

## Cohesive energy:

### What is cohesive energy?

It is the energy that must be supplied to the solid to separate its constituents into neutral free atoms at rest and at infinite separation with the same electronic configuration.

### What is the lattice energy of a solid?

It is the energy that must be supplied to an ionic crystal to separate its constituents into free ions at rest and at infinite separation.

### What are the forces responsible for the cohesion of solids?

There are three forces responsible for the cohesion of a solid:

1. Coulomb force: This is the major contribution to the cohesion of a solid; it is the attractive force between electrons and the nuclei.
2. Magnetic force: This has a weak contribution to cohesion.
3. Gravitational force: It has a negligible contribution to cohesion.

### Classification of solids due to their cohesion:

1. Van der Waals crystals: (e.g. Argon and other noble elements)
2. Ionic crystals: (e.g. NaCl and other corresponding structures).
3. Metallic crystals: (e.g. Na).
4. Covalent crystals (e.g. Diamond).

[Note: See different types of crystalline binding in figure 56].

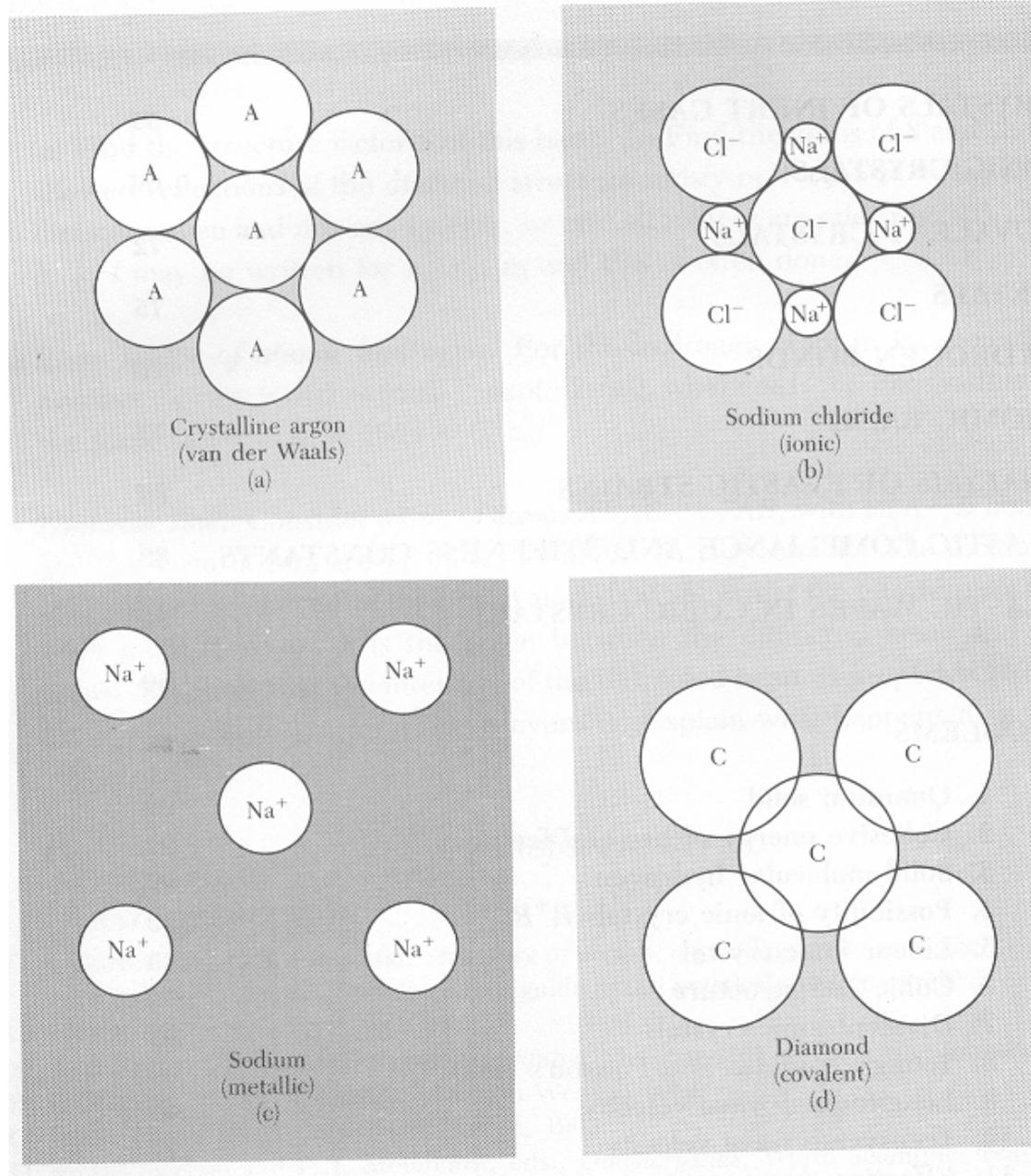


Figure 56: Different types of crystalline binding: (a) Van der Waals binding (b) Ionic binding (c) Metallic binding (d) Covalent binding.

### 1. Crystals of noble gases: (Molecular crystals).

The noble gases form the simplest crystals and crystallize as close-packed *fcc* except  $He^3$  and  $He^4$ . These crystals are transparent insulators, weakly bound with low temperature melting point temperature. The atoms have very high ionization energies.

Why do these crystals have cohesive energy of an atom 1% or may be less of the ionization energy of an atomic electron?

Some of the properties of these crystals at absolute zero temperature and zero pressure are listed in table 9.

Table 9: Properties of noble gas crystals (extrapolated to 0 K and zero pressure).

Crystal	Nearest neighbor distance ( $\text{\AA}$ )	Experimental cohesive energy (eV/atom)	Melting point (K)	Ionization potential of free atom (eV)	Lennard-Jone parameter $\epsilon$ ( $10^{-16}$ erg)	Lennard-Jone parameter $\sigma$ ( $\text{\AA}$ )
He	Liquid at zero temp.	-----	-----	24.58	14	2.56
Ne	3.13	0.02	24	21.56	50	2.74
Ar	3.76	0.08	84	15.76	167	3.40
Kr	4.01	0.116	117	14.00	225	3.65
Xe	4.35	0.17	161	12.13	320	3.98

### Van der Waals-London interaction:

The total potential energy of any two atoms (of a noble crystal) separated by a certain distance is due to two attractive and repulsive contributions.

### Attractive potential energy:

In an adopted model, it can be shown that induced dipole-dipole moment interaction between atoms of noble gases has an energy which is inversely proportional to the sixth power of the separation of two atoms, namely:

$U_{\text{attractive}} = -\frac{A}{r^6}$ , where the minus sign represents the attractive interaction and  $A$  is expressed as;

$A = \frac{\hbar\omega_0 e^4}{2C^2}$ . Here in this model each dipole is represented as a linear harmonic oscillator with frequency  $\omega_0$  and elastic constant of  $C = m\omega_0^2$ , where  $m$  is the mass of atom.

**Exercise:** Show that the induced dipole-dipole interaction for noble gases is expressed by  $U_{\text{attractive}} = -\frac{A}{r^6}$ . Consider each dipole as a linear oscillator with charges  $\pm e$  and separation  $x$  and oscillate along the x-axis, where  $r$  is the distance between atoms.

### Repulsive potential energy:

When the two atoms are close enough such that the charge distribution could overlap, such overlap gives repulsive energy. This repulsion is due to the Pauli Exclusion Principle. In the overlap of charge distribution, the electrons from atoms will have the chance to occupy states in the other atoms and vice versa.

How does the electron overlap increase the total energy of the system and give a repulsive contribution to the interaction?

**Answer:**

Let us take two hydrogen atoms that are pushed together until the protons are almost in contact, as shown in figure 57.

The energy of the resulted system is that of atomic *He* which is -78.98eV where there is no effect of Pauli principle when the two electrons from the two different hydrogen atoms align anti-parallel to each other in the new configuration, as shown in figure 57. When the electrons are parallel to each other the resulted energy is -59.38eV. The last configuration is less bound than the first one by 19.6eV. This amount of energy (19.6eV) which has increased the repulsion is due to the Pauli principle.

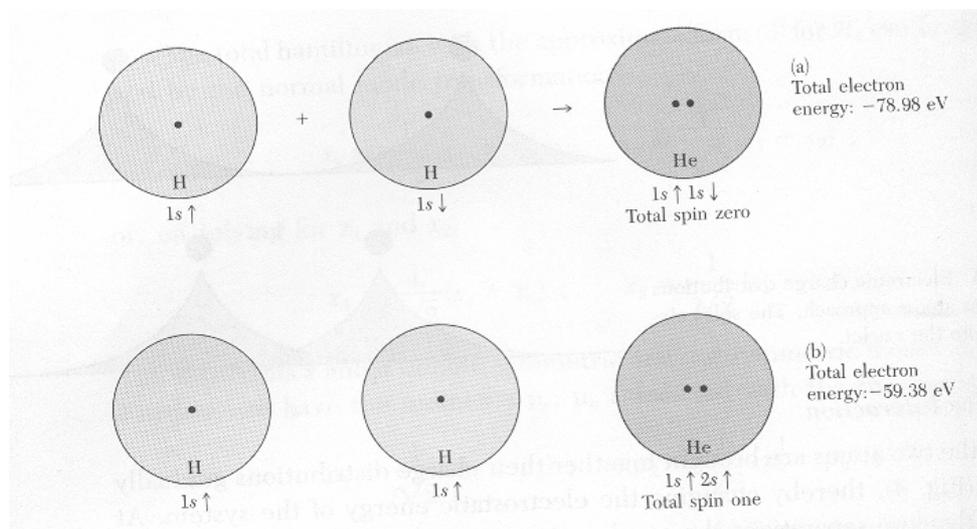


Figure 57: The effect of Pauli principle on the repulsive energy between two hydrogen atoms.