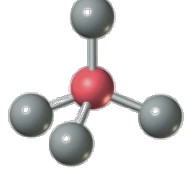
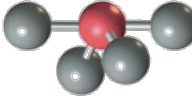
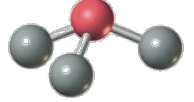
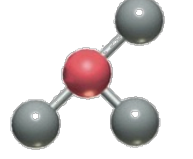
6: Octahedral



Shapes of Molecules

Table 7.4

The molecular shapes resulting from various combinations of the total number of electron pairs around the central atom and the number of lone pairs

Number of Electron Pairs	Number of Lone Pairs	Shape	Ball and Stick Model	Number of Electron Pairs	Number of Lone Pairs	Shape	Ball and Stick Model
3	0	BF₃ Trigonal planar		4	2	H₂O Bent (109.5°)	
3	1	SO₂ Bent (120°)		5	0	PCl₅ Trigonal bipyramidal	
4	0	SiH₄ Tetrahedral		5	1	SF₄ Seesaw	
4	1	NH₃ Trigonal pyramidal		5	2	BrF₃ T-shape	


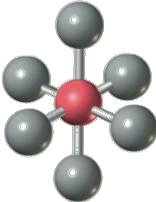
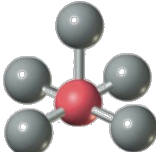
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- Molecular shapes for various combinations of bonding and nonbonding electron pairs.

Shapes of Molecules

Table ■ 7.4 (continued)

The molecular shapes resulting from various combinations of the total number of electron pairs around the central atom and the number of lone pairs

Number of Electron Pairs	Number of Lone Pairs	Shape	Ball and Stick Model
5	3	Linear	 I_3^-
6	0	Octahedral	 SF_6
6	1	Square pyramidal	 BrF_5

Chapter 8

Molecules and Materials

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Carbon

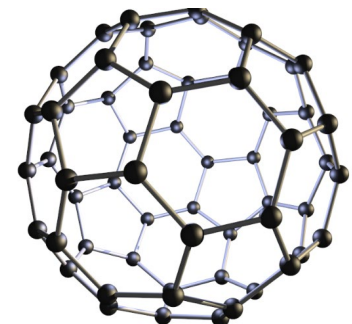
- There are three forms of the element carbon, they are **allotropes**.
 - **Graphite**, **diamond**, and **fullerenes**.
 - Graphite and diamond have been known for a long time.
 - Fullerenes were discovered in 1985 in the form of C_{60} .



Graphite



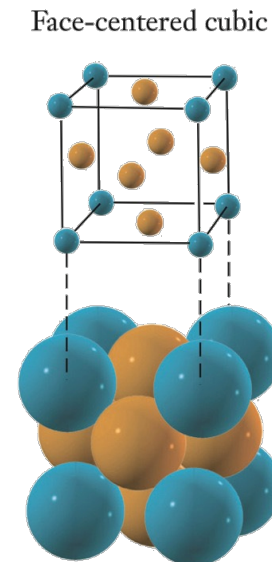
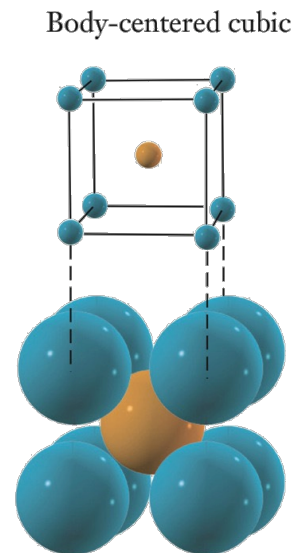
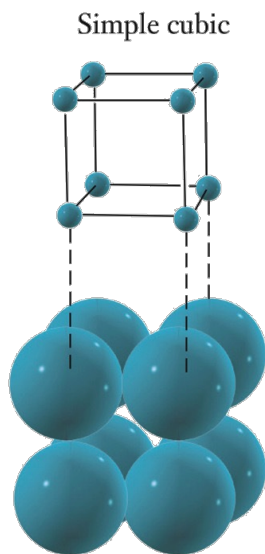
Diamond



C_{60} : Fullerene

Condensed Phases - Solids

- A **unit cell** is the smallest collection of atoms that displays all the features of the crystal structure.
 - Three types of cubic unit cells:
 - simple cubic (sc)** containing $1/8$ each of 8 corner atoms,
 - body-centered cubic (bcc)** containing one additional atom within,
 - face-centered cubic (fcc)** with an additional $1/2$ each of 6 atoms along the faces.



Calculation of Packing Efficiency

- To calculate packing efficiency:

$$\text{Packing efficiency} = \frac{\text{volume of atoms in unit cell}}{\text{total volume of unit cell}} \times 100$$

- To find the volume of the unit cell in terms of radius r :

$$V = a^3 \text{ (where } a \text{ is the edge length of the unit cell)}$$

$$a_{\text{fcc}} = (2\sqrt{2}) r; \quad a_{\text{bcc}} = \frac{4}{\sqrt{3}} r; \quad a_{\text{sc}} = 2r$$

- To find the total volume occupied by atoms:

$$\text{total volume occupied by atoms} = \# \text{ atoms in unit cell} \times \left(\frac{4}{3} \pi r^3 \right)$$

Calculation of Packing Efficiency

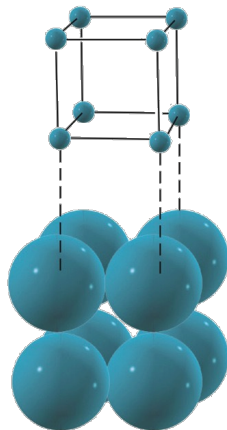
- To determine the number of complete atoms per unit cell:

$$\text{fcc} = \frac{1}{2} (\overset{6}{\# \text{ face-center atoms}}) + \frac{1}{8} (\overset{8}{\# \text{ corner atoms}}) = 4$$

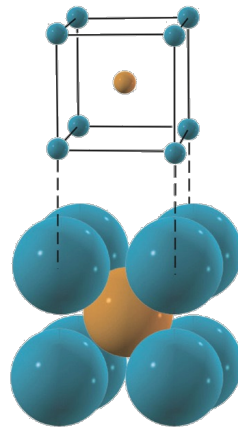
$$\text{bcc} = (\overset{1}{\# \text{ body-center atoms}}) + \frac{1}{8} (\overset{8}{\# \text{ corner atoms}}) = 2$$

$$\text{sc} = \frac{1}{8} (\overset{8}{\# \text{ corner atoms}}) = 1$$

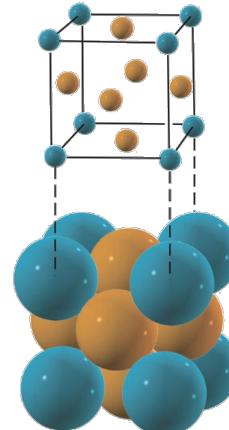
Simple cubic



Body-centered cubic



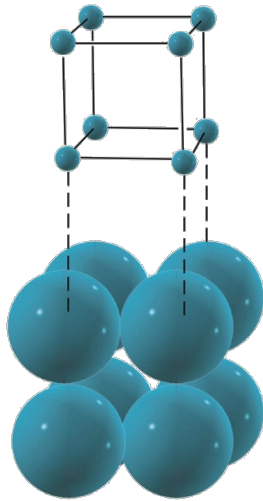
Face-centered cubic



Calculation of Packing Efficiency

52 %

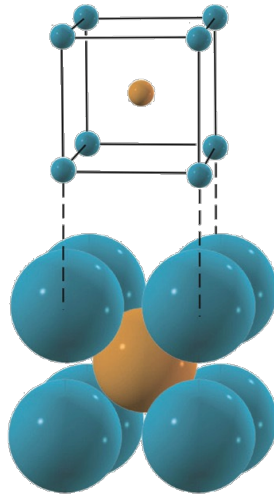
Simple cubic



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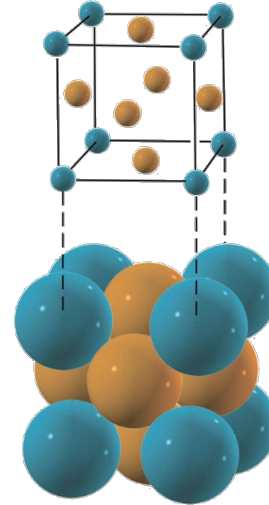
68 %

Body-centered cubic



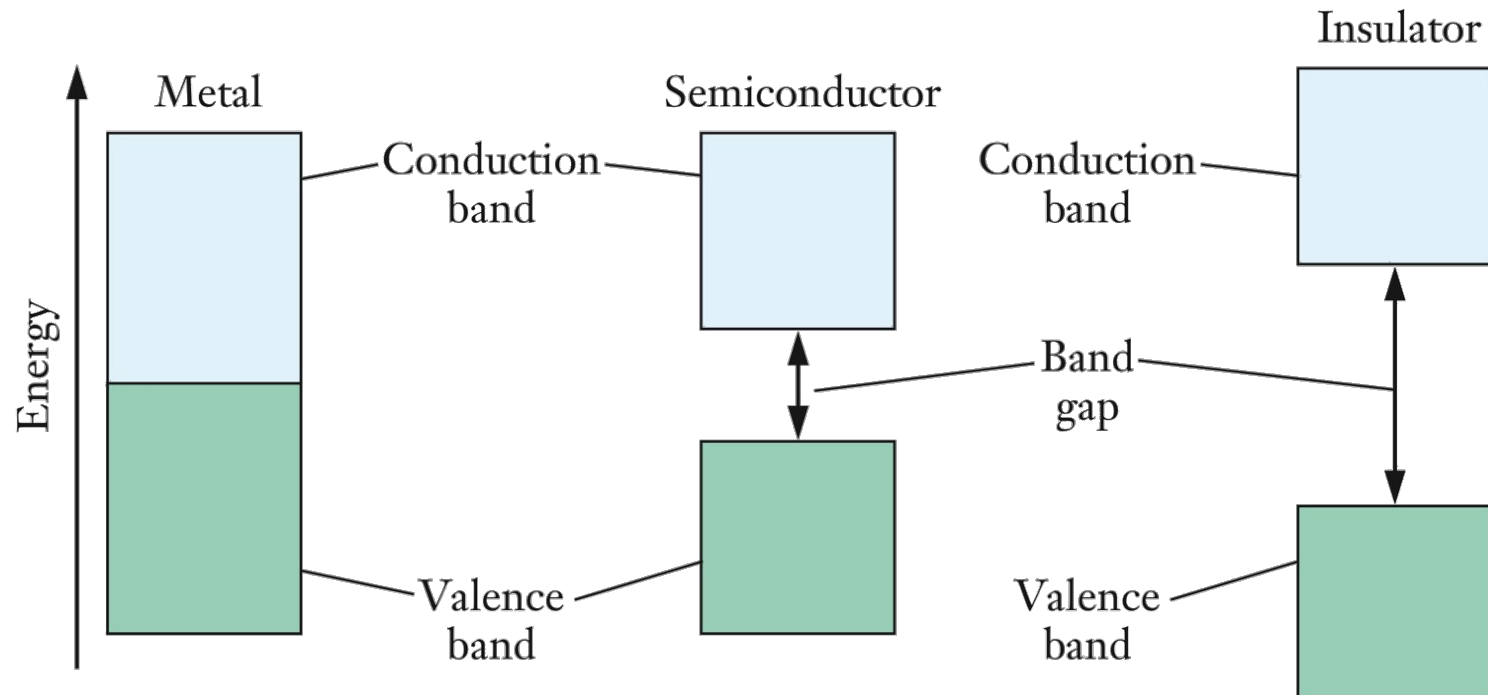
74 %

Face-centered cubic



Band Theory and Conductivity

- The wave functions of the valence electrons interact with each other.
- **Bonding molecular orbitals** result from constructive interference.
- **Antibonding molecular orbitals** result from destructive interference.



Semiconductors

- Electrical conductivity of semiconductors can be modified via doping.
- **Doping** - adding trace amounts of an element to a substance to modify its properties.
 - **n-type**: prepared by doping with a valence electron rich element; “negative”

Doping Si with P introduces an extra valence electron.

- **p-type**: prepared by doping with a valence electron deficient element; “positive”

Doping Si with Al means the dopant has fewer than 4 valence electrons (holes).

Intermolecular Forces

- **Intermolecular forces** - the attractive and repulsive forces between molecules. ($\text{H}_2\text{O}^{\delta-} \cdots \cdots \delta^+ \text{H}_2\text{O}$)
- **Dispersion forces** are common to all molecules.
 - Also referred to as **instantaneous dipole-induced dipole forces**.
- **Dipole-dipole forces** are the attractive and repulsive forces for molecules with a **permanent** dipole.
- **Hydrogen bonds** are a special case of dipole-dipole forces.
 - Hydrogen bonds occur only in compounds containing hydrogen covalently bonded to the highly electronegative elements F, O, or N.

Example Problem

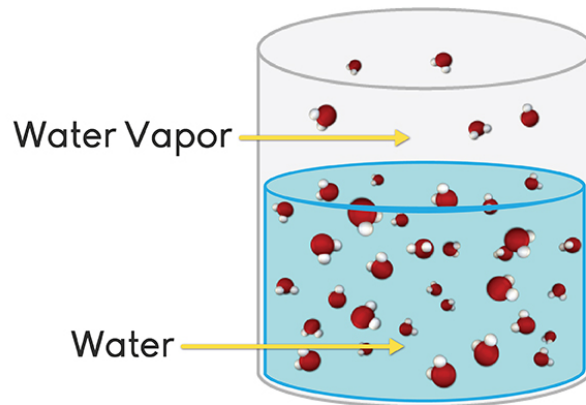
- Which type(s) of intermolecular forces need to be overcome to convert each of the following liquids to gases?

liquid \longrightarrow gas

- CH_4 **dispersion**
- CH_3F **dispersion dipole-dipole**
- CH_3OH **dispersion dipole-dipole**
 H-bonding

Vapor Pressure

- **Vapor pressure** - the gas phase pressure of a substance in dynamic equilibrium with the pure liquid in a pure substance.
 - Vapor pressure is a characteristic property of a particular substance at a particular temperature.



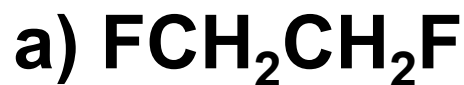
- Liquids with **strong** intermolecular forces have **lower** vapor pressures (**cooking oil; motor oil**).
- Liquids with **weak** intermolecular forces have **higher** vapor pressures & are described as **volatile (formaldehyde)**.

Example Problem

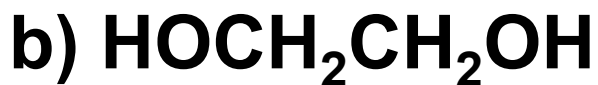
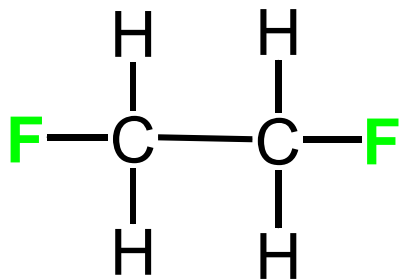
Q. Predict the order of increasing vapor pressure for the following compounds.

Weakest IMFs
highest VP

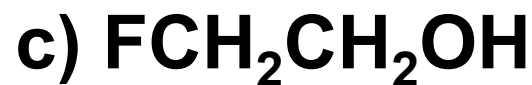
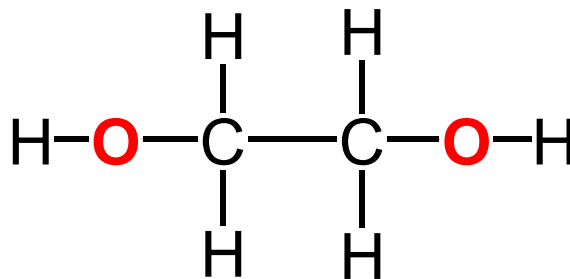
Strongest IMFs
lowest VP



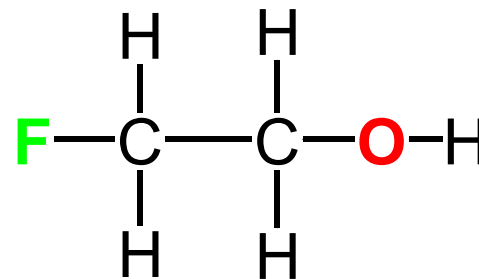
dispersion
dipole-dipole



dispersion
dipole-dipole
H-bonding



dispersion
dipole-dipole
H-bonding (less)



order of increasing vp: **b < c < a**

Chapter 9

Energy and Chemistry

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Energy Transformation

- For a system or surroundings, the only possible forms of energy flow are heat, q , and work, w .
- The delta, Δ , means “change in” and is defined as the difference in the final and initial states.

$$\Delta E = q + w$$

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

- The sign resulting from the difference in the final and initial states indicates the direction of the energy flow.
 - Negative values indicate energy is being released.
 - Positive values indicate energy is being absorbed.

Example Problem

- Calculate ΔE for the system in which 16 J of work is done on a gas by the surroundings and the gas absorbs 51 J of heat?

Heat added **TO** the system $q > 0$ $q = +51 \text{ J}$

Work done **TO** the system $w > 0$ $w = +16 \text{ J}$

$$\begin{aligned}\Delta E &= q + w \\ &= 51 \text{ J} + 16 \text{ J} = +67 \text{ J}\end{aligned}$$

Negative values indicate energy is being **released**.

Positive values indicate energy is being **absorbed**.

Heat Capacity

- Different systems will absorb different amounts of energy based on three main factors.
 - The amount of material, m or n .
 - m is mass and n is number of moles
 - The type of material, as measured by c or C_p .
 - c is the specific heat capacity, or specific heat, and C_p is the molar heat capacity.
 - The temperature change, ΔT .

$$q = mc\Delta T$$

$$q = nC_p\Delta T$$

Example Problem

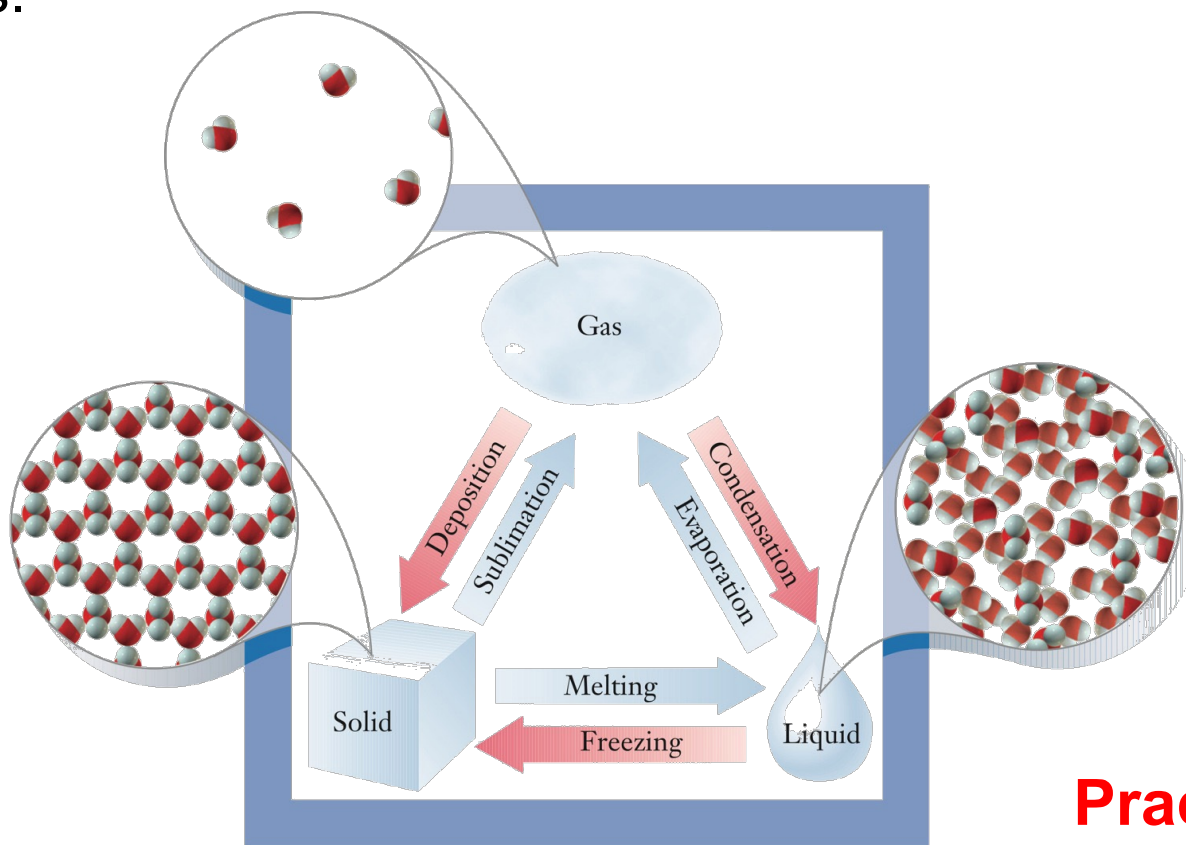
- Copper wires used to transport electrical current heat up because of the resistance in the wire. If a 140 g wire gains 280 J of heat, what is the change in temperature of the wire? Specific heat of Cu = 0.384 J/g°C

$$q = mc\Delta T$$

$$\begin{aligned}\Delta T &= \frac{q}{mc} = \frac{280 \text{ J}}{140 \text{ g} \cdot 0.384 \frac{\text{J}}{\text{g}^\circ\text{C}}} \\ &= 5.2^\circ\text{C}\end{aligned}$$

ΔH of Phase Changes

- Phase changes occur under constant pressure conditions.
 - The heat flow during a phase change is an enthalpy change.
 - During a phase change, temperature does not change with heat flow due to formation or breaking of intermolecular attractive forces.



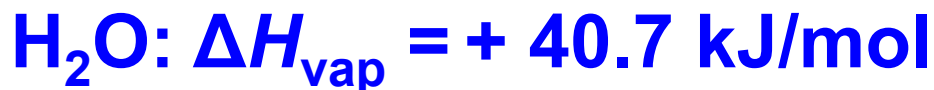
Practice 9.45

ΔH of Phase Changes

- The heat required to convert a liquid to a gas is the **heat of vaporization**, ΔH_{vap} .
 - ΔH_{vap} is endothermic with a positive value.
- The heat released to convert a gas to a liquid is the **heat of condensation**, ΔH_{cond} .
 - ΔH_{cond} is exothermic with a negative value.
- $\Delta H_{\text{cond}} = -\Delta H_{\text{vap}}$
 - The values of enthalpy changes in opposite directions have equal numeric values and differ only in their signs.
 - The magnitude of enthalpy change depends on the substance involved.

ΔH of Phase Changes

- The value of ΔH for a phase change is compound specific and has units of kJ/mol.



- The heat flow can be calculated using the number of moles of substance, n , and the value of the enthalpy change.

$$\Delta H = n \times \Delta H_{\text{phase change}}$$

Example Problem

- The heat of fusion of pure silicon is 43.4 kJ/mol. How much energy is needed to melt a 5.24 g-sample of silicon at its melting point of 1693 K?

$$n = m \times \frac{1}{M_{Si}} = 5.24 \times \frac{1}{28.1} = 0.186 \text{ mol}$$

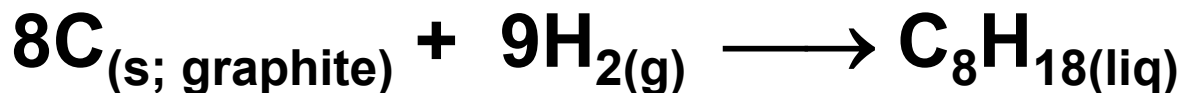
$$\Delta H = n \times \Delta H_{\text{phase change}}$$

$$= 0.186 \text{ mol} \times 43.4 \text{ kJ} / \text{mol}$$

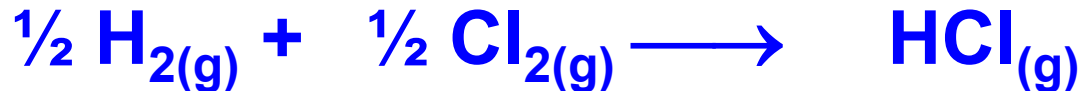
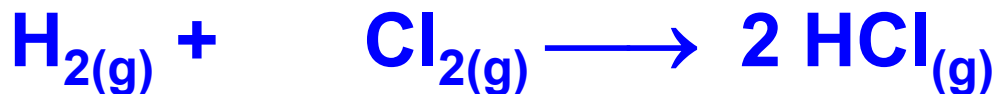
$$= 8.10 \text{ kJ}$$

Heats of Formation

- A **formation reaction** is the chemical reaction by which **one mole** of a compound is formed from its **elements** in their **standard states**.



- Fractional coefficients** are allowed for formation reactions because only one mole of product can be formed.



- The **standard state** is the most stable form of an element at room temperature, 25° C, and pressure, 1 atm, indicated with a superscript °.

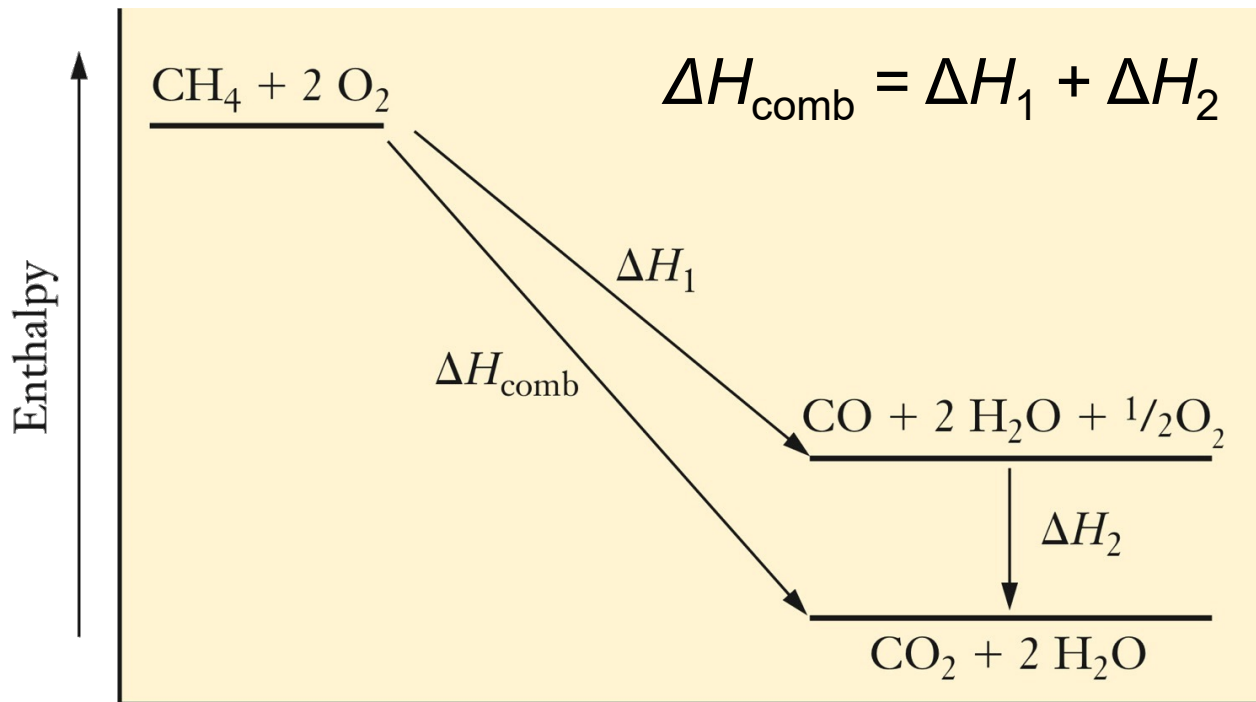
Practice 9.52, 9.53

- $\Delta H_{\text{f}}^{\circ} = 0$ for an element in its standard state.

Hess' s Law and Heats of Reaction

- Direct calorimetric determinations of some reactions may be too difficult or dangerous to perform.
 - An indirect method is needed to obtain heats of reaction.
- **Hess' s law**: the enthalpy change for any process is independent of the particular way the process is carried out.
 - Enthalpy is a state function.
 - A **state function** is a variable whose value depends only on the state of the system and not its history.

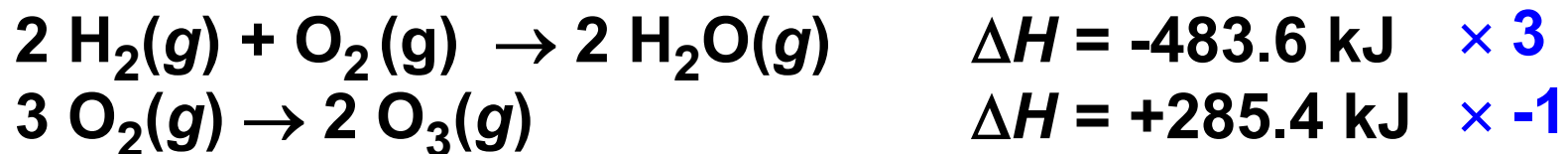
Hess' s Law



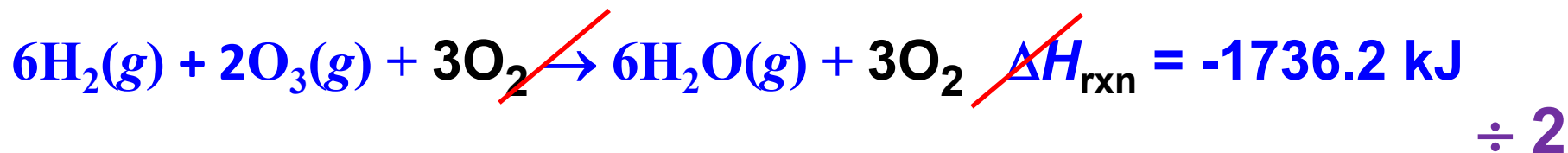
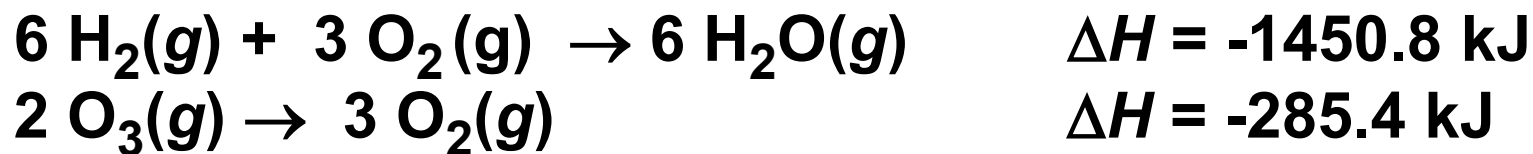
- Enthalpy diagram for the combustion of methane. The CH_4 is converted to CO , then the CO is converted to CO_2 . The ΔH for each step is used to calculate the ΔH for the overall reaction. The ΔH will be the same for both paths.

Example Problem

Use these two **given** reactions,



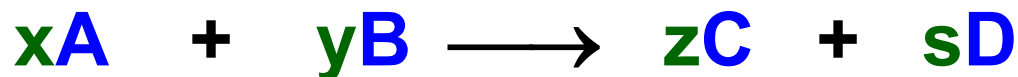
to solve ΔH_{rxn} for this reaction below:



Formation Reactions and Hess's Law

- The enthalpy change for a reaction can be calculated using Hess's law and heats of formation.

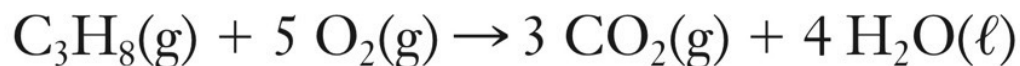
$$\Delta H_{rxn}^o = \sum_i v_i \Delta H_f^o(\text{products})_i - \sum_j v_j \Delta H_f^o(\text{reactants})_j$$



$$\Delta H_{rxn}^0 = [\mathbf{z}\Delta H_f^0(\mathbf{C}) + \mathbf{s}\Delta H_f^0(\mathbf{D})] - [\mathbf{x}\Delta H_f^0(\mathbf{A}) + \mathbf{y}\Delta H_f^0(\mathbf{B})]$$

Example Problem

- Use tabulated data to find the heat of combustion of one mole of propane, C_3H_8 , to form gaseous carbon dioxide and liquid water.



$$\Delta H^0_{\text{rxn}} = [\mathbf{z}\Delta H^0_{\text{f}}(\mathbf{C}) + \mathbf{s}\Delta H^0_{\text{f}}(\mathbf{D})] - [\mathbf{x}\Delta H^0_{\text{f}}(\mathbf{A}) + \mathbf{y}\Delta H^0_{\text{f}}(\mathbf{B})]$$

$$\Delta H^\circ = 3 \text{ mol } \Delta H^\circ_{\text{f}}[\text{CO}_2(\text{g})] + 4 \text{ mol } \Delta H^\circ_{\text{f}}[\text{H}_2\text{O}(\ell)] - 1 \text{ mol } \Delta H^\circ_{\text{f}}[\text{C}_3\text{H}_8(\text{g})] - 5 \text{ mol } \Delta H^\circ_{\text{f}}[\text{O}_2(\text{g})]$$

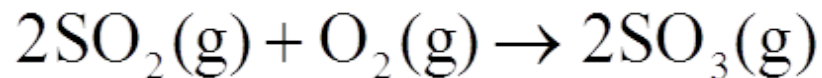
$$= 3 \text{ mol } (-393.5 \text{ kJ/mol}) + 4 \text{ mol } (-285.8 \text{ kJ/mol}) - 1 \text{ mol } (-103.8 \text{ kJ/mol}) - 5 \text{ mol } (0 \text{ kJ/mol})$$

$$= -2219.9 \text{ kJ}$$

Practice 9.58, 9.59₃₈

Energy and Stoichiometry

- A thermochemical equation allows for the stoichiometric treatment of energy.
- The thermochemical equation is used to convert between the number of moles of a reactant or product and the amount of energy released or absorbed.
 - The stated value of ΔH for a thermochemical equation corresponds to the reaction taken place exactly as written, with the indicated numbers of moles of each substance reacting.



$$\Delta H^\circ = -197.0 \text{ kJ}$$

2 moles

- 197.0 kJ

1 moles

- 98.5 kJ

Example Problem

- An engine generates 15.7 g of nitric oxide gas during a laboratory test. How much heat was absorbed in producing this NO?



Ratio to use: 2 mole NO need 180.5 kJ

$$n = m \times \frac{1}{M_{\text{NO}}} = 15.7 \text{ g} \times \frac{1 \text{ mol}}{30.0 \text{ g}} = 0.523 \text{ mol}$$

$$0.523 \text{ mol} \times \frac{180.5 \text{ kJ}}{2 \text{ mol}} = 47.2 \text{ kJ}$$

Practice 9.63, 9.65, 9.67