

University of Baghdad

College of Science

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Physical Chemistry

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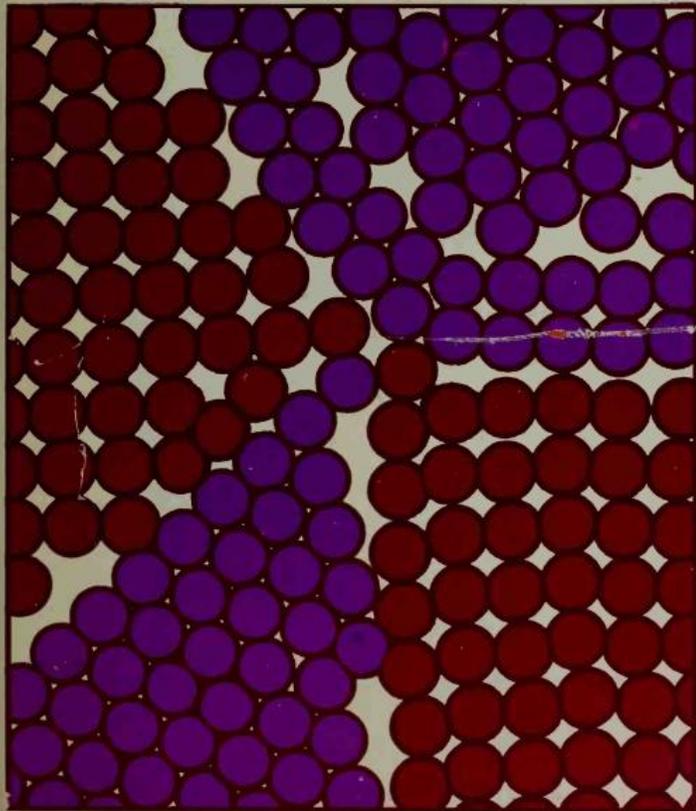
Department of Physics

Physical Chemistry

Chapter One: The States of Matter

Lecture 1

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Van Vlack Third Edition

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FOURTH EDITION

**MODERN
PHYSICAL
METALLURGY**

R.E. SMALLMAN

BUTTERWORTHS

Contents:

- Introduction
- Matter
- States of Matter
 - Gas Phase
 - Liquid Phase
 - Solid Phase

Introduction:

- ***Chemistry science***, in general, deals with matter and its changes. One of chemistry fields is **PHYSICAL CHEMISTRY** which focuses on the ***physical principles*** of which chemistry is based on.
- **Physical chemistry** explains the properties of matter via basic conceptual descriptions like atoms, electrons and energy. The importance of physical chemistry is manifested in all other fields of chemistry as well as in analysing and determination of structure.

Matter

- MATTER is anything that has mass and occupies space.
- The essential difference between gas, liquid, and solid states of matter is the *freedom* of the particles to move past one another. If the average separation of the particles is large, there is hardly any restriction on their motion and the substance is a **gas**. If the particles interact so strongly with one another that they are locked together rigidly, then the substance is a **solid**. If the particles have an intermediate mobility between these extremes, then the substance is a **liquid**.

Matter

- state of matter means a specific condition of a sample of matter that is described in terms of its **physical form** (gas, liquid, or solid) and the **volume, pressure, temperature, and amount of substance** present.
- 1 kg of hydrogen gas in a container of volume 10 dm^3 at a specified pressure and temperature is in a particular state. The same mass of gas in a container of volume 5 dm^3 is in a different state. Two samples of substance are in the same state if they are the same state of matter (both present as gas, liquid, or solid) and if they have the same mass, volume, pressure, and temperature.

Gas Phase

- A gas is a fluid of widely separated particles which owns a high flexibility to change its shape to fill any container that occupies. Molecules and atoms, which comprise a gas, weakly interact with one another and they in continuous and rapid disordered motion.

Ideal gas

- An Ideal gas is assumed to be consisted of very small particles in which interact only at their points of collision.

- At **low pressure**, a real gas can follow the behaviour of ideal gas due to the paths between molecules become sufficiently long enough. At moderate and high pressures, real gases are non-ideal gases and they no longer follow the ideal gas laws.
- Four parameters can represent an ideal gas: n (moles of gas, in moles), p (pressure, in Pascal), T (temperature, in Kelvin), V (volume, in dm^3 or m^3).
- Three historical laws represent ideal or perfect gas. Boyle's law, Charles' law and Avogadro's principle. All these laws are based on the relation **$pV = nRT$** , where R is the gas constant.

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Chapter One: The States of Matter

Lecture 2

Contents:

- States of Matter
 - Liquid Phase
 - Solid Phase
- Characterization of Atomic Structure

Liquid Phase

- A liquid is a fluid form of matter (of particles) which possesses a surface and fills a volume of the lower part of the container it occupies by the impact of gravitational field.

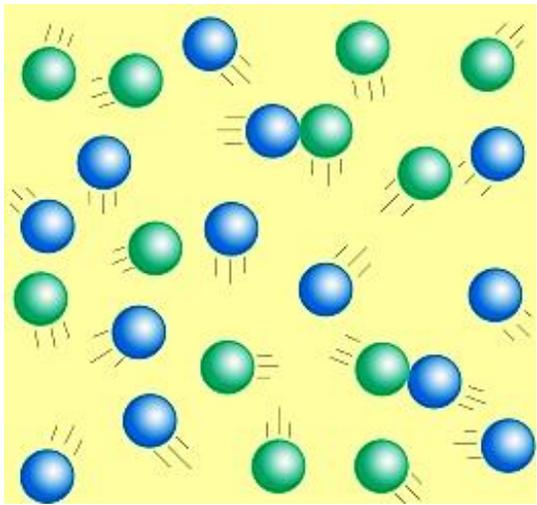
Some notes about liquids:

- The contacted particles of a liquid are able to move past each other (but with some restrictions) in their continuous motion.

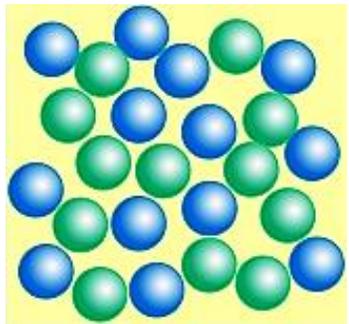
- ***Viscosity*** of a liquid characterizes the motion the liquid in the presence of a mechanical force. When a fluid passing through a capillary, it exposes to a retarding force from the capillary walls making the viscosity at the centre axis higher than at the walls.
- ***Surface tension*** is a phenomenon for liquids appears when no force affects a liquid and the free energy of the liquid is minimised, the liquid surface then takes the minimum possible area.

Solid Phase

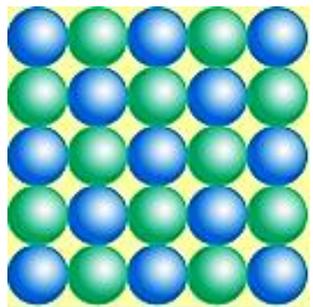
- A solid consists of particles that are in contact and only rarely able to move past one another. A solid retains its shape regardless of the shape of the container it occupies. Although the particles oscillate at an average location, they are essentially trapped in their initial positions, and typically lie in ordered arrays.
- We can understand the **melting** of a solid and the **vaporization** of a liquid in terms of the progressive increase in the liberty of the particles as a sample is **heated** and the particles become able to move more freely.



Gas phase



Liquid phase



Solid phase



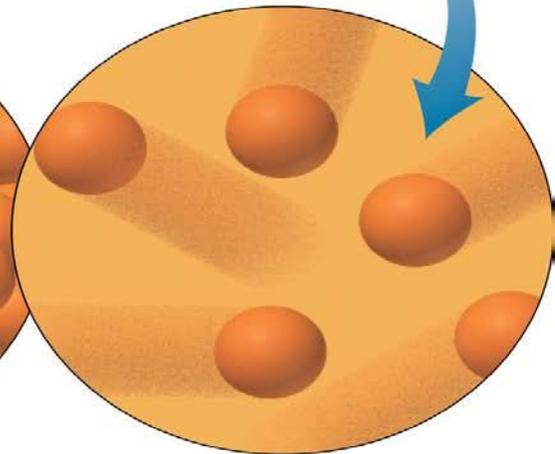
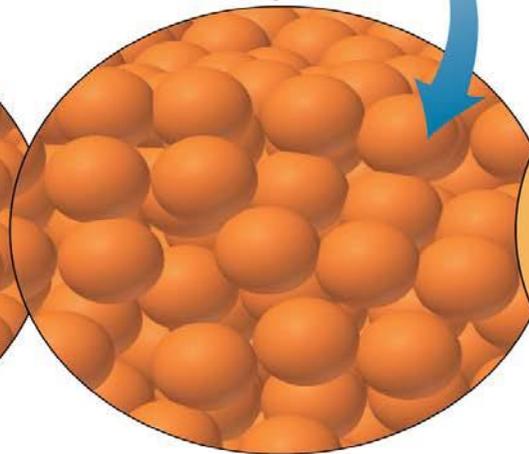
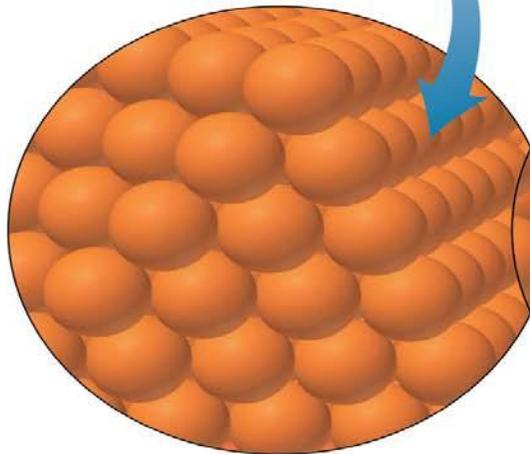
Solid



Liquid



Gas



- The **mass**, m , of a sample is a measure of the **quantity of matter** it contains. Thus, 2kg of lead contains twice as much matter as 1 kg of lead and indeed twice as much matter as 1 kg of anything.
- Mass is independent of location.
- **Weight** is the force exerted by an object, and depends on the pull of gravity (weight dependent of location).
- The ***Systeme International (SI) unit of mass*** is the kilogram (kg). Usually, more convenient to use a smaller unit and to express mass in grams (g), where **$1 \text{ kg} = 10^3 \text{g}$** .

Characterization of Atomic Structure

- **Atomic Number**: For an neutral atom, atomic number equals to the number of **protons** (of nucleus) which, at the same time, equals to the number of surrounding **electrons**.
- An **electron** has as much as **0.0005** mass of that of **proton** or **neutron**. This makes the atom is governed by both proton and neutron.

- **Atomic weight**=
$$\frac{\text{atomic number}}{\text{number of atoms in one mole}}$$

- **Atomic weight**=
$$\frac{\text{atomic number}}{\text{Avogadro number } (6.022 \times 10^{23})}$$

- **Example:** For natural carbon isotopes, the atom percent can be given as: 98.89 % C^{12} (mass=12.0000) and 1.11 % C^{13} (mass=13.0033). Calculate the atomic weight of natural carbon.

Answer:

$$9889 \times 12.0000 = 118668 \text{ amu} \quad (\text{atomic mass unit})$$

$$111 \times 13.0033 = 1443 \quad \text{amu}$$

$$120111 \text{ amu} / 10000 \text{ atoms}$$

$$\text{Atomic weight} = 12.0111 \text{ amu}$$

- **Example:** Argon has atomic weight of 39.95 gm/mole and a density of 1.75 gm/litre (at 1 atm and a temperature of 0 °C). How many atoms are there per cm³?

Answer:

$$\left(\frac{1.78 \text{ gm/liter}}{10^3 \text{ cm}^3/\text{liter}} \right) \left(\frac{6.022 \times 10^{23} \text{ atom/mole}}{39.95 \text{ gm/mole}} \right) = 2.68 \times 10^{19} \text{ atoms/cm}^3$$

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Chapter One: The States of Matter

Lecture 3

Contents:

- Electronic structure of atoms
- Quantum numbers

Electronic structure of atoms

- Electron mass = 9.109×10^{-28} gm = 9.109×10^{-31} kg
- Electron charge = 1.602×10^{-19} C

Quantum numbers

The **electrons** which surround an atomic nucleus do not all possess the same energy; therefore, we divide the electrons into **shells**, or groups with different energy levels. The first or **lowest quantum shell contains a maximum of 2** electrons; the **second shell contains a maximum of 8**; the third, **18**; and **the fourth, 32**. Thus the maximum number of electrons in a given shell is $2n^2$, where **n** is the **principal quantum number of the shell**.

Quantum numbers

Although the concept of the quantum shell is a convenient one, it is an oversimplification, because it implies that all electrons within a shell are equivalent.

A more complete discussion of electrons is necessary if the properties of materials are to be understood. Without rigorous explanation, we can approach the subject by way of the **Pauli exclusion principle**, which states that **no more than two interacting electrons in an atom can have the same orbital quantum number**.

Even these two electrons **are not identical**, because they possess opposite magnetic behaviours, or "**spins**."

Quantum numbers

Since the electrons in a quantum shell do not all possess the same energy, it is desirable to subdivide the shells into **subshells**.

Here again, **subshells with the lowest energy are filled before those with higher energy**; and, as with the main quantum shells, the **upper energy levels within a given subshell may be in a higher energy state than the lowest energy level in a succeeding subshell**.

Quantum number

- **Electron** *groupings* and *subgroupings* were verified through **spectrometric studies**.
- It was concluded that a **quantum of energy** is required to move an **electron** from a lower energy level to the next higher energy level.
- A quantum of energy (a photon) is released when an electron drops into a lower level. The energy, E , possessed by the photon may be calculated directly from the photon wavelength, λ : $E = hc/\lambda = h\nu$

Quantum number

- $E = \frac{hc}{\lambda} = h\nu$
- **h** is **Planck's constant** = 6.62×10^{-34} joule.sec or 6.62×10^{-27} erg.sec.
- **c** is the **velocity of light** = 2.998×10^{10} cm.sec.
- The **wave frequency** is **c/λ** or **ν** .
- The **sharpest spectral lines** are produced by the **electrons** which **drop to** the **lowest energy level** within a given quantum shell.

Homework??

Summarize “*Lecture Three*” with no more than two pages.

Quiz??

Quiz in “*Lecture Three*” only next week.

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Chapter One: The States of Matter

Lecture 4

Contents:

- Quantum numbers
- Electron configuration of elements
- Location probability

Quantum number

- Each succeeding shell has additional subshells, which are designated **p**, **d**, and **f**.
- The maximum numbers of electrons in these subshells are **6**, **10**, and **14**, respectively.
- Xeon, which has its **L-shell** (or **second quantum shell**) completely filled, possesses the electron notation $1s^2 2s^2 2p^6$, which indicates that two electrons are in the first shell and eight in the second, the latter containing two in its s-subshell and six in its p-subshell.

subshell	Maximum Number of electrons	
s	2	s^2
p	6	p^6
d	10	d^{10}
f	14	f^{14}

Example

With neutral atoms, two electrons go into the 4s-subshell before the 3d-subshell is filled; however, with ionization, the 4s-electrons are removed first. Show the electron notation for a single **iron atom**, and for **ferrous** and **ferric** iron ions.

Answer.



Example

We might pause at this point to compare the electronic orbitals of an uncharged vanadium atom and of a charged 3+ Fe ion. Although each has **23 electrons**, the **ferric ion** has **26 protons** against only **23** for **vanadium** ; therefore:



Element		K(n=1)	L (n=2)		M (n=3)			N (n=4)				O (n=5)				
Symbol Number		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	
H	1	1														$1S^1$
He	2	2														$1S^2$
Li	3	2	1													$1S^2 2S^1$
Be	4	2	2													$1S^2 2S^2$
B	5	2	2	1												$1S^2 2S^2 2p^1$
C	6	2	2	2												$1S^2 2S^2 2p^2$
N	7	2	2	3												$1S^2 2S^2 2p^3$
O	8	2	2	4												$1S^2 2S^2 2p^4$
F	9	2	2	5												$1S^2 2S^2 2p^5$
Ne	10	2	2	6												$1S^2 2S^2 2p^6$

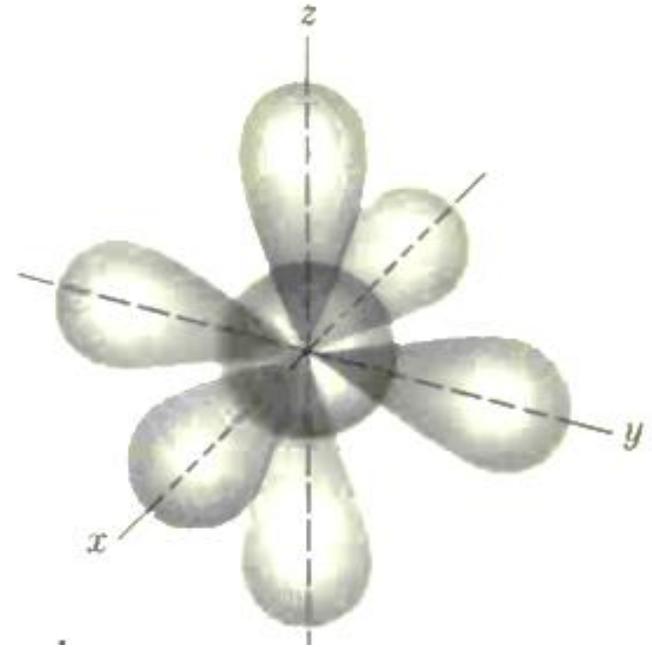
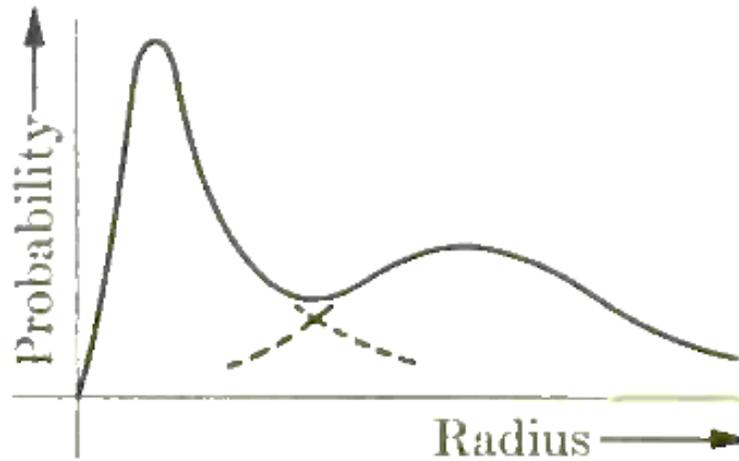
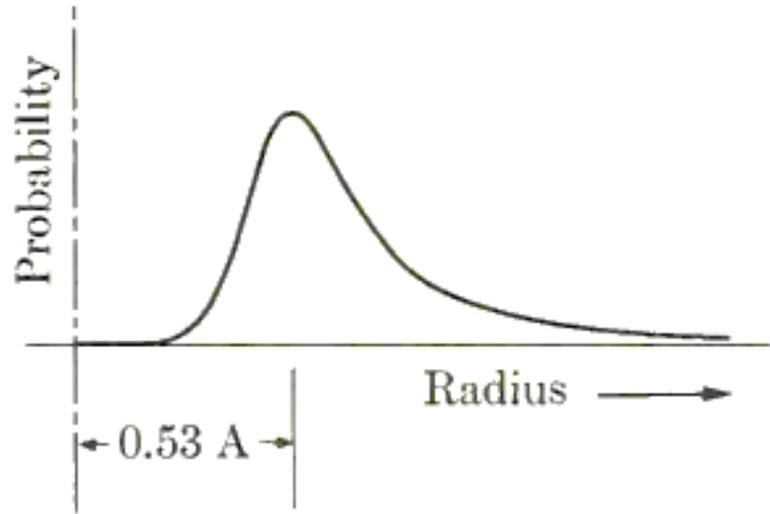
Element Symbol Number		K(n=1) 1s	L (n=2) 2s 2p		M (n=3) 3s 3p 3d			N (n=4) 4s 4p 4d 4f				O (n=5) 5s 5p 5d 5f				Electron configuration
Na	11	2	2	6	1											$1S^2 2S^2 2p^6 3s^1$
Mg	12	2	2	6	2											$1S^2 2S^2 2p^6 3s^2$
Al	13	2	2	6	2	1										$1S^2 2S^2 2p^6 3s^2 3p^1$
Si	14	2	2	6	2	2										$1S^2 2S^2 2p^6 3s^2 3p^2$
P	15	2	2	6	2	3										$1S^2 2S^2 2p^6 3s^2 3p^3$
S	16	2	2	6	2	4										$1S^2 2S^2 2p^6 3s^2 3p^4$
Cl	17	2	2	6	2	5										$1S^2 2S^2 2p^6 3s^2 3p^5$
Ar	18	2	2	6	2	6										$1S^2 2S^2 2p^6 3s^2 3p^6$

Location probability

- The **exact location of an electron** cannot be ascertained because any attempt to do so by light, x-rays, magnetic measurements, or other
- conceivable means would modify the wave characteristics of the electron.
- For hydrogen, with one electron, the probability is greatest that the electron will be located at a radius of 0.53 \AA from the nucleus. The probability is smaller, but still finite, that the moving electron will be nearer, or more remote, at any instant of time

Location probability

- The two electrons of helium have the same type of distribution as the electron of hydrogen because they differ only in their spin orientations.
- Lithium has an atomic number of 3. Its third electron goes into the second quantum shell, with a probable location as shown in the next slide.
- Next in order are beryllium, boron, carbon, nitrogen, oxygen, fluorine, and neon, each of which adds one more electron to the second quantum shell.
- Only two electrons can have the same energy state, and hence the same location probability.



The distribution probabilities for the eight valence electrons of the second shell of neon.

Homework??

Summarize “*Lecture Four*” with no more than two pages.

Quiz??

Quiz in “*Lecture Four*” only next week.

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Physical Chemistry

Chapter Two: The Structure of
Atoms and Crystals

Lecture 5

Contents:

- Metallic Characteristics
- Chemical behaviour and the metallic bond

Metallic Characteristics

- A **metal** is described as having a high lustre, good electrical and thermal conductivity, and as being malleable and ductile.
- Lots of metals do have all these properties, but many non-metallic substances can also exhibit one or more of them.
- There are large variations in the properties among the metals themselves.

Metallic Characteristics

- Great behaviour difference of metals can be realized when evaluate **malleability** and **ductility** of **lead** and compare them with the **hardness** and **brittleness** of **tungsten** at exact temperature.
- The *most characteristic property of a metal is its high **electrical** or **thermal** conductivity*. Among the **best** and **worst** conductors of electricity are **copper** and **lead**, respectively. The resistivity of **lead** is only twelve times **greater** than that of **copper**.

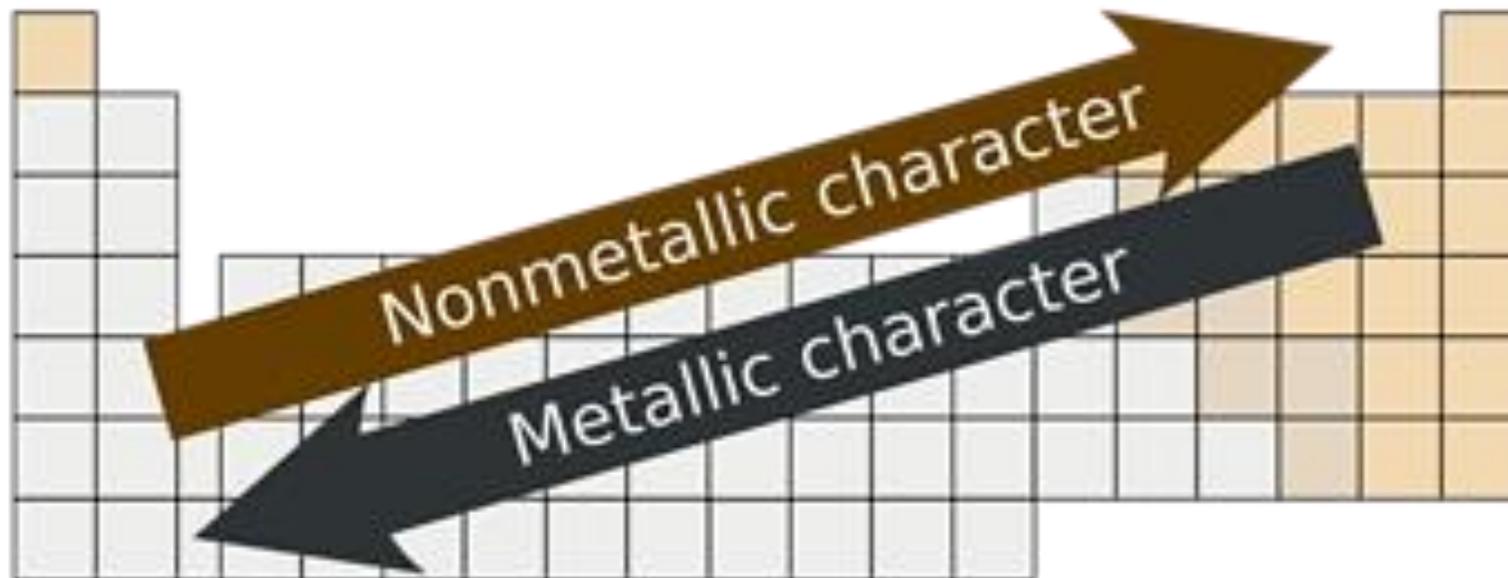
Metallic Characteristics

A non-metallic material (such as **diamond**) has a resistivity about one thousand million times greater than **copper**.

Why? The **reason** for the enormous difference in conductivity between **metal** and a **non-metal** is that electrons, which are negatively charged fundamental particles, can move freely through a metal under the action of a **potential difference**, whereas in a non-metal *this is not the case*.

Metallic Characteristics

Thus, the fundamental characteristics of the metallic state must be sought in the **electronic structure** of a metal.



Periodic table of the elements

group	1*	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
period 1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
lanthanoid series 6	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu				
actinoid series 7	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr				

*Numbering system adopted by the International Union of Pure and Applied Chemistry (IUPAC).

Chemical behaviour and the metallic bond

The chemical behaviour of the elements can be explained in terms of the *great stability* which arises when the *electron shells are filled*.

In the **inert gases** where this condition occurs in the atoms, it is very difficult to remove an electron from the outermost filled shell, and hence produce a **positively charged ion**, and equally difficult to add an extra electron outside the filled shells, and hence give rise to a **negatively charged ion**.

Chemical behaviour and the metallic bond

Thus, the **inert gases**, since they **cannot** readily be converted into ions, are unable to enter into chemical combinations.

Those elements having few electrons outside filled shells can readily shed their outer electrons to form **positively charged ions** (*cations*).

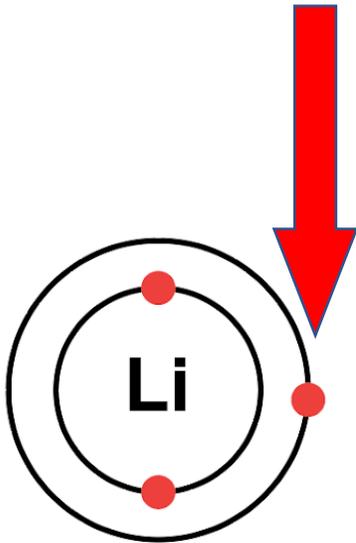
Those which have a large number of outer electrons find it easier to take up a sufficient number of electrons to fill the next shell, and thus form **negatively charged ions** (*anions*).

Chemical behaviour and the metallic bond

For example, lithium, sodium and potassium all have a single outer electron (valency electron), which when shed gives rise to singly charged positive ions. These elements are, therefore, univalent.

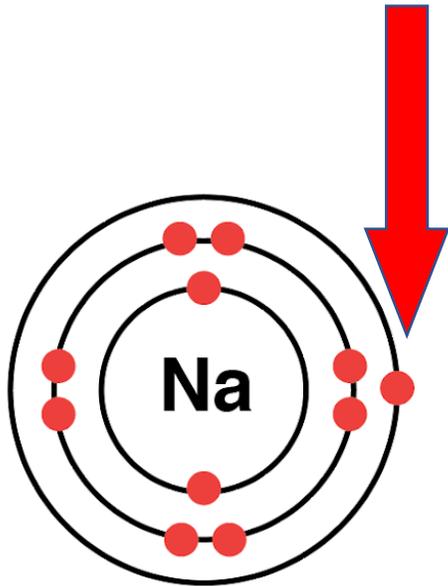
Chlorine, bromine and iodine, on the contrary, all have one electron short of the number required to fill an outer shell, and when they acquire the necessary electron to complete the shell they form highly stable, singly charged negative ions.

3e



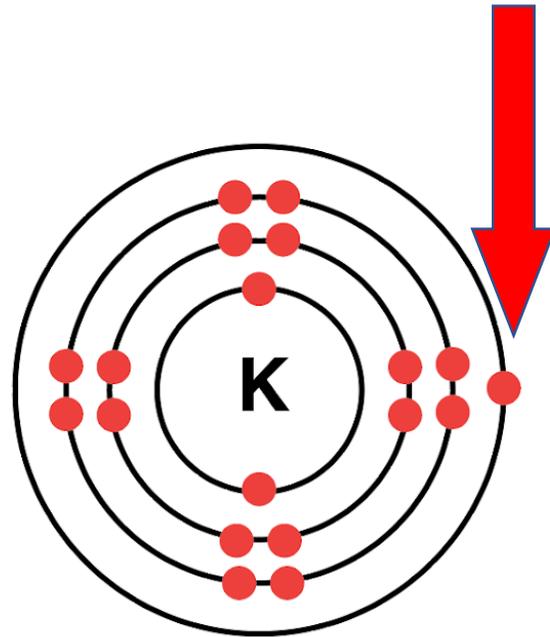
Lithium

11e



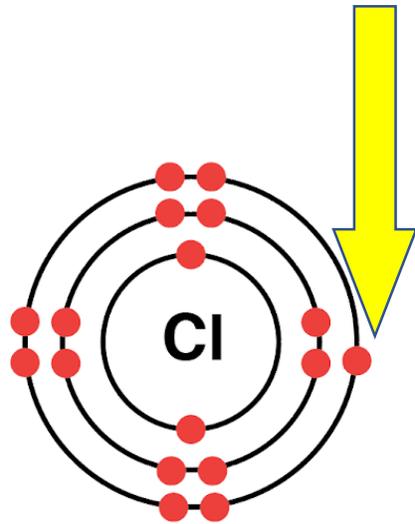
Sodium

19e



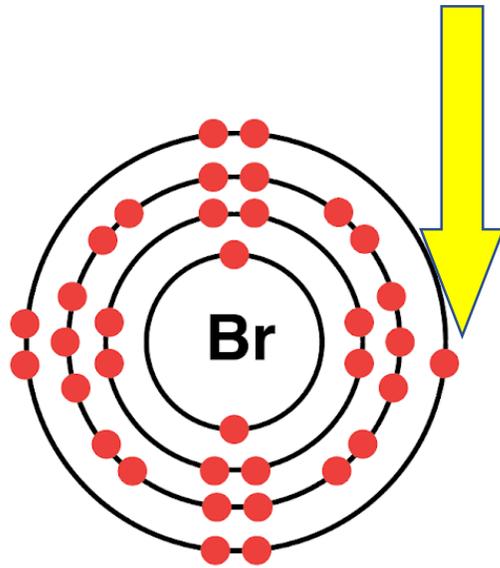
Potassium

17e



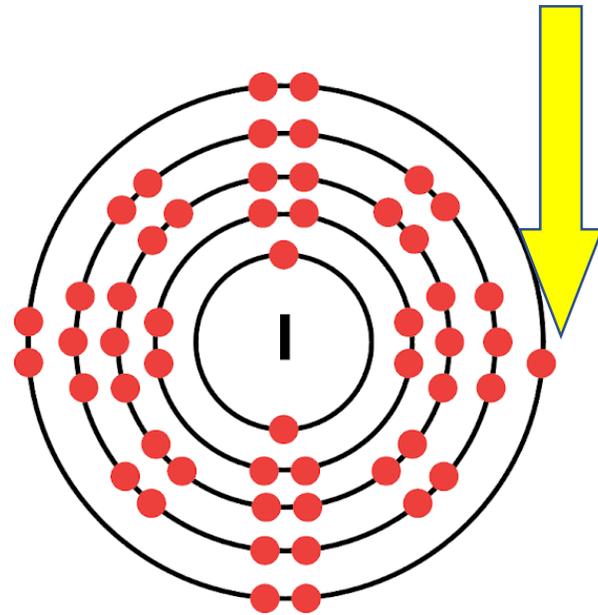
Chlorine

35e



Bromine

53e



Iodine

Homework??

Summarize “*Lecture Five*” with no more than two pages.

Quiz??

Quiz in “*Lecture Five*” only next week.

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Physical Chemistry

Chapter Two: The Structure of
Atoms and Crystals

Lecture 6

Contents:

- Chemical behaviour and the metallic bond -
Continued

Chemical behaviour and the metallic bond

The chemical affinity between **sodium** and **chlorine** can be easily explained in terms of the transfer of the outer electron of sodium to the chlorine atom, when both will now have the former electronic structure characterized by a full shell, and the two ions of opposite charge so produced will be held together by electrostatic attraction. This is the basis of **ionic** or **heteropolar** bonding.

Chemical behaviour and the metallic bond

The elements on the **left** of the **Periodic Table** form **positive ions**, and have **valencies** which increase as one proceeds along the periods from one group to the next starting from **Group I**. Similarly the elements on the **right-hand side** give rise to **negative ions** and, in this case, the **valencies** increase progressively on passing along the periods from **right** to **left**. The elements which have a **half-filled outer shell** of electrons, such as carbon, could form quadrivalent ions having either a **positive** or **negative** charge.

Periodic table of the elements

group	1*	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og
lanthanoid series 6	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu				
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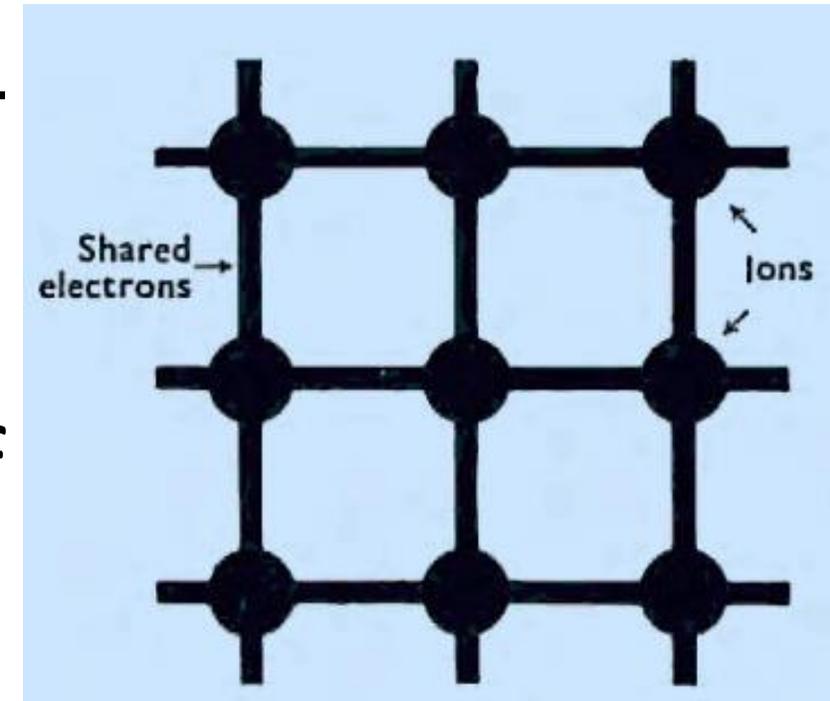
*Numbering system adopted by the International Union of Pure and Applied Chemistry (IUPAC).

Chemical behaviour and the metallic bond

- In fact, in some elements, although they sometimes enter into **ionic bonding** with other elements, more frequently make use of another type of bonding known as **covalent** or **homopolar bonding**. In this type of bonding neighbouring atoms share their outer valency electrons in such a way that each atom has effectively a full outer shell for part of the time.

Chemical behaviour and the metallic bond

- In covalent bonding, their atoms prefer to share only a single electron with their neighbours, as shown in the Figure.
- Therefore, the number of covalent bonds formed by an element is equal to $(8 - N)$ where N is the number of electrons outside the full shell.

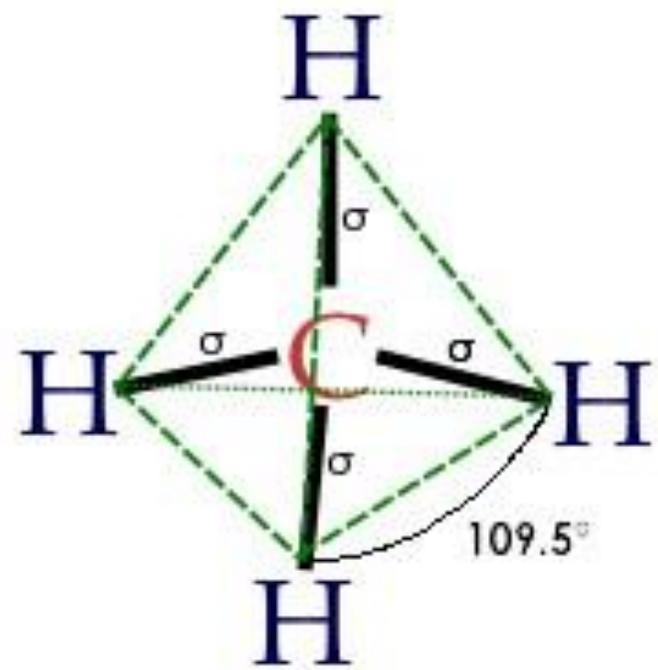
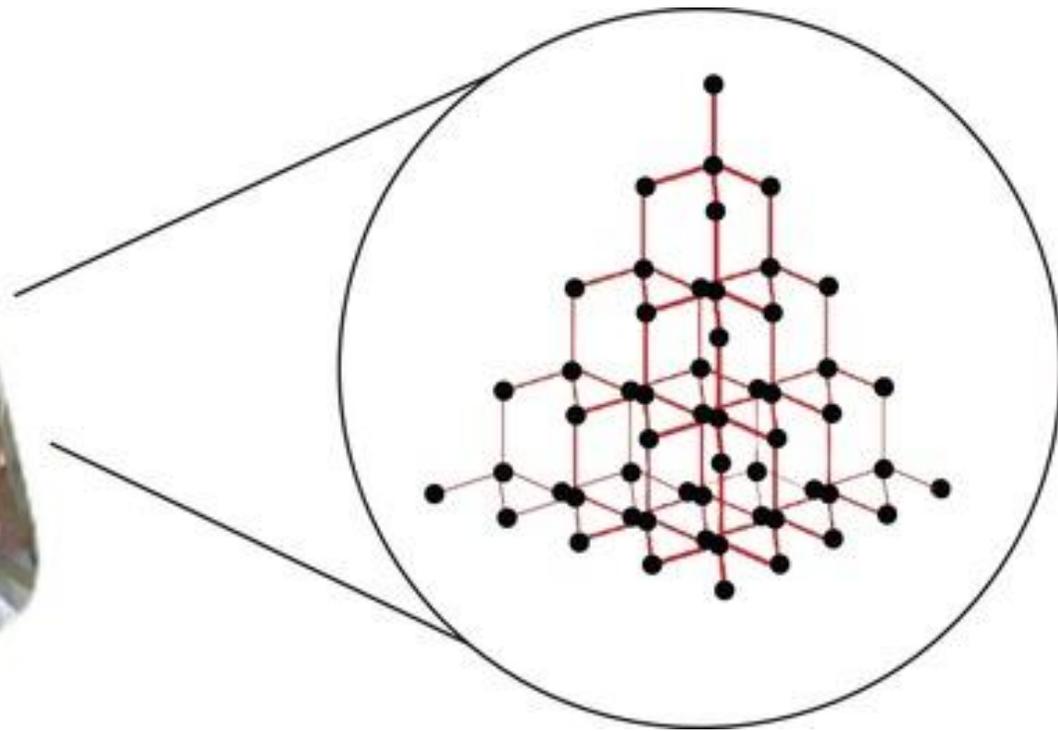


Chemical behaviour and the metallic bond

Another essential feature of **covalent bonding** is that the **shared electrons** are in **s**- and **p**-subshells.

Thus **carbon**, having **four outer electrons**, can *form covalent linkages with four other carbon atoms*.

In **diamond**, which is a form of solid carbon, **each carbon atom** is surrounded by **four** other atoms symmetrically situated at the corners of a regular tetrahedron. In this way a three dimensional network of carbon atoms can be built up.



Chemical behaviour and the metallic bond

In **solids** in which the bonding is either **ionic** or **covalent**, the electrons **are not free** to migrate under the action of an applied electromotive force and hence are **insulators**.

As we have seen, the most important characteristic of a **metal** is its **ability to conduct electricity**, and therefore **the bonding cannot be either ionic or covalent.**

Chemical behaviour and the metallic bond

All elements showing definite metallic characteristics are grouped on the left-hand side of the Periodic Table.

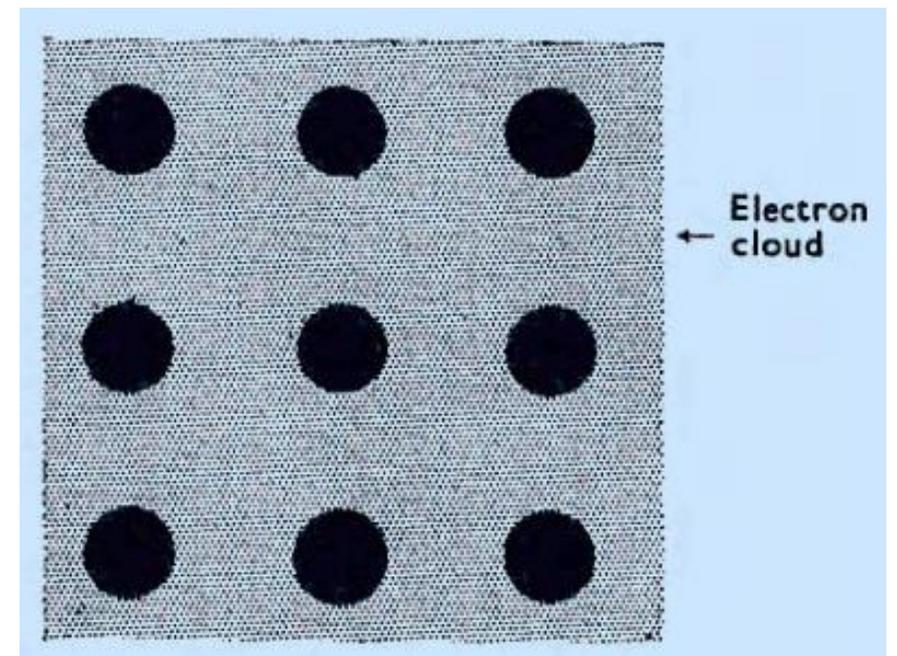
The atoms of the metallic elements all have a small number of electrons outside a full shell.

This is the case for all elements in **subgroups 1, 2 and 3**, for the elements of the **three transition series**, and for the **rare-earth** elements.

Chemical behaviour and the metallic bond

In a **metal** the outer electrons are essentially free to move throughout the material, and one must therefore picture a metal as an *array of positively charged ions completely permeated by a gas of freely moving electrons*.

The **bond** is caused mainly by the **attraction of the positive ions to the free electrons**.



Chemical behaviour and the metallic bond

One of the most important consequences of this mode of bonding is that the **bonding forces** are **not** spatially directed and the ions will, therefore, group themselves together in whatever geometrical form gives the most economical packing.

However, it must be remembered that when **two ions** approach each other there is a **repulsive force** brought into play, and this force limits the degree of economical packing.

Homework??

Summarize “*Lecture Six*” with no more than two pages.

Quiz??

Quiz in “*Lecture Six*” only next week.

University of Baghdad
College of Science
Department of Physics

Physical Chemistry

Chapter Two: The Structure of
Atoms and Crystals

Lecture 7

Contents:

- Arrangement of Atoms in Metals

Arrangement of Atoms in Metals

Metal ions are **very small**, and have diameters which are only a few times 10^{-7} mm, i.e. **less than a nanometer**. A millimetre cube of metal, therefore, contains something like 10^{20} atoms.

It has been shown that the ions in solid metal are **not** randomly arranged, but *are packed together in a highly regular manner*.

In majority of metals the ions are packed together so that the **metal occupies the minimum volume**.

Arrangement of Atoms in Metals

In **all** metals, including those in which the ions are **not** close-packed, the arrangement of ions follows a ***specific pattern***, and the structure of the metal is characterized by a simple unit of pattern, known as a **structure cell**, which, when it **is repeated** in a completely regular manner throughout the metal, defines the position of all the ions in the metal crystal.

Arrangement of Atoms in Metals

There are **TWO** methods of packing spheres of equal size together so that they occupy minimum volume:

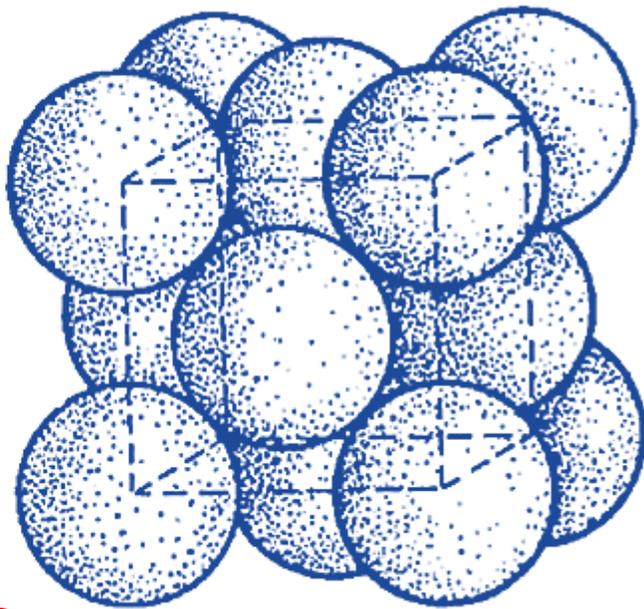
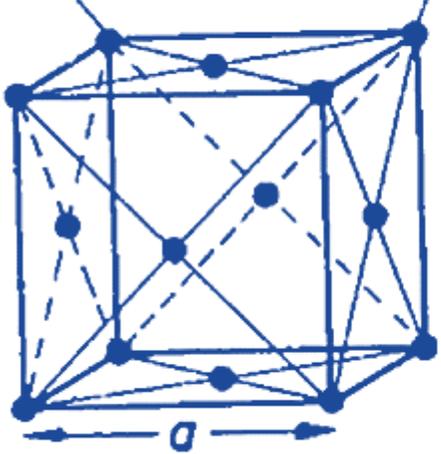
*1- face-centred cubic (**f.c.c.**) arrangement.*

*2- close-packed hexagonal (**c.p.h.**) arrangement.*

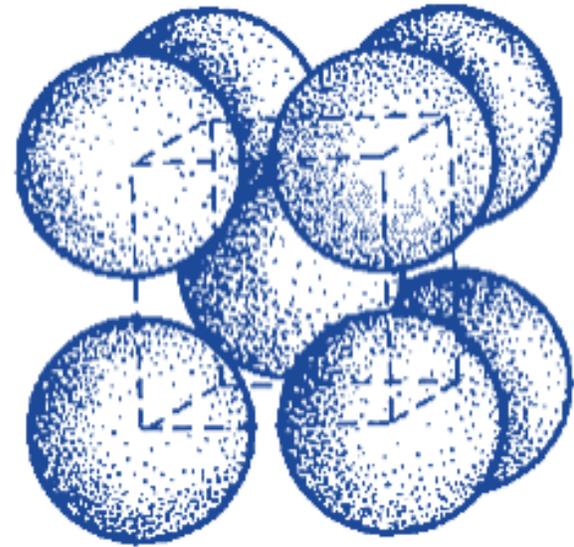
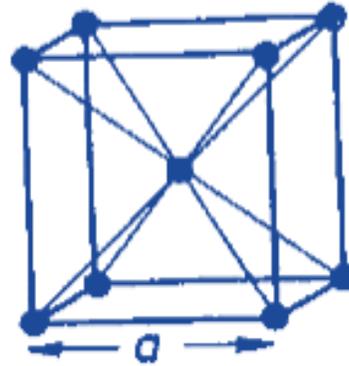
Also, there is **another method** which does not lead to close-packing but it is adopted by many metals.

*3- body-centred cubic (**b.c.c.**) arrangement.*

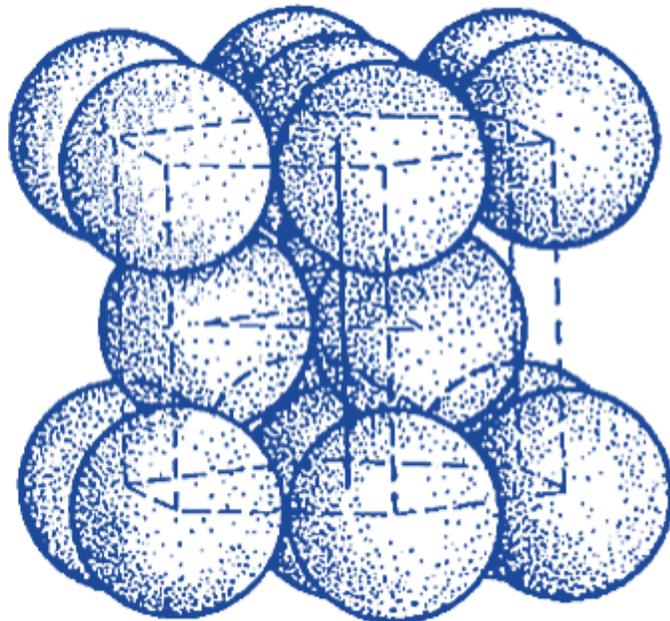
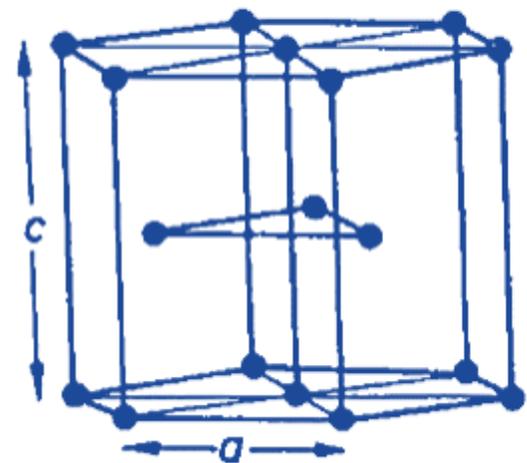
Position of the
centre of the atom



face-centred cubic (**f.c.c.**) structure



body-centred cubic (**b.c.c.**) structure



close-packed hexagonal (**c.p.h.**) structure

Arrangement of Atoms in Metals

Apart from the three crystal structures already mentioned, other structures such as:

- **orthorhombic** (e.g. gallium, uranium)
- **tetragonal** (e.g. indium, palladium)
- **rhombohedral** (e.g. arsenic, antimony, bismuth)

Arrangement of Atoms in Metals

To specify the structure of a metal, it is necessary to give *not only the type of crystal structure but also the dimensions of the **structure cell** of that metal.*

The number of quantities necessary to define a structure cell clearly depends on the **degree of geometric regularity** exhibited by the cell. Thus, in the **cubic** structure cells, it is only necessary to give the **length of an edge**, whereas in a **hexagonal** cell it is necessary to give the two lengths **a** and **c**.

Arrangement of Atoms in Metals

However, if the structure is ideally close-packed, the two quantities **a** and **c** must be in the ratio $c/a =$ 1.633.

In metal structures, the ratio c/a , known as the **axial ratio**, is never exactly 1.633, and the structures are, therefore, never quite ideally close-packed, e.g. for **zinc** $c/a =$ 1.86 and for **titanium** $c/a =$ 1.58. The quantities which give the size of a structure cell are termed the **lattice parameters**.

Arrangement of Atoms in Metals

A knowledge of the **lattice constants** permits the atomic radius **r** of the metal atoms *to be calculated* on the assumption that they are **spherical** and that they are in **closest possible contact**. It should be verified that in the **f.c.c.** structure $r = (a\sqrt{2})/4$, and in the **b.c.c.** structure $r = (a\sqrt{3})/4$, where **a** is in both cases the **lattice parameter**. As the quantities **a** and **r** are very small, it is customary to measure them in terms of nanometres (10^{-9} m).

Homework??

Summarize “*Lecture Seven*” with no more than two pages.

Quiz??

Quiz in “*Lecture Seven*” only next week.

University of Baghdad
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Physical Chemistry

Chapter Two: The Structure of
Atoms and Crystals

Lecture 8

Contents:

- Arrangement of Atoms in Metals - Continued

Arrangement of Atoms in Metals

An important concept dealing with crystal structures is the co-ordination number, which is defined as the number of equidistant nearest neighbouring atoms around any atom in the crystal structure. Thus, in the **body-centred cubic** structure, it is easily seen that the *atom at the centre of the cube* is surrounded by **eight** equidistant atoms at its corners, and the coordination number is **8**. The co-ordination number in the **face-centred cubic** structure is **12**.

Arrangement of Atoms in Metals

The co-ordination number of close-packed **hexagonal** structure (12) can be seen by considering once more *two cells stacked one on top of the other*, and *choosing the centre atom* of the common plane.

This plane is referred to as the **basal plane**.

The most densely packed plane in the ideally close-packed hexagonal structure is the basal plane, and has the same atomic arrangement as the closest packed plane in the face-centred cubic structure.

Arrangement of Atoms in Metals

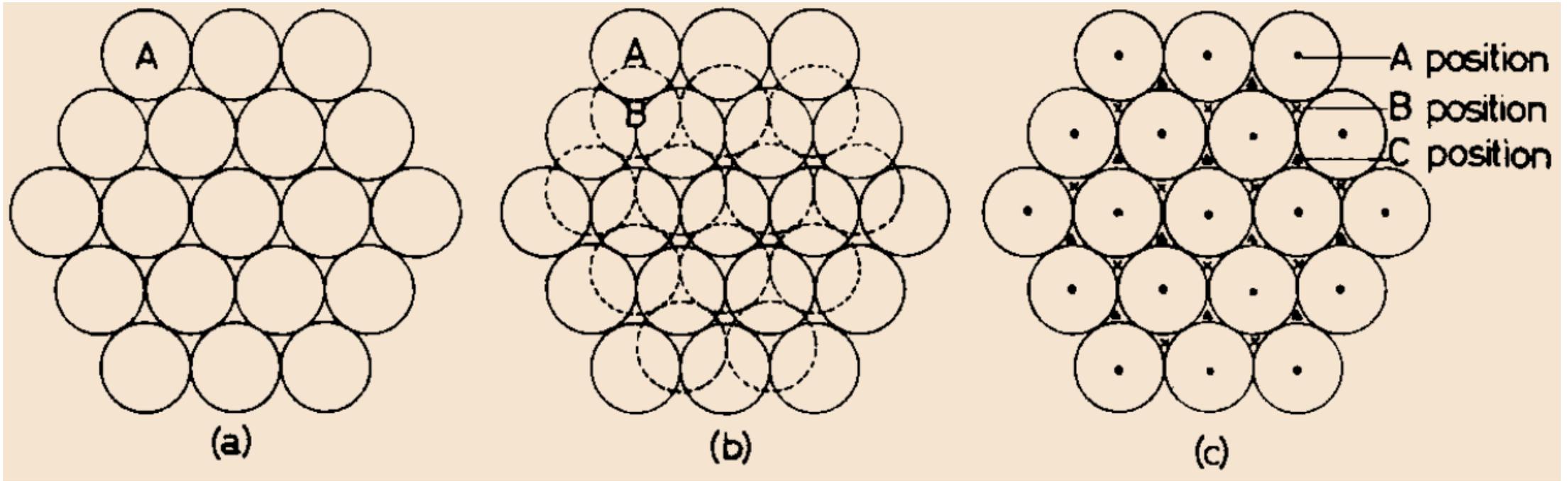
Both the **c.p.h.** and **f.c.c.** cubic structure represent two equally good methods of packing spheres.

The difference between them arises from the different way in which the close-packed planes are stacked.

Arrangement of Atoms in Metals

In laying down a **second plane** of close-packed atoms, the **first atom** may be placed in either position **B** or **C**, which are entirely equivalent sites. However, once the first atom is placed in **one** of the **two** types of site, all other atoms in the second plane must be in similar sites.

This is simply because neighbouring sites of the types **B** and **C** are **too close** together for both to be occupied in the same layer.



- (a)** Arrangements of atoms in a close-packed plane.
- (b)** positioning of two close-packed planes.
- (c)** the stacking of successive planes

Arrangement of Atoms in Metals

At this stage there is no difference between the **c.p.h.** and **f.c.c.** structure, and the difference arises only when the **third layer is put in position**. In building up the third layer, assuming that sites of type **B** have been used to construct the second layer sites **A** or **C** may be selected. If sites **A** are chosen, then the atoms in the **third layer** will be directly above those in the first layer, and the structure will be **c.p.h.**

Arrangement of Atoms in Metals

Whereas, if sites **C** are chosen this will not be the case and the structure will be **f.c.c.** Thus a **c.p.h.** structure consists of layers of closely packed atoms stacked in the sequence of **ABABAB** or, of course equally well, **ACACAC**.

An **f.c.c.** structure has the stacking sequence **ABCABCABC** so that the atoms in the fourth layer lie directly above those in the bottom layer.

Arrangement of Atoms in Metals

Some metals adopt more than one crystal structure, each of the exhibited crystal forms being stable only over a certain temperature range. The best known example of this phenomenon, called **polymorphism**, is exhibited by **iron** which is **b.c.c.** at temperatures **below 910 °C** and **above 1400 °C**, but **f.c.c.** **between 910-1400°C**. Other examples include **titanium** and **zirconium** which change from **c.p.h.** to **b.c.c.** at temperatures of 882 °C and 815 °C respectively.

Arrangement of Atoms in Metals

Tin which changes from **cubic** (grey) to **tetragonal** (white) at 13.2 °C, and the metals uranium and plutonium.

Plutonium is particularly complex in that it has six different crystal structures between *room temperature* and its melting point of 640 °C.

Homework??

Summarize “*Lecture Eight*” with no more than two pages.

Quiz??

Quiz in “*Lecture Eight*” only next week.

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Physical Chemistry

Chapter Two: The Structure of
Atoms and Crystals

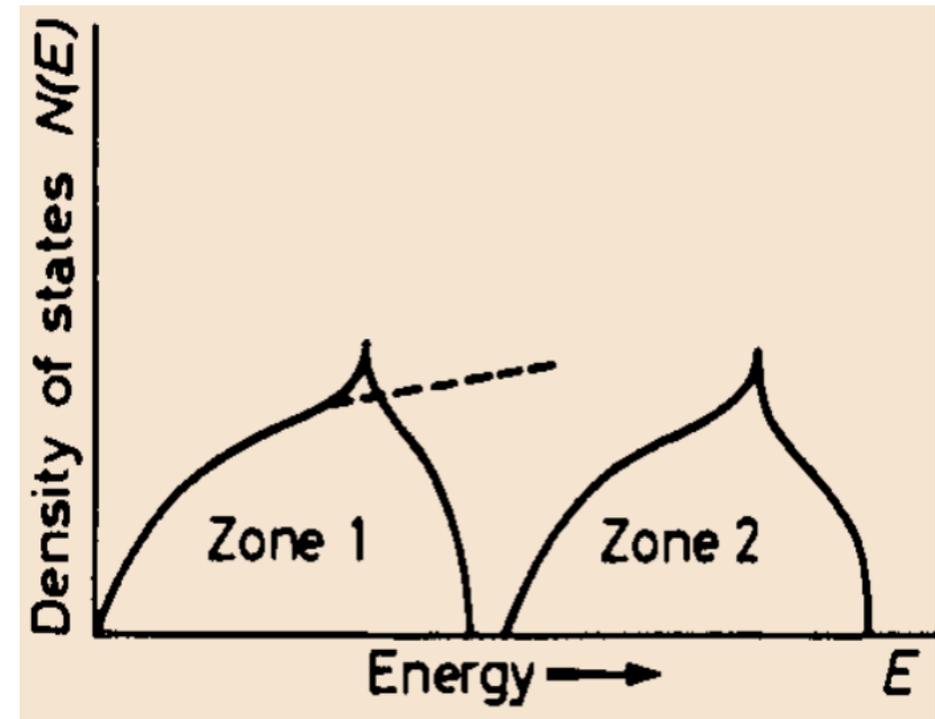
Lecture 9

Contents:

- Metals and insulators

Metals and insulators

- For electrical conduction to occur, it is necessary that the electrons at the top of a band should be able to increase their energy when an electric field is applied to materials so that a net flow of electrons in the direction of the applied potential, which manifests itself as an electric current, can take place.



Metals and insulators

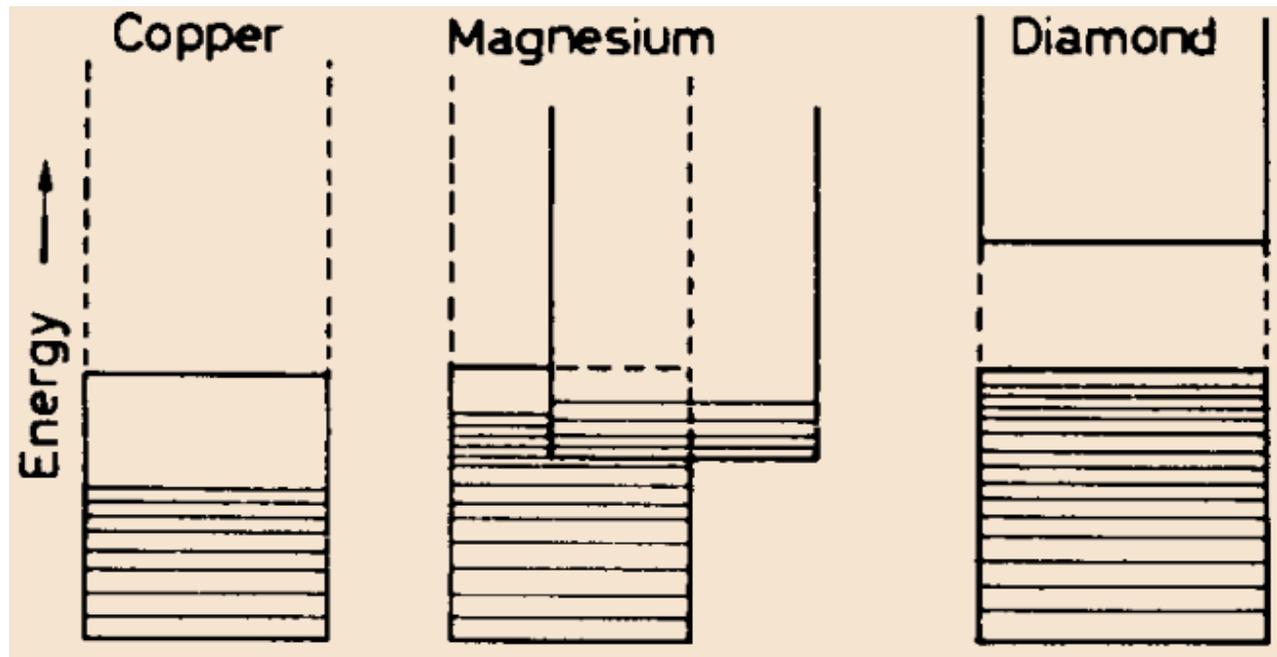
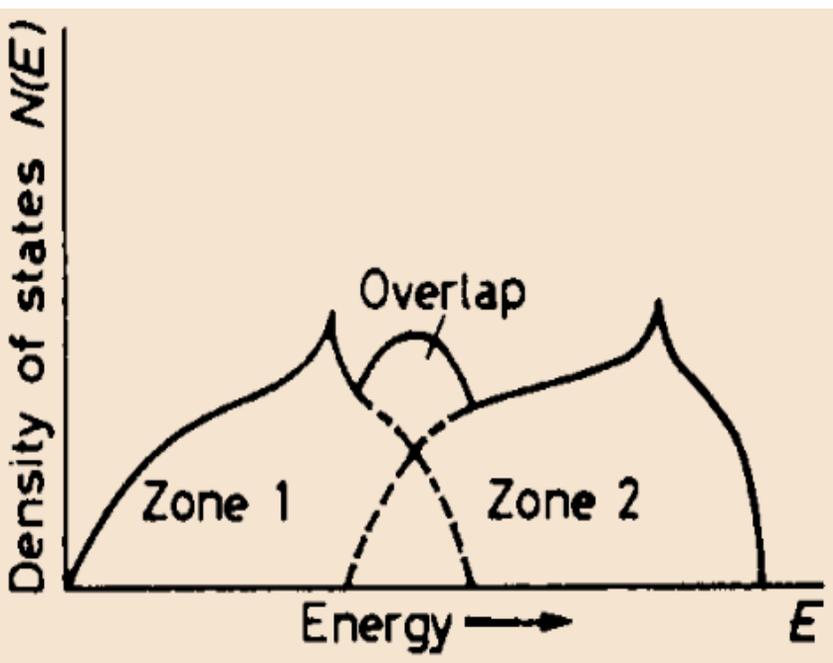
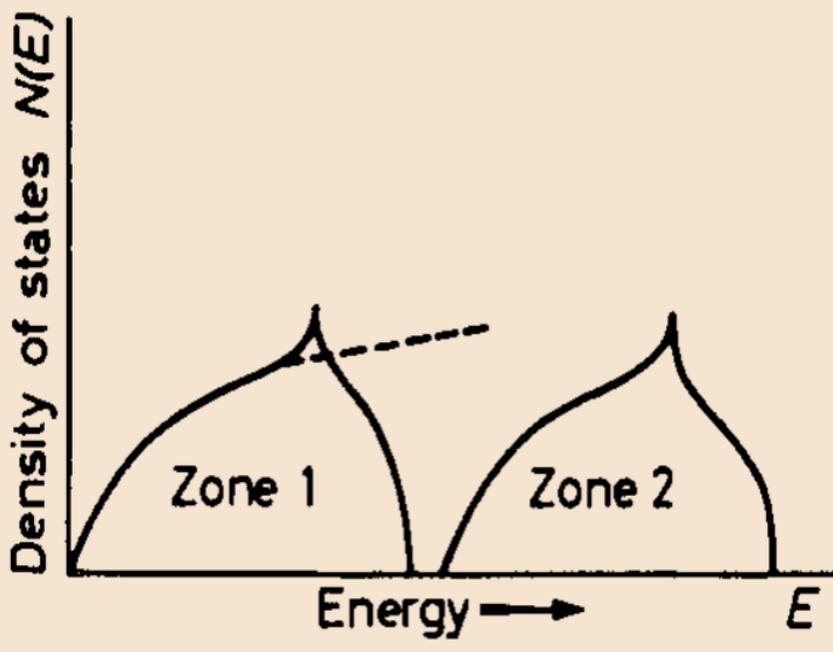
- If an energy gap between two zones of the type occurs, and if the lower zone is just filled with electrons, then it is impossible for any electrons to increase their energy by jumping into vacant levels under the influence of an applied electric field, unless the field strength is sufficiently great to supply the electrons at the top of the filled band with enough energy to jump the energy gap.

Metals and insulators

- Thus metallic conduction is due to the fact that in metals the number of electrons per atom is insufficient to fill the band up to the point where an energy gap occurs. In copper, for example, the 4s valency electrons fill only one half of the outer s-band. In other metals, e.g. Mg, the valency band overlaps a higher energy band and the electrons near the Fermi level are thus free to move into the empty states of a higher band.

Metals and insulators

- When the **valency band** is completely filled, and the next higher band, separated by an energy gap, is completely empty, the material is either an insulator or semiconductor.
- If the gap is several electron volts wide, such as in diamond where it is 7 eV, extremely high electric fields would be necessary to raise electrons to the higher band and the material is an insulator.

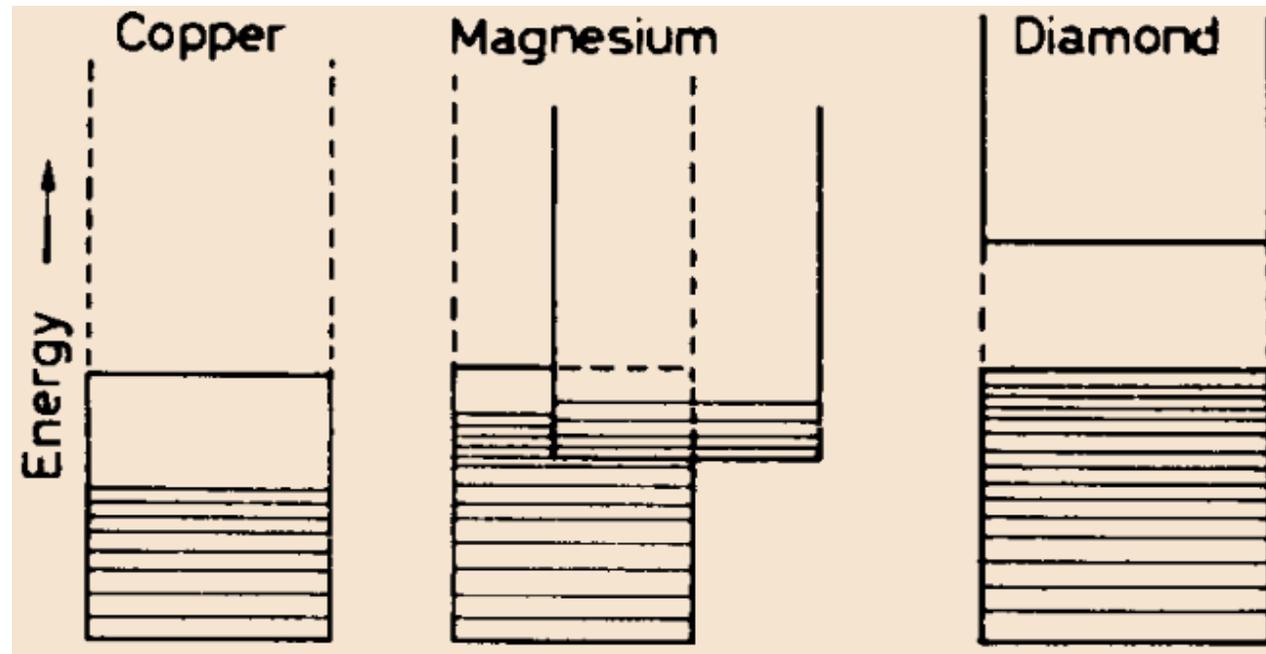


Metals and insulators

- If the gap is small enough, such as 1-2 eV as in silicon, then thermal energy may be sufficient to excite some electrons into the higher band and also create vacancies in the valency band, the material is a semiconductor.
- In general, the lowest energy band which is not completely filled with electrons is called a conduction band, and the band containing the valency electrons the valency band.

Metals and insulators

- For a conductor the valency band is also the conduction band. The electronic state of a selection of materials of different valencies is presented in the following figure.



Metals and insulators

- Although all metals are relatively good conductors of electricity, they exhibit among themselves a range of values for their resistivities. The resistivity of a metal depends on the density of states of the most energetic electrons at the top of the band, and the shape of the $N(E)$ — E curve at this point.
- It also depends on the degree to which the electrons are scattered by the ions of the metal which are *thermally vibrating*, and by *impurity atoms* or *other defects present in the metal*.

Homework??

Summarize “*Lecture Nine*” with no more than two pages.

Quiz??

Quiz in “*Lecture Nine*” only next week.

University of Baghdad
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Physical Chemistry

Chapter Two: The Structure of
Atoms and Crystals

Lecture 10

Contents:

- Real crystals and imperfections

Real crystals and imperfections

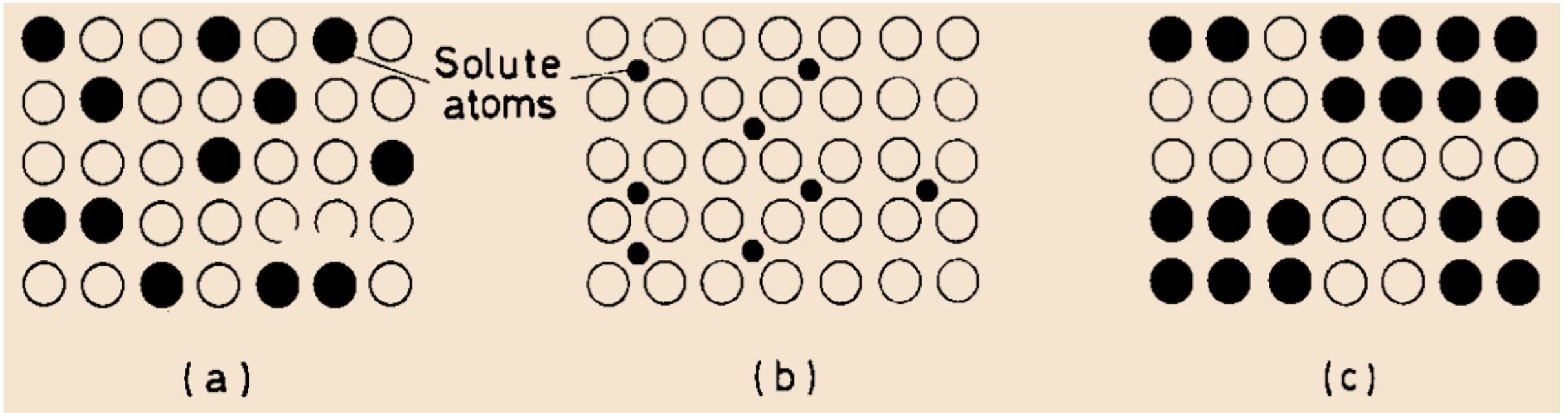
- Although real crystals are never quite so perfect. The basic structure of a real metal crystal is as regular, but lattice distortions as well as definite imperfections do exist. One source of irregularity can arise because the atoms are ***not at rest*** but ***vibrate*** about their mean lattice positions, with a frequency determined by the interatomic forces and with an amplitude governed by the **temperature** of the crystal.

Real crystals and imperfections

- The **second** complication is that the crystal may contain *foreign atoms*, added either intentionally as alloying elements or unintentionally as impurities which, **because of their different atomic size**, give rise to *local distortions* of the solvent lattice. These *solute atoms may be dispersed randomly throughout the crystal*, as shown in next slide (figures (a) and (b)) when they are said to be in solid solution.

Real crystals and imperfections

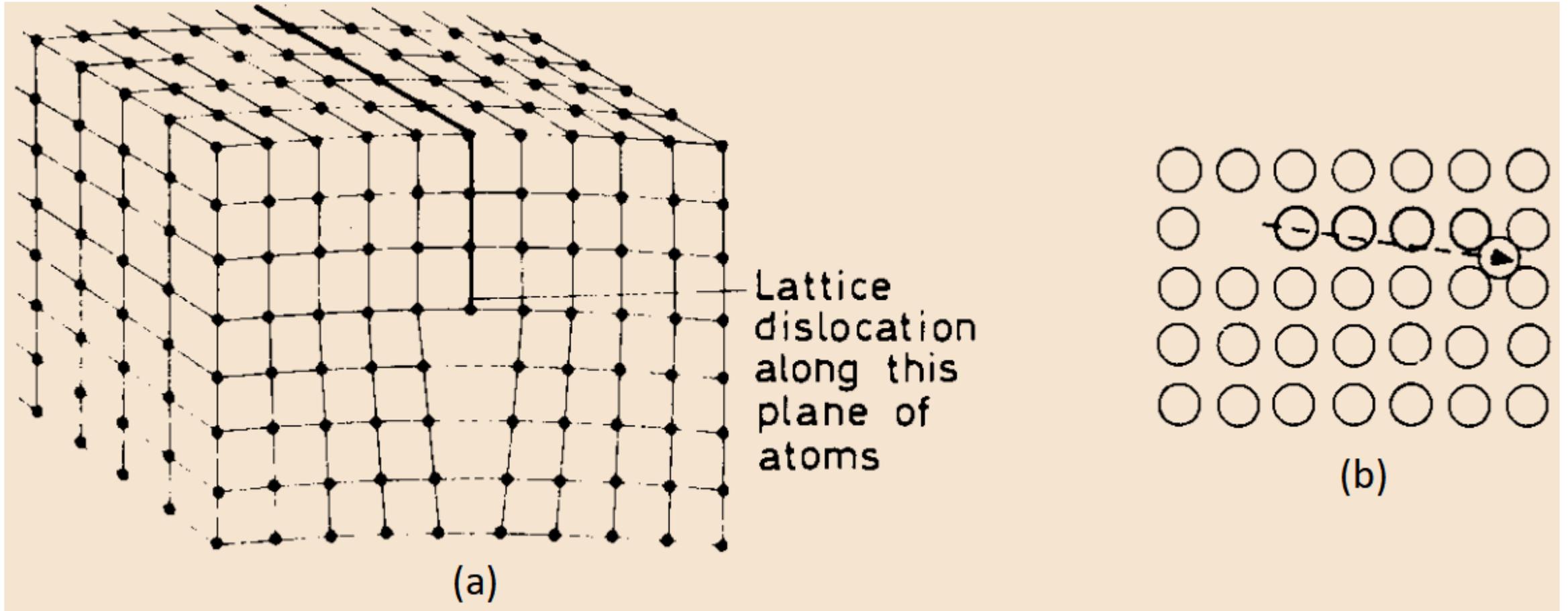
- or they may aggregate together to form particles of a second phase (figure (c)).



(a) substitutional solid solution, (b) interstitial solid solution, (c) phase mixture.

Real crystals and imperfections

- Apart from foreign atoms, other irregularities, classified generally as lattice imperfections, also occur in metal crystals. These imperfections may take the form of:
 - (i) volume defects, such as cracks or voids.
 - (ii) line defects, such as dislocations.
 - (iii) point defects, such as vacant lattice sites (or simply vacancies) and interstitial atoms (or simply interstitials).



(a) dislocation, and (b) vacancy-interstitial pair

Quiz??

Quiz in “*Lecture Ten*” only on Friday.