Molecules and Materials: Electronic basis of union of atoms leading to formation of molecules. Modes of atomic union (Ionic and Covalent bonding and their subsequent partial transformation into each other), Types of binding forces. Molecular association leading to formation of materials.

According to Dalton's atomic theory, all matter, whether an element, a compound or a mixture is composed of small particles called atoms. The postulates of this theory may be stated as follows:

•All matter is made of very tiny particles called atoms.
• Atoms are indivisible particles, which cannot be created or destroyed in a chemical reaction.
• Atoms of a given element are identical in mass and chemical properties.
• Atoms of different elements have different masses and chemical properties.
• Atoms combine in the ratio of small whole numbers to form compounds.
• The relative number and kinds of atoms are constant in a given compound.

An element is a pure substance consisting only of atoms that all have the same numbers of protons in their atomic nuclei. Unlike chemical compounds, chemical elements cannot be broken down into simpler substances by chemical means.

Atoms of most elements are not able to exist independently. Atoms form molecules and ions. These molecules or ions aggregate in large numbers to form the matter that we can see, feel or touch.

Under normal conditions no other element exists as an independent atom in nature, except noble gases.

Molecules

A molecule is in general a group of two or more atoms that are chemically bonded together, that is, tightly held together by attractive forces.

A molecule can be defined as the smallest particle of an element or a compound that is capable of an independent existence and shows all the properties of that substance. Atoms of the same element or of different elements can join together to form molecules.

The molecules of an element are constituted by the same type of atoms.

Molecules of many elements, such as argon (Ar), helium (He) etc. are made up of only one atom of that element.

But this is not the case with most of the non- metals. For example, a molecule of oxygen consists of two atoms of oxygen and hence it is known as a diatomic molecule, O_2. If 3 atoms of oxygen unite into a molecule, instead of the usual 2, we get ozone.

The number of atoms constituting a molecule is known as its atomicity.

Chemical bonding

Matter is made up of one or different type of elements.

However, a group of atoms is found to exist together as one species having characteristic properties. Such a group of atoms is called a molecule.

Obviously there must be some force which holds these constituent atoms together in the molecules.

The attractive force which holds various constituents (atoms, ions, etc.) together in different chemical species is called a chemical bond.

Since the formation of chemical compounds takes place as a result of combination of atoms of various elements in different ways, it raises many questions.
Why do atoms combine?
Why are only certain combinations possible?
Why do some atoms combine while certain others do not?
Why do molecules possess definite shapes?.

To answer such questions different theories and concepts have been put forward from time to time. These are
Kössel-Lewis approach,
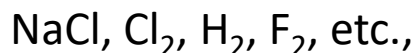Valence Shell Electron Pair Repulsion (VSEPR) Theory,
Valence Bond (VB) Theory
and Molecular Orbital
(MO) Theory.

KÖSSEL-LEWIS APPROACH TO CHEMICAL BONDING

Lewis postulated that atoms achieve the stable octet when they are linked by chemical bonds.

$$NaCl, Cl_2, H_2, F_2, \text{etc.,}$$

In the formation of molecules only the outer shell electrons take part in chemical combination and they are known as valence electrons

G. N. Lewis introduced simple notation to represent valence electrons in the atom. These notations called Lewis symbol. For example, Lewis symbols for the elements of second period are under

$$\text{Li} \quad \text{Be} \quad \cdot\text{B}\cdot \quad \cdot\text{C}\cdot \quad \cdot\text{N}\cdot \quad :\text{O}: \quad :\text{F}: \quad :\text{Ne}:$$
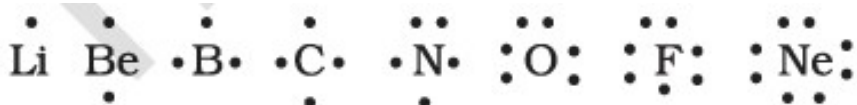
For example, the formation of NaCl from sodium and chlorine, according to the above scheme, can be explained as:

$$\text{Na} \rightarrow \text{Na}^+ + e^-$$
$$[Ne]\,3s^1 \qquad [Ne]$$
$$\text{Cl} + e^- \rightarrow \text{Cl}^-$$
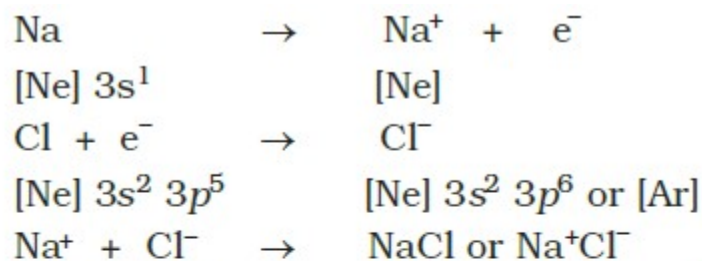
The bond formed, as a result of the electrostatic attraction between the positive and negative ions was termed as ionic bond

$$[Ne]\,3s^2\,3p^5 \qquad [Ne]\,3s^2\,3p^6 \text{ or } [Ar]$$
$$\text{Na}^+ + \text{Cl}^- \rightarrow \text{NaCl or Na}^+\text{Cl}^-$$

Similarly the formation of CaF_2 may be shown as:

$$\text{Ca} \rightarrow \text{Ca}^{2+} + 2e^-$$
$$[Ar]4s^2 \qquad [Ar]$$
$$\text{F} + e^- \rightarrow \text{F}^-$$
$$[He]\,2s^2\,2p^5 \qquad [He]\,2s^2\,2p^6 \text{ or } [Ne]$$
$$\text{Ca}^{2+} + 2\text{F}^- \rightarrow \text{CaF}_2 \text{ or } \text{Ca}^{2+}(\text{F}^-)_2$$
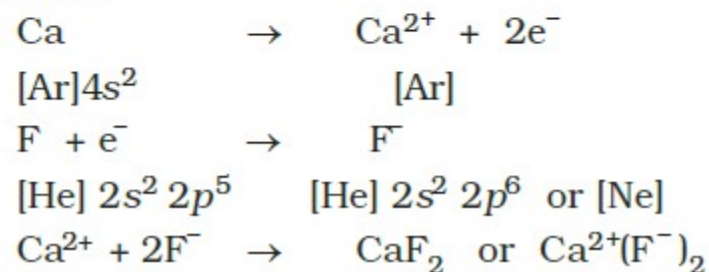
Atomic number	Symbol	Electron configuration
1	H	$1s^1$
2	He	$1s^2$
3	Li	$[He]2s^1$
4	Be	$[He]2s^2$
5	B	$[He]2s^2 2p^1$
6	C	$[He]2s^2 2p^2$
7	N	$[He]2s^2 2p^3$
8	O	$[He]2s^2 2p^4$
9	F	$[He]2s^2 2p^5$
10	Ne	$[He]2s^2 2p^6$
11	Na	$[Ne]3s^1$
12	Mg	$[Ne]3s^2$
13	Al	$[Ne]3s^2 3p^1$
14	Si	$[Ne]3s^2 3p^2$
15	P	$[Ne]3s^2 3p^3$
16	S	$[Ne]3s^2 3p^4$
17	Cl	$[Ne]3s^2 3p^5$
18	Ar	$[Ne]3s^2 3p^6$
19	K	$[Ar]4s^1$
20	Ca	$[Ar]4s^2$
21	Sc	$[Ar]4s^2 3d^1$

Octet rule

Kössel and Lewis in 1916 developed an important theory of chemical combination between atoms known as electronic theory of chemical bonding. According to this, atoms can combine either by transfer of valence electrons from one atom to another (gaining or losing) or by sharing of valence electrons in order to have an octet in in their valence shells. This is known as Octet rule

Langmuir (1919) refined the Lewis postulations by abandoning the idea of the stationary cubical arrangement of the octet and introducing the term Covalent bond
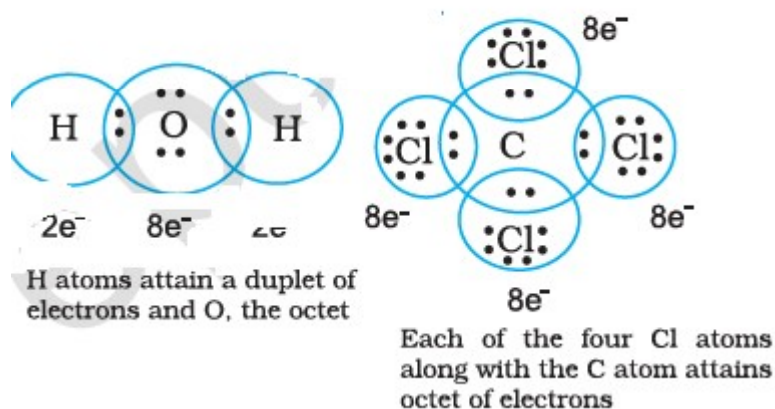
The formation of the Cl2 molecule can be understood in terms of the sharing of a pair of electrons between the two chlorine atoms, each chlorine atom contributing one electron to the shared pair. In the process both chlorine atoms attain the outer shell octet of the nearest noble gas (i.e., argon).

The dots represent electrons. Such structures are referred to as Lewis dot structures.

The Lewis dot structures can be written for other molecules also, in which the combining atoms may be identical or different. The important conditions being that:

• Each bond is formed as a result of sharing of an electron pair between the atoms.
• Each combining atom contributes at least one electron to the shared pair.
• The combining atoms attain the outer shell noble gas configurations as a result of the sharing of electrons.

Thus in water and carbon tetrachloride molecules, formation of covalent bonds can be represented as

2e⁻   8e⁻   2e

H atoms attain a duplet of
electrons and O, the octet

8e⁻

8e⁻

8e⁻

8e⁻

8e⁻

Each of the four Cl atoms
along with the C atom attains
octet of electrons

Thus, when two atoms share one electron pair they are said to be joined by **a single covalent bond.** In many compounds we have **multiple bonds** between atoms. The formation of multiple bonds envisages sharing of more than one electron pair between two atoms. **If two atoms share two pairs of electrons, the covalent bond between them is called a double bond.** For example, in the carbon dioxide molecule, we have two double bonds between the carbon and oxygen atoms. Similarly in ethene molecule the two carbon atoms are joined by a double bond.

C_2H_4 molecule
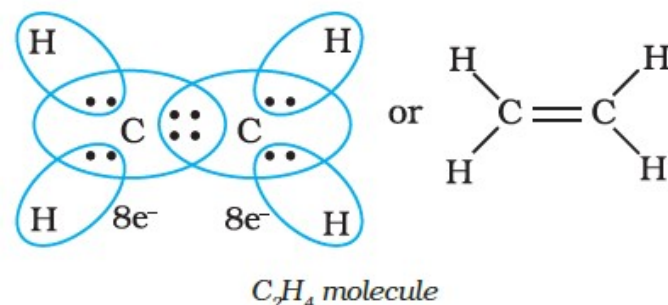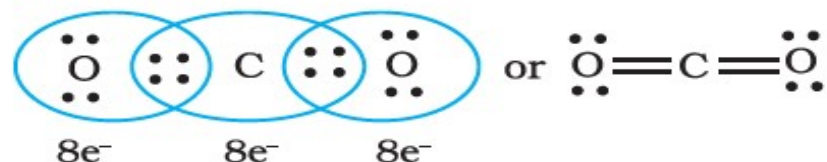
When combining atoms share three electron pairs as in the case of two nitrogen atoms in the N_2 molecule and the two carbon atoms in the ethyne molecule, a triple bond is formed.

N_2 molecule
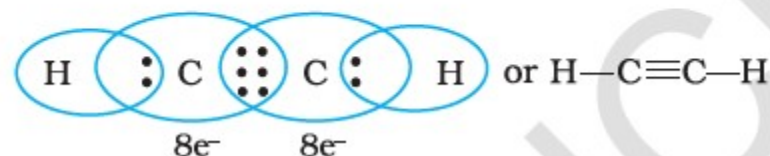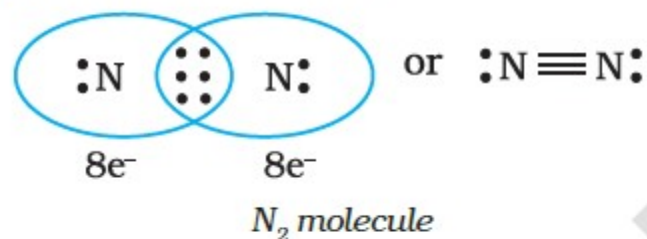
4.1.5 Limitations of the Octet Rule

The octet rule, though useful, is not universal. It is quite useful for understanding the structures of most of the organic compounds and it applies mainly to the second period elements of the periodic table. There are three types of exceptions to the octet rule.

The incomplete octet of the central atom

In some compounds, the number of electrons surrounding the central atom is less than eight. This is especially the case with elements having less than four valence electrons. Examples are $LiCl$, BeH_2 and BCl_3.

$$Li \! : \! Cl \qquad H \! : \! Be \! : \! H \qquad Cl \! : \! \overset{\overset{\displaystyle Cl}{\cdot\cdot}}{B} \! : \! Cl$$

Li, Be and B have 1,2 and 3 valence electrons only. Some other such compounds are $AlCl_3$ and BF_3.

Odd-electron molecules

In molecules with an odd number of electrons like nitric oxide, NO and nitrogen dioxide, NO_2, the octet rule is not satisfied for all the atoms

$$\overset{\cdot\cdot}{\underset{\cdot}{N}} \! = \! \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} \qquad\qquad \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} \! = \! \overset{\cdot\cdot\,+}{N} \! - \! \overset{\cdot\cdot\,-}{\underset{\cdot\cdot}{O}}$$
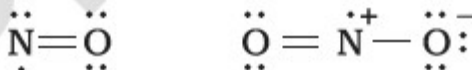
The expanded octet

Elements in and beyond the third period of the periodic table have, apart from 3s and 3p orbitals, 3d orbitals also available for bonding. In a number of compounds of these elements there are more than eight valence electrons around the central atom. This is termed as the expanded octet. Obviously the octet rule does not apply in such cases.

Some of the examples of such compounds are: PF_5, SF_6, H_2SO_4 and a number of coordination compounds.

PF₅

10 electrons around the P atom

SF₆

12 electrons a the S ato
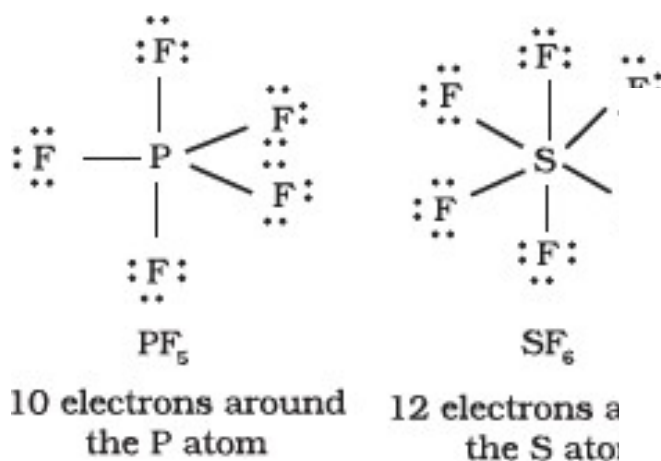
Interestingly, sulphur also forms many compounds in which the octet rule is obeyed. In sulphur dichloride, the S atom has an octet of electrons around it.
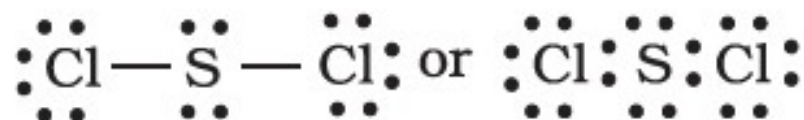
Other drawbacks of the octet theory

- It is clear that octet rule is based upon the chemical inertness of noble gases. However, some noble gases (for example xenon and krypton) also combine with oxygen and fluorine to form a number of compounds like XeF_2, KrF_2, $XeOF_2$ etc.,
- This theory does not account for the shape of molecules.
- It does not explain the relative stability of the molecules being totally silent about the energy of a molecule.

Ionic bond

Ionic bonding is a type of chemical bonding that involves the electrostatic attraction between oppositely charged ions, or between two atoms with sharply different electronegativities, and is the primary interaction occurring in ionic compounds.

$M(g) \rightarrow M^+(g) + e^-$;
Ionization enthalpy

$X(g) + e^- \rightarrow X^-(g)$;
Electron gain enthalpy

$M^+(g) + X^-(g) \rightarrow MX(s)$
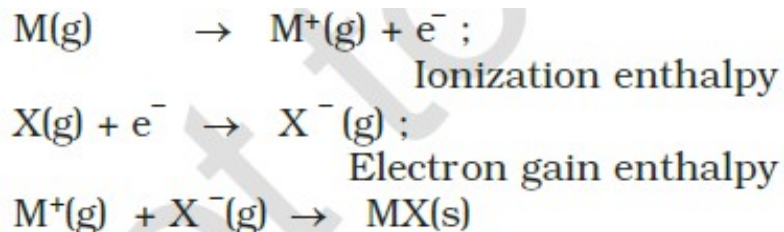
- The ease of formation of the positive and negative ions from the respective neutral atoms;
- The arrangement of the positive and negative ions in the solid, that is, the lattice of the crystalline compound.

Several properties distinguish ionic compounds from covalent compounds. These may be related rather simply to the crystal structure of ionic compounds, namely, a lattice composed of positive and negative ions in such a way that the attractive forces between oppositely charged ions are maximized and the repulsive forces between ions of the same charge are minimized. Before discussing some of the possible geometries, a few simple properties of ionic compounds may be mentioned:[1]

1. Ionic compounds tend to have very low electrical conductivities as solids but conduct electricity quite well when molten. This conductivity is attributed to the presence of *ions*, atoms charged either positively or negatively, which are free to move under the influence of an electric field. In the solid, the ions are bound tightly in the lattice and are not free to migrate and carry electrical current.

2. Ionic compounds tend to have high melting points. Ionic bonds usually are quite *strong* and they are *omnidirectional*. The second point is quite important, since ignoring it could lead one to conclude that ionic bonding was much stronger than covalent bonding—which is *not* the case. We shall see that substances containing strong, multidirectional covalent bonds, such as diamond, also have very high melting points. The high melting point of sodium chloride, for example, results from the strong electrostatic attractions between the sodium cations and the chloride anions, and from the lattice structure, in which each sodium ion attracts six chloride ions, each of which in turn attracts six

3. Ionic compounds usually are very hard but brittle substances. The hardness of ionic substances follows naturally from the argument presented above, except in this case we are relating the multivalent attractions between the ions with *mechanical* separation rather than separation through thermal energy. The tendency toward brittleness results from the nature of ionic bonding. If one can apply sufficient force to displace the ions slightly (e.g., the length of one-half of the unit cell in NaCl), the formerly attractive forces become repulsive

4. Ionic compounds are often soluble in polar solvents with high permittivities (dielectric constants). The energy of interaction of two charged particles is given by

$$E = \frac{q^+ q^-}{4\pi r \varepsilon} \tag{4.1}$$

where q^+ and q^- are the charges, r is the distance of separation, and ε is the permittivity of the medium. The permittivity of a vacuum, ε_0, is $8.85 \times 10^{-12} \, C^2 \, m^{-1} \, J^{-1}$. For common polar solvents, however, the permittivity values are considerably higher. For example, the permittivity is $7.25 \times 10^{-10} \, C^2 \, m^{-1} \, J^{-1}$ for water, $2.9 \times 10^{-10} \, C^2 \, m^{-1} \, J^{-1}$ for acetonitrile, and $2.2 \times 10^{-10} \, C^2 \, m^{-1} \, J^{-1}$ for ammonia, giving relative permittivities of $82 \, \varepsilon_0 \, (H_2O)$, $33 \, \varepsilon_0 \, (CH_3CN)$, and $25 \, \varepsilon_0 \, (NH_3)$. Since the permittivity of ammonia is 25 times that of a vacuum, the attraction between ions dissolved in ammonia, for example, is only 4% as great as in the absence of solvent. For solvents with higher permittivities the effect is even more pronounced.

Occurrence of ionic compounds

the requirements for ionic bonding are (1) the atoms of one element must be able to lose one or two (rarely three) electrons without undue energy input and (2) the atoms of the other element must be able to accept one or two electrons (almost never three) without undue energy input.

Ionic compounds in the crystalline state consist of orderly three-dimensional arrangements of cations and anions held together by coulombic interaction energies. These compounds crystallise in different crystal structures determined by the size of the ions, their packing arrangements and other factors. The crystal structure of sodium chloride, NaCl (rock salt), for example is shown below.
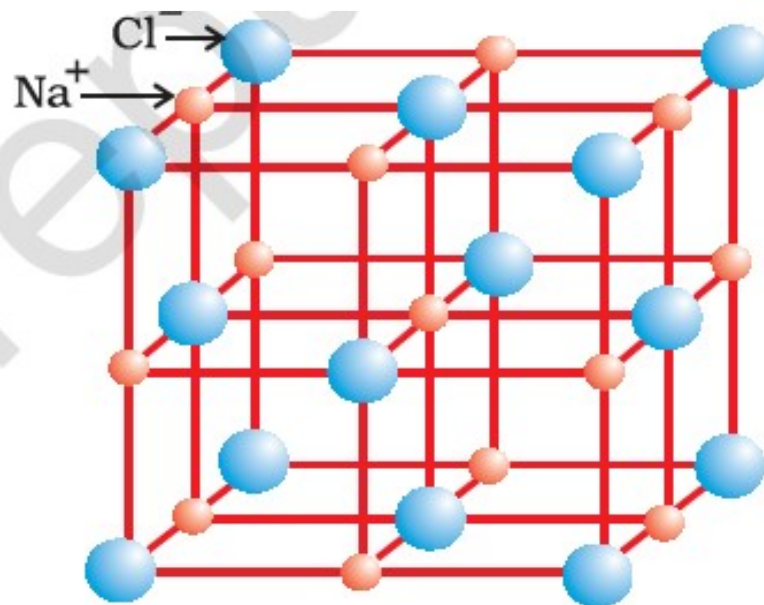
Face centered cubic structure

Eight sodium ions form the corners of the cube and six more are at the center

Chloride ions are similarly arranged , so that the sodium chloride lattice consts of two interpenetrating face centered cubic lattice

The coordination number of both ions in the sodium chloride lattice is 6, that is there are six chloride ions about each sodium ions and six sodium ions about each chloride ion

The sodium chloride structure is adopted by most of the alkali metal halides: All of the lithium, sodium, potassium, and rubidium halides plus cesium fluoride. It is also found in the oxides of magnesium, calcium, strontium, barium, and cadmium.

Cesium chloride body centered cube

Explaining Simple Ionic Structures

The crystal structure adopted depends mostly on:

· The relative sizes of the atoms/ions

· The relative number of the two types of atoms/ions

· The electronic structure of the atoms/ions

The radius ratio is typically defined as r^+/r^-, where r^+ is the radius of the cation and r^- is the radius of the anion.

How many anions (bigger) can be arranged around a cation (smaller)?

$\frac{r_{cation}}{r_{anion}}$	Coord #	
< 0.155	2	linear
0.155 - 0.225	3	triangular
0.225 - 0.414	4	T_D
0.414 - 0.732	6	O_H
0.732 - 1.000	8	cubic

ZnS (zincblende)

NaCl (sodium chloride)

CsCl (cesium chloride)
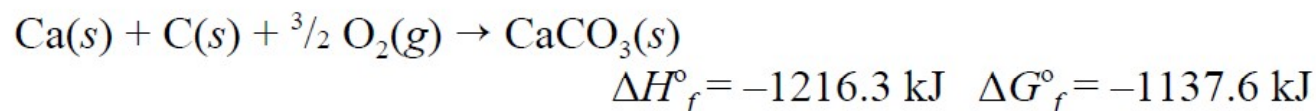
Radius Ratio Rules

In order to maximize the net electrostatic attraction between ions in a structure, the Coordination Number of the Cation will be Maximized subject to the criterion of Maintaining Cation-Anion Contact

stable　　　　　transitional　　　　unstable
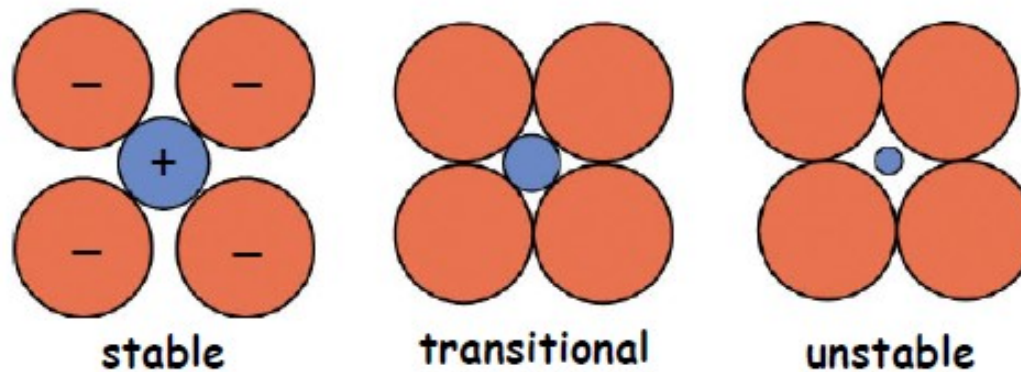
Determined by comparison of the ratio of the ionic radii (r+/r-), with values derived from the **geometric contact criterion**

Thermodynamics of Crystal Formation

- All stable ionic crystals have negative standard enthalpies of formation, ΔH°_f, and negative standard free energies of formation, ΔG°_f.

$$Na(s) + \tfrac{1}{2} Cl_2(g) \rightarrow NaCl(s) \qquad \Delta H^\circ_f = -410.9 \text{ kJ} \qquad \Delta G^\circ_f = -384.0 \text{ kJ}$$

$$Cs(s) + \tfrac{1}{2} Cl_2(g) \rightarrow CsCl(s) \qquad \Delta H^\circ_f = -442.8 \text{ kJ} \qquad \Delta G^\circ_f = -414.4 \text{ kJ}$$

$$Mg(s) + \tfrac{1}{2}O_2(g) \rightarrow MgO(s) \qquad \Delta H^\circ_f = -385.2 \text{ kJ} \qquad \Delta G^\circ_f = -362.9 \text{ kJ}$$

$$Ca(s) + C(s) + \tfrac{3}{2} O_2(g) \rightarrow CaCO_3(s)$$
$$\Delta H^\circ_f = -1216.3 \text{ kJ} \quad \Delta G^\circ_f = -1137.6 \text{ kJ}$$

- The exothermic and spontaneous formation of ionic solids can be understood in terms of a Hess's Law cycle, called the Born-Haber cycle.

- The lattice energy is the most important factor in making the formation of ionic crystals exothermic and spontaneous.

- Lattice energy, U, is defined as the enthalpy required to dissociate one mole of crystalline solid in its standard state into the gaseous ions of which it is composed; e.g.,

$$NaCl(s) \rightarrow Na^+(g) + Cl^-(g) \qquad U = +786.8 \text{ kJ}$$
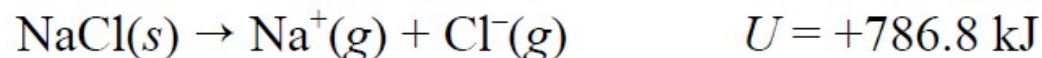
Defined in this way, lattice energy is a positive (endothermic) quantity.

Sometimes lattice energy is defined by the reverse reaction, in which case the values are negative (exothermic).

Born-Haber Cycle for NaCl(s)

$$Na^+(g) + Cl^-(g)$$

$I = +496$ kJ $A = -349$ kJ

$$Na(g) + Cl(g)$$

$-U = ?$

$\Delta H^o_{sub} = +107.7$ kJ $\frac{1}{2}D = +121.7$ kJ

$$Na(s) + \frac{1}{2}Cl_2(g) \longrightarrow NaCl(s)$$

$\Delta H^o_f = -410.9$ kJ

$Na(s) \rightarrow Na(g)$	$\Delta H^o_{sub} = 107.7$ kJ
$Na(g) \rightarrow Na^+(g) + e^-$	$I = 496$ kJ
$\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$	$\frac{1}{2}D = 121.7$ kJ
$Cl(g) + e^- \rightarrow Cl^-(g)$	$A = -349$ kJ
$Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$	$-U = ?$
$Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s)$	$\Delta H^o_f = -410.9$ kJ

Born-Haber Cycle for NaCl(s)

$$Na^+(g) + Cl^-(g) \quad\longrightarrow$$

$I = +496$ kJ	$A = -349$ kJ

$$Na(g) + Cl(g)$$

$\Delta H^o_{sub} = +107.7$ kJ	$\tfrac{1}{2}D = +121.7$ kJ

$$-U = ?$$

$$Na(s) + \tfrac{1}{2}Cl_2(g) \xrightarrow{\quad\Delta H^o_f = -410.9 \text{ kJ}\quad} NaCl(s)$$

$Na(s) \rightarrow Na(g)$	$\Delta H^o_{sub} = 107.7$ kJ
$Na(g) \rightarrow Na^+(g) + e^-$	$I = 496$ kJ
$\tfrac{1}{2}Cl_2(g) \rightarrow Cl(g)$	$\tfrac{1}{2}D = 121.7$ kJ
$Cl(g) + e^- \rightarrow Cl^-(g)$	$A = -349$ kJ
$Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$	$-U = ?$
$Na(s) + \tfrac{1}{2}Cl_2(g) \rightarrow NaCl(s)$	$\Delta H^o_f = -410.9$ kJ

$$\Rightarrow \quad \Delta H^o_f = \Delta H^o_{sub} + I + \tfrac{1}{2}D + A - U$$
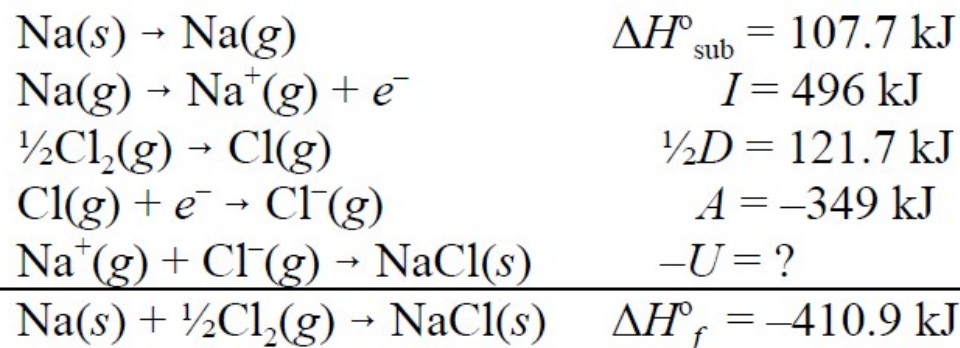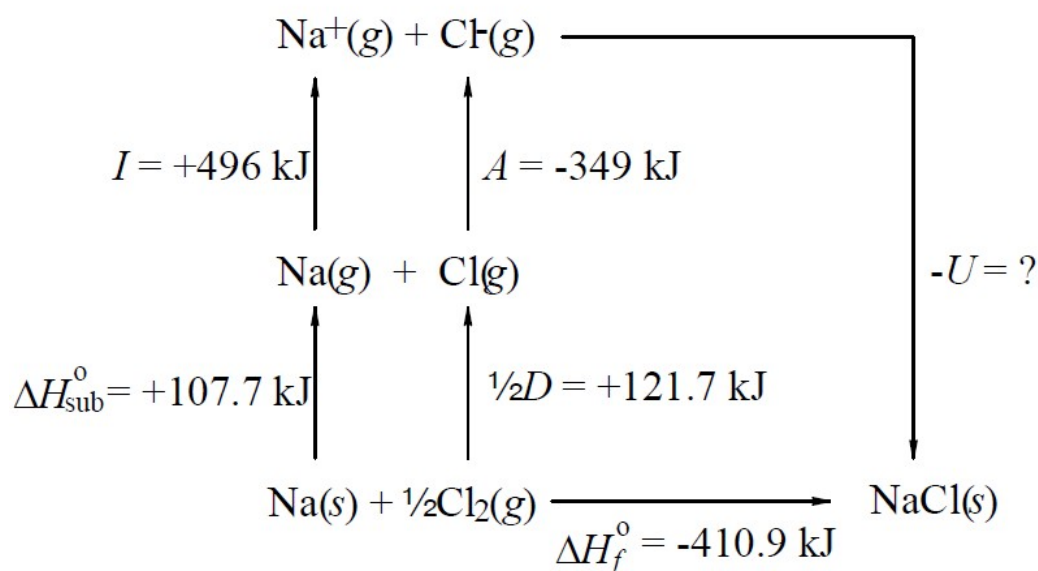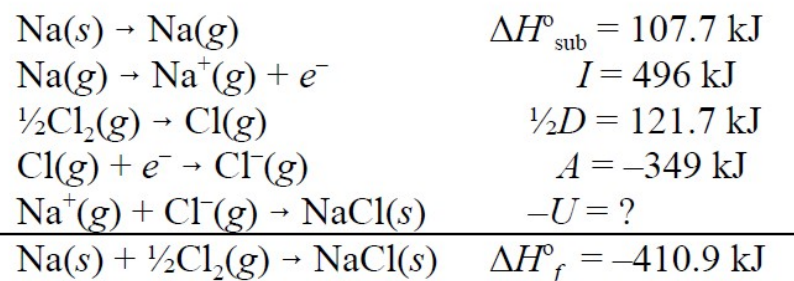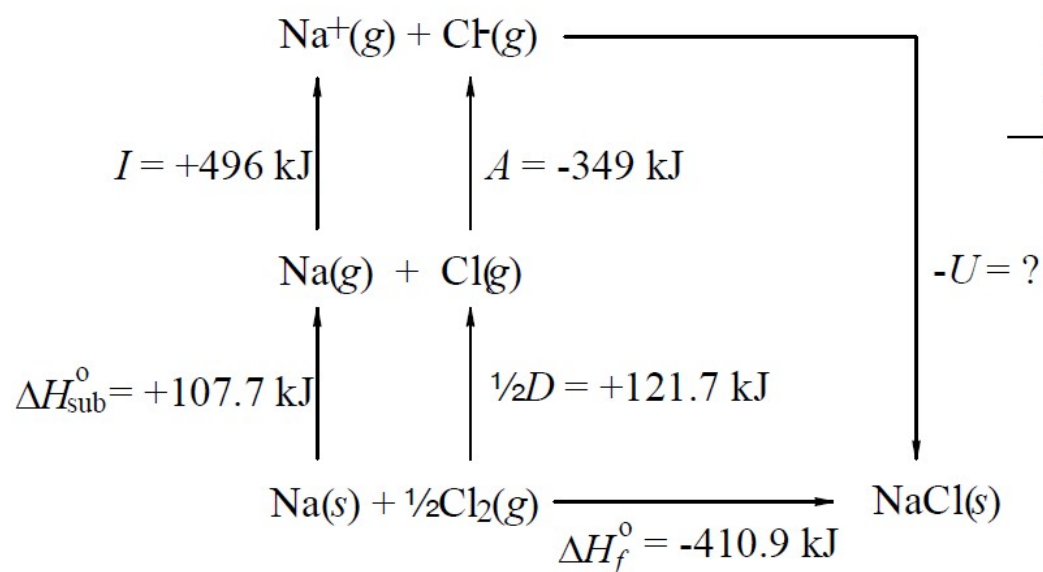
$$\therefore \quad U = \Delta H^o_{sub} + I + \tfrac{1}{2}D + A - \Delta H^o_f$$
$$= 107.7 \text{ kJ} + 496 \text{ kJ} + 121.7 \text{ kJ} + (-349 \text{ kJ}) - (-410.9 \text{ kJ})$$
$$= 787 \text{ kJ}$$

Factors Favoring a More Stable Crystal Lattice

Large values of lattice energy, U, are favored by
1. Higher ionic charges
2. Smaller ions
3. Shorter distances between ions

Selected Lattice Energies, U_o (kJ/mol)
(Born-Haber Cycle Data)

	F^-	Cl^-	Br^-	I^-	O^{2-}
Li^+	1049.0	862.0	818.6	762.7	2830
Na^+	927.7	786.8	751.8	703	2650
K^+	825.9	716.8	688.6	646.9	2250
Rb^+	788.9	687.9	612	625	2170
Cs^+	758.5	668.2	635	602	2090
Mg^{2+}		2522			3795
Ca^{2+}		2253			3414
Sr^{2+}		2127			3217