

3.0 Atomic Bonding

Periodic Table of the Elements

Column	I	II	Transitional elements										III	IV	V	VI	VII	VIII	Outer shell being filled						
Period (row) ↓	1																	2							
1	H 1s																		He 1s	K					
2	Li 2s	Be 2s																	Ne 2p	L					
3	Na 3s	Mg 3s																	Ar 3p	M					
4	K 4s	Ca 4s	Sc 3d	Ti 3d	V 3d	Cr 3d	Mn 3d	Fe 3d	Co 3d	Ni 3d	Cu 3d	Zn 3d	Ga 4s	Ge 4s	As 4p	Se 4p	Br 4p	Kr 4p	N						
5	Rb 5s	Sr 5s	Y 4d	Zr 4d	Nb 4d	Mo 4d	Tc 4d	Ru 4d	Rh 4d	Pd 4d	Ag 5s	Cd 5s	In 5s	Sn 5s	Sb 5p	Te 5p	I 5p	Xe 5p	O						
6	Cs 6s	Ba 6s	La 6d	Hf 5d	Ta 5d	W 5d	Re 5d	Os 5d	Ir 5d	Pt 6s	Au 6s	Hg 6s	Tl 6p	Pb 6p	Bi 6p	Po 6p	At 6p	Rn 6p	P						
7	Fr 7s	Ra 7s	Ac 6d	Rf 6d	Db 6d	Sg 6d	Bh 6d	Hs 6d	Mt 6d																Q

Atomic number → 26

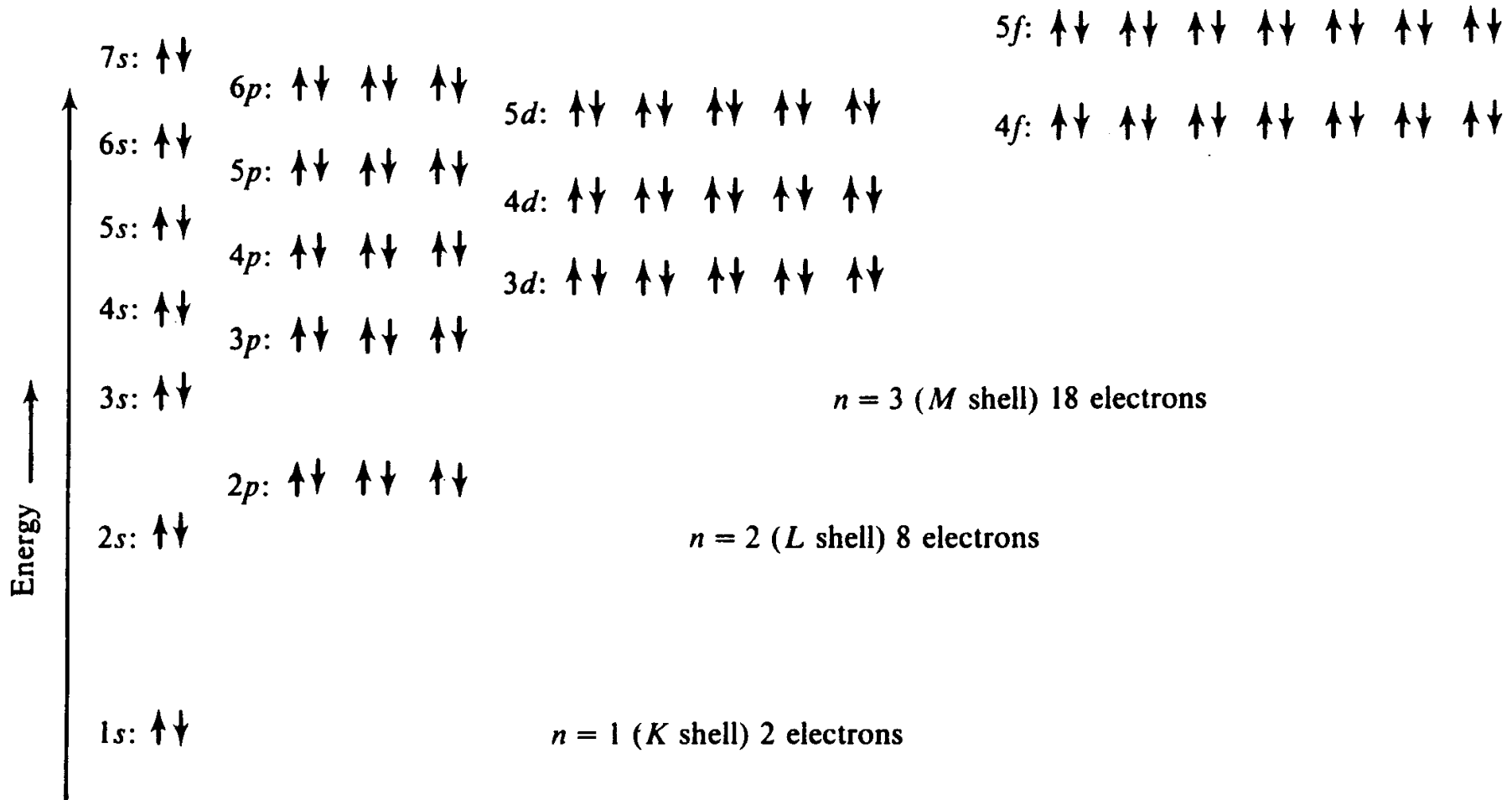
Symbol ← Fe

Orbital being filled ← 3d

Lanthanide series	58	59	60	61	62	63	64	65	66	67	68	69	70	71
	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Actinide series	90	91	92	93	94	95	96	97	98	99	100	101	102	103
	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

- Metallic elements
- Nonmetallic elements
- Inert gases
- Elements that do not occur naturally

ATOMIC BONDING



Relative energies of electrons in various orbitals. Each arrow denotes a single electron and its relative sense of spin. All electron configurations must be built up in order of increasing energy levels.

Atomic Number	Element	E_1	E_2	E_3
2	He	2371.91	5246.74	--
3	Li	520.07	7296.90	11811.43
4	Be	899.14	1756.86	14844.83
5	B	800.40	2426.72	3658.91
6	C	1086.17	2352.24	4619.14
7	N	1402.06	2856.84	4577.30
8	O	1313.78	3391.55	5301.13
9	F	1681.13	3375.23	6045.88
10	Ne	2080.28	3963.08	6276.00
11	Na	495.80	4564.74	6911.97
12	Mg	737.64	1450.17	7732.03
13	Al	577.39	1816.27	2744.29
14	Si	786.17	1576.53	3228.79
15	P	1062.74	1896.19	2909.97
16	S	999.56	2259.36	3376.49
17	Cl	1255.20	2296.60	3850.77
18	Ar	1520.47	2665.21	3946.77
19	K	418.82	3096.38	4602.40

First (E_1),
 Second (E_2)
 and Third (E_3)
 ionization
 energies of
 elements
 through atomic
 number 19.

**NOTE; All data
 are in kilo Joules
 per mole (kJ
 mol⁻¹)**

SHAPE OF THE ATOMS

From the sub-microscopical point of view they are considered to be spherical. Atoms orbitals show that the shape of atoms is complicated. STABLE STATE, half or completely filled shells and sub-shells may be spherical.

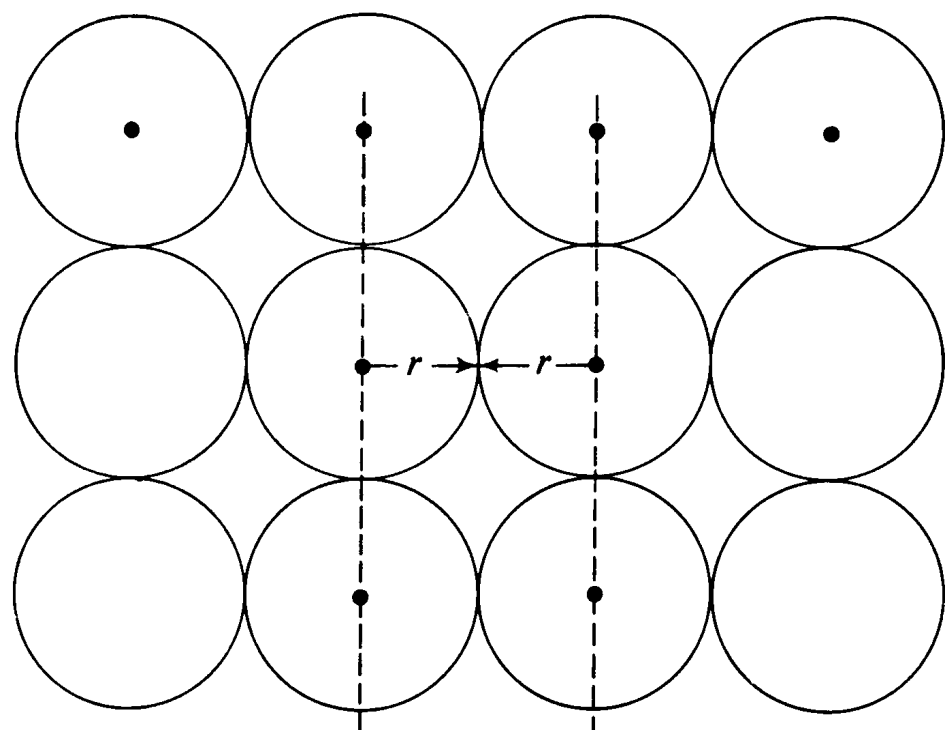
SIZE

Size is important for understanding of substitution. Size depends on the electron orbitals and it is not fixed.

We use the concept of effective radius rather than one fixed radius.

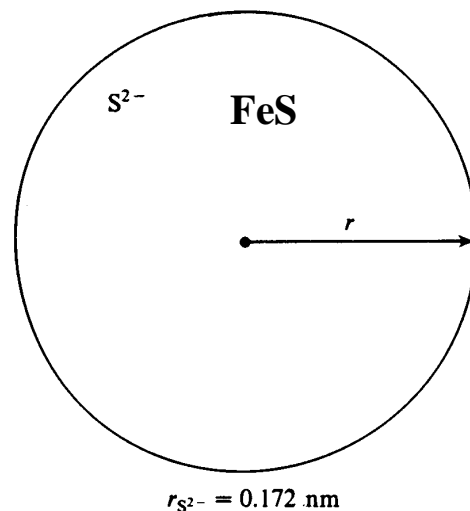
Interatomic distance can be measured by X-ray. To measure the radius of an element one of the radius interatomic configuration must be known.

RADIUS depends the outermost electrons S has 10 times higher or lower RADIUS depending on the electron configuration.

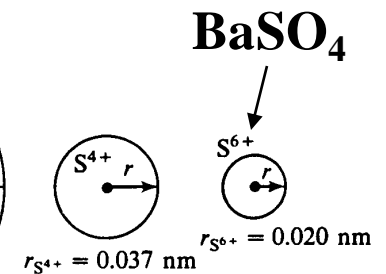
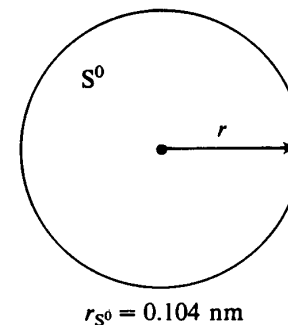


Closely packed arrangement of rigid, equal-sized spheres is typical of many elements. The interatomic distance d equals an atomic diameter $2r$

Relative ionic and atomic radii for various valence states of sulfur. Size varies in proportion to number of outer electrons, being greatest for S^{2-} and least for S^{6+} .



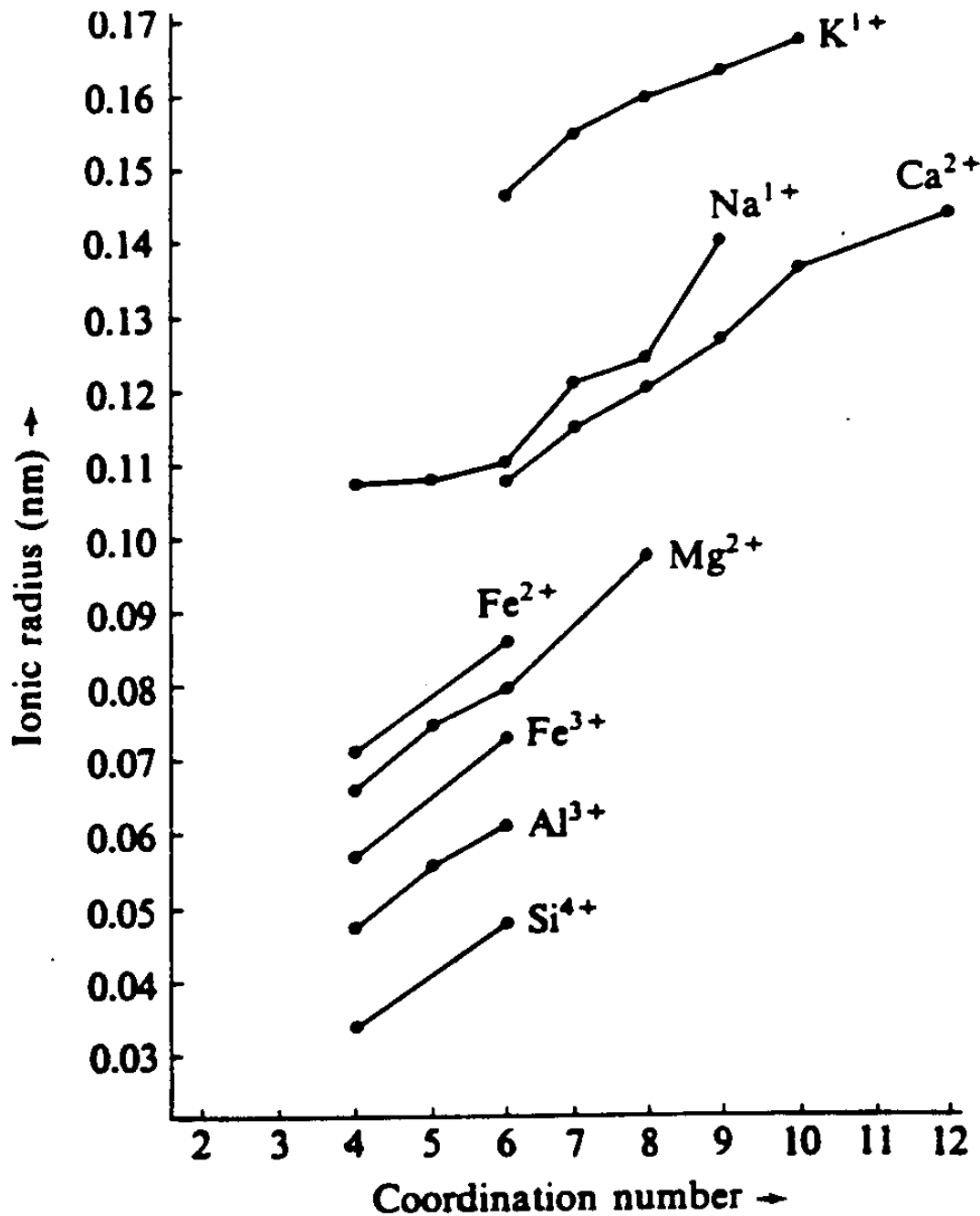
Atomic Num.16



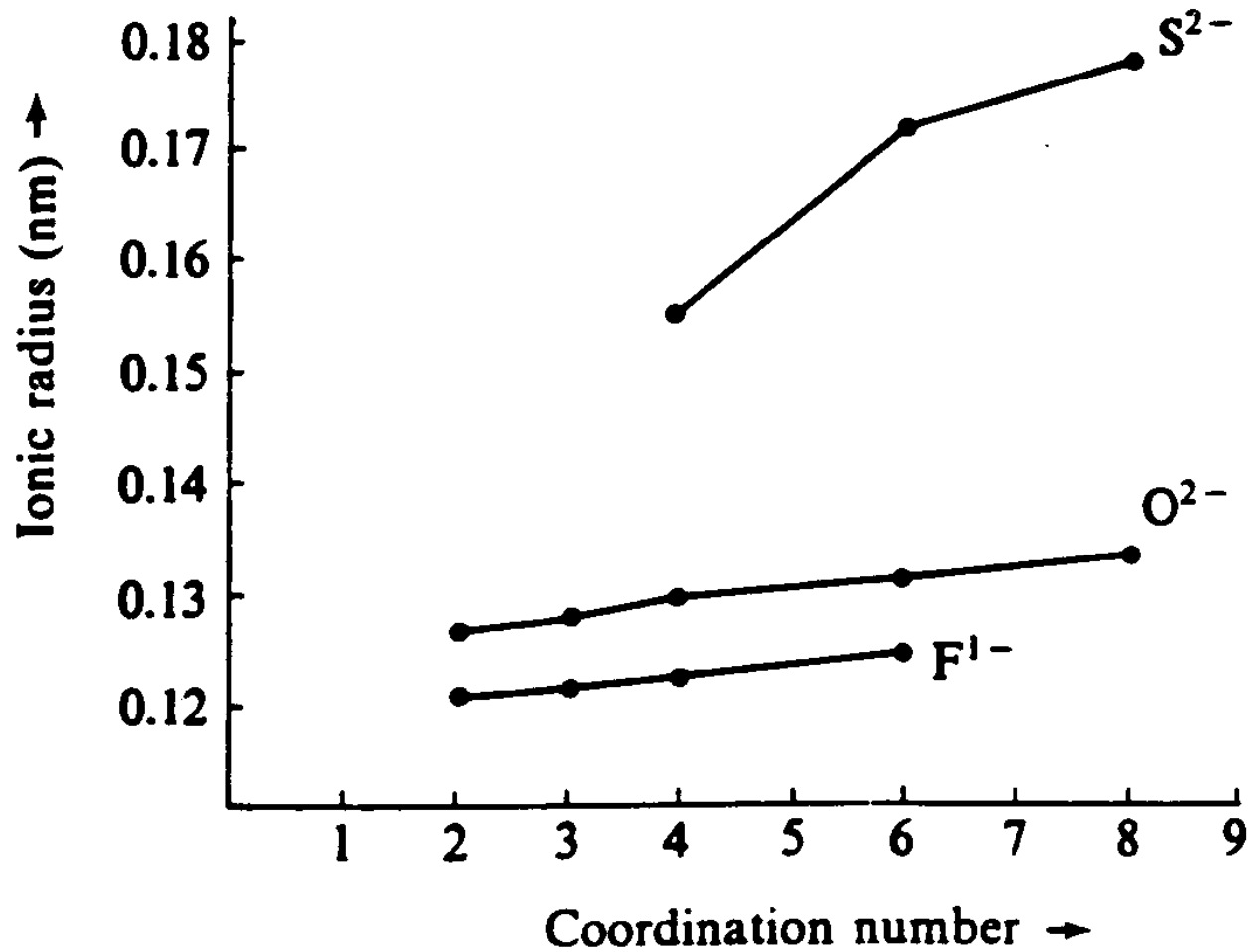
The problem of determining the effective radius is complicated further by the fact that ionic radius depends on coordination number.

COORDINATION NUMBER

The number of closest neighbors to which the ion is bonded.



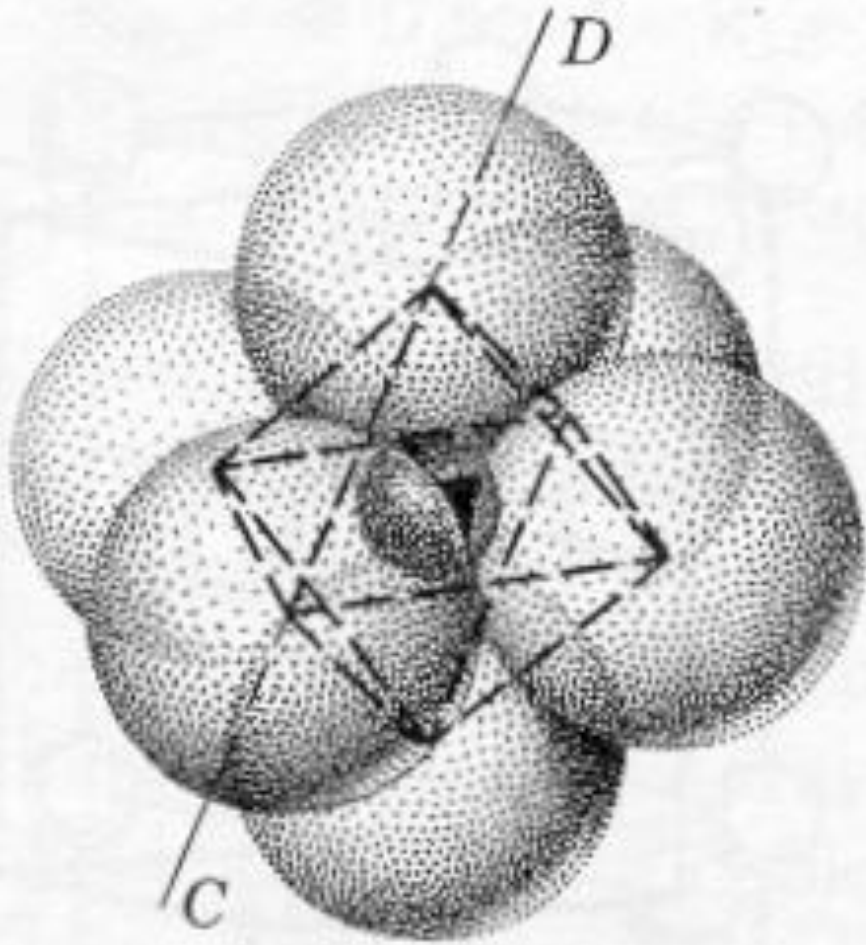
Variation of effective ionic radius of common cations with coordination number. Effective radius of an ion increases as its number of nearest neighbors increases.



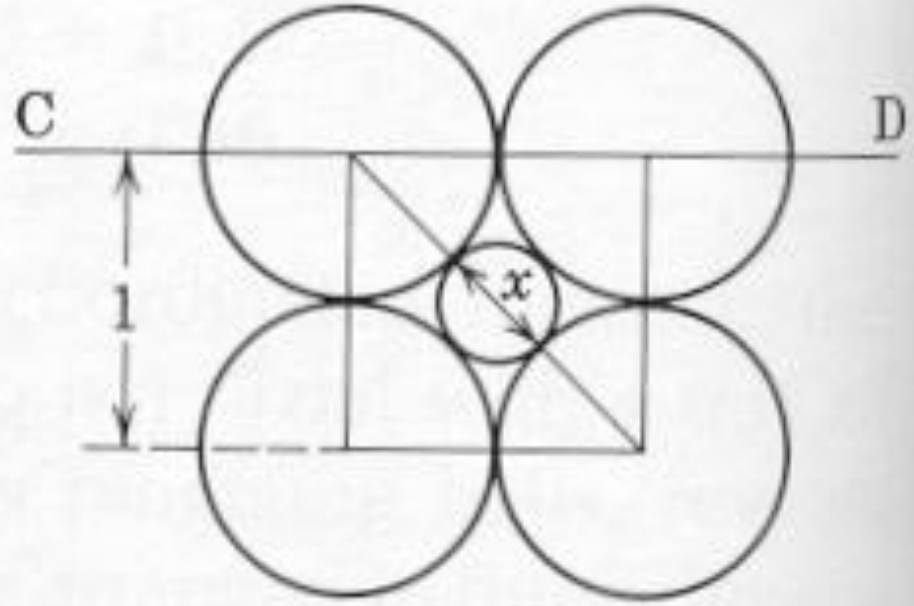
Variation of effective ionic radius of common anions with coordination number. Rate of radius increase is less than for cations.

Ion	CN*	Radius (nm)	Example	Ion	CN*	Radius (nm)	Example
O ²⁻	2	0.127	Quartz (SiO ₂)	Ca ²⁺	8	0.120	Fluorite (CaF ₂)
	3	0.128	Albite (NaSi ₃ AlO ₈)		12	0.143	Perovskite (CaTiO ₃)
	4	0.130	Forsterite (Mg ₂ SiO ₄)	Ti ⁴⁺	6	0.069	Rutile (TiO ₂)
F ¹⁻	6	0.132	Periclase (MgO)	Mn ²⁺	4	0.061	Hausmannite (MnMn ₂ O ₄)
	4	0.123	Fluorite (CaF ₂)		6(HS**)	0.091	Pyrochroite (Mn(OH) ₂)
Na ¹⁺	6	0.125	Villiaumite (NaF)	Mn ³⁺	6(LS†)	0.066	Groutite (MnO(OH))
	9	0.140	Nepheline (NaSiAlO ₄)		6(HS)	0.073	
Mg ²⁺	6	0.080	Forsterite (Mg ₂ SiO ₄)	Fe ²⁺	4(HS)	0.071	Staurolite (Al ₉ H Si ₄ Fe ₂ O ₂₄)
	4	0.066			6(LS)	0.069	Fayalite (Fe ₂ SiO ₄)
Al ³⁺	4	0.047	Anorthite (CaSi ₂ Al ₂ O ₈)	Fe ³⁺	6(HS)	0.086	
	5	0.056	Andalusite (AlAlOSiO ₄)		4(HS)	0.057	Cronstedtite (Fe ₃ (OH) ₄ SiFeO ₅)
	6	0.061	Kyanite (Al ₂ OSiO ₄)		6(LS)	0.063	Hematite (Fe ₂ O ₃)
Si ⁴⁺	4	0.034	Quartz (SiO ₂)		6(HS)	0.073	
	6	0.048	Stishovite (SiO ₂)	<p>SOURCE: Data from Whittaker, E. J. W., and Muntus, R., 1970. Ionic radii for use in geochemistry. <i>Geochimica Cosmochimica Acta</i> 34:945-956.</p> <p>NOTE: All radii are in nanometers (1 nm = 10 Å).</p> <p>*CN = coordination number.</p> <p>**HS = high-spin state.</p> <p>†LS = low-spin state.</p>			
S ²⁻	4	0.156	Sphalerite (ZnS)				
	6	0.172	Pyrite (FeS ₂)				
K ¹⁺	9	0.163	Microcline (KSi ₃ AlO ₈)				
	12	0.168	Muscovite (KAl ₂ (OH) ₂ Si ₃ AlO ₁₁)				

Selected ionic radii of most abundant ions in rock forming minerals



(a)



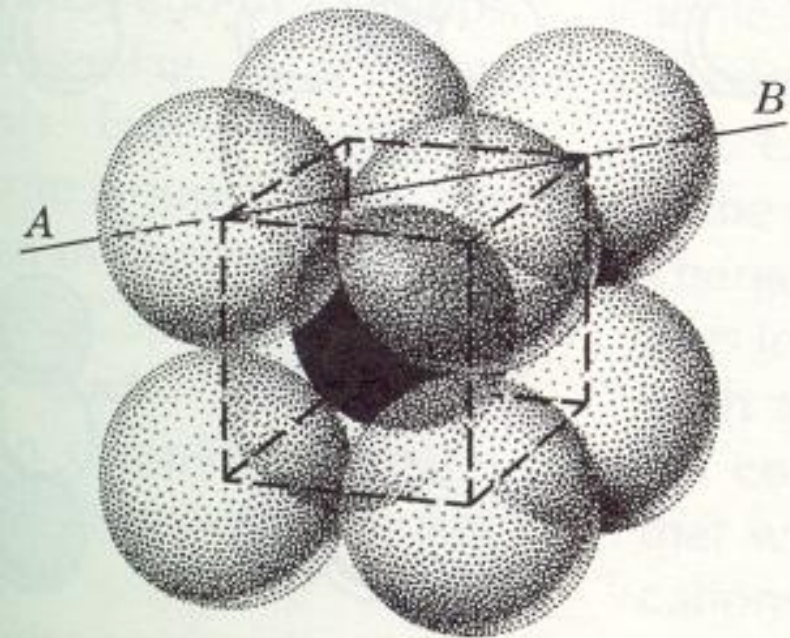
$$(1 + x)^2 = (1)^2 + (1)^2$$

$$1 + x = \sqrt{2} = 1.414$$

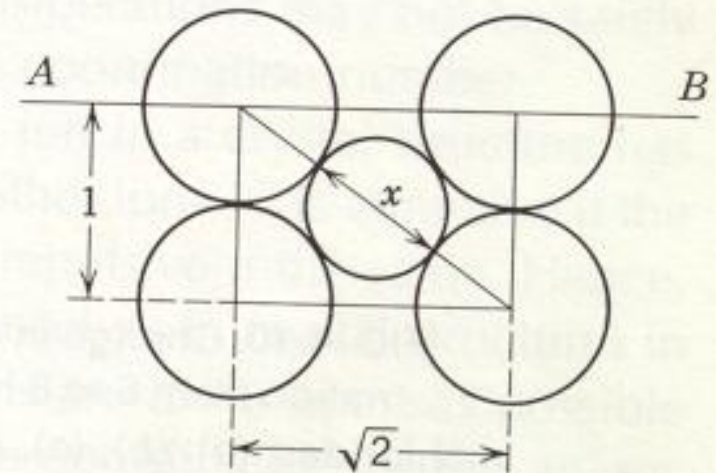
$$x = 0.414$$

(b)

a) Octahedral or 6 coordination of Z ions about an X ion. $R_x: R_z = 0.732-0.414$; b) limiting condition for octahedral coordination.



(a)



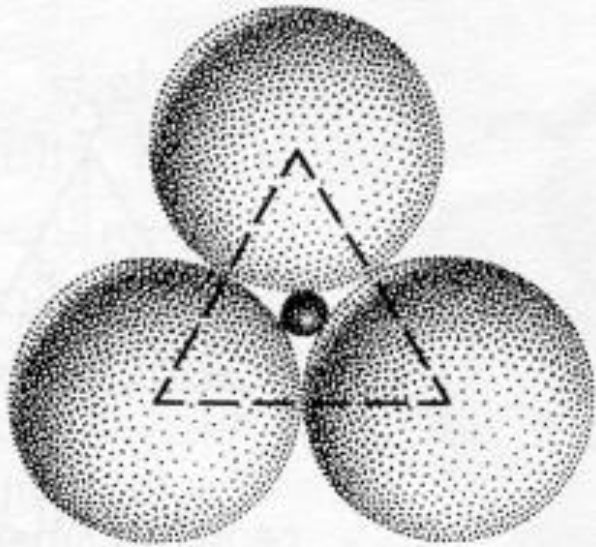
$$(1 + x)^2 = (1)^2 + (\sqrt{2})^2$$

$$1 + x = \sqrt{1 + 2} = 1.732$$

$$x = 0.732$$

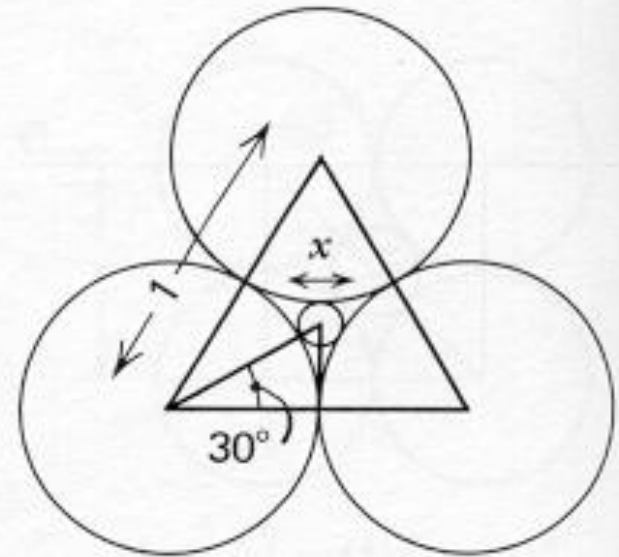
(b)

a) Cubic or 8 coordination of Z ions about an X ion. $R_x:R_z > 0.732$; b) limiting conditions for cubic coordination.



(a)

(a) Triangular or 3 coordination of Z ions about an X ion $R_x:R_z=0.225 - 0.155$. (b) limiting conditions for triangular coordination.



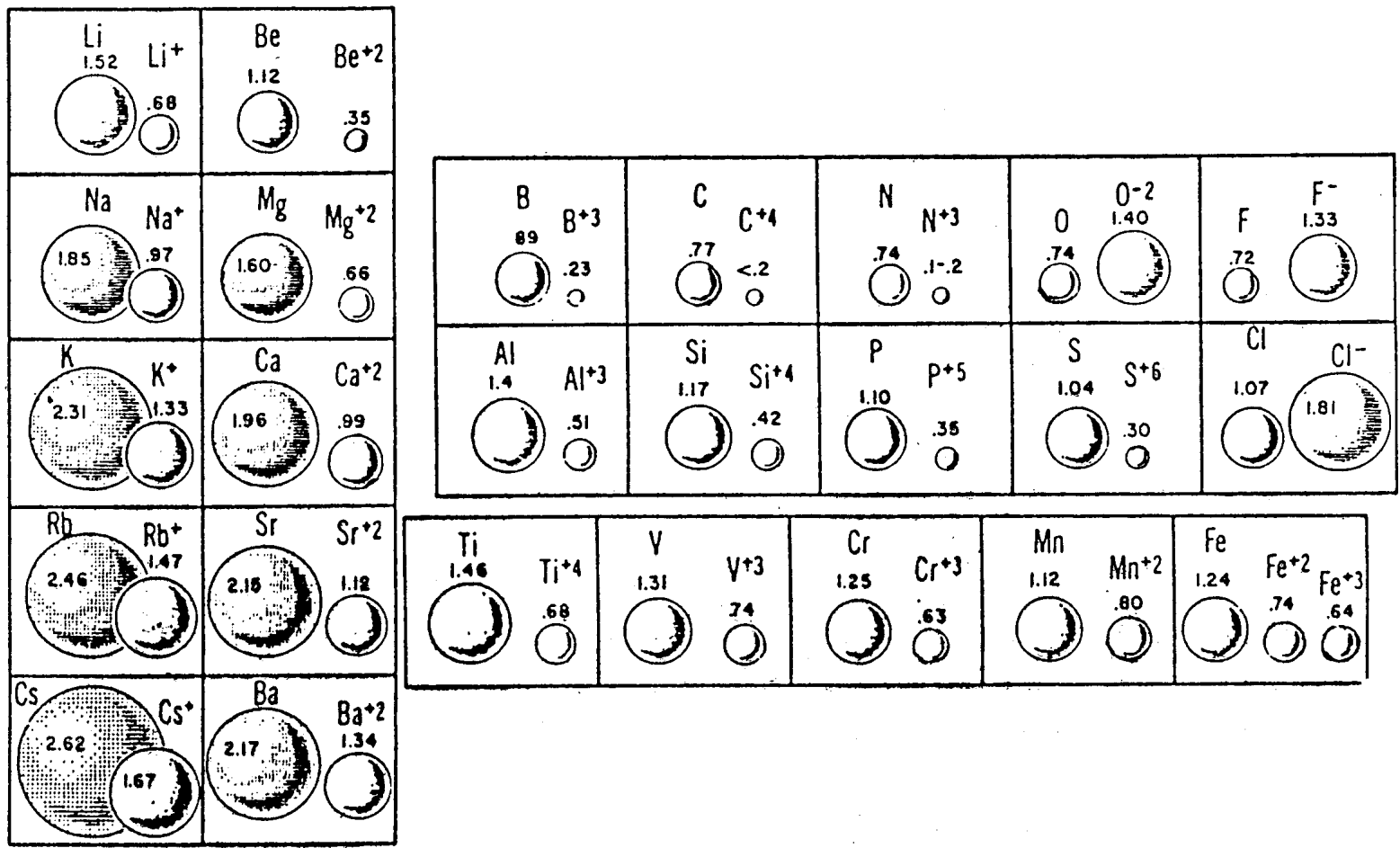
$$\cos 30^\circ = \frac{\frac{1}{2}}{\frac{1}{2} + \frac{1}{2} x}$$

$$\frac{1}{2} + \frac{1}{2} x = \frac{\frac{1}{2}}{\cos 30^\circ} = \frac{\frac{1}{2}}{0.8660} = 0.5774$$

$$\frac{1}{2} x = 0.5774 - 0.50 = 0.0774$$

$$x = 0.155$$

(b)



The size of more important atoms and ions drawn to scale (Å).

CHEMICAL BONDING BETWEEN ATOMS AND IONS

Elements that have a tendency to acquire electrons rather than to lose them are said to be *electronegative*.

Elements that tend to readily lose electrons are said to be *electropositive*.

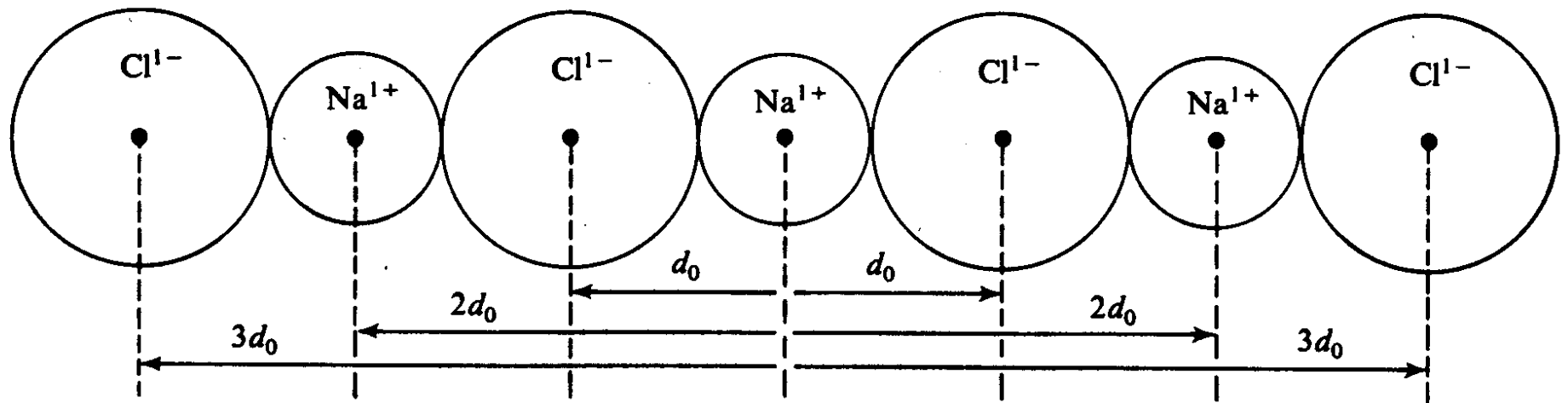
Bond strength fundamentally related to bond type.

1. IONIC BOND:

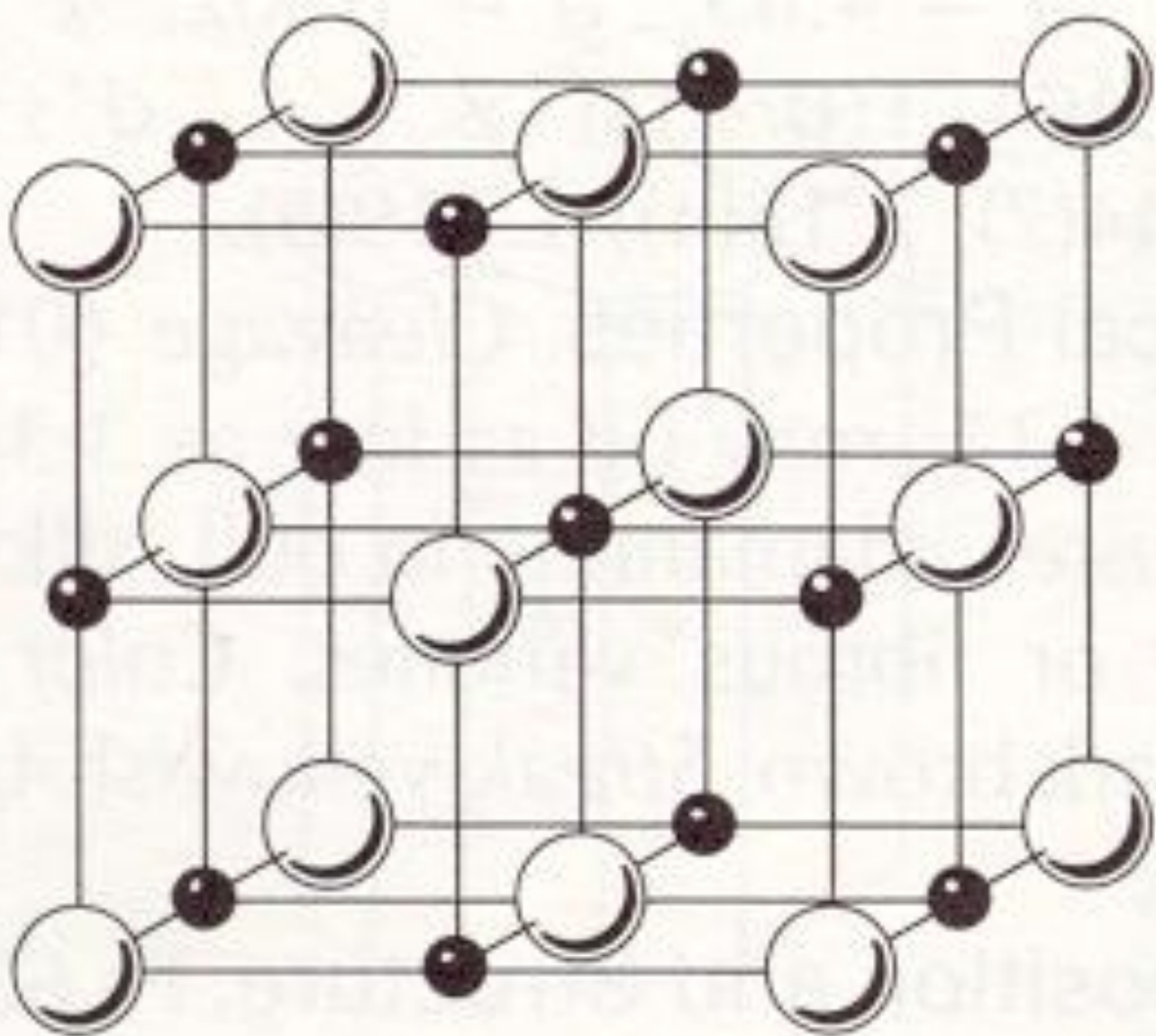
Chemical bonds between strongly electronegative and strongly electropositive elements are IONIC.

Examples for ionic bond are: NaCl, KCl.

The force of attraction is electrostatic



Hypothetical one-dimensional crystal of NaCl illustrating Madelung contribution by ordered array of ions. This array is more stable than an equivalent number of isolated ion pairs.



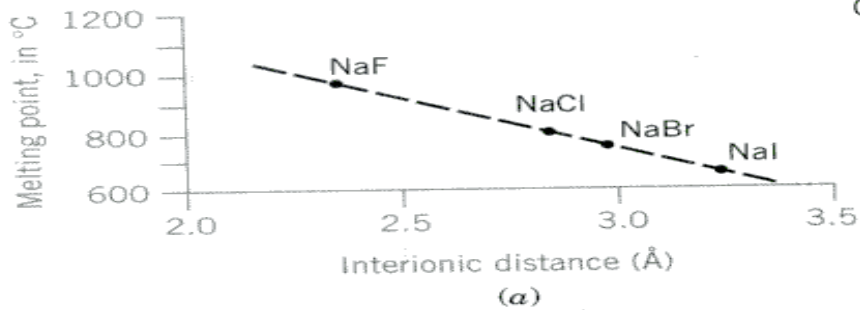
CHARACTERISTICS (Ionic Bond):

- **Highly symmetrical, brittle.**
- **Poor electrical conductivity.**
- **Ionic form in H₂O conducts electrons.**
- **High charge and oxygen (CaO), generally form strong ionic bond.**
- **Interionic distance.**
- **CN number.**

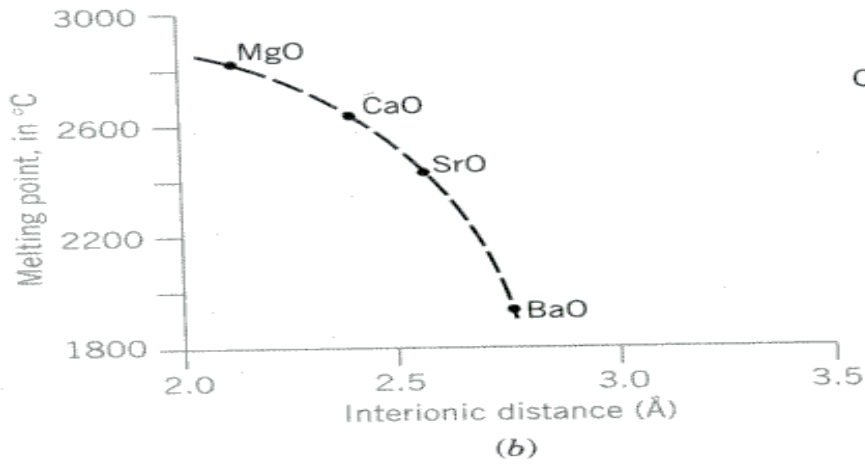
Ionic bond strength can be approximated by dividing the cation valance by the number of close, equally distant number to which cation is bonded.

A general relationship exist between the strength of the chemical bonds in a mineral and the mineral hardness.

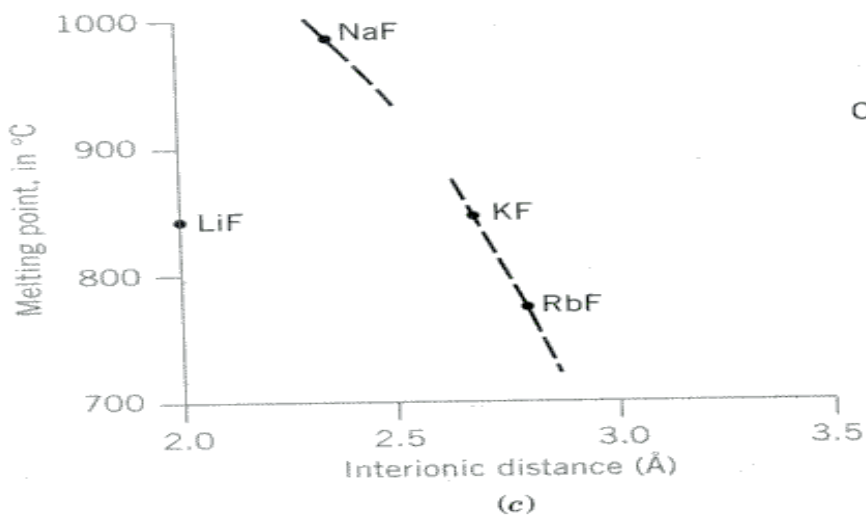
The properties of solubility and melting point, and Resistant weathering are also related bond strength (example is quartz; CN of Si and O).



Compound	Interionic distance (Å)	M.P. (°C)	Fl di (C p/B)
NaF	2.35	988	
NaCl	2.83	801	
NaBr	2.97	755	
NaI	3.22	651	



Compound	Interionic distance (Å)	M.P. (°C)
MgO	2.12	2820
CaO	2.40	2580
SrO	2.56	2430
BaO	2.76	1923



Compound	Interionic distance (Å)	M.P. (°C)
LiF	2.07	842
NaF	2.35	988
KF	2.69	846
RbF	2.80	775

2. COVALENT BOND:

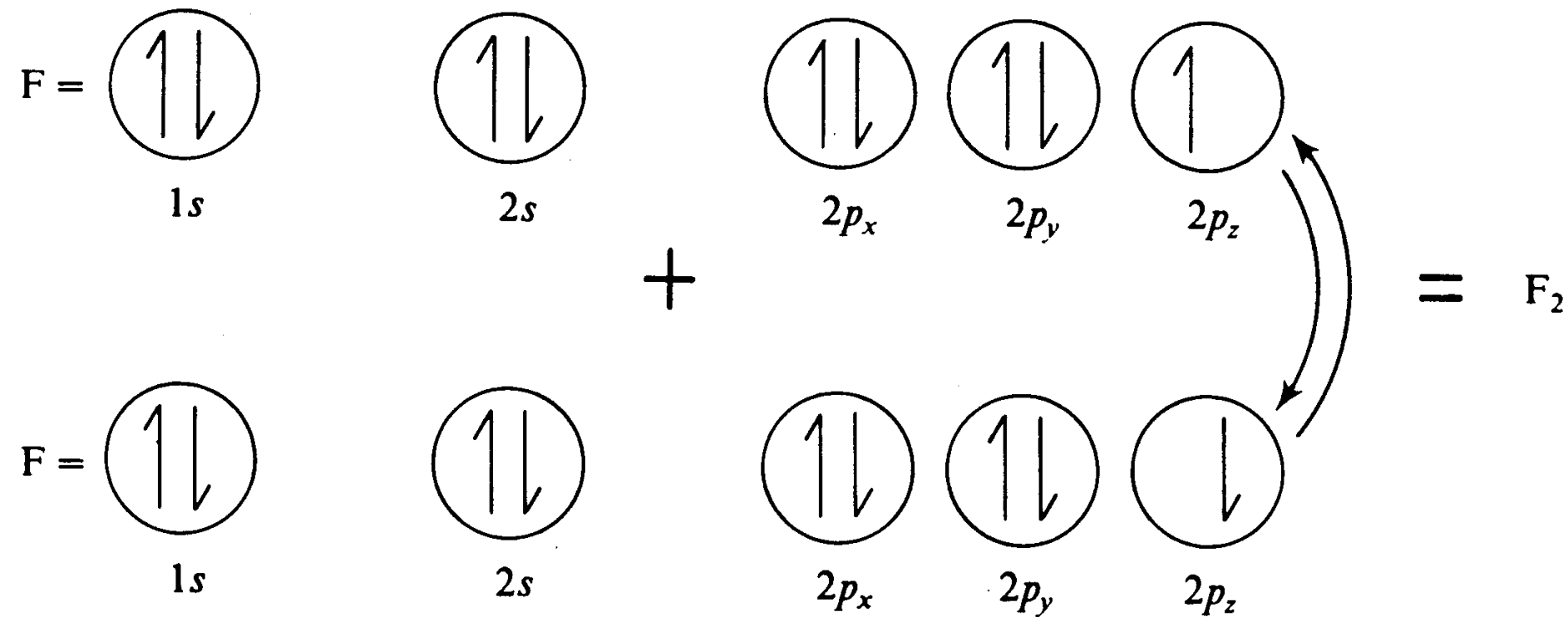
Chemical bonds between elements having little or no difference in their electronegativities are covalent (C diamond, graphite, metal Si, diatomic gas molecules H_2 , F_2 , Cl_2 , O_2 , N_2).

Share electrons.

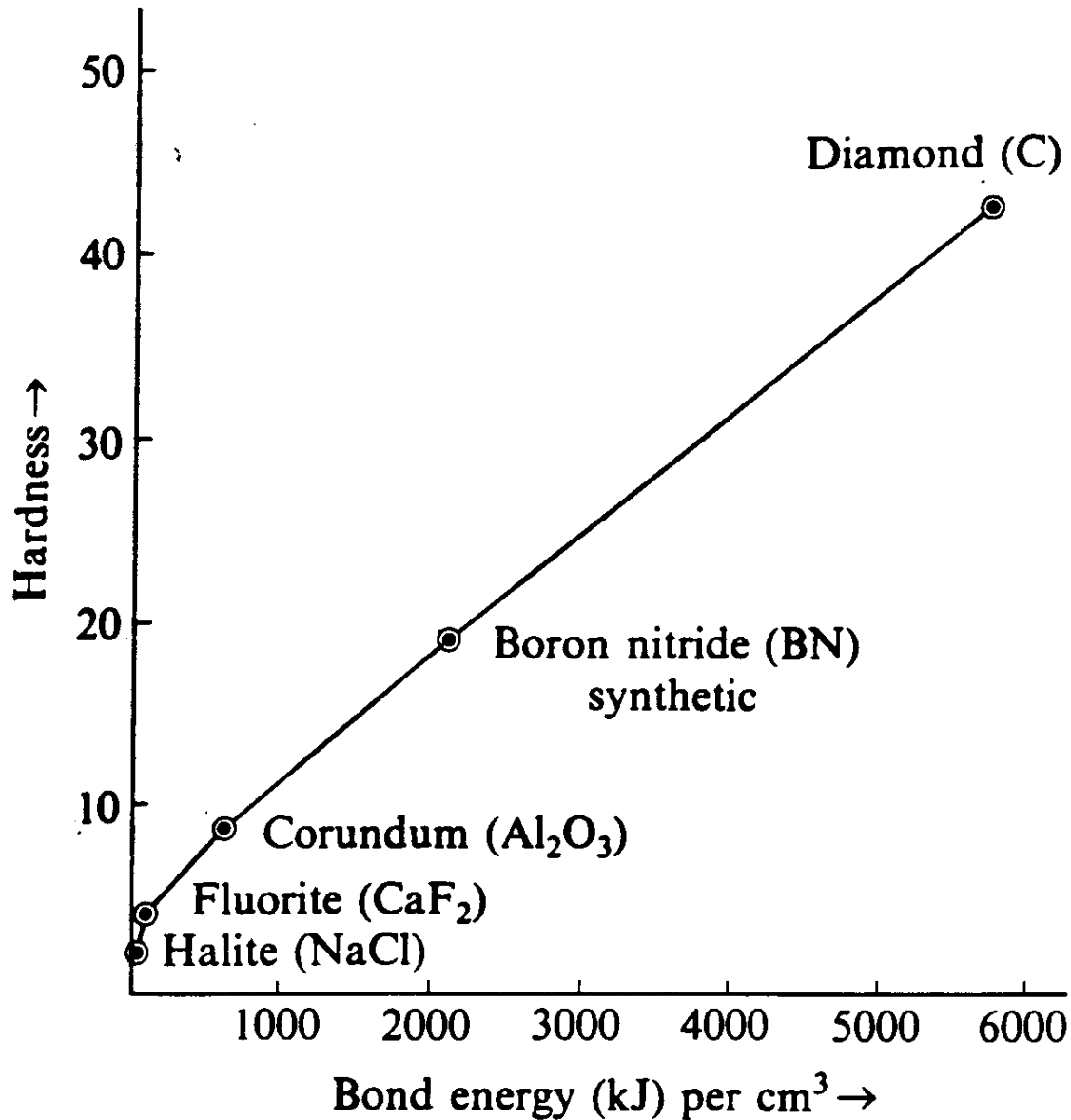
CHARACTERISTICS:

- Shorter interatomic distance,
- Overlap of atomic orbitals.

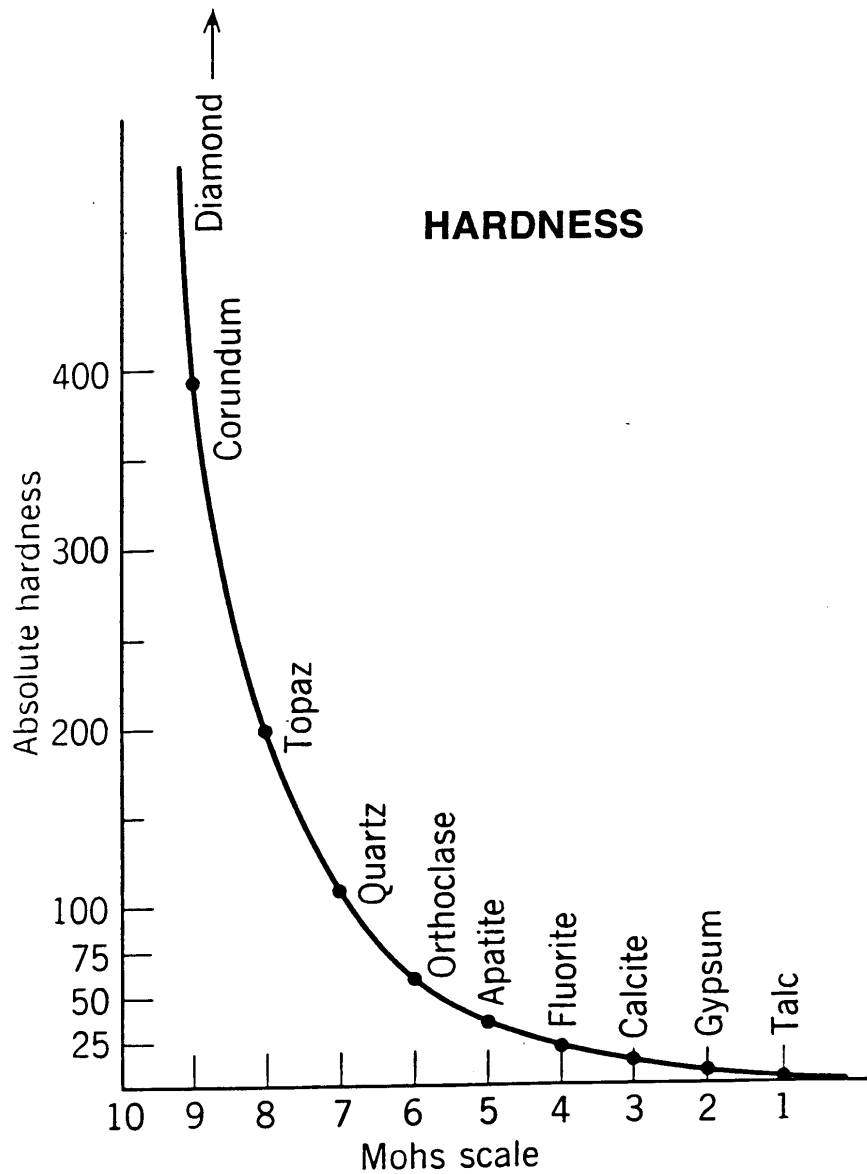
Most minerals have mixture of ideal ionic and covalent models. Average bond strength determines the hardness.



Electron configurations for F atoms that combine to form a stable F_2 molecules. A $2p^6$ Ne (neon) configuration is achieved by sharing a single electron in the $2p_z$ orbital. Note opposite spin of $2p_z$ electrons required for covalent bonding.



Hardness of some common minerals and synthetic abrasives versus bond strength per unit volume. Data converted to SI units. (After Bundy, F. P., 1974. Super-hard materials. *Scientific American* 231:64)



- | | |
|-------------|---------------|
| 1. Talc | 6. Orthoclase |
| 2. Gypsum | 7. Quartz |
| 3. Calcite | 8. Topaz |
| 4. Fluorite | 9. Corundum |
| 5. Apatite | 10. Diamond |

The Mohs hardness scale

Melting point vs. interionic distance in ionic-bonded compounds

Compound	Interionic Distance (X)	M.P (°C)	Compound	Interionic Distance (X)	M.P (°C)
NaF	2.31	988	SrO	2.57	2430
NaCl	2.81	801	BaO	2.76	1923
NaBr	2.98	755			
NaI	3.23	651	LiF	2.01	842
			NaF	2.31	988
MgO	2.10	2800	KF	2.67	846
CaO	2.40	2580	RbF	2.82	775

Data from Handbook of Chem. and Phys., 52nd ed., Chem. Rubber Publishing Co., 1972

Hardness vs. interionic distance and charge in ionic-bonded compounds

Compound	Interionic Distance (X)	Hardness (Mohs)	Compound	Interionic Distance (X)	Hardness (Mohs)
BeO	1.65	9.0	Na ⁺ F ⁻	2.31	3.2
MgO	2.10	6.5	Mg ²⁺ O ⁻²	2.10	6.5
CaO	2.40	4.5	Sc ³⁺ N ⁻³	2.23	7-8
SrO	2.57	3.5	Ti ⁴⁺ C ⁻⁴	2.23	8-9
BaO	2.76	3.3			

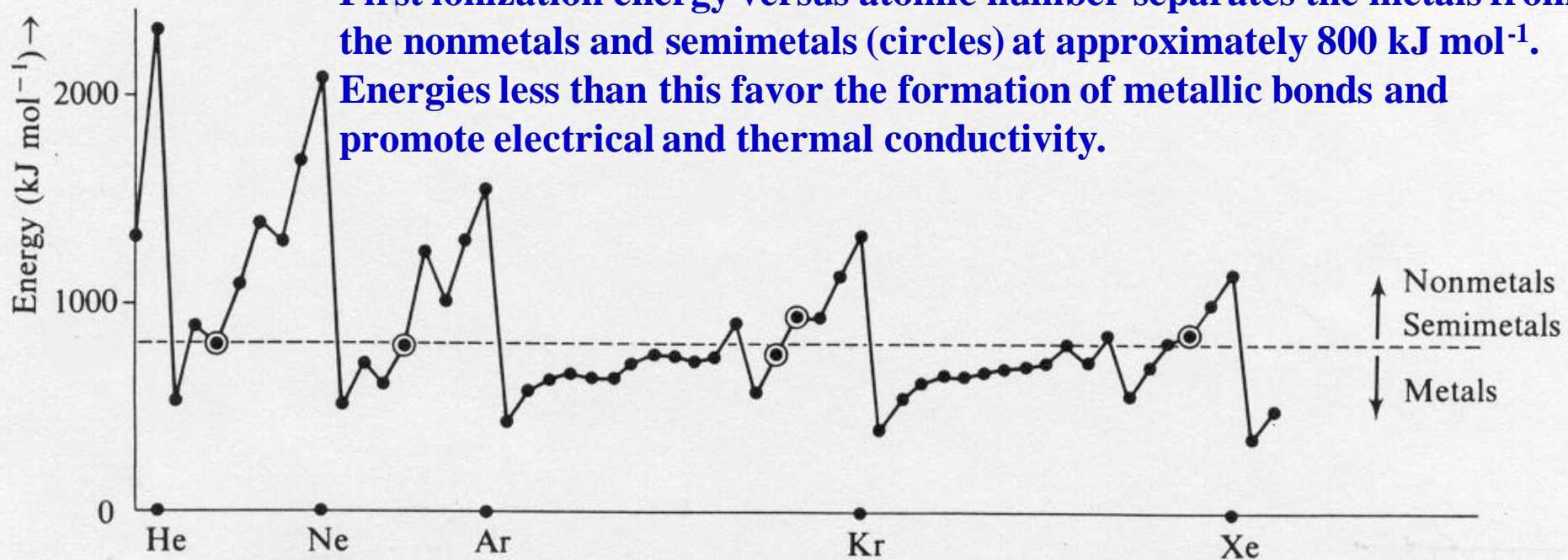
Data from Crystal Chemistry, R. C. Evans. Cambridge University Press, 1952.

3. METALIC BOND:

Chemical bonds bonding electrons are highly delocalized free to move from one atom to another.

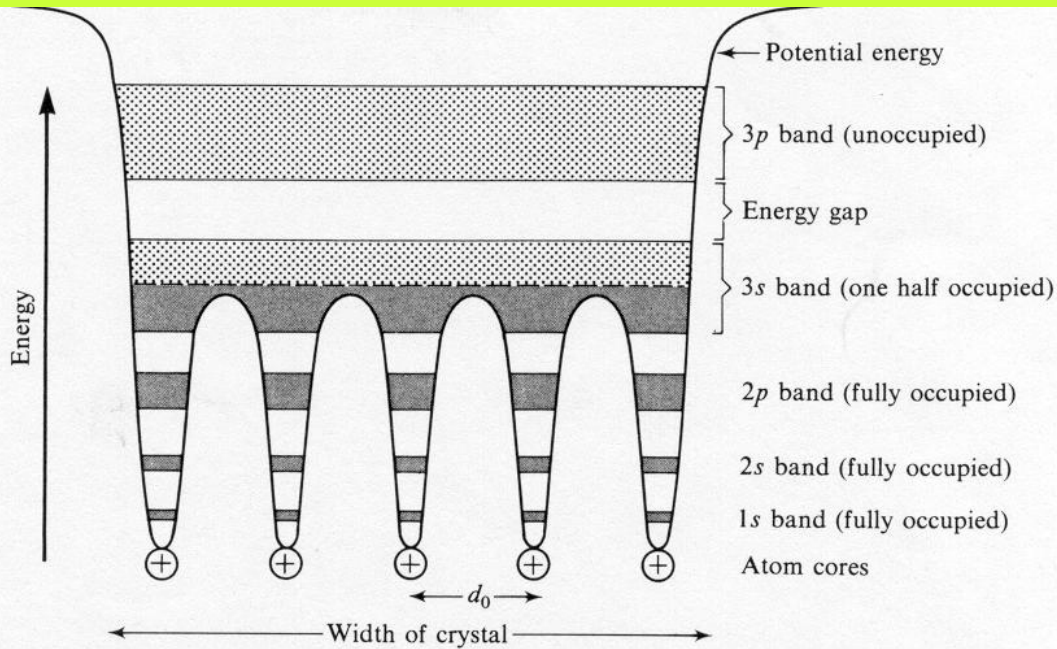
Their inner electrons held together by an “interatomic glues” of loosely bonded outer electrons.

First ionization energy versus atomic number separates the metals from the nonmetals and semimetals (circles) at approximately 800 kJ mol^{-1} . Energies less than this favor the formation of metallic bonds and promote electrical and thermal conductivity.



CHARACTERISTICS:

- Small number of outer electrons not shared.
- Low first ionization energies (see Table).
- High thermal and electrical conductivity.
- Low cohesive energy.
- Soft, low melting point, ductile.



Potential energy well for Na metal bounded by crystal surfaces. Internal subwells indicate positions of positively charged atom cores and localized electrons in the 1s, 2s, and 2p bands. The 3s band is the conduction band when voltage is applied across the metal.

4. MOLECULAR BOND: (Van der Waals)

At any given instant, each atom will have small but real electric dipole moment, as a result of higher electron density on one side of the nucleus. (exm. Graphite).

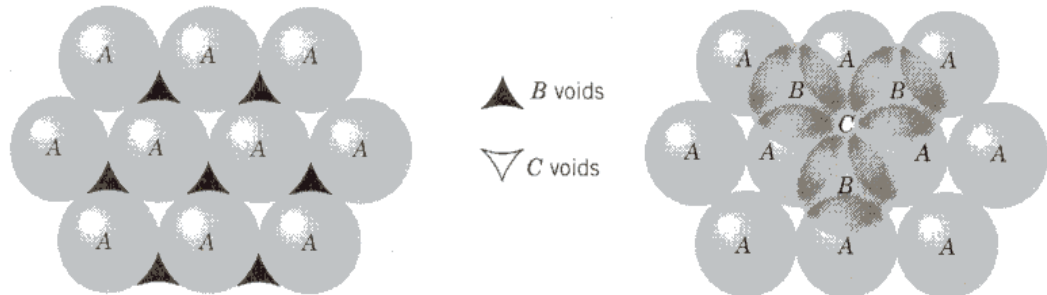
Small contribution to the bond.

5. Hydrogen BOND:

Is an electrostatic bond between a positively charged hydrogen ion and a negatively charged ion, such as O^{2-} or N^{3-} .

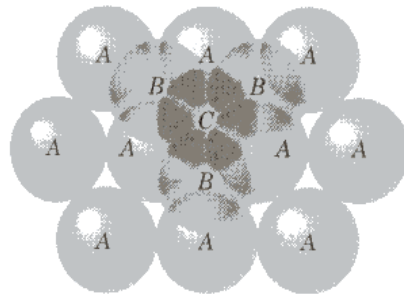
Small contribution to the bond.

FIG. 4.1 Closest packing of like-sized spheres (**C.N.** = 12). (a) Monolayer A of same size spheres showing six spheres in contact with a central sphere producing two types of voids. (b) Addition of another layer over B voids. (c) Addition of a third layer over C voids. (d) Oblique vertical view of packing in (c).



(a) Hexagonal closest packed layer

(b) Hexagonal closest packing sequence:
AB AB.....



(c) Cubic closest packing sequence:
ABC ABC.....

The plane of this drawing turns out to be perpendicular to the 3-fold axis at the corner of a cube

