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Field: Matter Sciences

Sector: Chemistry

Course Handout

Physical Chemistry of Surfaces and Interfaces

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This handout is intended for students enrolled in Master (M2) Specialty: Analytical Chemistry

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Good students are not those who display the trappings of studiousness (perfect attendance, rapt attention, meticulous work). Good students are those who learn. Whatever their preconceptions, barriers, or deficits - whatever their story - they take new information and new experiences and, to the best of their ability, make them tools for transforming themselves and their world. –M. Cohan

FORWORD

The content of the Physical Chemistry of Surfaces and Interfaces unit is designed to align with the analytical chemistry master's degree program offered at Boumerdes University, covering all aspects indicated in this educational field. While much of the content is conventional in nature and addresses the fundamentally important aspects of Physical Chemistry of Surfaces and Interfaces, it also comprehensively covers essential aspects of General and Physical Chemistry. This includes the chemical and physical properties of material surfaces, reactions on solid catalysts, metal corrosion, surface construction at the atomic level, terminology related to bulk crystals, interfacial phenomena such as surface tension, wetting, and adsorption, along with electrical and intermolecular forces. Additionally, fundamental experimental methods for measuring these phenomena are introduced. The topics are presented in a student-friendly manner, with worked examples and questions provided within each chapter. This guidebook aims to offer students a clear and straightforward presentation of these principles, avoiding overly complex mathematical treatments that may obscure understanding. Throughout the book, equations are provided to illustrate methods and relationships, helping students relate theoretical principles to practical situations. While this course guide does not aim to be a comprehensive compendium of facts, students are encouraged to consult other textbooks listed in the bibliography for additional resources to solve practical problems related to each topic. In order words, the course book is only skeleton which students must flesh and it serves as a framework that students must build upon. It is a valuable contribution to the discipline and profession of chemistry and will prove beneficial to students and beginning teachers in institutions and universities.

Constructive criticism and suggestions from students and colleagues are welcomed and appreciated as they contribute to the continuous improvement of this educational resource.

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Chapter I: Introduction to Surface Chemistry

I.1 Introduction

Surface chemistry is a branch of science focused on understanding the structures of matter across solids, liquids, and gases. It encompasses various essential concepts, with the interface or surface delineated by a hyphen or a slash between bulk phases (e.g., solid-gas or solid/gas). While gases exhibit complete miscibility, interfaces between solids, liquids, and gases are typically only a few molecules thick, their area contingent upon the size of bulk phase particles. Numerous significant phenomena, such as corrosion, electrode processes, and catalysis, occur at these interfaces. Surface chemistry finds diverse applications in industry, analytical work, and everyday life situations. Achieving meticulous surface studies requires exceptionally clean surfaces, often obtained under very high vacuums, to produce ultra-clean metal surfaces. Without proper storage under vacuum, solid materials risk contamination by molecules from the air, primarily dioxygen and dinitrogen.

I.2 Surfaces and interfaces

The surface of a solid material can be viewed as a distinct material with properties that depend on its composition and structure. The surface of a solid material consists of the top few atomic layers and has different chemical and electrical properties compared to the bulk material. Many of the electronic properties of a bulk material depend on the three-dimensional periodic structure inside the solid. The loss of periodicity in one dimension at the surface results in surface electronic properties that are different from the bulk. The lack of neighboring atoms on one side of the surface atoms may result in available chemical bonds, which “dangle” into the space outside the solid and are available for chemical reaction. This is illustrated in Figure below.

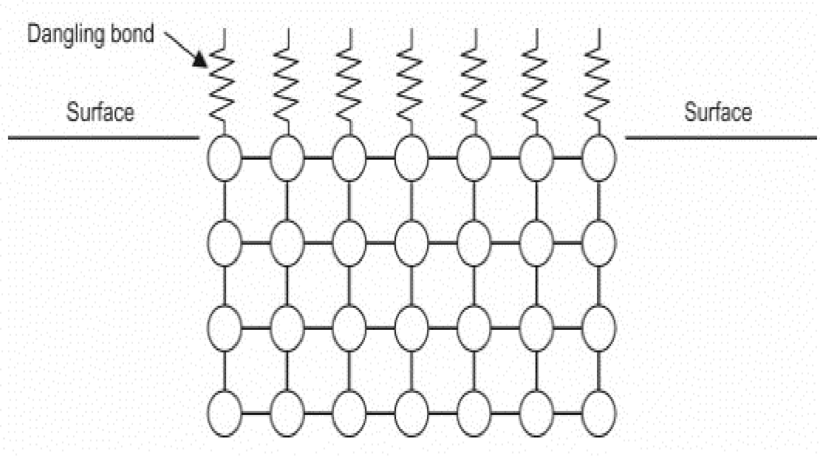


Figure I.1 Diagram of dangling bonds at a surface.

The composition of a material's surface often deviates from its bulk composition due to factors like surface oxidation and contamination. Metals, for instance, tend to develop thin oxide layers when exposed to air, while pollutants like hydrocarbons can deposit on surfaces. Additionally, handling or insufficient cleaning after processing can leave surface contaminants such as oils or dirt. These factors significantly influence surface properties and functionalities, impacting aspects like adhesion strength, electrical resistance, and material response to corrosion and wear. Surface structure, including both macroscopic and microscopic roughness, plays a pivotal role in determining bonding strength and electrical contact resistance. Molecules situated at interfaces exhibit distinct behaviors compared to those in bulk phases, affecting intermolecular forces and molecular orientations. In dense fluids, repulsive forces dominate, creating asymmetrical force fields at interfaces, which manifest as surface tension. Interface movements between phases generate adhesion forces, essential in various applications of surface and colloid science. As surface area increases, molecules migrate from the interior to the interface, influencing surface tension dynamics. While terminologies like "surface" and "interface" vary depending on the phases involved, they describe regions with gradated properties between two phases.

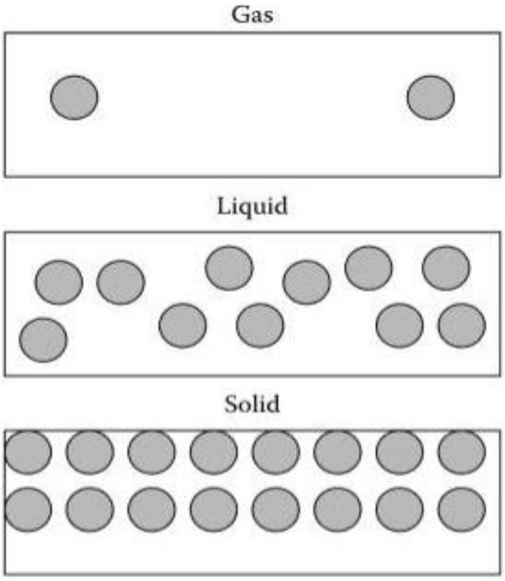


Figure I.1: Molecular structure of gas, liquid and solid.

Interfaces serve as boundaries separating two phases from each other, such as solid-liquid, solid-gas, and liquid-gas interfaces in solid, liquid, and gas phases, respectively. Additionally, liquid-liquid interfaces exist between immiscible liquids, and solid-solid interfaces are crucial for understanding solid material mechanics. Gas-gas interfaces, however, do not occur due to gas mixing. In colloid and surface science, "surface" refers to a phase boundary rather than a geometrical entity, with properties transitioning across molecular dimensions. While geometrically a surface lacks thickness, chemically it represents a region where phase properties change, often considered to have a thickness that approaches zero. "Interface" emphasizes the dividing region between phases. As a material becomes more finely subdivided, its surface area increases.

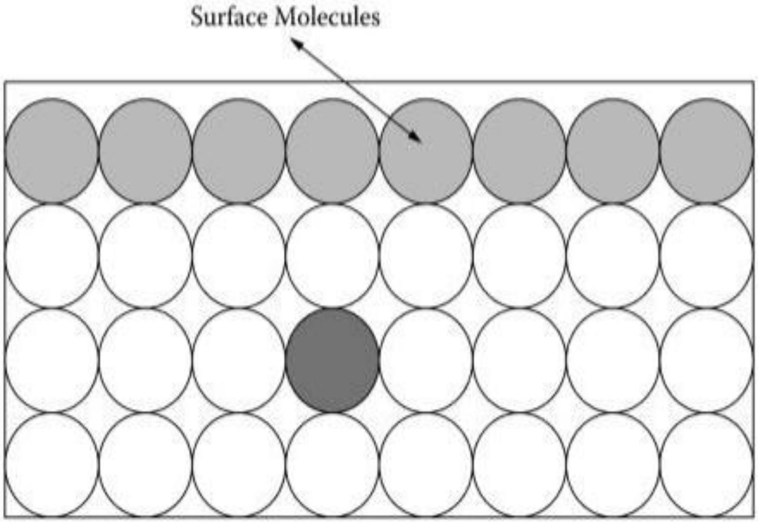


Figure I.2: Intermolecular forces around a molecule in the bulk liquid (dark) and around a molecule on the surface (light) layer.

The definition generally employed are as follows. Surface is term used when one considers the dividing phase between:

- Gas-liquid
- Gas-solid

Interface is the term used when one considers the dividing phase:

- Solid-liquid (colloids)
- Liquid1-Liquid2 (oil-water, emulsion)
- Solid1-solid2 (glue, adhesion, cement)

The term surface tension is used for solid-vapor or liquid-vapor interfaces. The term interfacial tension is more generally used for the interface between two liquids (oil-water), two solids, or a liquid and solid.

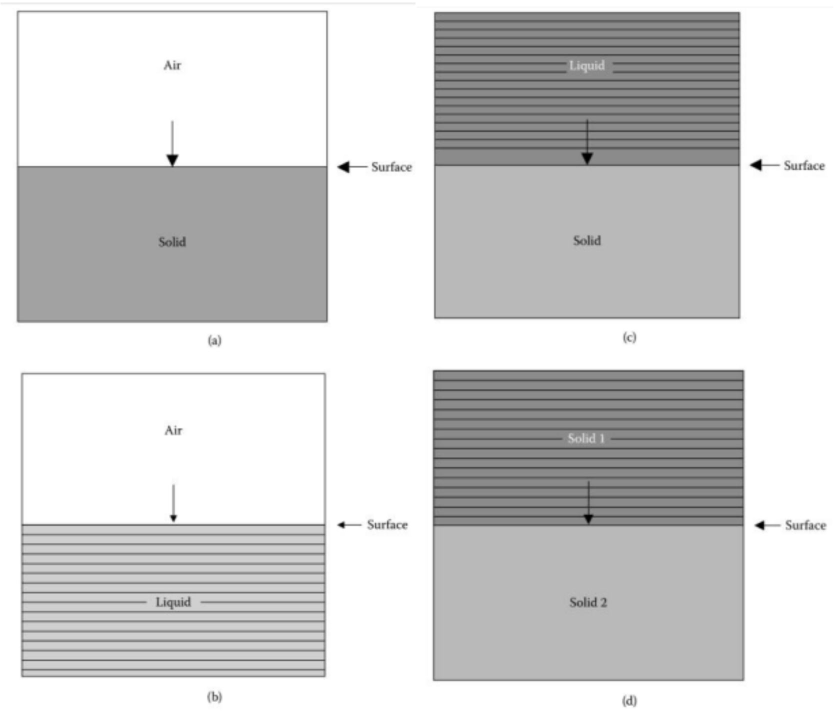


Figure I.3: Different interfaces (a) solid-gas (air), (b) liquid-gas, (c)solid-liquid-, (d) solid1-solid2.

1.3 Surface, interfacial tension and surface free energy

Consider, first, a soap film stretched over a wire frame, one end of which is movable. Experimentally one observes that a force is acting on the movable member in the direction opposite to that of the arrow in the diagram. If the value of the force per unit length is denoted by γ, then the work (W) done in extending the movable member a distance dx is:

$$W=\gamma \, b \, dx= \gamma \, dA \qquad (I.1)$$

Where dA= b dx is the change in area. In the second formulation, γ appears to be an energy per unit area (J/m^2 or $ergs/cm^2$) or dyn/cm or N/m.

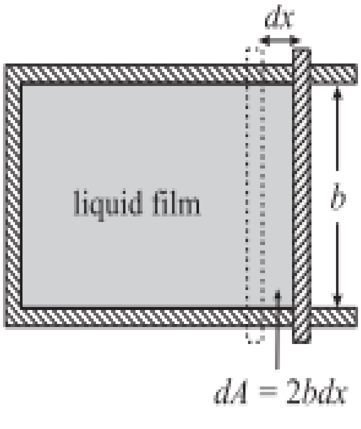


Figure I.4: Schematic set-up to verify Eq. (I.1) and define the surface tension.

The surface tension can also be defined by the force F that is required to hold the slider in place and to balance the surface tensional force:

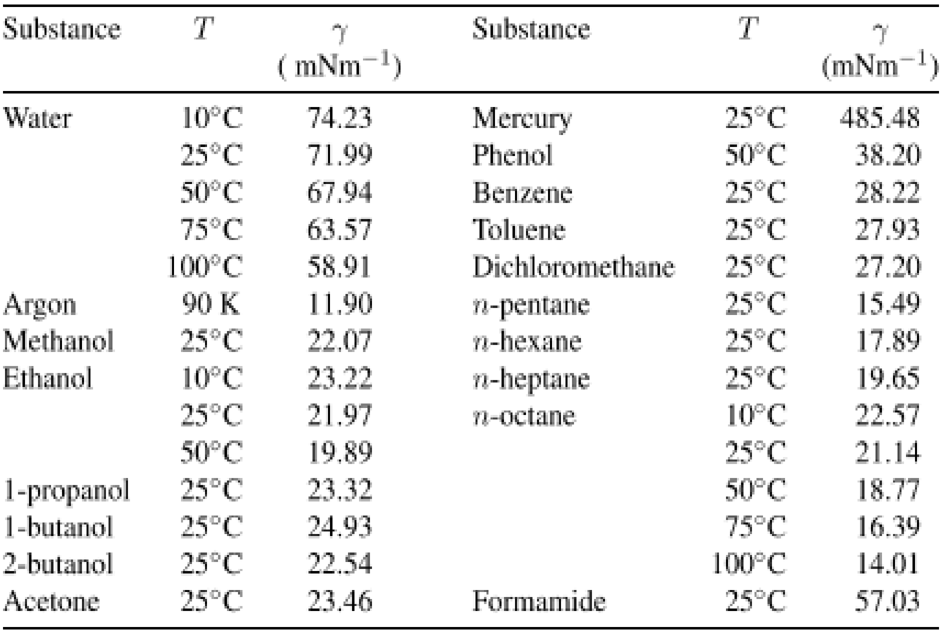
$$F = 2\gamma L \qquad (I.2)$$

Both forms of the law are equivalent, provided that the process is reversible. Then we can write:

$$F = \frac{dW}{dx} = -2\gamma b \qquad (I.3)$$

The force is directed to the left while x increases to the right. Therefore, we have a negative sign. The unit of surface tension is either J/m^2 or N/m.

Table I.1: Surface tensions γ of some liquids at different temperatures T.



Substance	T	γ (mNm^{-1})	Substance	T	γ (mNm^{-1})
Water	10°C	74.23	Mercury	25°C	485.48
	25°C	71.99	Phenol	50°C	38.20
	50°C	67.94	Benzene	25°C	28.22
	75°C	63.57	Toluene	25°C	27.93
	100°C	58.91	Dichloromethane	25°C	27.20
Argon	90 K	11.90	*n*-pentane	25°C	15.49
Methanol	25°C	22.07	*n*-hexane	25°C	17.89
Ethanol	10°C	23.22	*n*-heptane	25°C	19.65
	25°C	21.97	*n*-octane	10°C	22.57
	50°C	19.89		25°C	21.14
1-propanol	25°C	23.32		50°C	18.77
1-butanol	25°C	24.93		75°C	16.39
2-butanol	25°C	22.54		100°C	14.01
Acetone	25°C	23.46	Formamide	25°C	57.03

Surface tension is defined as the change in free energy per unit change in surface area. When surface area increases, molecules from the bulk phase must move to the surface, creating a force directed inward within the liquid. This inward force results from the attraction of surface molecules to those below and laterally, but not outward. Consequently, surface molecules behave as if wrapped in an elastic membrane, with cohesion among them supplying a tangential force. This behavior is observed in nature, where insects such as water striders exploit surface tension to skate on water without sinking, while heavier objects like metal needles can float due to the need to overcome surface forces to sink. Surface tension can also be seen in the smooth hulls of ships, which experience less resistance and save energy compared to rough bottoms. This tension arises from the unsaturation of bonds at the surface compared to the bulk, demonstrating the importance of surface properties in various natural and engineered systems.

Chapter II: Surface structure

II.1 Introduction

Molecules at a surface are arranged in a different way from molecules in the bulk. This statement is, in general, true for solids and liquids. There is, however, a major difference: when a solid is deformed by small external forces it reacts elastically while for a liquid the reaction is plastic. The shape of the solid was generated in the past and it is usually not determined by the surface tension. Individual atoms and molecules are only able to vibrate around their mean position and are otherwise fixed to a certain site. This applies, however, only within limits. Many solids are somewhat mobile and can flow very slowly. In that case methods and models of capillarity can be applied. One case where capillarity plays an important role is sintering. In sintering a powder is heated.

II.2 Liquid surfaces

A surface is not an infinitesimally sharp boundary in the direction of its normal; instead, it possesses a certain thickness. Density serves as one criterion for defining the thickness of an interface, but another parameter is the orientation of molecules. For instance, water molecules at the surface tend to orient with their negative sides facing outward towards the vapor phase, with this orientation diminishing as distance from the surface increases. The actual thickness of a surface depends on the relevant parameter being considered. For example, if we're interested in the density of a water surface, a realistic thickness would be on the order of 1 nanometer. However, if a salt is dissolved in the water, the concentration of ions may vary over a much larger distance, resulting in a greater thickness with respect to ion concentration. When in doubt, it's advisable to err on the side of choosing a larger value for the thickness. The surface of a liquid is a dynamic environment, characterized by molecules evaporating from the liquid into the vapor phase and vice versa, as well as diffusion into and from the bulk phase.

II.2.1 Surface tension on the molecular level

Molecules prefer to be surrounded by others due to attractive interactions like van der Waals forces and hydrogen bonds, crucial for the existence of condensed phases (Figure II.1). At the surface, molecules experience fewer adjacent molecules than in the bulk, requiring energy to bring them from the bulk to the surface. This energy, represented by surface tension (γ), is the energy required to create new surface area. Surface tension ensures γ is positive, preventing molecules from evaporating into the gas phase due to repulsive interactions.

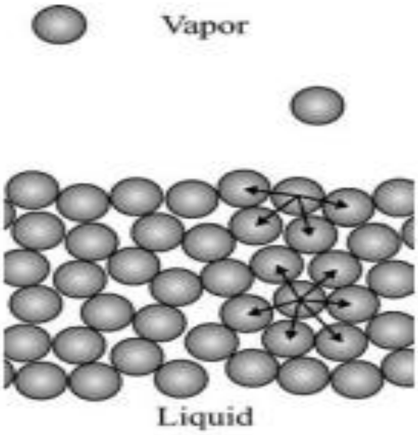


Figure II.1: Schematic molecular structure of a liquid-vapor interface.

II.2.2 Equation of Young and Laplace

In equilibrium, a curved liquid surface indicates a pressure difference across it. Surface tension works to minimize surface area, resulting in a planar surface geometry. To curve the surface, one side must experience higher pressure than the other, akin to a rubber membrane scenario. For instance, if a tube's end is closed with a tensioned rubber membrane, it remains planar as long as internal and external pressures are equal (Figure II.2). When pressure is increased by blowing into the tube, the membrane bulges out due to increased internal pressure. Conversely, sucking on the tube causes the membrane to bulge inward due to higher external pressure.

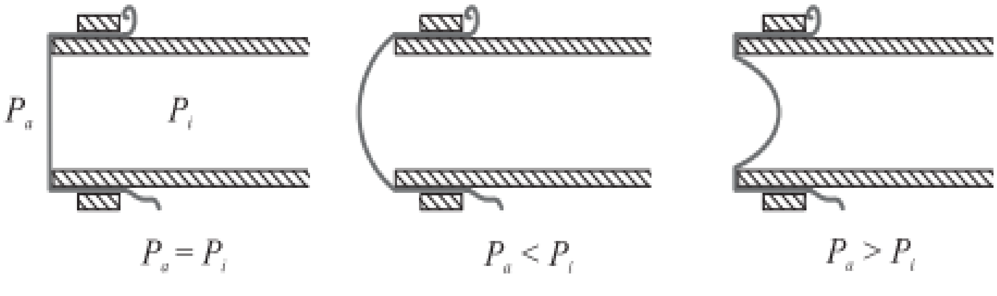


Figure II.2: Rubber membrane at the end of a cylindrical tube. An inner pressure Pi can be applied, which is different than the outside pressure Pa .

The Young-Laplace equation relates the pressure difference between the two phases ΔP and the curvature of the surface:

$$\Delta P = \gamma \left(\frac{1}{R1} + \frac{1}{R2}\right) \qquad (II.1)$$

R1 and R2 are the two principal radii of curvature. ΔP is also called Laplace pressure.

The Young–Laplace equation has several fundamental implications:

- If we know the shape of a liquid surface we know its curvature and we can calculate the pressure difference.

- In the absence of external fields (e.g. gravity), the pressure is the same everywhere in the liquid; otherwise there would be a flow of liquid to regions of low pressure. Thus, ΔP is constant and Young-Laplace equation tells us that in this case the surface of the liquid has the same curvature everywhere.

With the help of the Young–Laplace, it is possible to calculate the equilibrium shape of a liquid surface. If we know the pressure difference and some boundary conditions (such as the volume of the liquid and its contact line) we can calculate the geometry of the liquid surface. These considerations are valid for any small part of the liquid surface. Since the part is arbitrary the Young–Laplace equation must be valid everywhere.

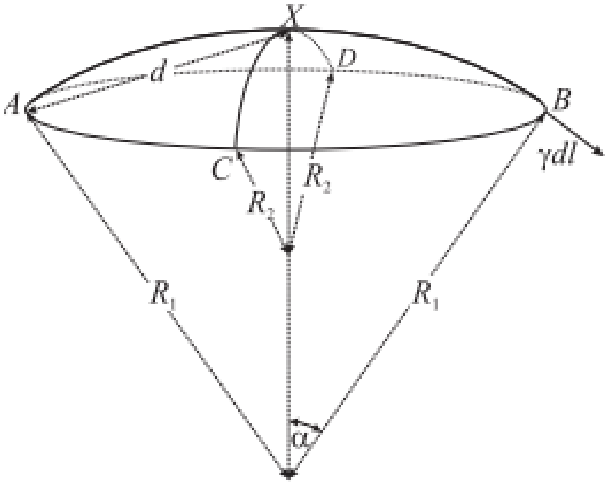


Figure II.3: Diagram used for deriving the Young–Laplace equation.

For a drop in a gaseous environment, the two principal curvatures are positive and given by $C_1 = C_2 = 1/R$. The pressure difference is positive, which implies that the pressure inside the liquid is higher than outside. For a bubble in a liquid environment the two principal curvatures are negative: $C1 = C2 = -1/R$. The pressure difference is negative and the pressure inside the liquid is lower than inside the bubble. For a drop hanging between the ends of two cylinders in a gaseous environment, one curvature is conveniently chosen to be $C_1 = 1/R_1$. The other curvature is negative, $C_2 = -1/R_2$. The pressure difference depends on the specific values of R_1 and R_2.

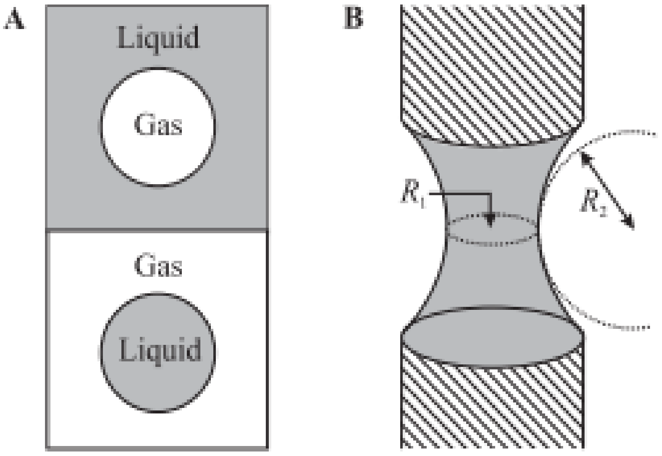


Figure II.4: (A) A gas bubble in liquid and a drop in a gaseous environment. (B) A liquid meniscus with radii of curvature of opposite sign between two solid cylinders.

The shape of a liquid surface is determined by the Young–Laplace equation. In large structures we have to consider also the hydrostatic pressure. Then the equation of Young and Laplace becomes:

$$\Delta P = \gamma\left(\frac{1}{R1}+\frac{1}{R2}\right)+\rho g h \qquad (II.2)$$

Here, g is the acceleration of free fall and h is the height coordinate.

II.2.3 The Kelvin equation

The Kelvin equation, akin to the Young-Laplace equation, universally describes the relationship between a liquid's vapor pressure and surface curvature. Droplets exhibit higher vapor pressure than flat surfaces, while bubbles experience reduced vapor pressure due to Laplace pressure. Elevated Laplace pressure in droplets promotes faster evaporation, while reduced pressure around bubbles impedes evaporation.

$$RTln\frac{P_0^K}{P_0} = \gamma V_m\left(\frac{1}{R1}+\frac{1}{R2}\right) \qquad (II.3)$$

P^K_0 is the vapor pressure of the curved, P0 that of the flat surface. At thermodynamic equilibrium, the curvature of a liquid surface is constant everywhere. V m is the molar volume of the liquid. For a sphere-like volume of radius r, the Kelvin equation can be simplified:

$$RTln\frac{P_0^k}{P_0} = \frac{2\gamma V_m}{r} \qquad (II.4)$$

In general, any change in the Gibbs free energy is given by the fundamental equation dG = V dP − SdT. The increase of the Gibbs free energy per mole of liquid, upon curving, at constant temperature is:

$$\Delta G_m = \int_0^{\Delta P} V_m \, dp = \gamma \; V_m \left(\frac{1}{R1} + \frac{1}{R2}\right) \qquad (II.5)$$

For a spherical drop in its vapor, we simply have ΔG m = 2γV m /r. The molar Gibbs free energy of the vapor depends on the vapor pressure P0 according to the formula:

$$G_m = G_m^0 + RT \; lnP_0 \qquad (II.6)$$

The change of the molar Gibbs free energy inside the vapor due to curving the interface is therefore

$$\Delta G_m = G_m^K - G_m = RTln\frac{P_0^K}{P_0} \qquad (II.7)$$

Since the liquid and vapor are supposed to be in equilibrium, the two expressions must be equal. This immediately leads to the Kelvin equation.

Bubble in a liquid: From previous equation, a negative sign has to be used for a bubble because of the negative curvature of the liquid surface. As a result:

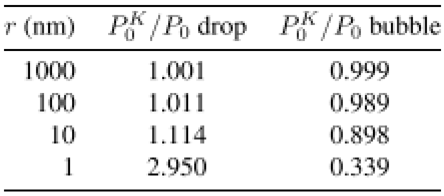
$$RTln\frac{P_0^K}{P_0} = -\frac{2\gamma V_m}{r} \qquad (II.8)$$

An important application of the Kelvin equation is the description of capillary condensation. This is the condensation of vapor into capillaries or fine pores even for vapor pressures below P0; P0 is the equilibrium vapor pressure of the liquid with a planar surface. The situation is analogous to that of a bubble and we have the equation II.8.

Capillary condensation leads to strong liquid adsorption into porous materials and the emergence of capillary forces, also known as meniscus forces. This phenomenon reinforces adhesion among fine particles and often governs powder behavior. When two particles come into contact, liquid, typically water, condenses into the gap between them, creating a curved meniscus. Consequently, the Laplace pressure in the liquid becomes negative, causing attraction between the particles. The capillary force is a result of this phenomenon. The capillary force is given by:

$$F = 2\pi\gamma R \qquad (II.9)$$

Table II.2: Relative equilibrium vapor pressure of a curved water surface at 25°C for spherical drops and bubbles of radius r.



r (nm)	P_0^K/P_0 drop	P_0^K/P_0 bubble
1000	1.001	0.999
100	1.011	0.989
10	1.114	0.898
1	2.950	0.339

II.2.4 Nucleation theory

The variation in vapor pressure with the curvature of a liquid surface impacts condensation and bubble formation during boiling. Homogeneous nucleation, where a new phase emerges without external surfaces, involves the formation of small molecular clusters that grow through condensation and aggregation. This process leads to the creation of macroscopic drops when vapor pressure significantly exceeds saturation levels. In contrast, heterogeneous nucleation occurs when vapor condenses onto surfaces like dust particles. A common example is observed when pouring sparkling water into a glass, where bubbles nucleate and ascend from the glass surface. Homogeneous nucleation theory dates back to 1920–1935, explaining the emergence of new phases in vapor. This process contrasts with heterogeneous nucleation, where vapor condensation occurs on external surfaces. The classical theory of homogeneous nucleation elucidates the formation of small clusters evolving into macroscopic drops. In order to describe nucleation, we calculate the change in the Gibbs free energy for the condensation of n moles vapor at a vapor pressure P, into a drop, with n is much smaller than one. To calculate the change in Gibbs free energy we first consider G_L-G_V. Here, G_L is the Gibbs free energy of the liquid drop and G_V is the Gibbs free energy of the corresponding number of molecules in the vapor phase. G_V is given by:

$$G_V = nG^0 + nRTlnP \qquad (II.10)$$

This, however, is not the whole energy difference. In addition, the drop has a surface tension which has to be considered. The total change in the Gibbs free energy is:

$$\Delta G = -nRTln\frac{P}{P_0^K} + 4\pi\gamma r^2 \qquad (II.11)$$

In a drop of radius r there are n = $4\pi r^3/3V$ m moles of molecules, where V m is the molar volume of the liquid phase. Inserting leads to:

$$\Delta G = \frac{4\pi RTr^3}{3V_m} ln\frac{P}{P_0^K} + 4\pi\gamma r^2 \qquad (II.12)$$

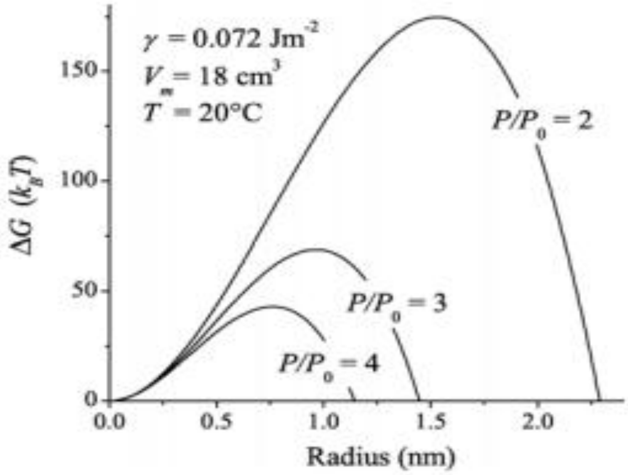


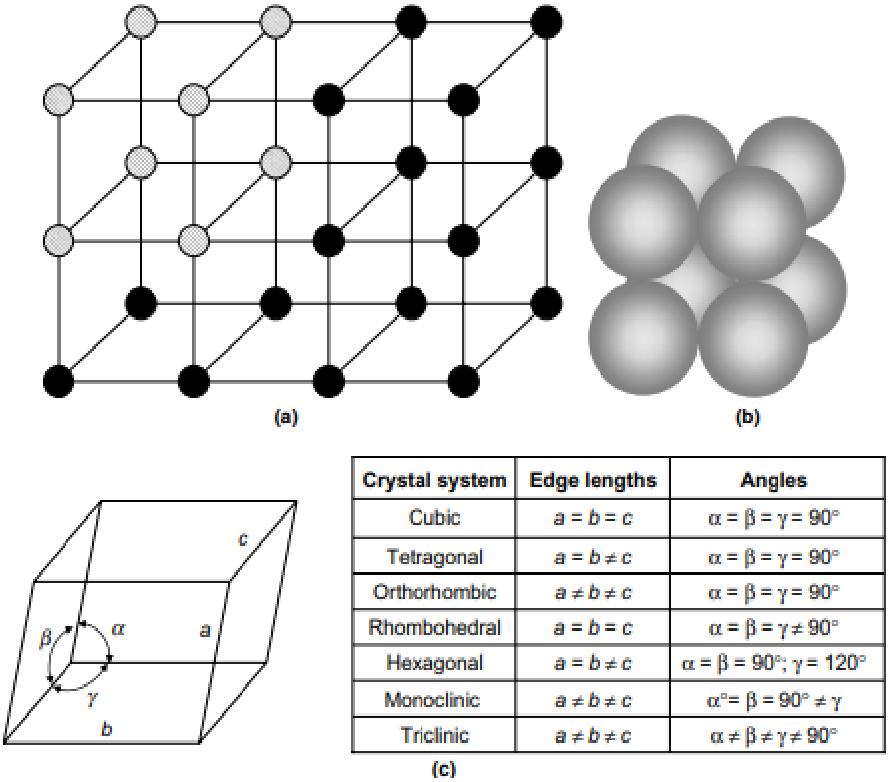
Figure II.5: Change of Gibbs free energy for the condensation of vapor to a drop of a certain radius.

II. 3 Structure of solid surfaces

The surfaces of most solids do not exhibit crystalline structures. This fact holds true not only for amorphous solids but also for the majority of crystalline or polycrystalline materials. The reason behind this is that, in many cases, the molecular arrangement on the surface differs from that in the bulk material. In fact, under typical ambient conditions, many surfaces undergo oxidation. An illustrative instance of this is aluminum, which promptly forms a robust oxide layer upon exposure to air. Interestingly, even in an environment devoid of reactivity, like an inert atmosphere or ultrahigh vacuum (UHV), surface molecules can give rise to an amorphous layer atop the underlying crystalline bulk solid.

II.3.1 Structure of crystalline surfaces

Materials in solid form exhibit a crystalline structure, with atoms arranged periodically in three dimensions within a single crystal. This periodic structure is represented by a point lattice, with atoms occupying lattice sites. The lattice is composed of repeating unit cells, depicted in Figure I.1 (a), with their size and shape described by lattice parameters—lengths of the three axes and angles between them. While Figure II.1 (b) offers a more accurate depiction, Figure II.1 (a) is commonly used for demonstration due to its simplicity.



Crystal system	Edge lengths	Angles
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°; \gamma = 120°$
Monoclinic	$a \neq b \neq c$	$\alpha° = \beta = 90° \neq \gamma$
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$

Figure II.6: (a) Crystal lattice. (b) Solid ball model. (c) The seven crystal systems.

II.3.1.1 Bulk Structures of Crystals

Crystalline surfaces are categorized into five Bravais lattices based on their symmetry, determined by lattice angle α and lengths of lattice vectors. Seven-unit cell types exist, stemming from permutations of lattice parameters, as depicted in Figure II.7. Predominant lattice structures in metals and alloys are face-centered cubic, body-centered cubic, and hexagonal. The actual arrangement of atoms in a crystal, termed the crystal structure, accounts for lattice structures, unit cell dimensions, and axis angles. While 14 lattice structures exist, the potential crystal structures are infinite considering various lattice parameters. The three most common basic crystal structures are fcc, hcp, and bcc.

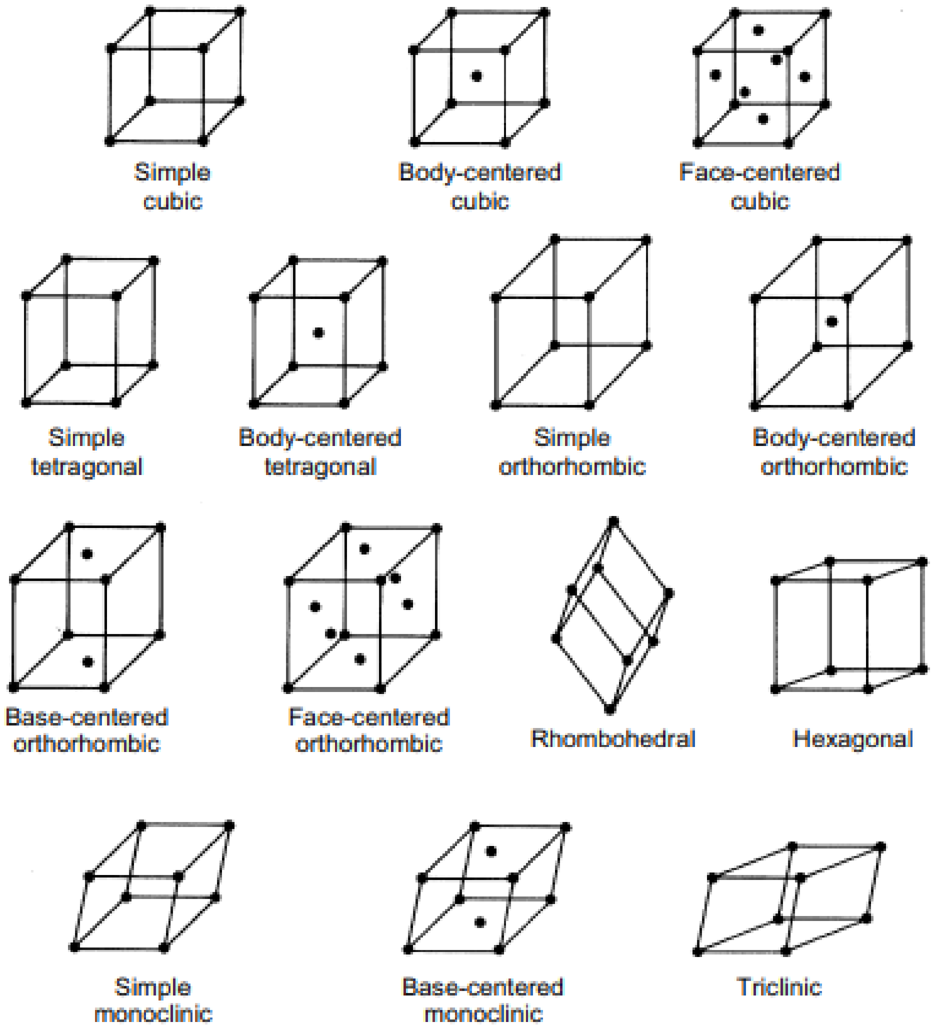


Figure II.7. The 14 lattice structures.

II.3.1.2 Miller Indices (hkl)

Surface or crystal plane orientation is defined by the intersection with primary crystallographic axes, determined by Miller Indices (hkl), facilitating unique identification of the plane. This process, focused on cubic crystal systems, simplifies with a step-by-step guide, considering an ideal crystal cut along a specific plane. Miller Indices, introduced by William Hallowes Miller, characterize plane orientation within a lattice concerning the unit cell. To determine Miller indices, intersections with crystal axes are expressed in terms of lattice constants, and inverse values are taken, then simplified to obtain a set of three integers (hkl). Negative values are denoted as ¯n, and {hkl} notation specifies symmetrical equivalent planes, like {100} in cubic crystals.

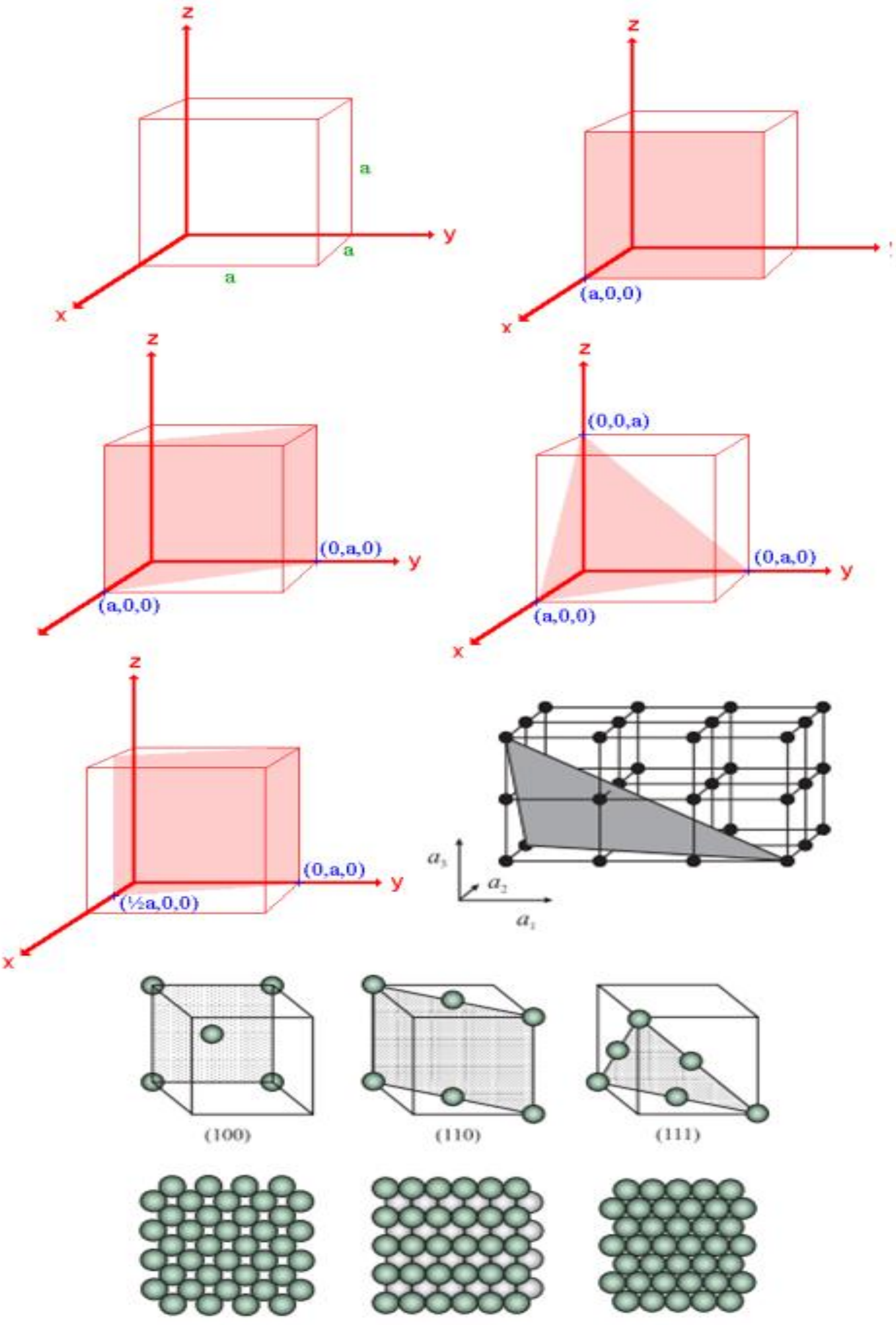
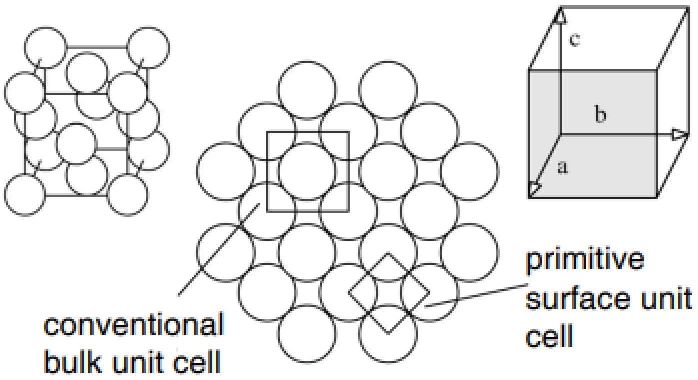
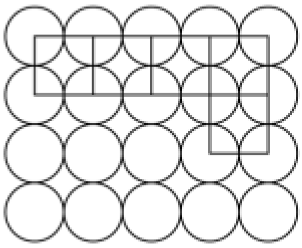


Figure II.8: Notation of a cutting plane by Miller indices. The three-dimensional crystal is described by the three-dimensional unit cell vectors a1, a2, and a3. The indicated plane intersects the crystal axes at the coordinates (3, 1, 2). The inverse is (1/3, 1/1, 1/2). The smallest possible multiplicator to obtain integers is 6. This leads to the Miller indices (263).

Example 1:

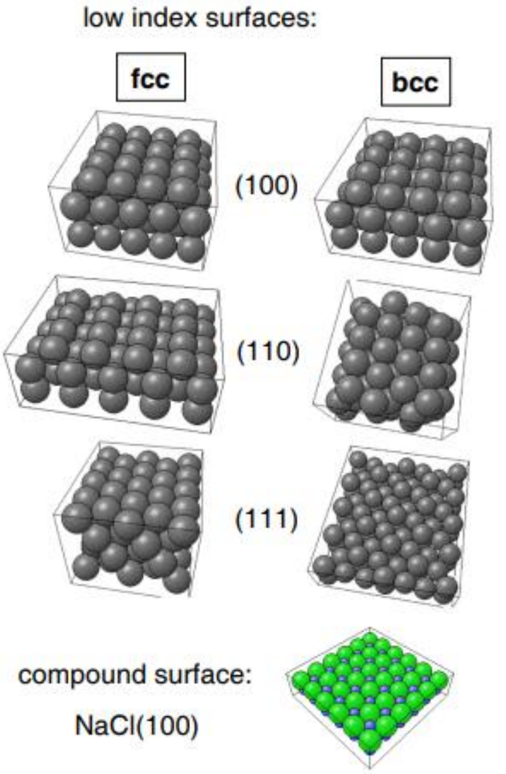
Au (100) surface





primitive cell obeys translation symmetry

Example 2:



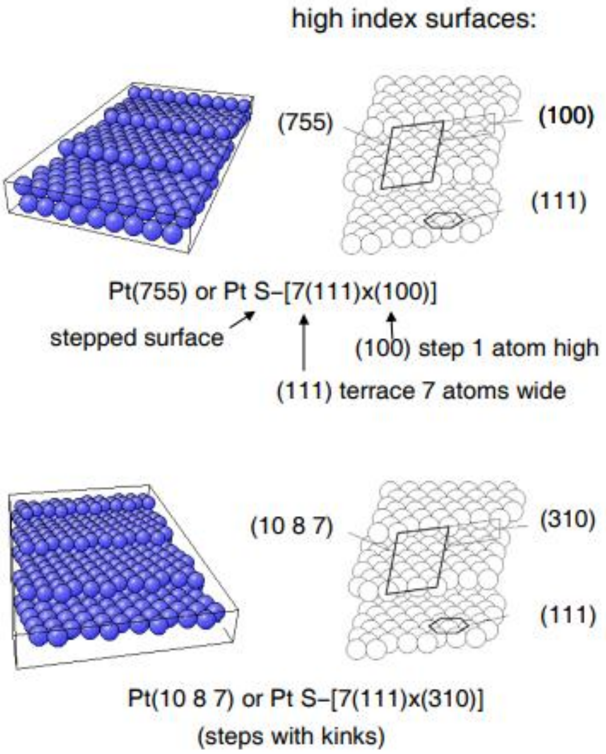
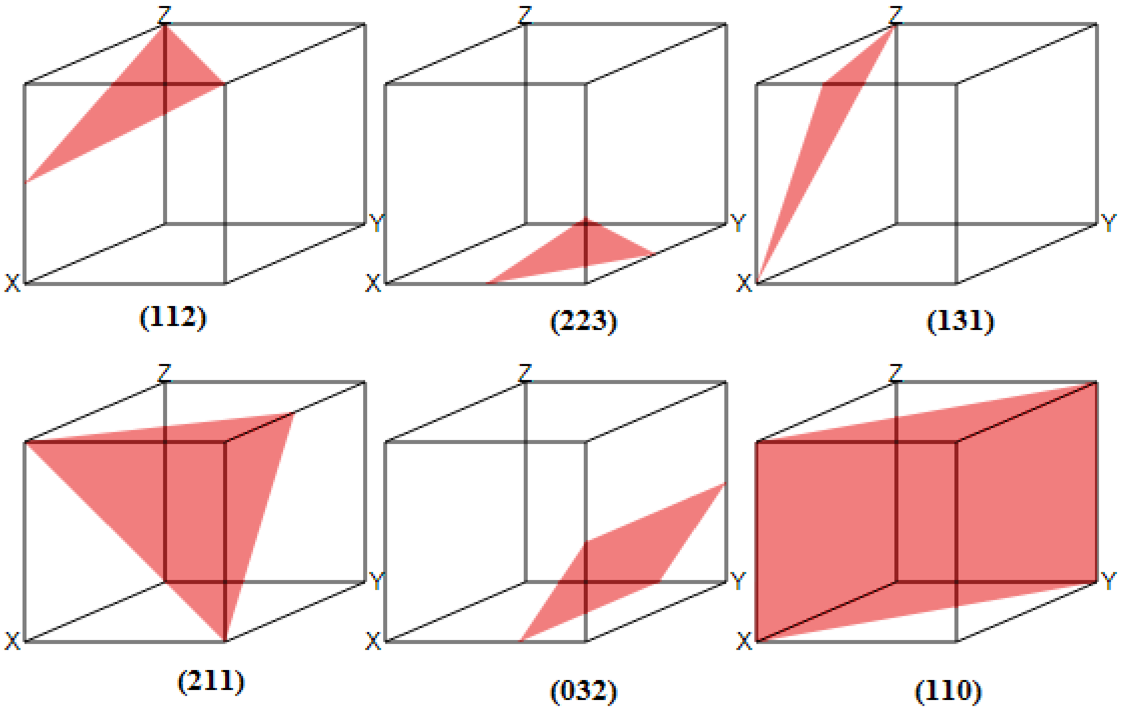


Table II. 3: crystal structure of some the more important metallic elements.

Face-Centered Cubic	Closed-Packed Hexagonal	Body-Centered Cubic
Iron (911.5 to 1396°C)	Magnesium	Iron (below 911.5 and from 1396 to 1538°C)
Copper	Zinc	Titanium (882 to 1670°C)
Silver	Titanium (below 882°C)	Zirconium (863 to 1855°C)
Gold	Zirconium (below 863°C)	Tungsten
Aluminum	Beryllium	Vanadium
Nickel	Cadmium	Molybdenum
Lead		Alkali Metals (Li, Na, K, Rb, Ca)
Platinum		

Exercise 1:

1. Identify the planes



2. What is the coordination number of the surface layer atoms on the fcc(100) surface, fcc(110) surface and on the fcc(111) surface??
3. Do the atoms in the second layer have the bulk coordination?

Response:

1. in the case of surface atoms, each atom is in proximity to four neighboring atoms within the first layer and an additional four in the layer directly beneath it, resulting in a total of eight neighboring

atoms. The coordination number of the topmost layer atoms on the fcc(100) surface is 7. This can be explained that each surface atom in the topmost layer has two nearest neighbors in the same layer, forming a pair. Additionally, there are four more nearest neighbors in the layer immediately below the surface layer, making a total of 6 nearest neighbors within the first two layers. However, there is one more nearest neighbor directly below the surface atom in the third layer. This atom is positioned right beneath the surface atom, and it contributes to the coordination of the surface atom. To confirm this, we can consider the atoms that have been removed from the layers above the surface layer. Specifically, there would have been 4 nearest neighbors in the layer immediately above the surface layer, equivalent to the four in the layer immediately below. Additionally, there would have been one nearest neighbor directly above each surface atom in the topmost layer, equivalent to the one directly below in the third layer. Therefore, when we account for the removed atoms from the layers above, we have 7 present nearest neighbors and 5 removed nearest neighbors, which adds up to the correct bulk coordination number of 12 for fcc metals. So, the coordination number of 7 for the topmost layer atoms is indeed consistent with the crystallographic structure.

The coordination number of the surface layer atoms is 9.

2. No, the fact that they are clearly visible at the surface implies that they have a lower CN than they would in the bulk.

Exercise 3 :

Determine the diffraction angle (θ) for the crystallographic planes represented by [220]. Given that the lattice parameter for iron is 0.2866 nm, the wavelength of the incident radiation is 0.179 nm, and we are dealing with the first-order reflection.

Response:

We have: $2\ d\sin\theta = n\lambda$

With: $\lambda=0.179$ nm, $n=1$, $a=0.2866$ nm, $(h,k,l)=[220]$

Half diffraction angle is given by

$\sin\theta = n\lambda = 2d$

For the cubic crystal structure, the intermolecular distance,

$d=d_{h,k,l}=\frac{a}{\sqrt{h^2+k2+L2}}=0.2866/\sqrt{8}=0.1013$ nm

So: $\theta=\sin^{-1}(1\times0.179)/2\times0.1013=62.13$

The diffraction angle:

$2\theta = 2\times 62.13 = 124.26°$.

II. 3.2 Surface relaxation and reconstruction

Atoms on the surfaces of solids often have missing neighbors on one side, leading to an inherent asymmetry. Consequently, the topmost surface atoms tend to adopt structures different from those found in the bulk material. To compensate for these missing bonds, they may form dimers or more complex structures to bond with the exposed dangling bonds. (Table II.4).

- **Surface relaxation**, a phenomenon observed in metals, involves an alteration in the distance between the topmost atomic layers while maintaining the lateral spacing of surface atoms. This change is primarily caused by the presence of a dipole layer at the metal surface, resulting from the distortion of electron wavefunctions at the surface.
- **Surface reconstruction** is the term used when the lateral distances between atoms on the surface are modified. This phenomenon is notably observed on the (100) crystallographic faces of materials like gold (Au), iridium (Ir), platinum (Pt), and tungsten (W). Surface reconstruction can lead to a doubling of the lattice spacing in one direction. Semiconductor surfaces are also prone to surface reconstruction due to the directional nature of the dangling bonds on their surfaces.

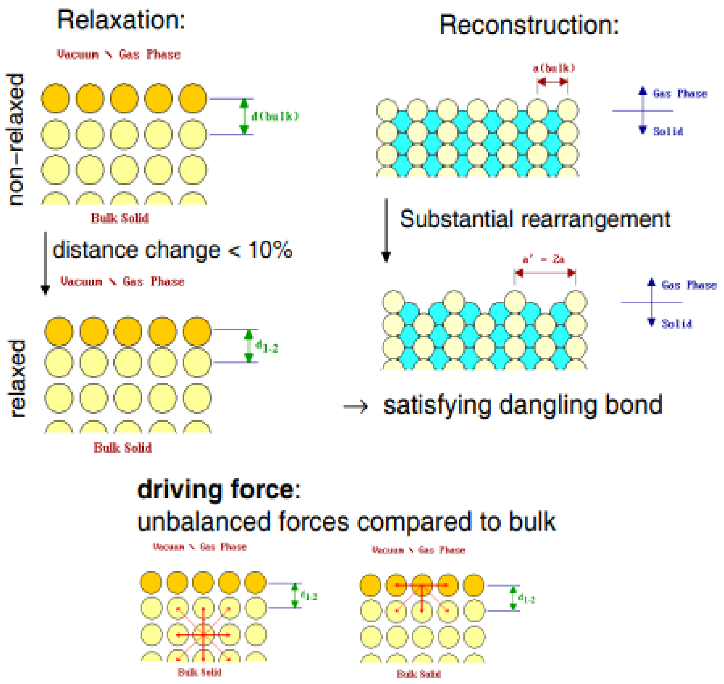


Figure II.9: Typical reconstructions of face centered cubic (110) surfaces.

Generally, surface structures can become more intricate when each lattice site accommodates more than one atom. To describe this, the concept of a "basis" is introduced, which signifies the fixed relative arrangement of these atoms or molecules. In such cases, providing both the lattice type and the basis becomes necessary for a comprehensive depiction of the crystal structure. Additionally, if surface atoms are situated at varying heights, the basis must be extended to more than just the surface layer of atoms.

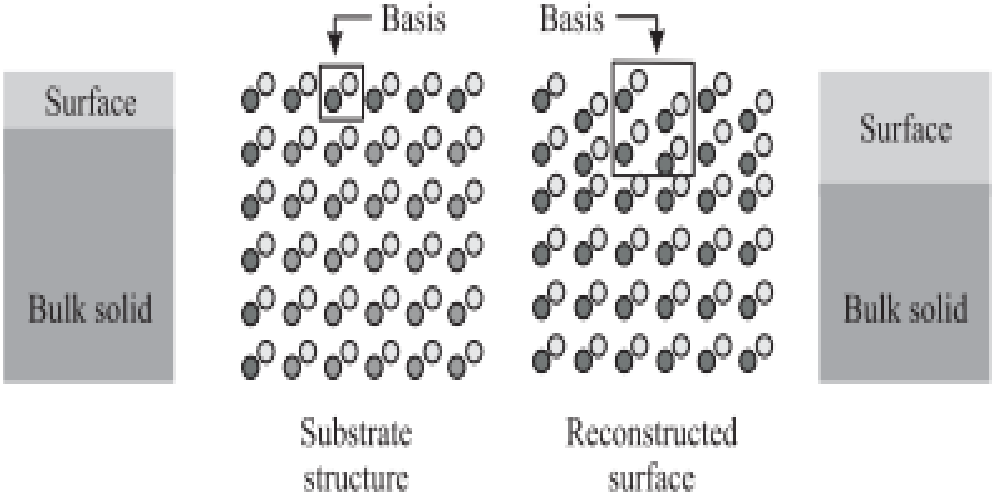


Figure II.10: Example of the necessary extension of the basis in the case of surface atoms positioned at different heights.

Table 4. Reduction of the interlayer spacing between the two top layers as compared to the bulk due to surface relaxation for the (110) surfaces of unreconstructed Cu, Ni, Au, and Pd.

Cu	Ni	Au	Pb
0.020 Å	0.156 Å	0.125 Å	0.080 Å

For reconstructed, crystalline surfaces the position vectors of the atoms have to be described by new unit cell vectors b1 and b2 and the surface structure is denoted in the form A (hkl) (p×q)

Where: A is the chemical symbol of the substrate; p and q being intergers.

Example 3:

The Gold (111) surface is an example of a surface without reconstruction and is represented as Au(111)(1 × 1). On the other hand, the (100) surface of silicon displays a (2 × 1) reconstruction, indicated as Si(100)(2×1). Another illustration of a complex surface reconstruction is the 7×7 surface reconstruction observed in Si(111).

II.3.3 Adsorbate structures

When molecules adhere to a crystalline surface, they frequently create a crystalline layer on top of it, known as a superlattice. This happens when the adsorbates exhibit a preference for specific sites on the surface. This together leads to the so-called Wood's notation: **A (hkl)c(p'×q') Rβ-B**.

With: A and B are the chemical symbols of substrate and adsorbate, respectively.

c is added in case of centered unit of adsorbate. p' and q' are integers.

The structure of the adsorbate lattice is expressed by the ratios of the lengths of the unit cell vectors: p'= c1/b1 and q'= c2/b2. If the adsorbate lattice is rotated with respect to the underlying substrate lattice by an angle β, the value of β preceded by an "R" is indicated. In general, the adsorption of atoms (e.g., Na, S, Cl) leads to high coordination surface sites on metal surfaces, while the smaller atomic adsorbates (H, C, N, O) conduced to high coordination and penetration within substrate.

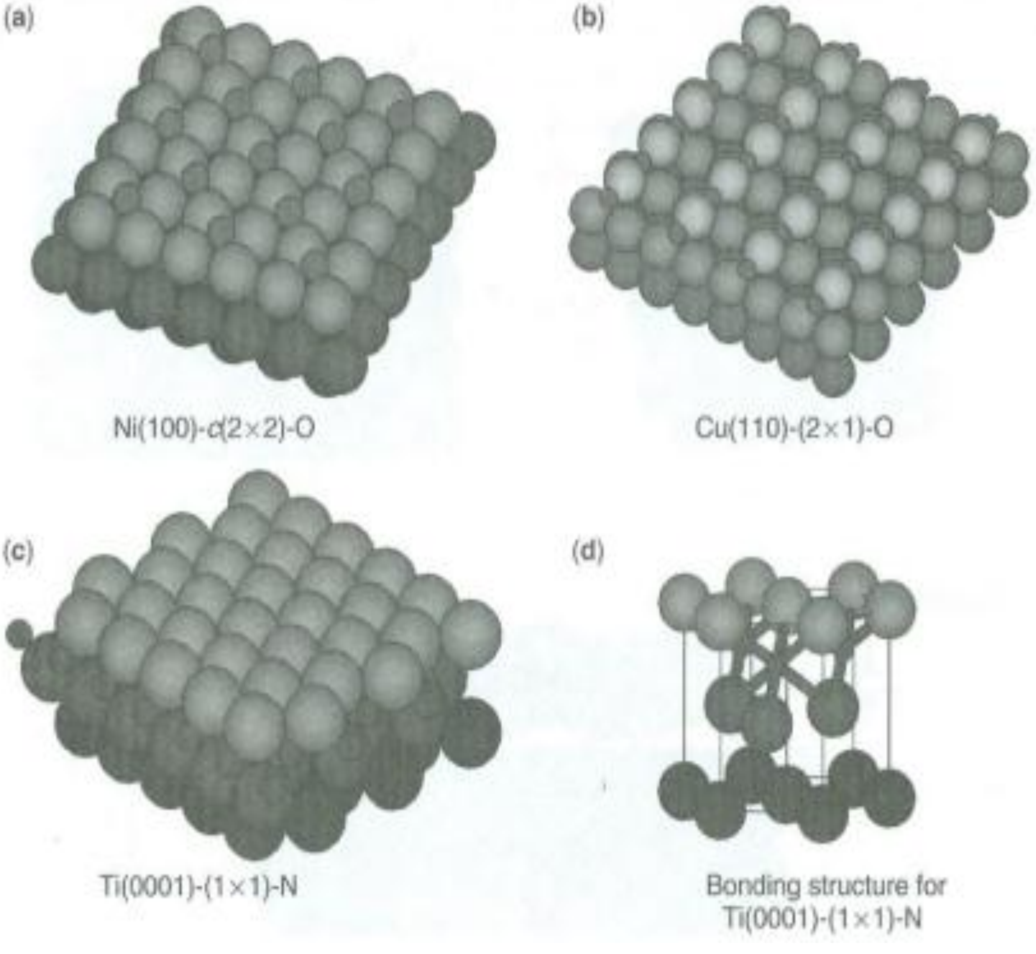


Figure II.11: (a) the O surface structure on Ni(100); (b) the O chemisorption induced surface structure on Cu(110); (c) the N surface structure on Ti(0001) and (d) the bonding structure for N on Ti(0001)

Example 5: adsorbate can also induce a new surface restructuring

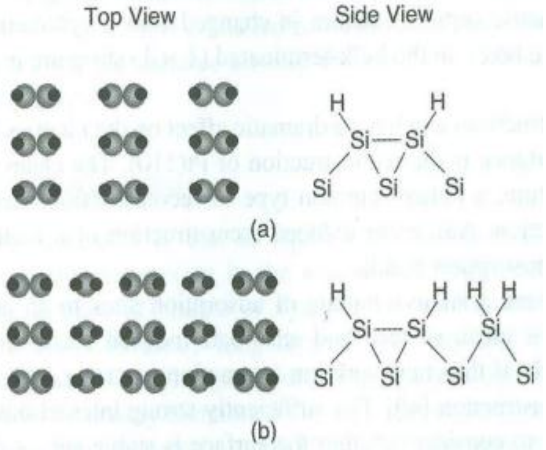


Figure II.12: The adsorption of H on to Si(100): (a) Si(100)-(2×1)H and (b) Si(100)-(3×1):H.

II.3.4 Surface steps and defects

Crystal defects have strong influence upon many properties of crystals, such as strength, electrical conductivity and hysteresis loss of ferromagnets. Thus, some important properties of crystals are controlled by as much as by defects and by the nature of the host crystals. For instance: the conductivity of some semiconductors is due entirely to trace amount of chemical impurities. Color, luminescence of many crystals arises from impurities and defects. Atomic diffusion may be accelerated enormously by impurities or defects. Mechnical and plastic properties are usually controlled by imperfections.

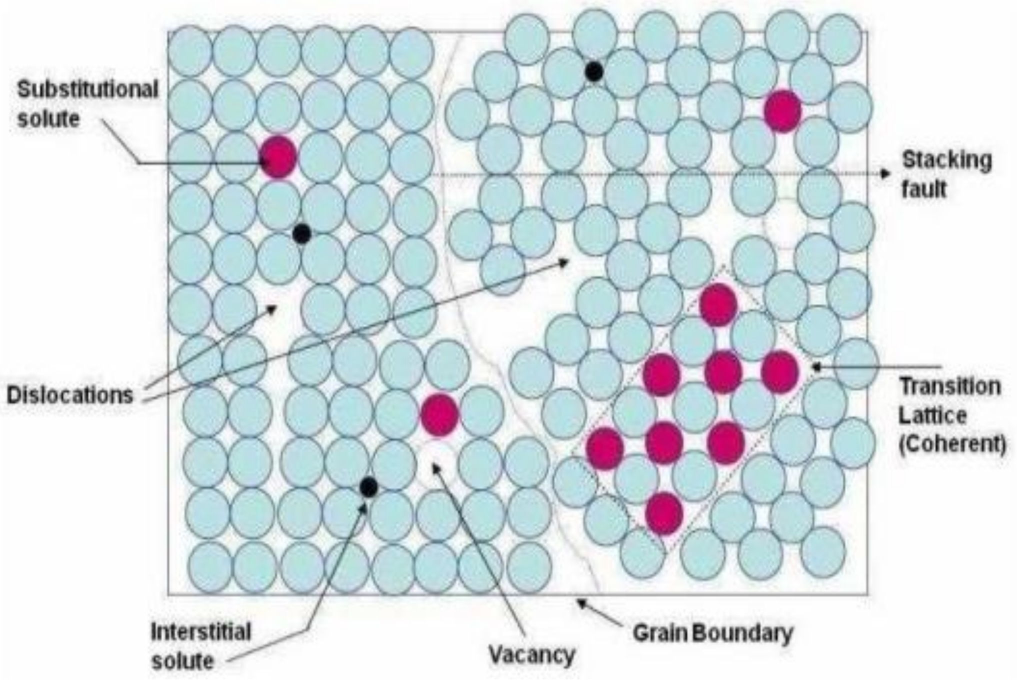


Figure II.13: Various crystal defects.

A few different types of defects exist within the crystal lattice of a metal or alloy. These defects are different from the manufacturing artifacts mentioned earlier in this chapter. Vacancies, interstitials, and substitutions are three of them.

■ **A vacancy** is where an atom is missing from its lattice site. The number of vacancies in a metal crystal increases as the temperature increases.

■ **An interstitial** is an atom that occupies the space between the atoms on the lattice sites. Interstitial atoms must be small (e.g., hydrogen, carbon, and nitrogen) in order to fit into the spaces between the atoms on the lattice sites. The number of interstitial sites in a metal crystal is constant.

■ **A substitution** is the occupation of a lattice site by an atom of a different element.

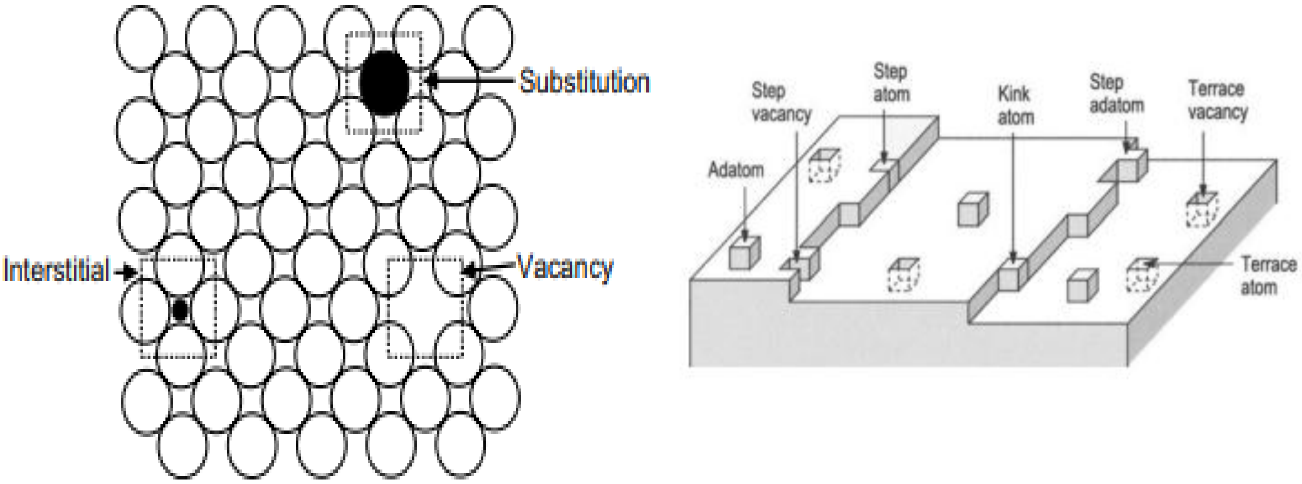
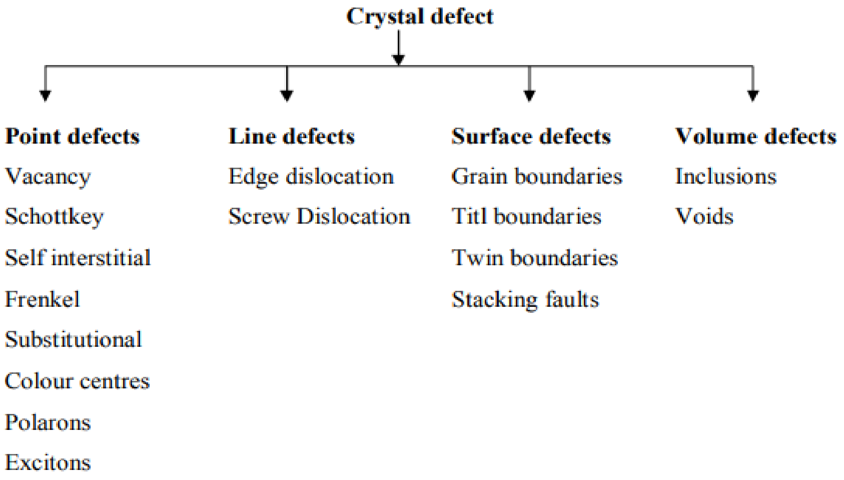


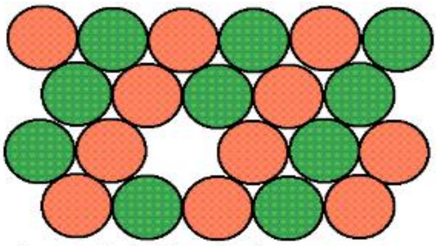
Figure II.14: Schematic of an interstitial, vacancy, and substitution.



II.3.4.1 Point Defects

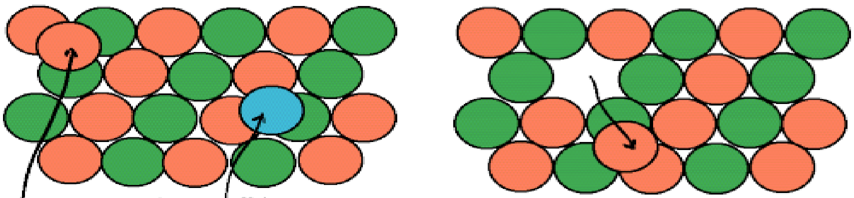
- ✓ **Stoichiometric Defect:** This type of point defect is characterized by maintaining the ratio of positive and negative ions, thereby preserving the electrical neutrality of the solid. It is sometimes referred to as an intrinsic or thermodynamic defect. In other words, this kind of defects doesn't change the symmetry of the solid. There are essentially two fundamental types of these defects :

1. **Vacancy Defect:** This defect occurs when an atom is absent from its designated lattice site, leaving that site vacant and resulting in a vacancy defect. As a consequence, the substance experiences a decrease in density.



An empty lattice site is a vacancy

2. **Interstitial Defect:** In this type of defect, an atom or molecule occupies the intermolecular spaces within the crystal lattice. This defect leads to an increase in the substance's density.

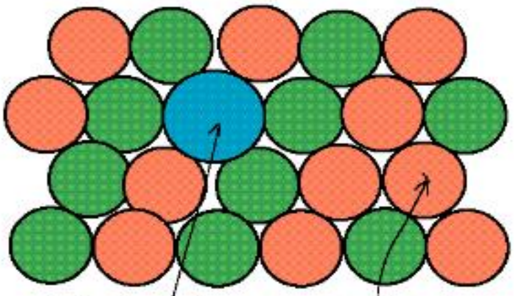


An interstitial is an off-lattice atom which may be a foreign atom or a regular atom

An interstitial may form by an atom moving to an off-lattice site and create a vacancy at the same time

Interstitials An Interstitial is an atom on a non-lattice

3. **Impurity Defect:** When molten NaCl crystallizes with SrCl2, Sr2+ ions replace two Na+ ions, leaving a vacant lattice site. This vacancy constitutes an impurity defect in the crystal structure. Point defects in crystals typically range from 0.1% to 1% of atomic sites, crucial for controlling color and deformation. However, advancements allow the growth of extremely pure materials, affecting defect concentrations and movement.



A foreign atom, or a regular atom out of place, is an impurity.

Non-ionic compounds primarily exhibit vacancy and interstitial defects, while **ionic compounds** manifest similar defects in the forms of Frenkel and Schottky defects.

4. **Frenkel Defect:** In ionic solids, a common phenomenon involves the smaller ion, which is typically the cation, moving from its original position to occupy an interstitial space within the crystal lattice. This relocation results in the creation of a vacancy defect at its original site and an interstitial defect at its new location. This type of defect is also referred to as a dislocation defect. Importantly, it does not alter the density of the substance. Dislocation defects tend to occur when there is a significant disparity in the sizes of the anions and cations within the compound.

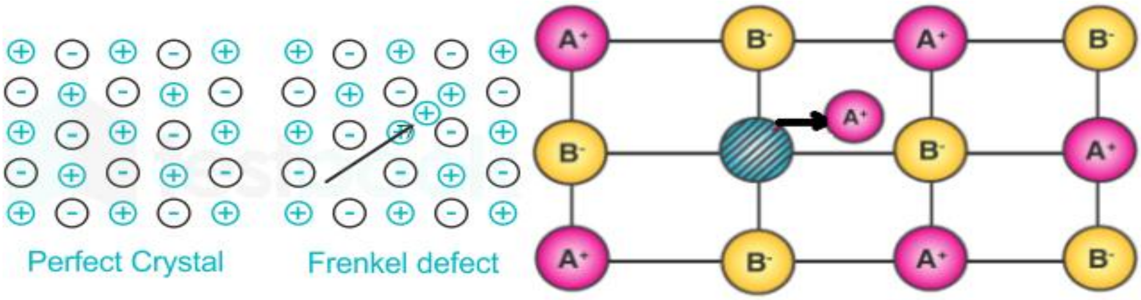
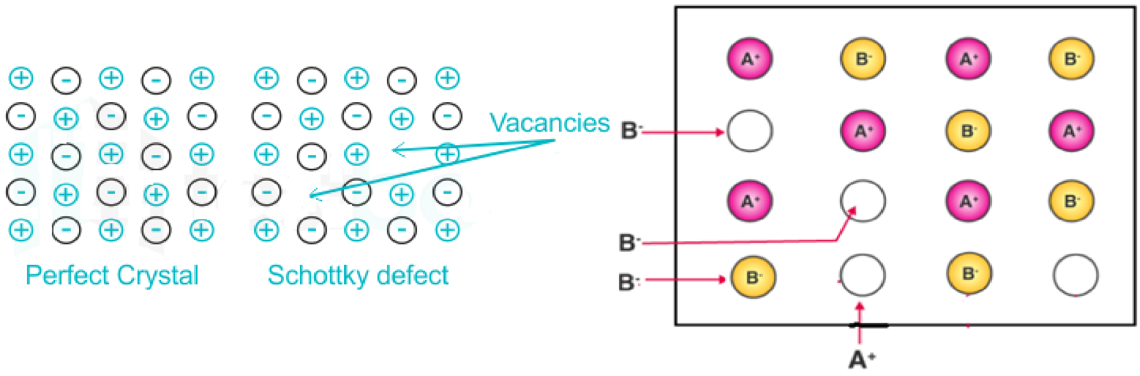


Figure II.15: Frenkel Defect.

Examples of compounds exhibiting this behavior include ZnS, AgI, AgBr and AgCl, etc.

5. **Schottky Defect:** This type of vacancy defect is commonly observed in ionic solids. In ionic compounds, it is essential to maintain the electrical neutrality of the compound, which means an equal number of anions and cations will be missing from the compound due to these defects. As a result of these vacancy defects, the density of the substance is reduced. This phenomenon typically occurs when the sizes of cations and anions in the compound are relatively similar.



Figure

II. 16: Schottky Defect.

Examples: NaCl, CsCl, KCl, AgBr, etc.

- **Non-stoichiometric defects**

These types of defects disrupt the stoichiometry of the compounds. They occur when the number of cations and anions is not present in the equal ratio, as indicated by the chemical formula. This defect can be happened due to two reasons:

- In a lattice, substances have a cation whose proportion is more than in an anion. Hence, known as a metal excess defect.
- In a lattice, substances have a cation whose proportion is lesser than in an anion. And hence known as the metal deficiency defect.

These defects can manifest in the following ways.

a) **Metal excess defects**: Metal excess defects occur when there's an excess of metal cations compared to anions in a lattice, involving the presence of free electrons. Unlike Schottky and Frenkel defects, they don't involve holes or interstitial electrons. These defects can generate electricity and often exhibit color due to the presence of free electrons. Anionic sites occupied by unpaired electrons are termed F centres, responsible for the crystal's color by absorbing energy from visible light. Examples include yellow (NaCl), pink (LiCl), and violet (KCl) colors.

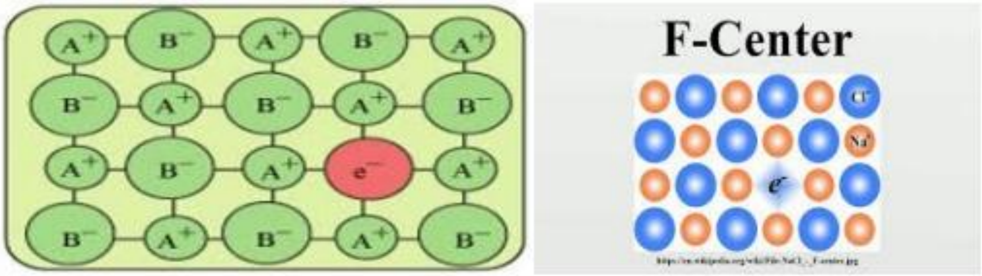


Figure II.17: Metal excess defects.

Two additional types of defects in crystal lattices are anionic vacancies and extra cations.

b) **An anionic vacancy** occurs when electrons fill the space left by a released anion, forming an f-center and causing colored centers in the lattice. This defect is common in ionic compounds like NaCl and LiCl.

c) **Extra cations defects** involve additional cations occupying interstitial sites, introducing a positive charge. To maintain electrical neutrality, an appropriate number of electrons accompany these extra cations. This phenomenon ensures the crystal's electrical balance and stability. **Example**: Zinc oxide. For example ZnO is white in color at room temperature when heated give yellow color. Now there is excess of Zn+2 in the crystal and its formula become Zn1+x. the excess Zn+2 ions moves to the interstitial sites and electron to the neighboring interstitial site when these electron are excited by absorbing energy from the visible light and thus show color to the crystal.

$$ZnO \xrightarrow{Heat} Zn^{2+} + \frac{1}{2} O_2 + 2e^-$$

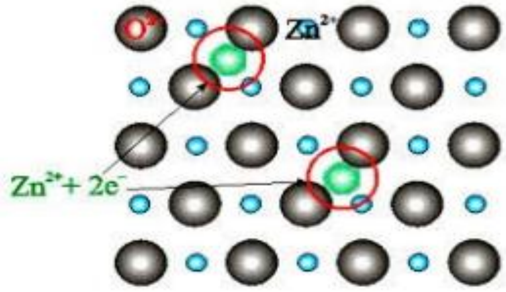


Figure II.18: Zn excess defect due to Zn-cations.

d) **Metal deficiency defect:** Solids cannot be prepared in the composition of stoichiometric and hence vary lower amounts of metals, (for example-FeO). It happens when in a lattice, cation has less ratio than in anion. Different oxidation states are varied by compound cations. Negative ions sizes are comparatively large and hence it is expected that negative ions would not be fixed into interstitial positions. A positive ion may be missing from its lattice site and extra positive charge is balance by the adjacent metal ions by increasing its positive charge by 1 unit. In this defect, positive can act as a semiconductor. Examples: Iron compound crystal and copper compound crystal. This defect is shown by metals having variable valences for example Fe_2O_3 it is a mixed oxide of $FeO.Fe_2O_3(Fe_3O_4)$. It is also shown by transition metals for example dblock elements.

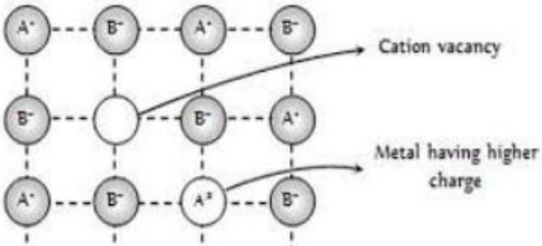


Figure II.19: Metal deficiency defect.

- **Line Imperfections:** known as dislocations, arise when groups of atoms occupy irregular positions within a crystal lattice. These deviations from a perfectly periodic arrangement along a line are considered line imperfections. Dislocations manifest as boundaries separating two regions of the surface, each structurally perfect but misaligned with respect to the other. Typically lying within the slip plane, the line imperfection is termed a dislocation and concentrates distortion along a specific line. Dislocations are generated and can move under external stress, significantly influencing the strength and ductility of metals. The two extreme types of dislocations are edge dislocations and screw dislocations..

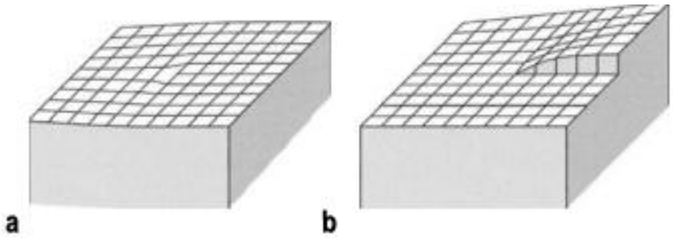


Figure II 20.: Emergence of (a) an edge dislocation and (b) a screw dislocation on the (100) surface of the TSK model crystal

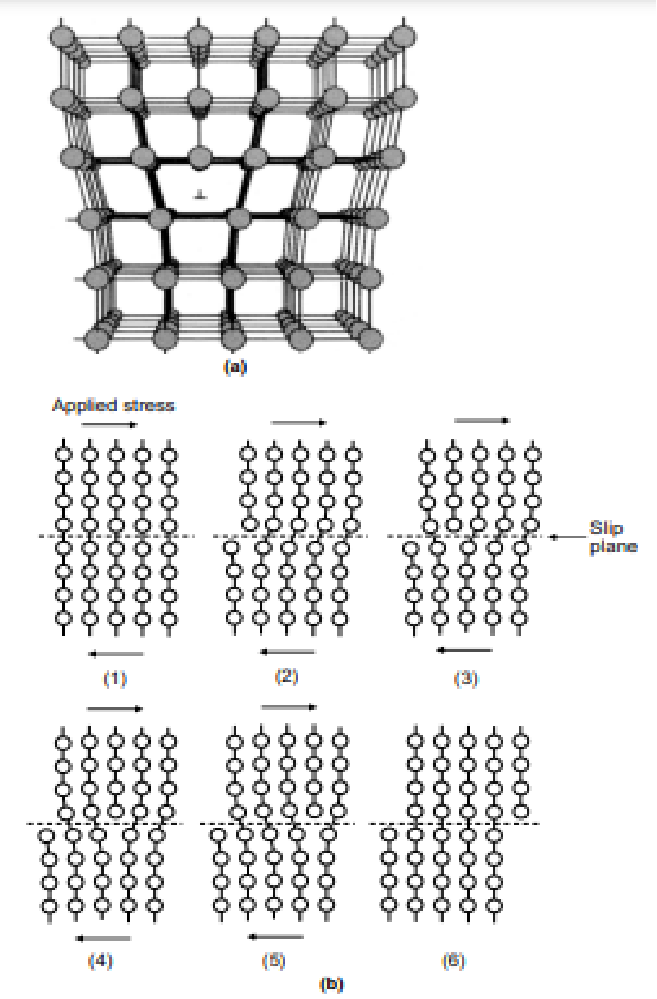


Figure II.21. Schematics of (a) a dislocation in a crystal lattice and (b) a dislocation moving through a crystal lattice.

II.3.5 Free surfaces

The interface that exists between a crystalline solid and a vapor or liquid plays a crucial role in governing the interactions between these two phases. Moreover, it has a significant influence on the behavior of the solid. Additionally, this interface affects the shape of the solid itself. The characteristics and properties of the free surface are determined by a combination of its structural features and its energy content. Importantly, these two parameters are interconnected and influence each other.

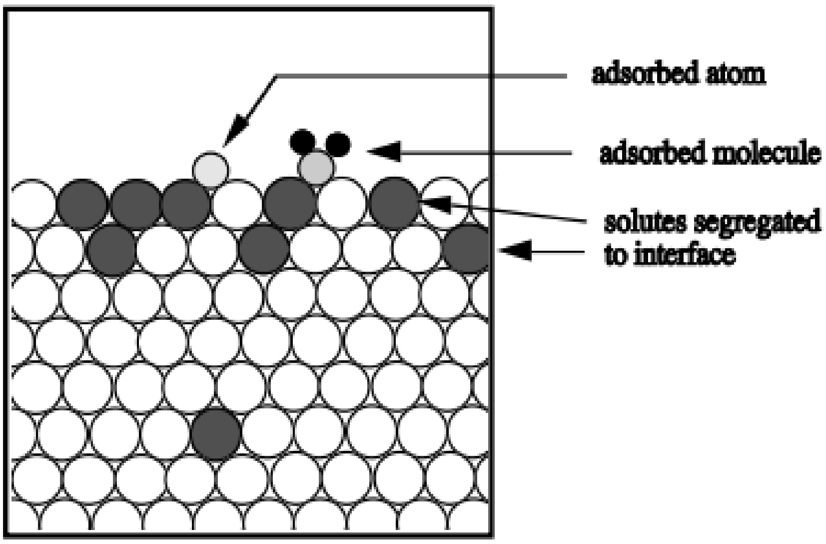


Fig. II.22: Solid surface showing segregated solutes and adsorbates.

The atomic arrangement of a solid's surface reflects the packing pattern of atoms on the parallel crystal plane. However, surface structure differs somewhat from bulk crystal planes due to one-sided bonding at the free surface. Real interfaces are complex, influenced by bonding interactions across the interface and chemical changes at the interfacial plane. Dangling bonds at interfaces attract atoms, enriching solute species like oxygen, sulfur, and phosphorus. Interfacial tension depends on disrupted bonds due to the absence of a continuous crystal structure, varying with surface orientation. Metallic solids exhibit weak orientation-dependent interfacial tension due to non-directional bonding, while covalent solids show stronger anisotropy with directional bonds. External surfaces often align with close-packed atomic planes, influencing interfacial plane structures. Non-parallel interfaces may feature stepped structures with close-packed segments, increasing surface area while maintaining lower overall surface tension. In ionic solids, the interfacial tension is strongly affected by the distribution of electric charge. In strongly ionic materials like NaCl, the electrically neutral surfaces (e.g., {100} in NaCl) have much lower interfacial tensions than the charged surfaces (e.g., {111}). The relative interfacial tensions of charged and uncharged surfaces can be altered by the addition of surfactants, which are often attracted to the charged surfaces.

a) **Crystals bounded by free surfaces** minimize total interfacial energy, often adopting shapes close to spherical in simple metals. For ionic or strongly covalent solids, crystal planes with low surface tensions lead to polygonal shapes with large, flat facets parallel to these planes, creating less spherical and more faceted crystal shapes.

b) **Interfaces between solids and liquids** exhibit diffusion, contrasting with sharp interfaces between crystalline solids and vapor. Near the solid surface in contact with the liquid, there's a high atom density, and the local arrangement may resemble the crystalline pattern. Solid-liquid interface tension weakly depends on surface orientation, resulting in a diffuse interfacial structure. This diffuse interface facilitates smooth and rapid solidification processes from a molten state, allowing atoms from the liquid to integrate seamlessly into the solid.

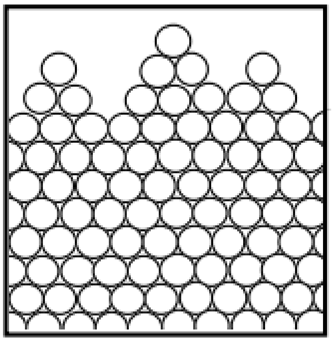


Fig. II.23: Possible configuration of a diffuse interface.

II.3.6 Interfaces between crystals

The most important internal interfaces in a typical solid are those that separate the individual crystallites it contains. Almost all crystalline solids are polycrystalline. They are composed of many small crystallites (grains) of the primary constituent and may also contain several distinct constituents (phases) of different composition and crystal structure. The interfaces that separate grains are called grain boundaries. Those that separate phases are called two-phase interfaces.

a) **Grain Boundaries/** A grain boundary is a common planar defect found in polycrystalline solids, and it serves as a boundary that separates regions of varying crystalline orientation, commonly referred to as grains. Within the grain boundary, the atomic arrangement is not in a perfect crystalline order, and these boundaries typically emerge due to uneven growth during the solidification process. Grain sizes can range from 1 μm to 1 mm.

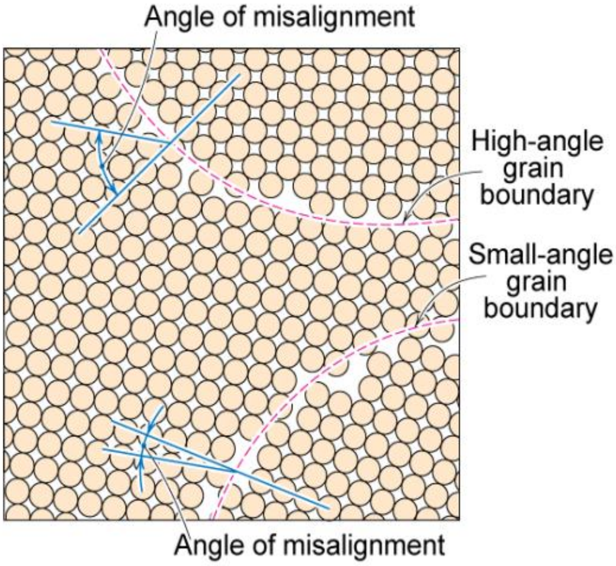


Figure II.24: Grain Boundaries.

Two-phase interfaces resemble grain boundaries and possess specific structures and interfacial energies. The critical feature of a two-phase interface is coherency, where both phases align on the same crystal lattice. Coherent interfaces are common, such as in precipitate formation within solids, where slight atomic arrangement variations lead to coherent interfaces. In thin-film electronics, multi-layer structures are built by depositing atom layers sequentially, resulting in coherent heterostructures of different compositions.

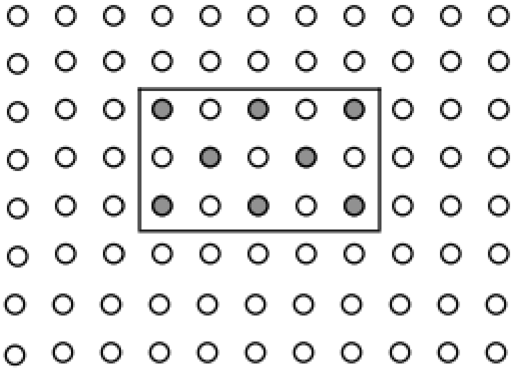


Figure II.25: Coherent, ordered precipitate in a two-dimensional crystal.

b) **Tilt boundary:** A tilt boundary, found between two grains with slight misalignment, often presents itself as an array of edge dislocations.

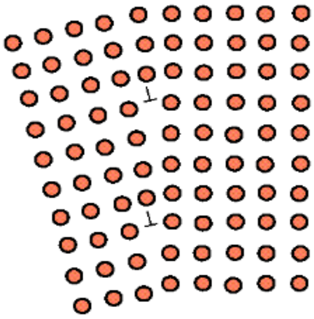


Figure II.26: Tilt Boundaries.

c) **Twin boundaries :** They occur when crystals on either side of a plane are exact mirror images of each other. Along the boundary, there is a single plane of atoms, and no disorder is present. The atoms at the boundary can be considered as part of the crystal structures of both twin crystals. Twins can form during crystallization or as a result of mechanical or thermal processes.

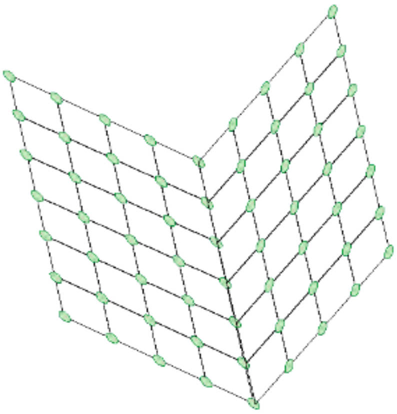


Figure II. 27: Twin Boundaries.

Coherency between different crystalline phases in two-phase interfaces presents challenges as both phases undergo distortion to fit together, especially as precipitate particles grow larger. Larger particles often lose coherency due to dislocation accumulation at the interface. Coherent interfaces exhibit high anisotropy in surface tension, with the volumetric distortion of the precipitate dependent on its shape and crystallographic fit. Coherent second-phase particles adopt characteristic shapes and interfaces aligned along a specific crystallographic plane, known as the habit plane, but lose definition when incoherent. Despite positive interfacial tension, coherent particles experience decreased energy per unit volume as they grow. In systems with varying precipitate sizes and high temperatures, larger particles grow at the expense of smaller ones, leading to overall energy reduction and coarsening of the particle distribution.

II.3.7 Interfaces within crystals

Surface defects that are typically found within a crystal can be categorized into two types: stacking faults and antiphase boundaries. Stacking faults involve a disruption in the regular sequence of planes of atom positions within the crystal structure. In contrast, antiphase boundaries represent a defect in the arrangement of atoms over the crystal planes and are exclusive to ordered compounds.

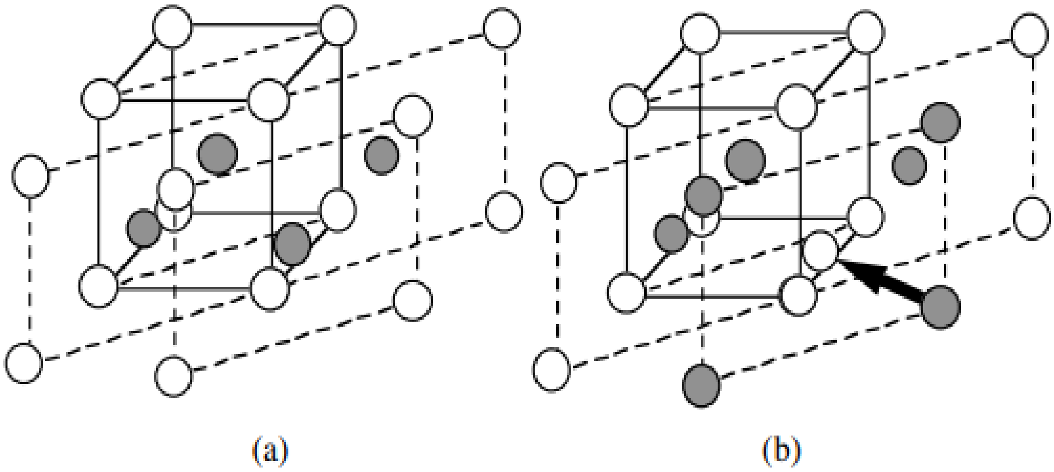


Figure II.29: (a) The CsCl structure drawn as a stacking of {110} planes. (b) An antiphase boundary in the CsCl structure made by a displacement of the type 1 2 in the third plane.

II.3.7.1 Microcracks

Microcracks are small fractures that occur on the surface or at structural irregularities within a solid, typically around 10 μm in size. They form when internal bonds break, creating new surfaces known as separation planes. Microcracks are often a result of abrasion or impacts from dust particles and play a significant role in determining the fracture behavior of solids. In crystals with multiple atom types, both chemical and physical disorder can be observed at grain boundaries.

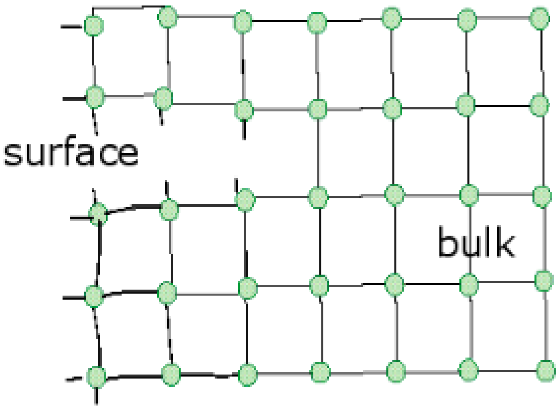


Figure II.30: Microcracks.

II.4 Volume Defects

Volume defects in crystalline materials are three-dimensional clusters of atoms or vacancies, categorized by their size and impact on the material.

1. Precipitates are small, dispersed within the crystal, often used to enhance structural alloy strength by impeding dislocation motion.
2. Second-phase particles vary in size and are intentionally introduced into the material's microstructure, affecting properties like mechanical strength and conductivity.
3. Inclusions, ranging from microns to macroscopic sizes, are undesirable particles introduced as contaminants or through precipitation, detrimental in microelectronics due to their interference and alteration of electrical properties.
4. Voids or pores are empty spaces formed by trapped gases or vacancies, reducing mechanical strength and promoting fracture under small loads. Precipitates modify matrix behavior rather than act as separate phases. Dispersants influence properties as an average of their phase and the parent material. Inclusions disturb device geometry or alter electrical properties in microelectronics. Voids decrease mechanical strength and promote fracture.

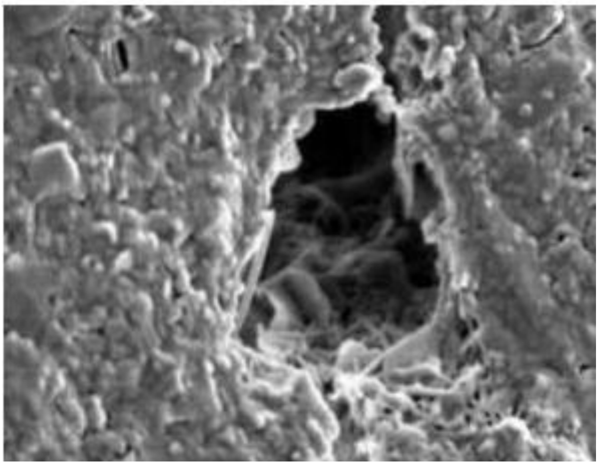


Figure II.31: Volume defects.

Chapter III: Surface electronic states

III.1 Introduction

The surface electronic structure of solid materials is determined by factors such as atom type, arrangement, and atomic order or disorder. It differs from bulk materials due to broken bonds and surface reconstructions. Early methods like Tight Binding approximate electronic wave functions by combining atomic wave functions. Electrons in solids exhibit collective behavior, forming energy bands instead of discrete states. Surface charges create an electric field, attracting counter ions to form an electric double layer. Initially, counter ions were thought to directly bind to the surface, forming the Helmholtz layer. However, Gouy and Chapman proposed a diffuse layer model to explain electric double layer capacitance. Debye and Hückel expanded upon this, calculating potential and ion distribution around spherical surfaces. The electronic structure at a material's surface is influenced by atomic arrangement and disorder. Tight Binding approximates electronic wave functions by combining atomic wave functions. The presence of surface charges creates an electric field attracting counter ions. Initially, counter ions were thought to directly bind to the surface, forming the Helmholtz layer. However, Gouy and Chapman proposed a diffuse layer model to explain electric double layer capacitance. Debye and Hückel expanded upon this, calculating potential and ion distribution around spherical surfaces.

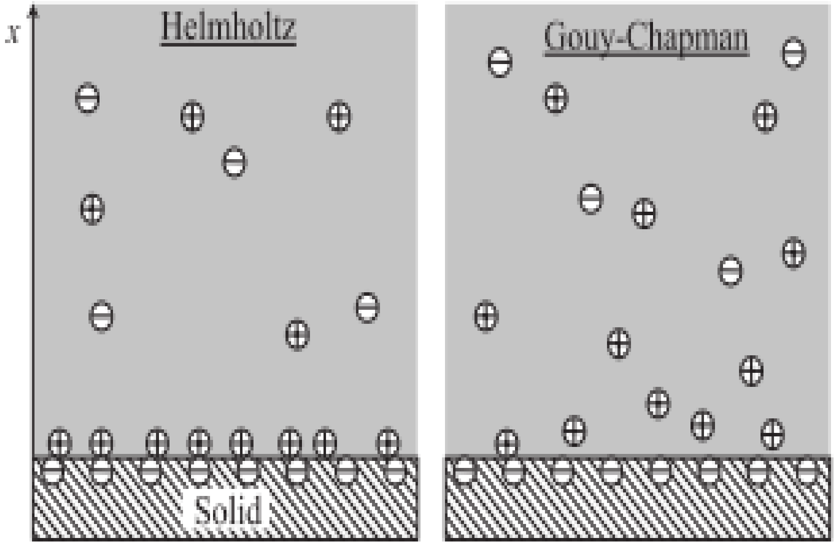


Figure III. 1: Helmholtz and Gouy–Chapman model of the electric double layer.

The Gouy-Chapman and Debye-Hückel theories are continuum models that treat the solvent as a continuous medium with a specific dielectric constant. They consider ions as continuous charge distributions rather than individual point charges. Despite their suitability for many applications and alignment with experimental observations, these models do not account for the molecular characteristics of the liquid and have limitations discussed in the concluding section.

III.2 Electronic surface states

In the early 1930s, Tamm and Shockley introduced the concept of localized states at crystalline lattice terminations, influencing surface properties like energy and reactivity. Schrieffer (1957) described a surface state in semiconductor physics, crucial for MOSFET technology and phenomena like the quantum Hall effect.

In the 1950s and 1960s, experiments on superfluid helium revealed significant findings. Rayfield and Reif (1964) discovered quantized vortex rings, enabling measurement of their anomalous energy-momentum relation. Levine and Sanders (1967) identified a transition in helium density, from delocalized to localized "bubble" states, analogous to localization in disordered media. This transition, influenced by the exclusion principle's repulsive interaction between helium atoms and electrons, plays a pivotal role in condensed matter physics. The delocalized and bubble states serve as valuable tools for probing fundamental properties of superfluid helium. These discoveries underscore the intricate relationship between localized states, surface properties, and fundamental phenomena in both semiconductor physics and condensed matter physics.

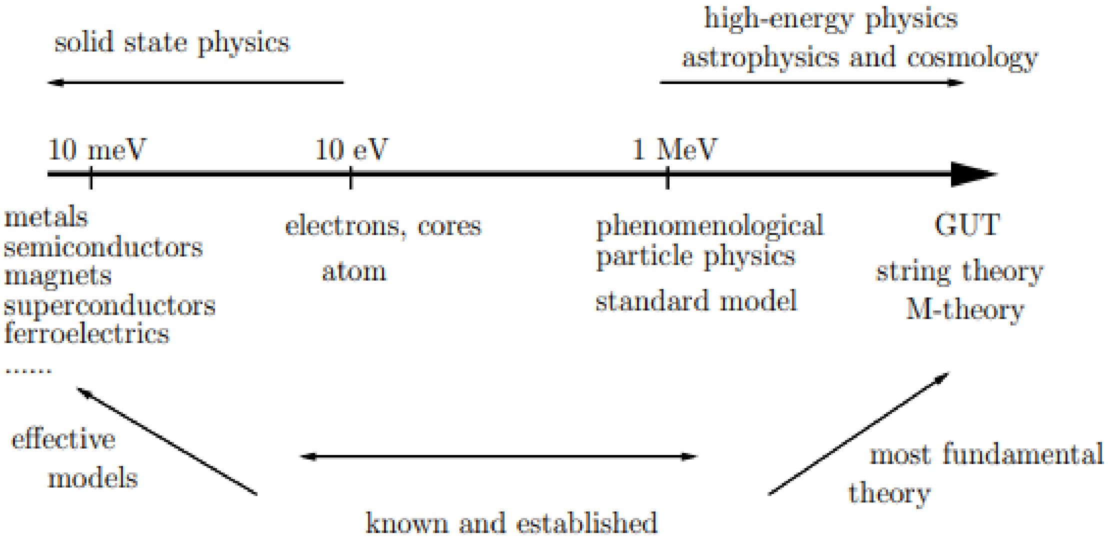


Figure III. 2: Energy scales in physics.

In contrast, in solid state physics we are dealing with phenomena occurring at room temperature (T ~ 300K) or below, i.e., at characteristic energies of about E ~ kBT ~ 0.03eV = 30meV, which is even much smaller than the energy scale of one Hartree. Correspondingly, the important length scales are given by the extension of the system or of the electronic wave functions.

In solid state physics, while the standard model successfully describes low energies, the underlying theory for higher energies remains unknown. The Hamiltonian captures 'high-energy' physics, with an aim to describe low-energy properties using effective theories, a non-trivial task. Condensed matter theory encompasses various states like metals, semiconductors, and insulators, along with phenomena such as magnetism, superconductivity, and ferroelectricity, all originating from electron-ion Coulomb interactions. Microscopic formulations are often too complex for understanding low-energy behavior, necessitating effective theories. Ground state characterization is crucial, but measurable quantities rely on excited states, highlighting the importance of 'elementary excitations' like Landau quasiparticles, phonons, and magnons.These excitations are treated as particles on an effective vacuum, often the Fermi sea or a state with broken symmetry, like a ferromagnet or a superconductor. The concept of second quantization helps in understanding ground state dynamics and the behavior of elementary excitations in condensed matter systems.

Condensed matter (solid bodies) consists of atomic nuclei (ions), usually arranged in a regular (elastic) lattice, and of electrons (see Figure 1). As the macroscopic behavior of a solid is determined by the dynamics of these constituents, the description of the system requires the use of quantum mechanics. Thus, we introduce the Hamiltonian describing nuclei and electrons.

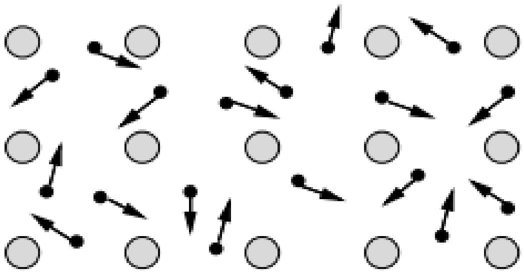


Figure II. 3: Atom cores and the surrounding electrons.

$$\boldsymbol{\hat{H} = \widehat{He} + \widehat{Hn} + \hat{H}n - e} \qquad (\boldsymbol{III}.1)$$

Where :

$\widehat{He}$

$(\widehat{Hn})\ describes\ the\ dynamics\ of\ the\ electrons\ (nuclei) and\ their\ mutua$

$\hat{H}n - e\ \ includes\ the\ interaction\ between\ ions\ and\ electrons.$

The Planck scale is an energy scale so large that even gravity is thought to be affected by quantum effects, as:

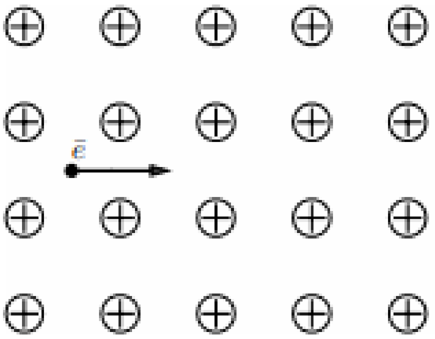
$$E_{Plank} = c^2\sqrt{\frac{hc}{G}} = 10^{19}\ GeV \qquad (III.2)$$

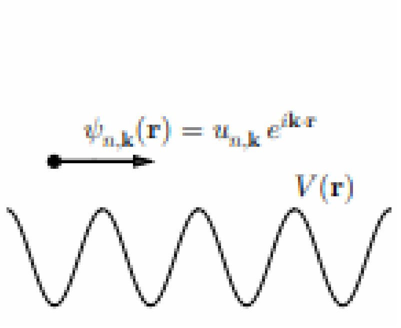
$$I_{Plank} = \sqrt{\frac{hG}{C^3}} = 1.6\times10^{-35} m \qquad (III.3)$$

where G = $6.673 \times 10^{-11} m^3 kg^{-1}\ s^{-2}$ is the gravitational constant. This is the realm of the GUT (grand unified theory) and string theory. The goal is not to provide a better description of electrons or atomic cores, but to find the most fundamental theory of physics.

III.3 Band spectrum of crystals: general consideration

We consider an electron in a crystal with periodic arrangement of positively charged ions.





It is well known that the solutions of the stationary Schrödinger equation:

$$\hat{H}\psi(r) = E\psi(r) \qquad (III.4)$$

for electron in an arbitrary periodic potential V(r) = V(r + a) have a form of so-called Bloch states – modulated plane waves of constant amplitudes.

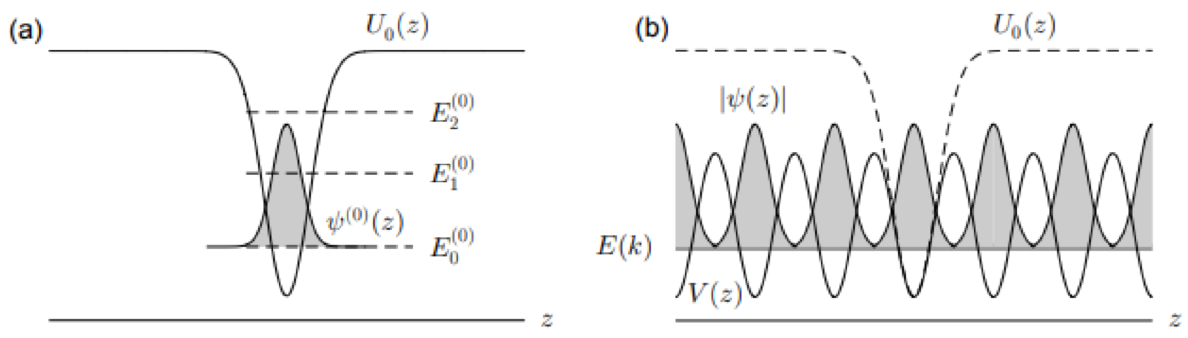
$$\psi_{n,k}(r) = u_{n,k}(r)e^{ik-r} \qquad (III.5)$$

where n is integer index, un,k (r) = un,k (r + a) is an arbitrary periodic function, and k is the wave vector (quasi-momentum).

III.3.1 Band spectrum and wave functions

Let U0(z) be non-perturbed potential energy of an electron around an isolated ion (see Figure below).

The eigenfunctions $\psi^{(0)}$n (z) and eigenenergies $E^{(0)}$n , describing an electron in this single-well potential, should meet the stationary Schr¨odinger equation:



$$\boldsymbol{\widehat{H}0\psi_n^{(0)}(z) = \psi_n^{(0)}(z)} \qquad (\boldsymbol{III}.6)$$

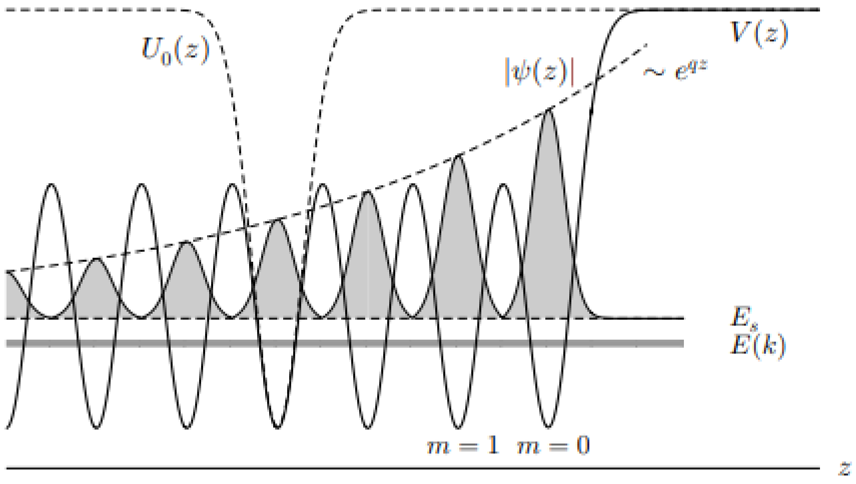
A potential, corresponding to the sum of the isolated potential wells:

$$\boldsymbol{V(z) = \sum_m U_0\,(z + ma)} \qquad (\boldsymbol{III}.7)$$

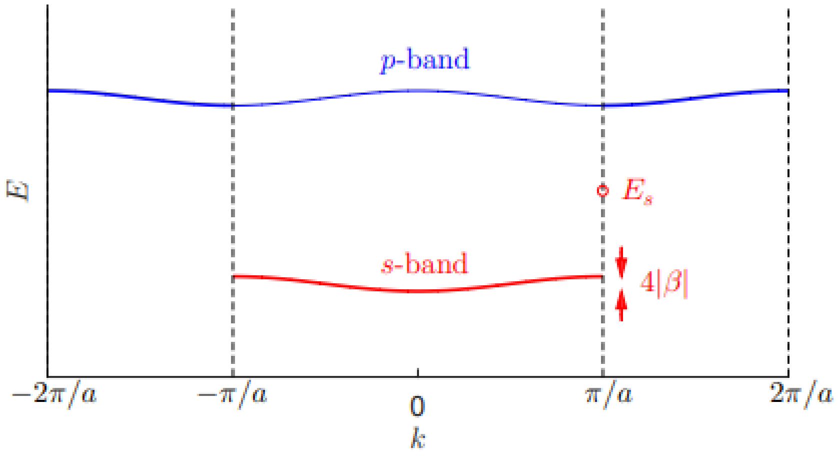
should be the periodic function with the period a, where a is the lattice constant. Wave functions ψ(z) of electron in the periodic potential V(z) of arbitrary shape should be the solutions of the stationary Schr¨odinger equation. For simplicity we consider the formation of the s−band, corresponding to n = 0. If overlapping of the wave functions localized at neighbour cites are negligibly small, then we can find the solution in the form of the superposition of non-perturbed wave functions ψ (0) (z + ma), localized near m−th ion.

III.3.1.1 Band spectrum for 1D semi-infinite crystal

It should be repeated that any boundaries and defects break periodicity and leads to nonapplicability of the Bloch theorem. Let the index m = 0 corresponds to the potential well at the edge. It is reasonable to introduce a modified parameter α0 for the last potential well, what meets the criterion α < α0 < 0.



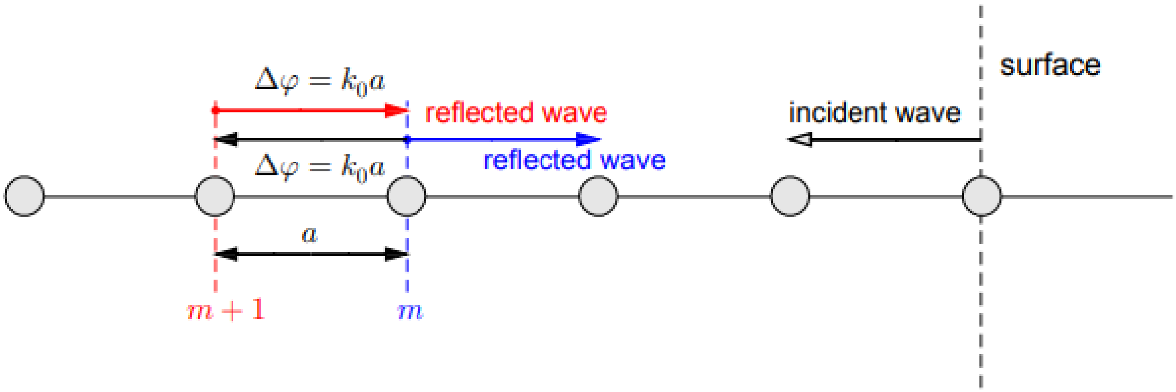
It is easy to see that this energy is larger than the top of the allowed s−band



III.3.1.2 Surface states and Wullf-Bragg-von Laue resonance

The condition $k_0 = \pi/a$ corresponds to the Bragg resonance on the periodic structure. The criterion of the coherent back-scattering of electronic waves by neighbor atoms with indexes m and m + 1.

$$\Delta\varphi_{total} = 2 \cdot k_0 a = 2\pi n \quad \text{or} \quad k_0 = \frac{\pi n}{a}.$$



Important conclusion: if the real part of the wave vector k0 of the incident electronic wave meets the Bragg condition of resonant back-scattering ($k0 = \pi n/a$), such wave cannot pass through the periodic structure. As a result, crystal acts like ideal mirror fully reflecting the incident wave with $k0 = \pi n/a$.

III.3.2 Bandgap energies of solid materials

In solid-state physics, the bandgap of a solid material defines the difference in energy between electron orbitals in which the electrons are not free to move (i.e., the valence band) and orbitals in which the electrons are mobile and able to carry a current (i.e., the conduction band). In other words, the bandgap represents the energy between a solid's nonconductive and conductive states. In conductors, such as most metals, the valence and conduction bands overlap, and therefore, outer orbital electrons are free to carry electrical currents (Figure 1). Conversely, outer orbital electrons in semiconductors and insulators are restricted to the valence band and thus immobilized. In general, semiconductors (e.g., Si, Ge, and GaAs) are characterized by small but nonzero bandgaps; at absolute 0 (0 K or − 273 °C), these materials behave as insulators, but electrons can be thermally excited into the conduction band at higher temperatures. Alternatively, insulators (e.g., diamond, glass, and ceramic) are defined by large bandgaps regardless of temperature.

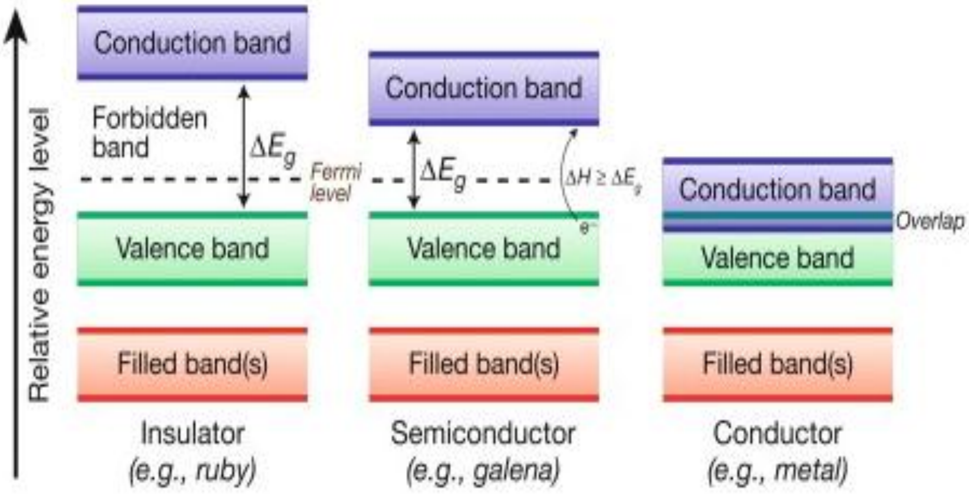


Figure III.4. Schematic representation of the bandgap energies (ΔE_g) of a representative conductor, semiconductor, and insulator.

The valence and conduction bands overlap in conductors, such as most metals, and therefore, there is no bandgap energy to overcome and outer orbital electrons are free to carry electrical currents. Semiconductors such as galena (PbS) are characterized by small but nonzero bandgap energies that can be overcome by thermal excitations at temperatures T> 0 K (when $\Delta H \geq \Delta E_g$). Alternatively, thermal energy is not sufficient to raise electrons from the valence band to the empty conduction band in insulators and dielectrics (e.g., diamond, ruby, and ceramic). The Fermi level describes the energy of the least tightly held electrons within a solid at absolute 0 (0 K or − 273.15 °C).

III.4 Electrical potential

The binding potential, due to the interaction between the electron and the dielectric, is most easily derived by putting an artificial image charge in the dielectric. Asymptotically, the interaction takes the classical form:

$$\boldsymbol{V} = -\frac{\boldsymbol{q}^2}{\boldsymbol{z}} \qquad (\boldsymbol{III}.8)$$

$$\left(\frac{\boldsymbol{q}}{\boldsymbol{e}}\right)^2 = \frac{(\boldsymbol{\varepsilon} - 1)}{[4(\boldsymbol{\varepsilon} + 1)]} \qquad (\boldsymbol{III}.9)$$

where ε is the dielectric constant of the fluid, which occupies the half-space z<O. Close to the surface, this functional form is not applicable and a many-body potential is required.

III.5 Schrödinger equation

Within the medium, the electron encounters an effective potential energy that approaches the bulk positive energy *Vo*. Given that *Vo* is significantly larger than the eventual binding energy of the electron, one might initially assume that Equation 1 remains applicable right up to the *z*=0 plane, where the potential becomes infinite within the fluid. The corresponding Schrödinger equation is then derived as follows:

$$-\left(\frac{\hbar^2}{2\boldsymbol{m}}\right)\nabla^2\boldsymbol{\psi}-\left(\frac{\boldsymbol{q}^2}{\boldsymbol{z}}\right)\boldsymbol{\psi} = \boldsymbol{E\psi} \quad (\boldsymbol{z}>0) \qquad (\mathbf{III}.10)$$

III.4 Electronic states at the surface

Surface states refer to electronic states that exist specifically at the surfaces of materials. These states emerge due to the abrupt transition between the solid material and the surface, and they are localized in the atomic layers nearest to the surface. When a material terminates at a surface, it results in an alteration of the electronic band structure, transitioning from the bulk material to the vacuum. This change in the potential energy profile at the surface creates an opportunity for the formation of new electronic states, commonly referred to as surface states.

- **Tight-binding approximation**: In the approach, the electronic wave functions are usually considered as a linear combination of localized atomic orbitals (LCAO). Surface states described in the framework of a tight-binding model are often referred to as Tamm states (1932).
- **Approximation of nearly-free electrons**: In the approach, the electronic wave functions are usually considered as plane delocalized electronic waves. Surface states described in the framework of a nearly-free-electron model are often referred to as Shockley states (1939). Thus, there is no strict physical distinction between Tamm and Shockley states, but the mathematical approaches used in describing them are completely different. We prefer to use generalized terms ’surface electronic states’ or ’Tamm-Shockley states’.

III.4.1 Electronic states at the surfaces of crystals

We are examining a simple cubic crystal structure comprising a block that is N atomic layers thick in the *a*-direction but extends infinitely in the perpendicular directions. More precisely, we are disregarding the effects at the ends in these perpendicular directions. The atoms are located at points defined by their position vectors.

$$\boldsymbol{Tlmn} = (-\boldsymbol{c}(\boldsymbol{l} - 1), \boldsymbol{cm}, \boldsymbol{cn})$$

Here, *m* and *n* are unrestricted integers, while *l* takes values from 1 to *N*. We focus solely on the s-states of the individual atoms. First, let's denote by *Hl* the Hamiltonian for an electron moving in the field of the *l*th layer of atoms only. This refers to the infinite layer of atoms whose poEsitions are given by r*lmn* . This Hamiltonian has the form:

$$\boldsymbol{Hl} = \frac{\hbar}{2\boldsymbol{m}} \nabla^2 + \sum_{\boldsymbol{mn}} \boldsymbol{U}\,(|\boldsymbol{r} - \boldsymbol{r_{lmn}}|) \qquad (\boldsymbol{III}.11)$$

The corresponding wave functions of electrons moving in the field of such a twodimensional array of atoms are solutions of the wave equation:

$$(\boldsymbol{H_l} - \boldsymbol{E})\boldsymbol{\psi} = 0 \qquad (\boldsymbol{III}.12)$$

Such solutions are found, as in the usual case of a three-dimensional crystal, to be of the type:

$$\boldsymbol{\psi_{lk_2k_3}} = \boldsymbol{N_l} \sum_{\boldsymbol{mn}} \boldsymbol{e^{io(mk2+nk3)}}\, \boldsymbol{\phi}(|\boldsymbol{r} - \boldsymbol{r_{lmn}}|)_{\boldsymbol{s}} \qquad (\mathbf{III}.13)$$

with the corresponding energy, independent of I, given by:

$$\boldsymbol{E_{k2k3}} = \boldsymbol{E_0} - \boldsymbol{\alpha} - 2\boldsymbol{\gamma}(\boldsymbol{cosck}2 + \boldsymbol{cosck}3) \qquad (\boldsymbol{III}.14)$$

Now two states of the type (4a) but with different k2, k3 are non-combining**J**. We accordingly approximate to W by a series of the form

$$\boldsymbol{\psi} = \sum_{\boldsymbol{l}=1}^{\boldsymbol{N}} \boldsymbol{a_1}\, \boldsymbol{\psi_{lk2k3}} \qquad (\mathbf{III}.15)$$

Now if Nt of (4 a) is chosen so that, neglecting the overlap integral S, we have:

$$\int \boldsymbol{\psi^{*} l k_2 k_3 \psi l k_2 k_3 dr} = 1 \qquad (\boldsymbol{III}.16)$$

In this way we obtain two series of states:

$$\boldsymbol{\psi_{\theta k2k3}} = \sum_{\boldsymbol{S=mn}}^{\boldsymbol{N-1}} \sum_{\boldsymbol{mn}} \boldsymbol{cos}\left(\frac{1}{2}\boldsymbol{N} - \frac{1}{2}\boldsymbol{S}\right)\boldsymbol{\theta e^{ic(mk_2+nk_3)}\phi}\left(|\boldsymbol{r} - \boldsymbol{r_{S+1,m,n}}|\right) \qquad (\boldsymbol{III}.17)$$

$$\boldsymbol{\psi_{\theta k_2 k_3}} = \sum_{\boldsymbol{S}=0}^{\boldsymbol{N-1}} \sum_{\boldsymbol{mn}} \mathbf{sin}(\frac{1}{2}\boldsymbol{N} - \frac{1}{2}\boldsymbol{S})\boldsymbol{\theta e^{ic(mk_2+nk_3)}\phi}(|\boldsymbol{r} - \boldsymbol{r_{S+1,m,n}}) \qquad (\boldsymbol{III}.18)$$

and the values of 6 being exactly as before. Thus 0 < θ < π.

The energies) for the range 0 < θ < π clearly give the usual band of energies forming the first Brillouin zone for a simple cubic crystal. Indeed, if θ is replaced by π-ck$_1$ the forms of the expressions are identicalf. This zone now contains only M(N— 2) possible states, where M is the number of atoms in a monatomic layer parallel to the x-axis:

We observe that, if we neglect the electron spin, the number of surface states corresponding to any given surface is equal to the number of atoms in that surface. This result is also true for the case of nearly free electrons discussed in I, as is easily seen if we consider the density of states in phase space§. If we consider a finite cube of metal we obtain "surface states" corresponding to all six surfaces," line states" corresponding to all twelve edges and finally" point states" corresponding to the eight corners.

III.4.2 degeneracy of the atomic s- and p-states

When the s- and p-states are to be taken as degenerate we consider the case of a semi-infinite linear chain and, as in previously, concentrate on the relations between the coefficients of the wave function. We solve these as a set of recurrence relations and hence we are able to predict the existence of a surface state lying above the higher allowed band with another lying between the two bands but with no such state below the lower band. It is, however, impossible to find the energy of either of these states.

- **The allowed bands:** We take the atoms to be situated at the points:

$$r_l = (-cl, 0, 0) \quad (l = 0, 1, \dots \infty)$$

For such a chain only the p-states combine with the s-states. Denoting the p_x-states by $\phi_1(pl)$, we therefore write for the zero-order wave function:

$$\boldsymbol{\psi} = \sum_{l=0}^{\infty} \boldsymbol{a}_1 \emptyset_0(\boldsymbol{p}_l) + \sum_{l=0}^{\infty} \boldsymbol{b}_1 \emptyset_0(\boldsymbol{p}_l) \qquad (\boldsymbol{III}.19)$$

Applying the perturbation theory and neglecting the interactions of all but nearest neighbours, we obtain an infinite number of relations between the coefficients a_l and b_l and then one of the roots θ_1 is real and the other is complex of the form iμ or π + iμ. The general solution of the equations is:

$$\boldsymbol{a}_l = \boldsymbol{A}_1^+ \boldsymbol{e}^{il\theta_1} + \boldsymbol{A}_1^- \boldsymbol{e}^{-il\theta 1} + \boldsymbol{A}_2^+ \boldsymbol{e}^{il\theta_2} + \boldsymbol{A}_2^- \boldsymbol{e}^{-il\theta_2} \qquad (\boldsymbol{III}.20)$$

$$\boldsymbol{b}_l = \boldsymbol{B}_1^+ \boldsymbol{e}^{il\theta_1} + \boldsymbol{B}_1^- \boldsymbol{e}^{-il\theta_1} + \boldsymbol{B}_2^+ \boldsymbol{e}^{il\theta_2} + \boldsymbol{B}_2^- \boldsymbol{e}^{-il\theta_2} \qquad (\boldsymbol{III}.21)$$

Now let us consider first the case when E lies within either of the bands (15). Then the term $e^{-il\theta}$ increases exponentially with I and so for a physically possible state we must have $A_2^- = B_2^- = 0$. Actual substitution shows that the equations have a unique solution for any value of E which lies within one of the bands (15). These bands are, therefore, completely occupied by electronic states and are seen to correspond exactly to the allowed bands obtained for the infinite metal in the case when the s- and p-states are degenerate, being, in fact, their one-dimensional counterpart.

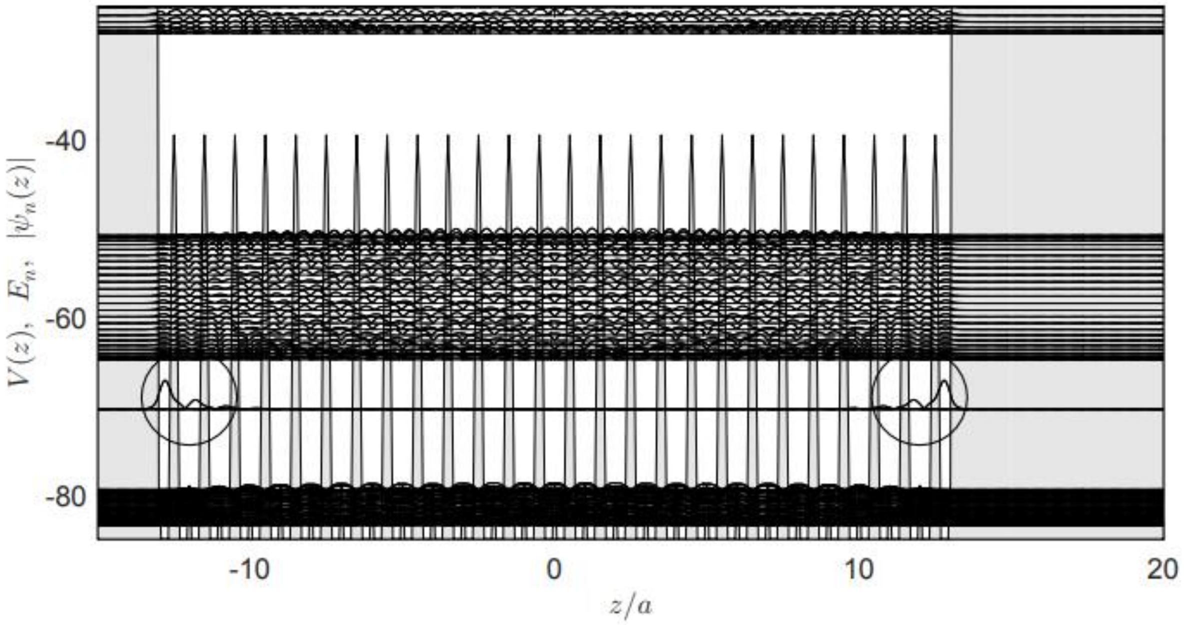
- **The forbidden bands**: We proceed now to the case when E does not lie in either of the bands. Then both $e^{-il\theta_1}$ and $e^{-il\theta_2}$ increase exponentially with I, and thus for the solution to be physically significant we must have:

$$\boldsymbol{A}_1^- = \boldsymbol{A}_2^- = \boldsymbol{B}_1^- = \boldsymbol{B}_2^- = 0$$

This situation is unfortunate since an attempt to consider the effect of these states on any phenomenon would naturally require a knowledge of whether at the absolute zero of temperature the states are to be regarded as full, partly full, or empty. In such a case it would be necessary to consider both possibilities of derivation of the states to see which, if either, leads to results compatible with experiment. However, this position is perhaps no less satisfying than it is in problems in which the possible overlapping or non-overlapping of the zones has to be considered. Here again the distribution of the electronic states is deduced from an attempted correlation with experiment; the experimental results are not predicted from a known electron distribution. The number of electronic surface states, if we neglect the spin, is equal to the number of atoms in the surface, just as the number of normal states is equal to the total number of atoms in the lattice (here considering, of course, just one band of levels). They are thus greatly outnumbered by the normal electronic states and their effect can only be expected to be appreciable in what are essentially surface phenomena or in crystals in which the number of electrons available for an interaction has for some reason been drastically cut down. The method of the previous paper is extended to determine the surface states of a simple cubic crystal on the approximation of tight binding. It is also applied to the case of a semi-infinite linear chain when the atomic s- and ^3-states are to be regarded as degenerate, the existence of surface states being again predicted.

III.4.3 Surface electronic states: numerical simulation

Considered model profile of potential energy (V1 < 0 and V2 > 0).

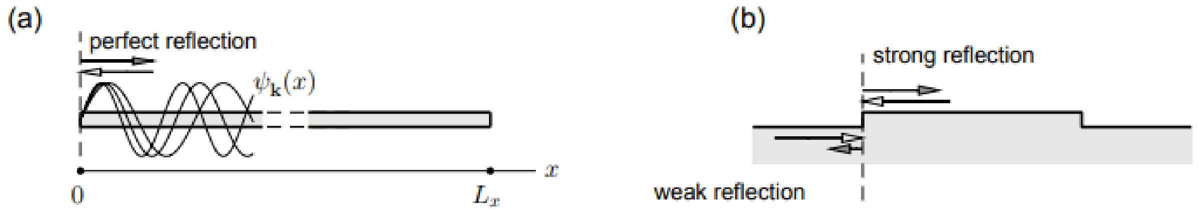


The potential is equal to:

$$\boldsymbol{V}(\boldsymbol{z}) = \boldsymbol{V}_0 + 2\boldsymbol{V}_1 \cos\left(\frac{2\pi z}{a}\right) + 2\boldsymbol{V}_2 \cos\left(\frac{4\pi z}{a}\right) \tag{III.22}$$

III.4.4 Quasiparticle interference (QPI) near defects at surface

Elastic scattering of surface waves at defects leads to peculiar interference patterns as seen in previous chapter.



With nonuniform local density of states.

III.5 Image potential in electrostatics

It is known that a probe charge located outside a conductive sample generate a charge at the surface of the opposite sign. The interaction of the probe charge with the charged flat surface of bulk sample can be viewed as the electrostatic interaction of the probe charge and the mirror (image) charge. A Coulomb force acting between point charges e and −e at a distance 2h as well as corresponding potential are equal:

$$\boldsymbol{F}_2(\boldsymbol{h}) = -\frac{1}{\epsilon}\frac{\boldsymbol{e}^2}{(2\boldsymbol{h})^2} \qquad (\boldsymbol{III}.23)$$

$$\boldsymbol{U}(\boldsymbol{z}) = \boldsymbol{E}_{\boldsymbol{vac}} - \int_{\boldsymbol{Z}}^{+\infty} \boldsymbol{F}_2 (\boldsymbol{h}')\boldsymbol{d}\boldsymbol{h}' = \boldsymbol{E}_{\boldsymbol{vac}} - \frac{1}{\epsilon}\frac{\boldsymbol{e}^2}{4\boldsymbol{z}} \qquad (\boldsymbol{III}.24)$$

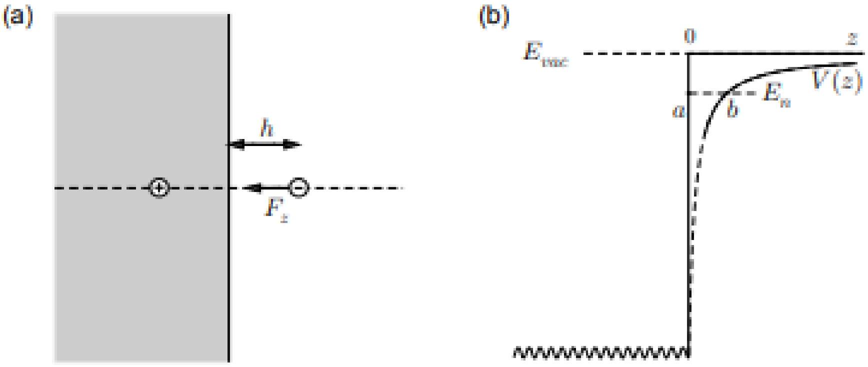


Figure III.5: Energy and spatial scales characterizing image states on metal surface.

Electrons can be potentially localized in the effective potential well formed by the Coulomb image potential from one side and the surface of the crystal from the other side. If the energy of the image-potential states is in the forbidden band of bulk crystal, such states can be quasi-stationary and slowly decaying, affecting optical and transport properties of nanostructured samples.

III.6 Surface electronic states in the image potential

Let us assume that (i) Evac = 0 and (ii) the energy of the localized states belongs to the forbidden band of bulk crystal. The effective potential for non-transparent wall at z = 0 can be written in the form:

$$U(\boldsymbol{z}) = \begin{cases} \infty & at\ z < 0 \\ \dfrac{-\boldsymbol{e}^2}{4\boldsymbol{z}} & at\ z > 0 \end{cases} \qquad (\boldsymbol{III}.25)$$

where z is the distance measured from the surface, a = 0 and b = e 2 /4|En| are classical turning points for a particle with energy En = −|En|. Within quasi-classical Wentzel-Kramers-Brillouin (WKB) approximation, one can estimate the change of the phase of the electronic wave function for the round trip (a → b → a):

$$\frac{1}{\boldsymbol{h}}\int_{\boldsymbol{a}}^{\boldsymbol{b}} \boldsymbol{p}(\boldsymbol{z})\boldsymbol{dz} + \qquad \boldsymbol{\varphi_b}$$

$$+\frac{1}{\boldsymbol{h}}\int_{\boldsymbol{b}}^{\boldsymbol{a}} \left(-\boldsymbol{p}(\boldsymbol{z})\right)\boldsymbol{dz} + \boldsymbol{\varphi_a}$$

$$= 2\boldsymbol{\pi n} \qquad (\boldsymbol{III}.26)$$

where ϕa and ϕb are the phase shifts for reflected waves at points a and b, correspondingly; n = 0, 1 . . . is the number of quantum-well state. After rearranging, we come to the Bohr-Sommerfeld quantization rule :

$$\frac{1}{2\boldsymbol{\pi}\text{Ћ}}\oint \boldsymbol{p}(\boldsymbol{z})\boldsymbol{dz} = \boldsymbol{n} + \boldsymbol{\gamma} \qquad (\boldsymbol{III}.27)$$

Where: $\boldsymbol{\gamma} = -\frac{\boldsymbol{\varphi_a}}{2\boldsymbol{\pi}} - \frac{\boldsymbol{\varphi_b}}{2\boldsymbol{\pi}} \approx \frac{3}{4}$

Afetr substituting $\boldsymbol{p}(\boldsymbol{z}) = \sqrt{2\boldsymbol{m}(\boldsymbol{E} - \boldsymbol{U}(\boldsymbol{z})}$ into the Bohr-Sommerfeld quantization rule, we get:

$$\frac{1}{2\boldsymbol{\pi}\text{Ћ}}\oint \boldsymbol{p}(\boldsymbol{z})\boldsymbol{dz} = \frac{1}{\boldsymbol{\pi}\text{Ћ}}\int_0^{\boldsymbol{b}} \sqrt{2\boldsymbol{m}_0\left(\boldsymbol{E_n} - \boldsymbol{U}(\boldsymbol{z})\right)\boldsymbol{dz}} = \frac{\boldsymbol{e}^2}{\boldsymbol{\pi}\text{Ћ}}\sqrt{\frac{2\boldsymbol{m}_0}{|\boldsymbol{E_n}|}\frac{\boldsymbol{\pi}}{8}} = \boldsymbol{n} + \boldsymbol{\gamma} \qquad (\boldsymbol{III}.28)$$

As a result, the spectrum of the localized electronic states in the image-potential with non-penetrable well is given by a simple relationship:

$$\boldsymbol{E_n} = -\frac{\boldsymbol{m}_0\boldsymbol{e}^4}{32\text{Ћ}^2} \qquad \frac{1}{(\boldsymbol{n}+\boldsymbol{\gamma})^2}$$

$$= -\frac{1}{16} \qquad \frac{\boldsymbol{R_Y}}{(\boldsymbol{n}+\boldsymbol{\gamma})^2}$$

$$(\mathbf{III}.29)$$

Chapter IV: Thermodynamic of surfaces

IV. Introduction

Surface thermodynamics provides interesting investigative possibilities because of the increase of parameters and variables as compared to bulk phenomena. Thus, additional possibilities of behavior develop in capillary systems. As is well known, classical thermodynamics for continuous systems, as well as for surfaces, is concerned with equilibrium situations.The presence of an interface influences generally all thermodynamic parameters of a system. To consider the thermodynamics of a system with an interface, we divide that system into three parts: The two bulk phases with volumes Vα and V β, and the interface σ. In the Gibbs model the interface is ideally thin (Vσ = 0) and the total volume is :

$$\boldsymbol{V = V^{\alpha} + V^{\beta}} \qquad (\boldsymbol{IV}.1)$$

All other extensive quantities can be written as a sum of three components: one of bulk phase α, one of bulk phase β, and one of the interfacial region σ. Examples are the internal energy U, the number of molecules of the ith substance Ni, and the entropy S:

$$U = U^{\alpha} + U^{\beta} + U^{\sigma}$$

$$n = n^{\alpha} + n^{\beta} + n^{\sigma}$$

$$S = S^{\alpha} + S^{\beta} + S^{\sigma}$$

IV.2 Estimate of the Excess Energy Associated with Surfaces

In the treatment of the equilibrium of phases the effect of the surface that separates the various phases was neglected. In other words, no distinction was made between systems that had an abundance of surface and those that do not—there was no distinction made between:

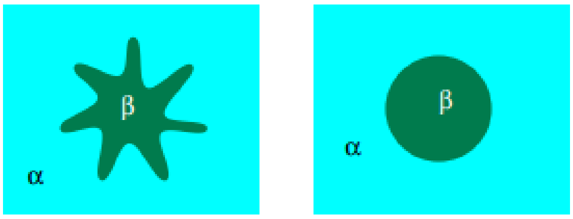


Figure IV.1: Including the effect of interfaces and surfaces. The treatment of equilibrium up until now treated these two systems as being alike even though one obviously has much more surface (and thus any energy associated with that surface) than the other.

Consider, as an example, that an atom on a surface as having a 50% higher energy than those in the bulk, then there will be an extra energy associated with the surface of a sphere.

To estimate how much energy is associated with the surface let:

surface area ≡ surface area of α-phase =$4\pi R_s^2$

volume ≡ volume of α-phase =$\frac{4}{3}\pi R_s^3$

The energy of the system is:

$$\overline{U}^{xs} = \frac{N^{\text{surf}}U^{\text{surf}} + N^{\text{bulk}}U^{\text{bulk}}}{N^{\text{total}}} \qquad \textbf{(IV.2)}$$

Letting the energy of an atom on the surface be half again that of the bulk:

$$U^{\text{surf}} \approx \frac{3}{2}U^{\text{bulk}} \quad \text{(assumption)}$$
$$\overline{U}^{xs} = \left(1 + \frac{1}{2}\frac{N^{\text{surf}}}{N^{\text{total}}}\right) \qquad \textbf{(IV.3)}$$

If Ω is the volume per atom and RA is the radius of an atom, then:

$$N^{\text{surf}} = \frac{(\text{Surface Area})R_A}{\Omega} \qquad \textbf{(IV.4)}$$
$$N^{\text{bulk}} = \frac{(\text{Volume})}{\Omega}$$

IV.3 Gibbs Interfacial Energy

Note the atoms at the surface were treated as being somehow different than those of the bulk. This idea can be extended rigorously to treat the interface as a relatively thin layer. This thin layer will be treated as a separate “quasi-two-dimensional phase.” The original Gibbs idea was as follows: Suppose the composition is different between to phases (but dictated by μ α i = μ β i , of course). There is no requirement that the concentration should be uniform in the vicinity of the interface. Subtract the real system in Figure 35-2 from its idealization in following Figure to define an excess quantity associated with the mathematical surface “The Gibbs Surface” which has no volume associated with it, but excess extensive quantities.

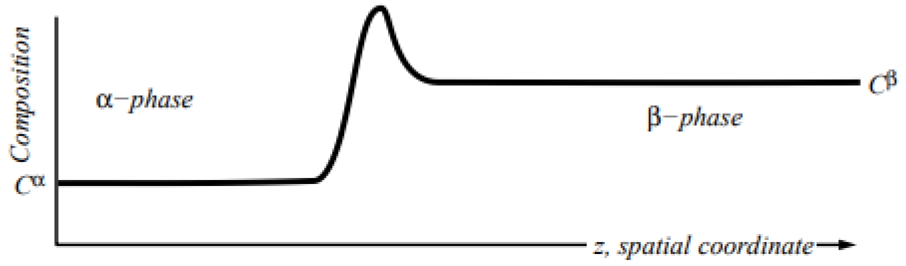


Figure IV. 2: Illustration of the composition in the vicinity of a real interface.

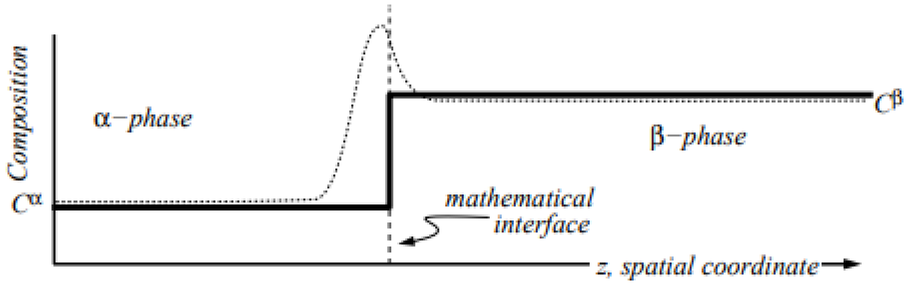


Figure IV. 3: Gibbs idealization of the interface as a mathematical dividing surface.

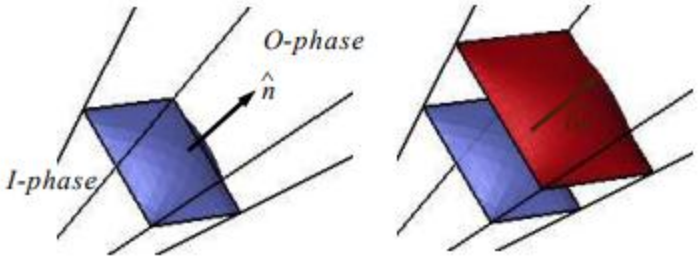


Figure IV. 4: Illustration of an interface separating two phases.

In the Gibbs model of an ideal interface there is one problem: where precisely do we position the ideal interface? Let us therefore look at a liquid–vapor interface of a pure liquid more closely. The density decreases continuously from the high density of the bulk liquid to the low density of the bulk vapor (see Fig. 3.2). There could even be a density maximum in between since it should in principle be possible to have an increased density at the interface. It is natural to place the ideal interface in the middle of the interfacial region so that $\Gamma = 0$. In this case the two dotted regions, left and right from the ideal interface, are equal in size. If the ideal interface is placed more into the vapor phase the total number of molecules extrapolated from the bulk densities is higher than the real number of molecules, $N < c\ \alpha\ V\ \alpha + c\ \beta\ V\ \beta$.

Therefore the surface excess is negative. Vice versa: if the ideal interface is placed more into the liquid phase, the total number of molecules extrapolated from the bulk densities is lower than the real number of molecules, N > c α V α + c β V β, and the surface excess is positive.

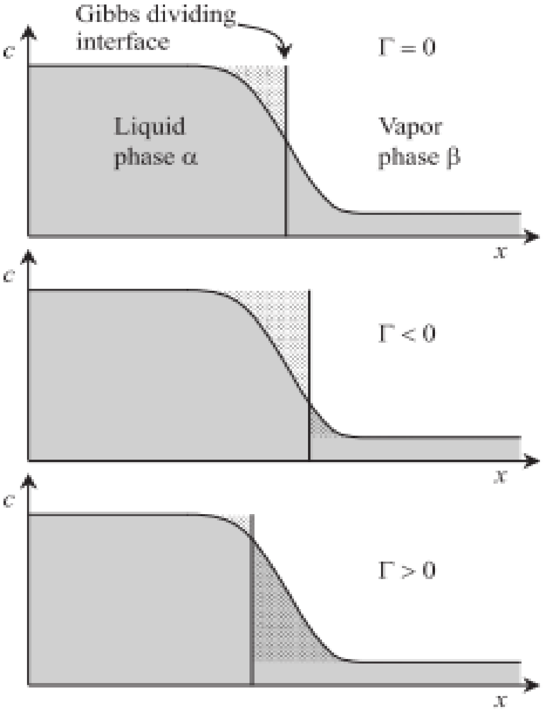


Figure IV.5: Dependence of the surface excess Γon the position of the Gibbs dividing plane.

In this figure the concentration profiles for solute 2 dissolved in liquid 1 are illustrated. We assume that the solute is enriched at the surface. The area of the dotted region corresponds to the surface excess Γ(1)2 of solute.

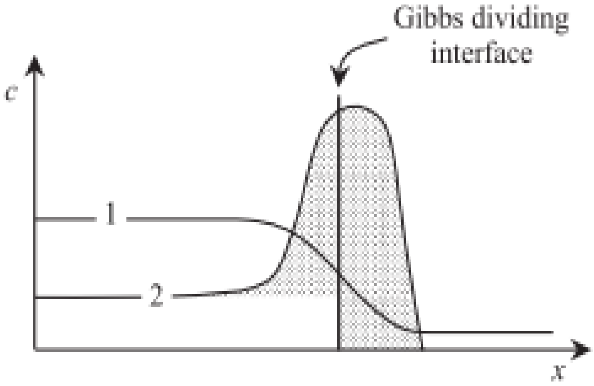


Figure IV.6: Concentration profile of a solute (2) dissolved in a liquid (1). The area of the dotted region corresponds to the surface excess Γ(1)2 of solute.

For the surface phase :

$$dU^{\text{surf}} = TdS^{\text{surf}} + \gamma dA + \sum_{i=1}^{C} \mu_i dN_i^{\text{surf}} \tag{IV.5}$$

where A is the surface area of the interface.

This is the surface tension, it has units of force per unit length or, equivalently, surface energy per area. It is the energy associated with creating surface. Consider the entire system, it is possible to define something like a surface concentration, the so called interfacial excess:

$$\begin{aligned}\delta U^{\text{total}} &= \delta U^{\text{inside}} + \delta U^{\text{surf}} + \delta U^{\text{outside}} \\ &= T\delta S^{\text{inside}} - P\delta V^{\text{inside}} + \sum_{i=1}^{C} \mu_i \delta N_i^{\text{inside}} \\ &+ T\delta S^{\text{surf}} + \gamma\delta A + \sum_{i=1}^{C} \mu_i \delta N_i^{\text{surf}} \\ &+ T\delta S^{\text{outside}} - P\delta V^{\text{outside}} + \sum_{i=1}^{C} \mu_i \delta N_i^{\text{outside}}\end{aligned} \tag{IV.6}$$

Because the surface represents an object that can resist pressure, it can no longer assumed that the pressures on the inside and the outside phase are equal.

VI.3.1 Internal energy and Helmholtz energy

Let us consider a process in a system with two phases, α and β, which are divided by an interface; we could, for instance, do work on that system. As a consequence, the state quantities like the internal energy, the entropy, etc. change. How do they change and how can we describe this mathematically? In contrast to the usual “bulk” thermodynamics we have to take the interface into account. We start the analysis with the internal energy. A variation of the internal energy of a two-phase system is, according to the first and second principle of thermodynamics,

dU=TdS-PdV+$\sum \boldsymbol{\mu_i} + \boldsymbol{dN_i} + \boldsymbol{dW}$

Here, W is the work done on the system without expansion work P dV . It contains the surface work γdA. The sum runs over all components, that means over all substances that are chemically different. μ i is the chemical potential of the ith substance. We first analyze the internal energy, and not the enthalpy, the free energy, or the Gibbs free energy, because the internal energy only contains extensive quantities (S, V, N i , A) as variables. This simplifies the following calculation. We split the internal energy:

$$\begin{aligned} dU &= dU^{\alpha} + dU^{\beta} + dU^{\sigma} \\ &= TdS^{\alpha} + \sum \mu_i^{\alpha} dN_i^{\alpha} - P^{\alpha} dV^{\alpha} + TdS^{\beta} \qquad \text{l)} \\ &+ \sum \mu_i^{\beta} dN_i^{\beta} - P^{\beta} dV^{\beta} + TdS^{\sigma} + \sum \mu_i^{\sigma} dN_i^{\sigma} + \gamma dA \end{aligned}$$

The TdS terms stands for the change in internal energy, which is caused by an entropy change, e.g. a heat flow. The μ i dN i terms consider the energy change caused by a change in the composition. Both P dV terms correspond to the volume-work of the two phases. Since the interface is infinitely thin it cannot perform volume work. With dV = dV α + dV β ⇒ dV α = dV − dV β and summing up

$$\begin{aligned} dU &= TdS - P^{\alpha} dV - \left(P^{\beta} - P^{\alpha}\right) dV^{\beta} \\ &+ \sum \mu_i^{\alpha} dN_i^{\alpha} + \sum \mu_i^{\beta} dN_i^{\beta} + \sum \mu_i^{\sigma} dN_i^{\sigma} + \gamma dA \end{aligned}$$

Now we consider the Helmholtz free energy. The change in free energy of the system is

dF = −SdT − P dV +Σμ i dN i + dW . It follows that

$$\begin{aligned} dF &= -SdT - P^{\alpha} dV - \left(P^{\beta} - P^{\alpha}\right) dV^{\beta} \\ &+ \sum \mu_i^{\alpha} dN_i^{\alpha} + \sum \mu_i^{\beta} dN_i^{\beta} + \sum \mu_i^{\sigma} dN_i^{\sigma} + \gamma dA \end{aligned}$$

When the temperature and volume are constant (dV = 0, dT = 0) the first two terms are zero.

the entropy terms, the equation simplifies as:

Equilibrium condition

We assume that there is no exchange of material with the outside world (dN i = 0); we have a closed system. Then the three parameters N αi, Nβi, and N σi are not independent because N i = N αi+ Nβi+ N σi is constant. Only two at a time, as an example N αi and Nβi, can be varied independently. N σi is then determined by the other two amounts because dN σi= −dN αi − dNβi. Therefore we can write:

$$dF = -\left(P^{\beta} - P^{\alpha}\right) dV^{\beta} + \gamma dA + \sum (\mu_i^{\alpha} - \mu_i^{\sigma}) dN_i^{\alpha} + \sum (\mu_i^{\beta} - \mu_i^{\sigma}) dN_i$$

At equilibrium, with constant volume, temperature, and constant amounts of material, the free energy is minimal. At a minimum the derivatives with respect to all independent variables must be zero:

$$\frac{dF}{dN_i^\alpha} = \mu_i^\alpha - \mu_i^\sigma = 0, \quad \frac{dF}{dN_i^\beta} = \mu_i^\beta - \mu_i^\sigma = 0$$

It follows that

$$\mu_i^\alpha = \mu_i^\sigma = \mu_i^\beta = \mu_i$$

Hence, in equilibrium the chemical potentials are the same everywhere in the system. With this, we can further simplify :

$$dF = -\left(P^\beta - P^\alpha\right) dV^\beta + \gamma dA + \sum \mu_i dN_i$$

The surface tension tells us how the Helmholtz free energy of the system changes when increasing the surface area while keeping the temperature, the total volume, the volume of phase β and the total numbers of all components constant. Is this a useful equation? It is not so difficult to control T, V , and N i but V β might be difficult to keep constant. As we shall see later, for planar surfaces (and practically those which have small curvatures) the condition that V β has to be kept constant can be dropped.

IV.4 Fundamental thermodynamic relations for surfaces

Consider:

$$dU^{\text{surf}} = TdS^{\text{surf}} + \gamma dA + \sum_{i=1}^{C} \mu_i dN_i^{\text{surf}}$$

since the dependent variables are all extensive, we can integrate (i.e. homogeneous degree 1 in all of its variables), therefore

$$U^{\text{surf}} = TS^{\text{surf}} + \gamma A + \sum_{i=1}^{C} \mu_i N_i^{\text{surf}}$$

Taking the derivative (as was done when deriving the Gibbs-Duhem equation);

$$dU^{\text{surf}} = TdS^{\text{surf}} + S^{\text{surf}}dT + \gamma dA + Ad\gamma + \sum_{i=1}^{C} \mu_i dN_i^{\text{surf}} + \sum_{i=1}^{C} N_i^{\text{surf}} d\mu_i$$

So:

$$0 = S^{\text{surf}} dT + A d\gamma + \sum_{i=1}^{C} N_i^{\text{surf}} d\mu_i$$

which expresses a relation between variations of the intensive degrees of freedom for a surface to remain in equilibrium. Dividing through by the total surface area (so as to normalize by the area, creating derived intensive variables) and defining

$$\widetilde{S^{\text{surf}}} = \frac{S^{\text{surf}}}{A}$$

as the entropy of the surface per area, then,

$$\begin{aligned} 0 &= d\gamma + \widetilde{S^{\text{surf}}} dT + \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2 + \ldots \Gamma_C d\mu_c \\ &= d\gamma + \widetilde{S^{\text{surf}}} dT + \sum_{i=1}^{C} \Gamma_i d\mu_i \end{aligned}$$

Where

$$\Gamma_i \equiv \widetilde{N_i^{\text{surf}}}$$

is the standard notation for the excess surface concentration. Holding everything (temperature, et cetera) constant except μ1, we get a relation that expresses the relation between the change in surface tension to the change in chemical potential of an absorbing species:

$$\left(\frac{\partial \gamma}{\partial \mu_i}\right)_{\text{constant}_{T,\mu_j \neq \mu_i}} = -\Gamma_i$$

This is the “Gibbs Absorption Isotherm.”

It is well known that the surface tension of water decreases when a detergent is added. Detergents are strongly enriched at the surface, which lowers the surface tension. This change of surface tension upon adsorption of substances to the interface, is described by the Gibbs adsorption isotherm. Note that if a species absorbs to the surface Γi > 0 and the surface tension decreases as the chemical potential of that species is increased.

The choice of the ideal interface in the Gibbs adsorption isotherm (3.52) for a two-component system is, in a certain view, arbitrary. It is, however, convenient. There are two reasons: First, on the right side there are physically measurable quantities (a, γ, T), which are related in a simple way to the interfacial excess. Any other choice of the interface would lead to a more complicated expression. Second, the choice of the interface is intuitively evident, at least for c1 >>c2. One should, however, keep in mind that different spatial distributions of the solute can lead to the same $\Gamma(1)2$. Figure 3.6 shows two examples of the same interfacial excess concentration $\Gamma(1)2$. In the first case the distribution of molecules 2 stretches out beyond the interface, but the concentration is nowhere increased. In the second case, the concentration of the molecules 2 is actually increased.

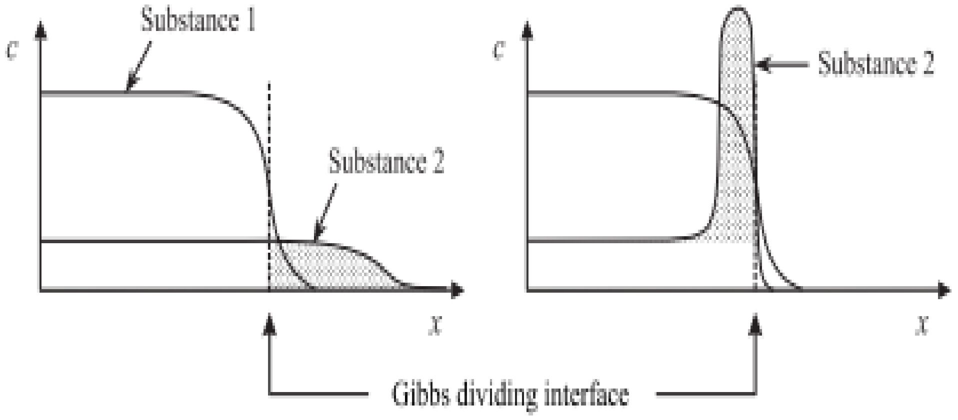


Figure IV.7: Examples of two different concentration profiles leading to the same interfacial excess concentration $\Gamma(1)2$.

There are two common and widely used definitions of the interfacial excess enthalpy. We can argue that enthalpy is equal to the internal energy minus the total mechanical work $\gamma A - P V^\sigma$. Since in the Gibbs convention $P V^\sigma = 0$ we define

$$H^\sigma \equiv U^\sigma - \gamma A \tag{3.32}$$

This definition is recommended by the IUPAC. One consequence is that $H = H \alpha + H \beta + H \sigma + \gamma A$. The differential is again easily obtained to be

$$dH^\sigma = TdS^\sigma + \sum \mu_i dN_i^\sigma - Ad\gamma$$

Alternatively, one could argue that the enthalpy is equal to the internal energy minus the volume work $P V \sigma$. Since the volume work is zero in the Gibbs convention we simply get

$$H'^\sigma \equiv U^\sigma$$

The difference between $U \sigma$ and $F \sigma$ should be the same as the one between $H \sigma$ and $G \sigma$. Therefore we define

$$G^{\sigma} \equiv H^{\sigma} - TS^{\sigma} = F^{\sigma} - \gamma A = \sum \mu_i N_i^{\sigma}$$

One consequence is that G = G α + G β + G σ + γA. The differential is

$$dG^{\sigma} = -S^{\sigma} dT + \sum \mu_i dN_i^{\sigma} - A d\gamma$$

With the alternative definition of H'$^{\sigma}$ we obtain

$$G'^{\sigma} \equiv H'^{\sigma} - TS^{\sigma} = F^{\sigma}$$

and $G = G^{\alpha} + G^{\beta} + G'^{\sigma}$.

Consider the case where three different phases make contact:

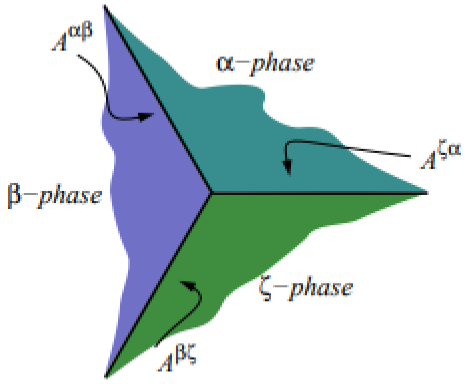


Figure IV.8: Intersection, or triple line, where three phases make contact in space.

Considering

$$dU^{\text{surf}} = \gamma^{\alpha\beta} dA^{\alpha\beta} + \gamma^{\beta\zeta} dA^{\beta\zeta} + \gamma^{\zeta\alpha} dA^{\zeta\alpha}$$

must be a minimum, one may derive two relations for the angles of contact:

$$\frac{\sin\phi_{\alpha\beta}}{\gamma_{\alpha\beta}} = \frac{\sin\phi_{\beta\zeta}}{\gamma_{\beta\zeta}} = \frac{\sin\phi_{\zeta\alpha}}{\gamma_{\zeta\alpha}}$$

which is the general equation the angles at a triple line, called Young’s equation, where

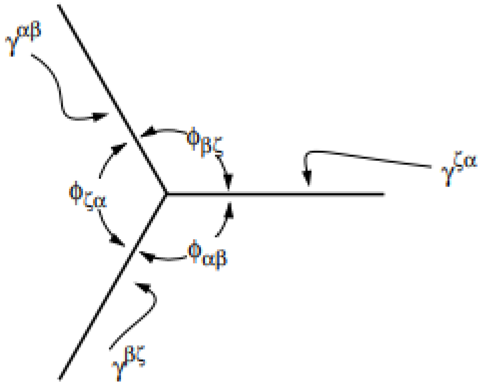


Figure IV.9: The definitions of the terms in Young's Equation.

which is equivalent to the "force balance" where each of the γ are considered the forces applied to the vertex.

IV. 4.1 Temperature dependence of specific surface free energy

For the temperature range that are typically used in the studies of surface-tension, Gs=γ. Temperature dependence can be determined by differentiating with respect to temperature

$$\left(\frac{\partial G^s}{\partial T}\right)_P = \left(\frac{\partial \gamma}{\partial T}\right)_P = -S^s$$

Thus, temperature dependence of surface tension leads to the specific surface entropy. • Temperature dependence of g predicting by a semi-empirical equation (van der Waals and Guggenheim:

$$\gamma = \gamma^o (1 - T / T_o)^n$$

where g o = g at T = 0 K, Tc = critical temperature (temperature at which condensed phase no longer can exist) and n is a constant that varies from 11/9 for organic substances to 1 for metals. –Notice γ = 0 when T=Tc.

Another empirical relationship for metals:

$$\gamma_m = \frac{3.6 T_m}{V_m^{2/3}}$$

where m = melting point of the metal; g is in dynes per centimeter. • Specific surface enthalpy can be determined from the specific free energy and entropy:

$$H^s = G^s + TS^s$$

$$H^s = \gamma - T\left(\frac{\partial \gamma}{\partial T}\right)_P$$

IV.4.2 Specific Surface Energy and Heat Capacity

At constant pressure the heat absorbed upon creation of unit surface area is given by previous equation. If volume is constant, then we can immediately see that the specific surface energy and specific surface enthalpy are equal to each other:

$$E^s = \gamma - T\left(\frac{\partial \gamma}{\partial T}\right)_P$$

Specific Heat Capacity

Remember the heat capacity, C, is defined as C = dq/dt. This leads to:

$$C_v = \left(\frac{\partial q}{\partial T}\right)_v = \left(\frac{\partial E}{\partial T}\right)_v \wedge C_P = \left(\frac{\partial q}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P$$

Take derivative with respect to temperature of equation 4 to find the heat capacity at constant pressure.

$$C_P^s = \left(\frac{\partial H^s}{\partial T}\right)_P = \frac{\partial}{\partial T}\left[\gamma - T\left(\frac{\partial \gamma}{\partial T}\right)_P\right]_p = \left(\frac{\partial \gamma}{\partial T}\right)_p - \left(\frac{\partial T}{\partial T}\right)_P\left(\frac{\partial \gamma}{\partial T}\right)_P - T\left(\frac{\partial^2 \gamma}{\partial T^2}\right)_P$$

$$C_P^s = -T\left(\frac{\partial^2 \gamma}{\partial T^2}\right)_P$$

Also, using H = G + TS and taking the derivative of both sides with respect to T leads to:

$$\left(\frac{\partial H}{\partial T}\right)_P = \frac{\partial}{\partial T}(G + TS)_P = \left(\frac{\partial G}{\partial T}\right)_P + \left(\frac{\partial T}{\partial T}\right)_P S + T\left(\frac{\partial S}{\partial T}\right)_P = -S + S + T\left(\frac{\partial S}{\partial T}\right)_P$$

$$\left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P =$$

- Surface heat capacity is equal to T times temperature derivative of entropy at constant pressure.
- On metal surfaces Cv and CP are usually consider approximately equal to each other.
- Accurate surface tension measurements should lead to accurate estimates of surface heat capacity.
- Direct Surface Heat capacities are often not reliable since the data is often not accurate enough.

- Better results are obtained from direct measurements of surface heat capacity measurements on finely divided powders with large surface – to – volume ratio.
- Difference between this and heat capacity of large crystallites of the same material yield the surface heat capacity.

Chapter V: Surface Electronic Proprieties and Chemical Bonds

V. 1 Introduction

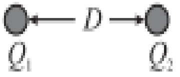
A vast array of phenomena within interface science revolves around the intricate dynamics of surface forces. In practical terms, many applications in colloid science boil down to the challenge of regulating the forces acting between colloidal particles, between particles and surfaces, and between two surfaces. Consequently, scientists have invested considerable effort in comprehending surface forces and their manipulation. When we discuss "surface forces," our initial thoughts often drift towards the interaction between two solid particles immersed in a fluid medium. This scenario is particularly pertinent when considering the stability of sols. If attractive forces prevail, the particles tend to aggregate, whereas dominance of repulsive forces ensures dispersion stability. However, the realm of "surface forces" extends beyond this specific scenario. For instance, it encompasses the interaction between two liquid-gas interfaces within a liquid lamella—a critical aspect governing foam stability. In this case, the interaction occurs between the two-opposing liquid-vapor interfaces. Should these interactions prove attractive, the liquid lamella becomes unstable and eventually ruptures. Conversely, a repulsive interaction ensures the stability of the lamella. Another illustration lies in thin liquid films adhering to solid surfaces, where both solid-liquid and liquid-vapor interfaces interact. In this context, a repulsive interaction results in a stable film that tends to spread across the solid surface, whereas attractive interactions tend to destabilize thin films.

V.2 Van der Waals forces between molecules

These forces have their origin in the dipole or induced-dipole interactions at the atomic level and are therefore of extreme importance in almost all aspects of the study of materials. The strength of van der Waals forces increases in the case of interaction between macroscopic objects such as colloidal particles since typically each particle has a large number of atoms or molecules. One of the most important things to bear in mind in studying van der Waals forces is that this topic has ramifications that extend far beyond our discussion here. Van der Waals interactions, for example, contribute to the nonideality of gases and, closer to home, gas adsorption. Almost all interfacial phenomena are influenced to various extents by forces that have their origin in atomic- and molecular-level interactions due to the induced or permanent polarities created in molecules by the electric fields of neighboring molecules or due to the instantaneous dipoles caused by the "positions" of the electrons around the nuclei. These forces consist of three major categories known as Keesom interactions (permanent dipole/permanent dipole interactions), Debye interactions (permanent dipole/induced dipole interactions), and London interactions (induced dipole/induced dipole interactions). The three are known collectively as the van der Waals interactions and play a major role in determining material properties and behavior important in colloid and surface chemistry. Of the three forces mentioned above, the London force is always present (like the gravitational force) because it does not require the existence of permanent polarity or charge-induced polarity in the molecules. Even neutral atoms or molecules such as helium or hydrocarbons give rise to the London interaction. As a consequence, the London interaction plays a special role in colloid and surface chemistry. As mentioned above, it influences physical adsorption and surface tension; in addition, it is important in adhesion, wetting phenomena, structure of macromolecules such as proteins and other biological and nonbiological polymer molecules, and stability of foams and thin films. It also plays a very important part in determining the strengths of solids, properties of gases and liquids, heat of melting and vaporization of solids, and the like.

Forces between macroscopic objects result from a complex interplay of the interaction between molecules in the two objects and the medium separating them. The basis for an understanding of intermolecular forces is the Coulomb 1 force. The Coulomb force is the electrostatic force between two charges Q1 and Q2:

$$F = \frac{Q_1 Q_2}{4\pi\varepsilon\varepsilon_0 D^2}$$



)

The potential energy between two electrical charges which are a distance D apart is:

$$W = \frac{Q_1 Q_2}{4\pi\varepsilon\varepsilon_0 D} \qquad 2)$$

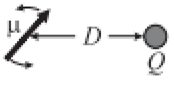
For charges with opposite sign the potential energy is negative. They reduce their energy when they get closer. If the two charges are in a medium, the dielectric permittivity ε is higher than one and the electrostatic force is reduced accordingly.

Example 1. The potential energy between Na$^+$ and Cl$^-$, being 1 nm apart, in a vacuum is:

$$W = -\frac{\left(1.60 \times 10^{-19}\mathrm{C}\right)^2}{4\pi \cdot 8.85 \times 10^{-12}\mathrm{AsV}^{-1}\mathrm{m}^{-1} \cdot 10^{-9}\mathrm{m}} = -2.30 \times 10^{-19}\,\mathrm{J}$$

The average potential energy is

$$W = -\frac{Q^2\mu^2}{6(4\pi\varepsilon_0)^2 k_B T D^4}$$

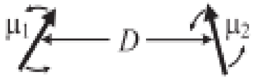


Example 2. Calculate the potential energy between Na+ and a water molecule (dipole moment 6.17 × 10^{-30} Cm) being 1 nm apart in vacuum at 25◦C.

$$
\begin{aligned}
W &= -\frac{\left(1.60\times10^{-19}\mathrm{C}\right)^2\left(6.17\times10^{-30}\mathrm{Cm}\right)^2}{6\left(4\pi\cdot 8.85\times10^{-12}\mathrm{AsV^{-1}m^{-1}}\right)^2\cdot 4.12\times10^{-21}\mathrm{J}\cdot\left(10^{-9}\mathrm{m}\right)^4}\\
&= -3.20\times10^{-21}\ \mathrm{J}
\end{aligned}
$$

Two freely rotating dipoles attract each other because they preferentially orient with their opposite charges facing each other. This randomly oriented dipole–dipole interaction is often referred to as the Keesom energy :

$$W = -\frac{C_{orient}}{D^6} = -\frac{\mu_1^2\mu_2^2}{3(4\pi\varepsilon_0)^2 k_B T D^6}$$



Example 3. The polarizability of a water molecule is 1.65 × 10−40 C2m2J−1. Which dipole moment is induced by a unit charge which is 1 nm away and what is the potential energy between the two? The electric field of a point charge at a distance D is

$$E = \frac{Q}{4\pi\varepsilon_0 D^2} = 1.44\times10^9\ \frac{\mathrm{V}}{\mathrm{m}}$$

If the dipole can freely rotate, the Helmholtz free energy is

$$W = -\frac{C_{ind}}{D^6} = -\frac{\mu^2\alpha}{(4\pi\varepsilon_0)^2 D^6}$$

for different molecules. If the molecules are identical, a factor of two has to be inserted.

V.3 Concepts for the description of surface forces

V.3.1 The Derjaguin approximation

The Derjaguin approximation relates the energy per unit area between two planar surfaces w which are separated by a gap of width x to the energy between two bodies of arbitrary shape W which are at a distance D:

$$W(D) = \int_D^\infty w(x)\,\frac{dA}{dx}dx$$

The integration runs over the entire surface of the solid. Please note that here A is the cross-sectional area. Often we have to deal with rotational-symmetric configurations.

The approximation is only valid if the characteristic decay length of the surface force is small in comparison to the curvature of the surfaces.

For the force we can use a similar equation as for the energy:

$$\begin{aligned}
F(D) &= \int_D^\infty f(x)\,\frac{dA}{dx}dx = -\int_D^\infty \frac{A_H}{6\pi x^3}\cdot 2\pi\cdot\tan^2\alpha\cdot(x-D)\cdot dx \\
&= -\frac{A_H\tan^2\alpha}{3}\cdot\int_D^\infty \frac{x-D}{x^3}dx \\
F(D) &= -\frac{A_H\tan^2\alpha}{3}\cdot\left[-\frac{1}{x}+\frac{D}{2x^2}\right]_D^\infty = \frac{A_H\tan^2\alpha}{3}\cdot\left(-\frac{1}{D}+\frac{1}{2D}\right) \\
&= -\frac{A_H\tan^2\alpha}{6D}
\end{aligned}$$

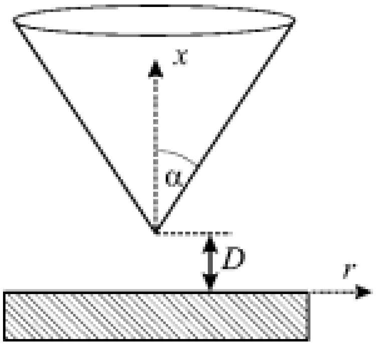


Figure V.1: Interaction between a cone and a planar surface.

A special, but nevertheless important, case is the interaction between two identical spheres. It is important to understand the stability of dispersions. For the case of two spheres of equal radius **R**, the parameters x and r are related by :

$$x(r) = D+2R-2\sqrt{R^2-r^2} \Rightarrow dx = \frac{2r}{\sqrt{R^2-r^2}}dr \Rightarrow 2rdr = \sqrt{R^2-r^2}\cdot dx$$

If the range of the interaction is substantially smaller than **R**, then we only need to consider the outer caps of the two spheres and only the contributions with a small r are effective. We can simplify

$$2rdr = \sqrt{R^2-r^2}\cdot dx \approx Rdx$$

From the potential energy we can calculate the force between two spheres:

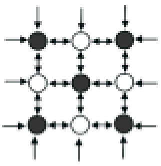
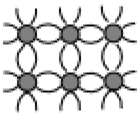
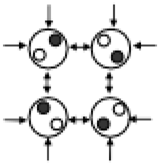
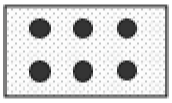
$$F = -\frac{dW}{dD} = -\pi R\cdot\frac{d}{dD}\left(\int_D^\infty w(x)\,dx\right) = \pi R\cdot w(D)$$

Derjaguin's approximation has a fundamental consequence. In general, the force or energy between two bodies depends on the shape, on the material properties, and on the distance. Now it is possible to divide the force (or energy) between two solids into a purely geometrical factor and into a material and distance-dependent term w(x). Thus, it is possible to describe the interaction independent of the geometry. This also gives us a common reference, which is w(x). In the following we only discuss w(x).

V.4 Bonds in solid

A solid consists of atoms, ions, or molecules packed cosly together and forces that hold them in place give rise to the distinctive properties of the various kind of solids. The covalent bonds that can link a fixed number of atoms to forms a certain molecule can also link an unlimited number of molecules to form a solid. I addition ionic, Van der Waals, and metallic bonds provide the cohesive forces in solids. Whose structural elements afre respectively ion, molecules, and metal atoms.

Table V.1: Types of Crytalline solids on the basis of bonding types:

Types	Lattice	Bond	Properties	Example
Ionic		Electron attraction	• Hard • Melting point high • Solube in polar liquids • Elelctrical insulators (Conductors in solution)	Alkali Halides, Alkaline oxides (Na_2O), etc.
Covalent		Shared Electrons	• Very hard • High melting points • Insoluble in nearly all liquids • Semiconductors (Except diamond)	Diamond, C, Etc.
Molecular		Van der Waals forces	• Soft • Low melting and boiling points • Soluble in covalent liquids • Electrical insulators	Methane (CH_4)
Metallic		Electron gas	• Ductile • Metallic luster • High electrical and thermal conductivity	Sodium (Na)

Thus, on the basis of bonding type, we have following five categories of solids:

1. Ionic solids (NaCl, NaOH, etc.)

2. Covalent solids (Diamond, Silicon)
3. Metallic solids (various metals and alloys)
4. Van der waals bonded solids/ molecules (O_2 , H_2 , Solid He, Kr, Xe)
5. Hydrogen bonded solids (Ice, Some fluorides)

Note:

- The reason of condensation is due to van der Waals bonding.
- Hydrogen bonding is a special type of van der Waals bonding containing Hydrogen atoms.
- Ioninc bonds come into being when atoms that have low ionization energies, and hence loss electron readily interect with other atoms that tend to aquire excess electrons. The formar atoms give up electrons to the later, and they thereupon become positive and negative ions respectively. In ionic crystals this ion assembles themselves in an equilibrium configuration in which the attaractive forces between the positive and negative ions balance the repulsive forces between ions.
- Electron affinity: It is the energy, ralesed when an electron si addede to an atm of a given elements; the greater the electro, the more such atoms tends to becobe negative ions. Sodium, with an ionization energy of 5.14 eV, tends to form Na^+, and Chlorine atom wioth an electron affinity, tends to form Cl^- ions.

Definition of the chemical bond

Once an atom in a molecule has been defined, it is possible to distinguish between bonded and nonbonded atoms. In the first case, two atoms A and B ai;e separated by a common zero-fliux surface S (A, B). In the second case, the two atomic subspaces are separated by at least one other subspace belonging to a third atom. We conclude that a necessary condition for the existence of a chemical bond between atoms A and B is the existence of a common zero-flux surface S (A, B). This condition is certainly not sufficient as becomes immediately clear when considering the van der Waals complex Hez or two atoms A and B separated by such a distance that bonding is no longer possible. In these cases, the atomic regions of A and B are still separated by a common surface S (A, B). The same applies if A and B belong to two different molecules described by the wave function of the corresponding supermolecule (for examples, see Figure 2). In order to distinguish between bonding and nonbonding situations, a second condition has to complement the first one. The second condition should be sufficient to detect a bond AB.

We speak of a chemical bond between two atoms A and B if and

1. a saddle point rp and, hence, a zero-flux surface S exists between A and B (necessary condition)

2. the local energy density H (rp) is smaller than zero (sufficient condition). We denote the bond as a covalent bond and distinguish it from noncovalent bonds to be discussed in the next section.

Ionic bonding is non-directional because an ion has the same attraction from all directions for an ion of opposite charge. Explanation: ... This means that packing efficiency in the crystal lattice determines the arrangement of ions in a crystal. There is no preferred direction for the bonds.

V.4.1 Ionic bonding

Metal atoms lose electrons to become positively charged ions. Nonmetal atoms gain electrons to become negatively charged ions. The ions produced by metals in Groups 1 and 2 and by non-metals in Groups 6 and 7 have the electronic structure of a noble gas (Group 0). The electron transfer during the formation of an ionic compound can be represented by a dot and cross diagram, eg for sodium chloride. The charge on the ions produced by metals in Groups 1 and 2 and by non-metals in Groups 6 and 7 relates to the group number of the element in the periodic table.

V.4.1.2 Electronic structures of cations

When forming a cation, an atom of a main group element tends to lose all of its valence electrons, thus assuming the electronic structure of the noble gas that precedes it in the periodic table. For groups 1 (the alkali metals) and 2 (the alkaline earth metals), the group numbers are equal to the numbers of valence shell electrons and, consequently, to the charges of the cations formed from atoms of these elements when all valence shell electrons are removed. For example, calcium is a group 2 element whose neutral atoms have 20 electrons and a ground state electron configuration of 1s 2 2s 2 2p 6 3s 2 3p 6 4s 2 . When a Ca atom loses both of its valence electrons, the result is a cation with 18 electrons, a 2+ charge, and an electron configuration of 1s 2 2s 2 2p 6 3s 2 3p 6.

The Ca2+ ion is therefore isoelectronic with the noble gas Ar. For groups 12–17, the group numbers exceed the number of valence electrons by 10 (accounting for the possibility of full d subshells in atoms of elements in the fourth and greater periods). Thus, the charge of a cation formed by the loss of all valence electrons is equal to the group number minus 10. For example, aluminum (in group 13) forms 3+ ions (Al3+).

Exceptions to the expected behavior involve elements toward the bottom of the groups. In addition to the expected ions Tl3+, Sn4+, Pb4+, and Bi5+, a partial loss of these atoms' valence shell electrons can also lead to the formation of Tl+ , Sn2+, Pb2+, and Bi3+ ions. The formation of these 1+, 2+, and 3+ cations is ascribed to the inert pair effect, which reflects the relatively low energy of the valence s-electron pair for atoms of the heavy elements of groups 13, 14, and 15. Mercury (group 12) also exhibits an unexpected behavior: it forms a diatomic ion, Hg_2^{2+} (an ion formed from two mercury atoms, with an Hg-Hg bond), in addition to the expected monatomic ion Hg^{2+} (formed from only one mercury atom). Transition and inner transition metal elements behave differently than main group elements. Most transition metal cations have 2+ or 3+ charges that result from the loss of their outermost s electron(s) first, sometimes followed by the loss of one or two d electrons from the next-to-outermost shell. For example, iron ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$) forms the ion Fe^{2+} ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$) by the loss of the 4s electron and the ion Fe^{3+} ($1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$) by the loss of the 4s electron and one of the 3d electrons. Although the d orbitals of the transition elements are—according to the Aufbau principle—the last to fill when building up electron configurations, the outermost s electrons are the first to be lost when these atoms ionize. When the inner transition metals form ions, they usually have a 3+ charge, resulting from the loss of their outermost s electrons and a d or f electron.

V.4.1.2 Electronic structures of anions

Most monatomic anions form when a neutral nonmetal atom gains enough electrons to completely fill its outer s and p orbitals, thereby reaching the electron configuration of the next noble gas. Thus, it is simple to determine the charge on such a negative ion: The charge is equal to the number of electrons that must be gained to fill the s and p orbitals of the parent atom. Oxygen, for example, has the electron configuration $1s^2 2s^2 2p^4$, whereas the oxygen anion has the electron configuration of the noble gas neon (Ne), $1s^2 2s^2 2p^6$. The two additional electrons required to fill the valence orbitals give the oxide ion the charge of 2– (O^{2-}).

V.4.2 Covalent bonding

In ionic compounds, electrons are transferred between atoms of different elements to form ions. But this is not the only way that compounds can be formed. Atoms can also make chemical bonds by sharing electrons equally between each other. Such bonds are called covalent bonds. Covalent bonds are formed between two atoms when both have similar tendencies to attract electrons to themselves (i.e., when both atoms have identical or fairly similar ionization energies and electron affinities). For example, two hydrogen atoms bond covalently to form an H_2 molecule; each hydrogen atom in the H_2 molecule has two electrons stabilizing it, giving each atom the same number of valence electrons as the noble gas He. Compounds that contain covalent bonds exhibit different physical properties than ionic compounds. Because the attraction between molecules, which are electrically neutral, is weaker than that between electrically charged ions, covalent compounds generally have much lower melting and boiling points than ionic compounds. In fact, many covalent compounds are liquids or gases at room temperature, and, in their solid states, they are typically much softer than ionic solids. Furthermore, whereas ionic compounds are good conductors of electricity when dissolved in water, most covalent compounds are insoluble in water; since they are electrically neutral, they are poor conductors of electricity in any state.

V.4.3 Ionic bond strength and lattice energy

An ionic compound is stable because of the electrostatic attraction between its positive and negative ions. The lattice energy of a compound is a measure of the strength of this attraction. The lattice energy (ΔHlattice) of an ionic compound is defined as the energy required to separate one mole of the solid into its component gaseous ions. For the ionic solid MX, the lattice energy is the enthalpy change of the process:

$$\mathrm{MX}(s) \longrightarrow \mathrm{M}^{n+}(g) + \mathrm{X}^{n-}(g) \qquad \Delta H_{\mathrm{lattice}}$$

Note that we are using the convention where the ionic solid is separated into ions, so our lattice energies will be endothermic (positive values). Some texts use the equivalent but opposite convention, defining lattice energy as the energy released when separate ions combine to form a lattice and giving negative (exothermic) values. Thus, if you are looking up lattice energies in another reference, be certain to check which definition is being used. In both cases, a larger magnitude for lattice energy indicates a more stable ionic compound. For sodium chloride, ΔHlattice = 769 kJ. Thus, it requires 769 kJ to separate one mole of solid NaCl into gaseous Na+ and Cl– ions. When one mole each of gaseous Na+ and Cl– ions form solid NaCl, 769 kJ of heat is released. The lattice energy ΔHlattice of an ionic crystal can be expressed by the following equation (derived from Coulomb's law, governing the forces between electric charges):

$$\Delta H_{\mathrm{lattice}} = \frac{\mathrm{C}(\mathrm{Z}^{+})(\mathrm{Z}^{-})}{\mathrm{R}_{\mathrm{o}}}$$

in which C is a constant that depends on the type of crystal structure; Z+ and Z– are the charges on the ions; and Ro is the interionic distance (the sum of the radii of the positive and negative ions). Thus, the lattice energy of an ionic crystal increases rapidly as the charges of the ions increase and the sizes of the ions decrease. When all other parameters are kept constant, doubling the charge of both the cation and anion quadruples the lattice energy. For example, the lattice energy of LiF (Z+ and Z– = 1) is 1023 kJ/mol, whereas that of MgO (Z+ and Z– = 2) is 3900 kJ/ mol (Ro is nearly the same—about 200 pm for both compounds). Different interatomic distances produce different lattice energies. For example, we can compare the lattice energy of MgF2 (2957 kJ/mol) to that of MgI2 (2327 kJ/mol) to observe the effect on lattice energy of the smaller ionic size of F – as compared to I–.

Formation of covalent bonds

Nonmetal atoms frequently engage in covalent bonding with other nonmetal atoms. For instance, the hydrogen molecule, H2, exemplifies a covalent bond formed between its two hydrogen atoms. Figure V.2 provides insight into the rationale behind this bond formation. Initially, on the far right of the figure, we observe two distinct hydrogen atoms, each with its specific potential energy, as indicated by the red line. Along the x-axis lies the distance separating the two atoms. As these atoms approach each other (progressing left along the x-axis), their valence orbitals (1s) start to overlap. Consequently, the single electrons on each hydrogen atom begin to interact with both atomic nuclei, occupying the space around both atoms. This interaction results in a strong attraction between each shared electron and both nuclei, leading to system stabilization and a decrease in potential energy as the bond distance decreases. However, if the atoms continue to draw nearer, the positive charges in the two nuclei begin to repel each other, causing the potential energy to increase. Ultimately, the bond length is determined by the distance at which the system achieves its lowest potential energy.

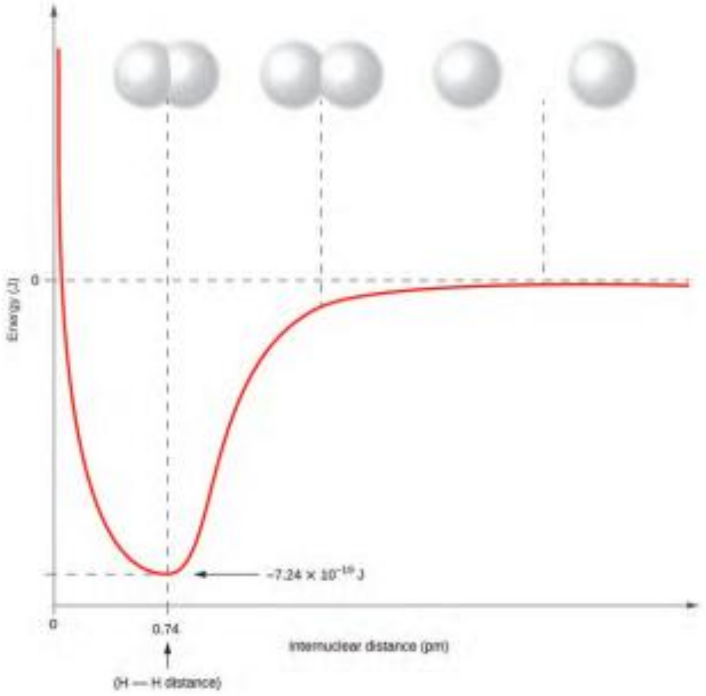


Figure V.2: The potential energy of two separate hydrogen atoms (right) decreases as they approach each other, and the single electrons on each atom are shared to form a covalent bond. The bond length is the internuclear distance at which the lowest potential energy is achieved.

It is essential to remember that energy must be added to break chemical bonds (an endothermic process), whereas forming chemical bonds releases energy (an exothermic process).

If the atoms that form a covalent bond are identical, as in H2, Cl2, and other diatomic molecules, then the electrons in the bond must be shared equally. We refer to this as a pure covalent bond. Electrons shared in pure covalent bonds have an equal probability of being near each nucleus. In the case of Cl2, each atom starts off with seven valence electrons, and each Cl shares one electron with the other, forming one covalent bond. The total number of electrons around each individual atom consists of six nonbonding electrons and two shared (i.e., bonding) electrons for eight total electrons, matching the number of valence electrons in the noble gas argon. Since the bonding atoms are identical, Cl2 also features a pure covalent bond. When the atoms linked by a covalent bond are different, the bonding electrons are shared, but no longer equally. Instead, the bonding electrons are more attracted to one atom than the other, giving rise to a shift of electron density toward that atom. This unequal distribution of electrons is known as a polar covalent bond, characterized by a partial positive charge on one atom and a partial negative charge on the other. The atom that attracts the electrons more strongly acquires the partial negative charge and vice versa. For example, the electrons in the H–Cl bond of a hydrogen chloride molecule spend more time near the chlorine atom than near the hydrogen atom. Thus, in an HCl molecule, the chlorine atom carries a partial negative charge and the hydrogen atom has a partial positive charge. Note that the shaded area around Cl is much larger than it is around H. Compare this to Figure V.2, which shows the even distribution of electrons in the H2 nonpolar bond. We sometimes designate the positive and negative atoms in a polar covalent bond using a lowercase Greek letter "delta," δ, with a plus sign or minus sign to indicate whether the atom has a partial positive charge (δ+) or a partial negative charge (δ–).

Bond Strength

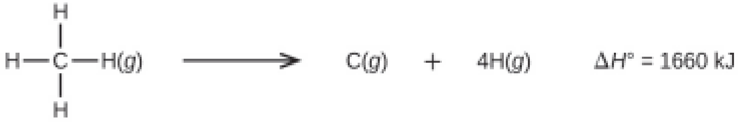
Covalent Bonds Stable molecules exist because covalent bonds hold the atoms together. We measure the strength of a covalent bond by the energy required to break it, that is, the energy necessary to separate the bonded atoms. Separating any pair of bonded atoms requires energy (see Figure 7.4). The stronger a bond, the greater the energy required to break it. The energy required to break a specific covalent bond in one mole of gaseous molecules is called the bond energy or the bond dissociation energy. The bond energy for a diatomic molecule, DX–Y, is defined as the standard enthalpy change for the endothermic reaction:

$$XY(g) \longrightarrow X(g) + Y(g) \qquad D_{X-Y} = \Delta H^\circ$$

For example, the bond energy of the pure covalent H–H bond, DH–H, is 436 kJ per mole of H–H bonds broken:

$$H_2(g) \longrightarrow 2H(g) \qquad D_{H-H} = \Delta H^\circ = 436\ \text{kJ}$$

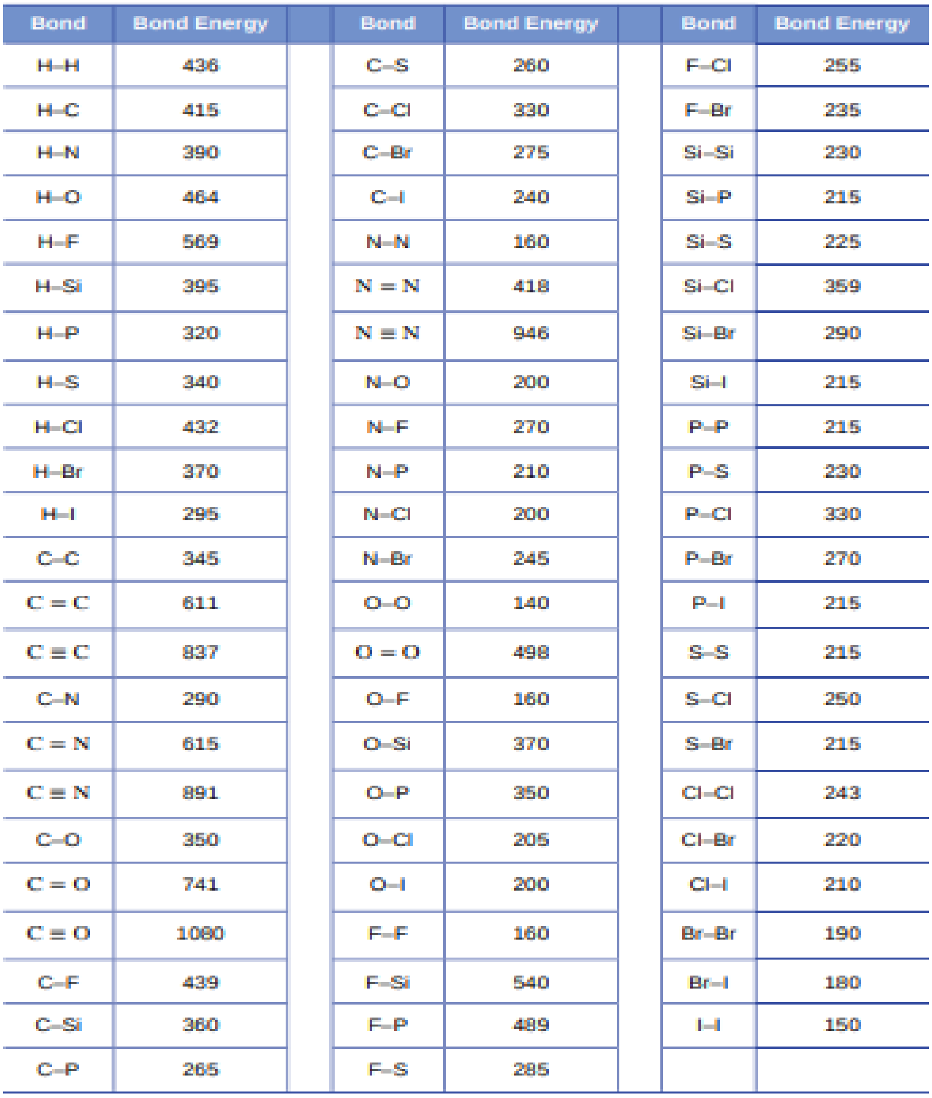
Molecules with three or more atoms have two or more bonds. The sum of all bond energies in such a molecule is equal to the standard enthalpy change for the endothermic reaction that breaks all the bonds in the molecule. For example, the sum of the four C–H bond energies in CH4, 1660 kJ, is equal to the standard enthalpy change of the reaction:



$$\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}-\text{H}(g) \\ | \\ \text{H} \end{array} \longrightarrow C(g) + 4H(g) \qquad \Delta H^\circ = 1660\ \text{kJ}$$

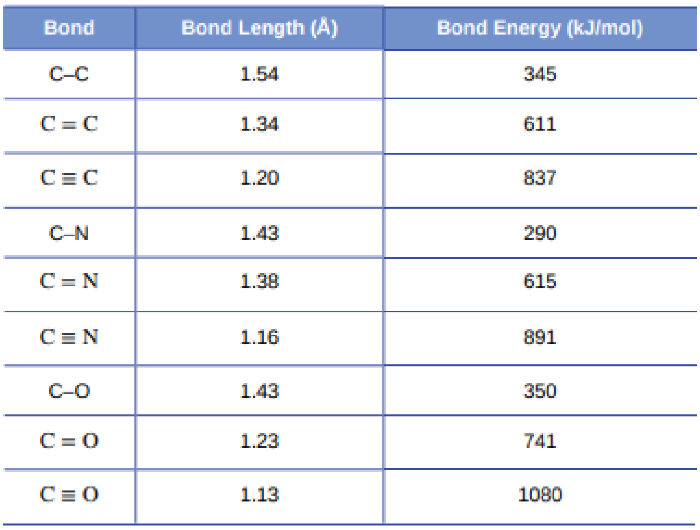
The average C–H bond energy, DC–H, is 1660/4 = 415 kJ/mol because there are four moles of C–H bonds broken per mole of the reaction. Although the four C–H bonds are equivalent in the original molecule, they do not each require the same energy to break; once the first bond is broken (which requires 439 kJ/mol), the remaining bonds are easier to break. The 415 kJ/mol value is the average, not the exact value required to break any one bond. The strength of a bond between two atoms increases as the number of electron pairs in the bond increases. Generally, as the bond strength increases, the bond length decreases. Thus, we find that triple bonds are stronger and shorter than double bonds between the same two atoms; likewise, double bonds are stronger and shorter than single bonds between the same two atoms. Average bond energies for some common bonds appear in Table 7.2, and a comparison of bond lengths and bond strengths for some common bonds appears in Table 7.3. When one atom bonds to various atoms in a group, the bond strength typically decreases as we move down the group. For example, C–F is 439 kJ/mol, C–Cl is 330 kJ/mol, and C–Br is 275 kJ/mol.

Table V.1: Bond Energies (kJ/mol).



Bond	Bond Energy	Bond	Bond Energy	Bond	Bond Energy
H–H	436	C–S	260	F–Cl	255
H–C	415	C–Cl	330	F–Br	235
H–N	390	C–Br	275	Si–Si	230
H–O	464	C–I	240	Si–P	215
H–F	569	N–N	160	Si–S	225
H–Si	395	N = N	418	Si–Cl	359
H–P	320	N ≡ N	946	Si–Br	290
H–S	340	N–O	200	Si–I	215
H–Cl	432	N–F	270	P–P	215
H–Br	370	N–P	210	P–S	230
H–I	295	N–Cl	200	P–Cl	330
C–C	345	N–Br	245	P–Br	270
C = C	611	O–O	140	P–I	215
C ≡ C	837	O = O	498	S–S	215
C–N	290	O–F	160	S–Cl	250
C = N	615	O–Si	370	S–Br	215
C ≡ N	891	O–P	350	Cl–Cl	243
C–O	350	O–Cl	205	Cl–Br	220
C = O	741	O–I	200	Cl–I	210
C ≡ O	1080	F–F	160	Br–Br	190
C–F	439	F–Si	540	Br–I	180
C–Si	360	F–P	489	I–I	150
C–P	265	F–S	285		

Table V.2: Average Bond Lengths and Bond Energies for Some Common Bonds.



Bond	Bond Length (Å)	Bond Energy (kJ/mol)
C–C	1.54	345
C = C	1.34	611
C ≡ C	1.20	837
C–N	1.43	290
C = N	1.38	615
C ≡ N	1.16	891
C–O	1.43	350
C = O	1.23	741
C ≡ O	1.13	1080

We can use bond energies to calculate approximate enthalpy changes for reactions where enthalpies of formation are not available. Calculations of this type will also tell us whether a reaction is exothermic or endothermic. An exothermic reaction (ΔH negative, heat produced) results when the bonds in the products are stronger than the bonds in the reactants. An endothermic reaction (ΔH positive, heat absorbed) results when the bonds in the products are weaker than those in the reactants. The enthalpy change, ΔH, for a chemical reaction is approximately equal to the sum of the energy required to break all bonds in the reactants (energy "in", positive sign) plus the energy released when all bonds are formed in the products (energy "out," negative sign). This can be expressed mathematically in the following way:

$$\Delta H = \Sigma \mathrm{D}_{\text{bonds broken}} - \Sigma \mathrm{D}_{\text{bonds formed}}$$

Example:

Consider the following reaction:

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$

$$H\text{–}H(g) + Cl\text{–}Cl(g) \longrightarrow 2H\text{–}Cl(g)$$

To form two moles of HCl, one mole of H–H bonds and one mole of Cl–Cl bonds must be broken. The energy required to break these bonds is the sum of the bond energy of the H–H bond (436 kJ/mol) and the Cl–Cl bond (243 kJ/mol). During the reaction, two moles of H–Cl bonds are formed (bond energy = 432 kJ/mol), releasing 2 × 432 kJ; or 864 kJ. Because the bonds in the products are stronger than those in the reactants, the reaction releases more energy than it consumes:

$$\begin{aligned}\Delta H &= \Sigma \mathrm{D}_{\text{bonds broken}} - \Sigma \mathrm{D}_{\text{bonds formed}}\\ \Delta H &= [\mathrm{D}_{\mathrm{H-H}} + \mathrm{D}_{\mathrm{Cl-Cl}}] - 2\mathrm{D}_{\mathrm{H-Cl}}\\ &= [436 + 243] - 2(432) = -185\ \mathrm{kJ}\end{aligned}$$

This excess energy is released as heat, so the reaction is exothermic. Twice that value is –184.6 kJ, which agrees well with the answer obtained earlier for the formation of two moles of HCl.

V.4.4 Metallic Bonds

Metallic bonds, as the name suggests, are bonds found only in metals. Metals are elements of the electropositive nature; thus, it is very easy for the constituent atoms to lose their outer shell electrons and form ions. In metals, these positively charged ions are held together in a sea of negatively charged free electrons. These free electrons are responsible for the high electric and thermal conductivities of metals. Metallic bond' is a term used to describe the collective sharing of a sea of valence electrons between several positively charged metal ions. Metallic bonding is a type of chemical bonding and is responsible for several characteristic properties of metals such as their shiny lustre, their malleability, and their conductivities for heat and electricity. The factors that affect the strength of a metallic bond include: • Total number of delocalized electrons. • Magnitude of positive charge held by the metal cation. • Ionic radius of the cation • An illustration describing the way electrons are delocalized over a rigid lattice of metal ions in a metallic bond is provided below. Metallic bonds are not broken when the metal is heated into the melt state. Instead, these bonds are weakened, causing the ordered array of metal ions to lose their definite, rigid structure and become liquid. However, these bonds are completely broken when the metal is heated to its boiling point.

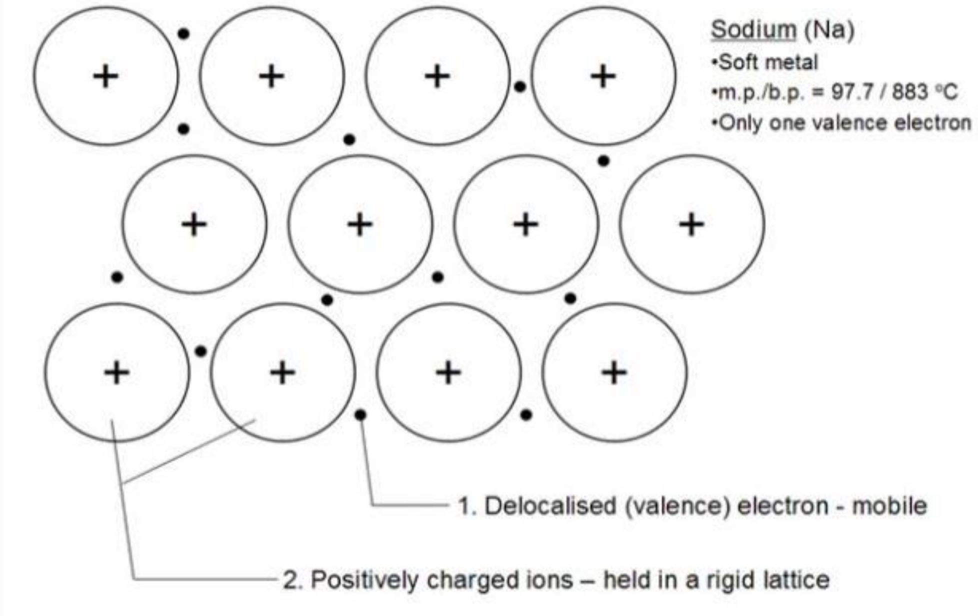


Figure V.3: Metallic bonding.

The softness and low melting point of sodium can be explained by the relatively low number of electrons in the electron sea and the relatively small charge on the sodium cation. For example, metallic magnesium consists of an array of Mg2+ ions. The electron sea here contains twice the number of electrons than the one in sodium (since two 3s electrons are delocalized into the sea). Due to the greater magnitude of charge and the greater electron density in the sea, the melting point of magnesium (˜650o C) is significantly higher than that of sodium.

V.4.4.1 Properties attributed by metallic bonding

Metallic bonds impart several important properties to metals that make them commercially desirable. Some of these properties are briefly described in this subsection.

- **Electrical Conductivity** is a measure of the ability of a substance to allow a charge to move through it. Since the movement of electrons is not restricted in the electron sea, any electric current passed through the metal passes through it, as illustrated below. When a potential difference is introduced to the metal, the delocalized electrons start moving towards the positive charge. This is the reason why metals are generally good conductors of electric current.

- **Thermal Conductivity** of a material is a measure of its ability to conduct/transfer heat. When one end of a metallic substance is heated, the kinetic energy of the electrons in that area increases. These electrons transfer their kinetic energies to other electrons in the sea via collisions. The greater the mobility of the electrons, the quicker the transfer of kinetic energy. Due to metallic bonds, the delocalized electrons are highly mobile and they transfer the heat through the metallic substance by colliding with other electrons.

- **Malleability and Ductility** When an ionic crystal (such a sodium chloride crystal) is beaten with a hammer, it shatters into many smaller pieces. This is because the atoms in the crystals are held together in a rigid lattice that is not easily deformed. The introduction of a force (from the hammer) causes the crystal structure to fracture, resulting in the shattering of the crystal. In the case of metals, the sea of electrons in the metallic bond enables the deformation of the lattice. Therefore, when metals are beaten with a hammer, the rigid lattice is deformed and not fractured. This is why metals can be beaten into thin sheets. Since these lattices do not fracture easily, metals are said to be highly ductile.

- **Metallic Luster** When light is incident on a metallic surface, the energy of the photon is absorbed by the sea of electrons that constitute the metallic bond. The absorption of energy excites the electrons, increasing their energy levels. These excited electrons quickly return to their ground states, emitting light in the process. This emission of light due to the de-excitation of electrons attributes a shiny metallic lustre to the metal.

- **High Melting and Boiling Points** As a result of powerful metallic bonding, the attractive force between the metal atoms is quite strong. In order to overcome this force of attraction, a great deal of energy is required. This is the reason why metals tend to have high melting and boiling points. The exceptions to this include zinc, cadmium, and mercury (explained by their electron configurations, which end with ns2). The metallic bond can retain its strength even when the metal is in its melt state. For example, gallium melts at 29.76o C but boils only at 2400o C. Therefore, molten gallium is a nonvolatile liquid.

Difference between Metallic Bonding and Ionic Bonding

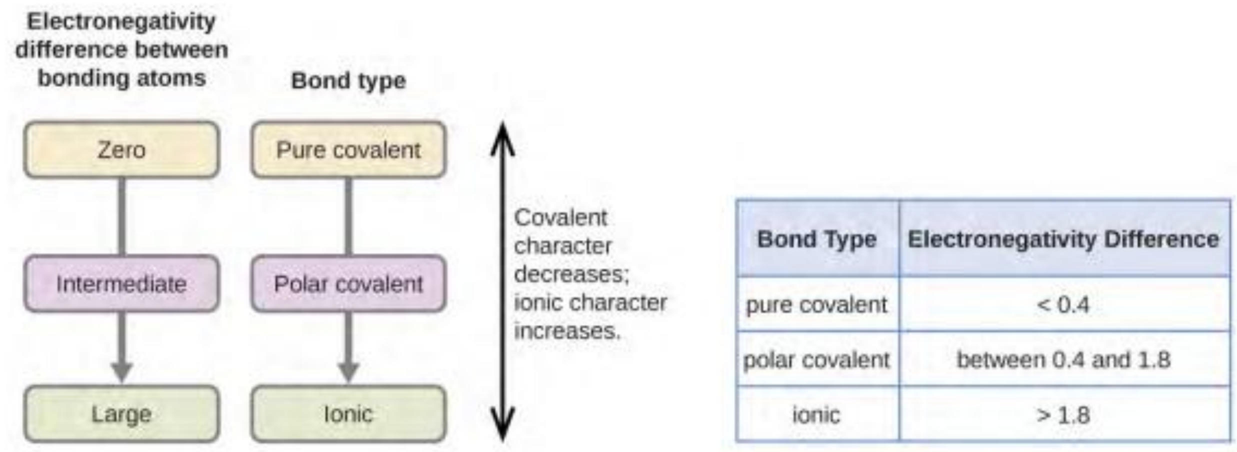
Ionic bonds involve the transfer of electrons between two chemical species. They arise from a difference in the electronegativities of the bonded atoms. On the other hand, metallic bonds are formed when a rigid, definite lattice of metal cations share a sea of delocalized valence electrons. However, both these types of bonding involve electrostatic forces of attraction.

V.4.5 Polar covalent bonding

Polar covalent bonding is described in terms of covalent bonding with unequal sharing of electrons. This inequality is described as occurring when a bond forms between atoms with different electronegativities (Silberberg, 2003; Lagowski, 1997c), resulting in a bond with one partially negative pole and one partially positive pole (Silberberg), or a bond in which the electron density is shifted toward the more electronegative atom (Lagowski, 1997c). This unequal sharing can also be described without drawing on the concept of electronegativity, for instance by saying that the electron pair is held more closely by one of the atoms (Parker, 1997) or that the electrons lie closer to one of the two atoms in the bond because of differences in the attractive forces 32 acting on the bonding electron pair (Hopp & Henning, 1983). Other reasons given for the unequal sharing are that the electrons spend more time in the vicinity of one atom, which can be framed as a partial electron transfer or shift in electron density. Using this model, the electronegativity of the participating atoms can be used to distinguish between polar and non-polar covalent bonds (Chang, 2005). Lewis (2007) does not use the term polar covalent bonds; instead, covalent bonds are said to exist on a spectrum with non-polar bonds having evenly shared electrons at one extreme and very polar bonds with extremely uneven sharing at the other. According to Atkins (1994), a covalent bond is non-polar if the electron sharing is equal and polar if it is unequal.

V.5 Electronegativity and bond type

The absolute value of the difference in electronegativity (ΔEN) of two bonded atoms provides a rough measure of the polarity to be expected in the bond and, thus, the bond type. When the difference is very small or zero, the bond is covalent and nonpolar. When it is large, the bond is polar covalent or ionic. The absolute values of the electronegativity differences between the atoms in the bonds H–H, H–Cl, and Na–Cl are 0 (nonpolar), 0.9 (polar covalent), and 2.1 (ionic), respectively. The degree to which electrons are shared between atoms varies from completely equal (pure covalent bonding) to not at all (ionic bonding). Figure 7.8 shows the relationship between electronegativity difference and bond type.

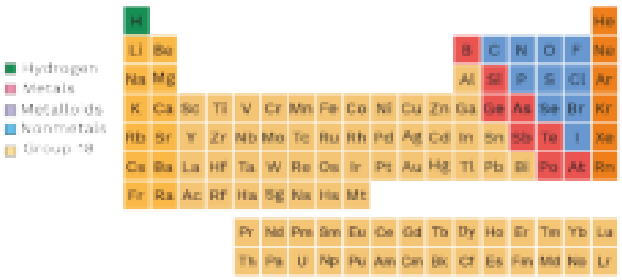


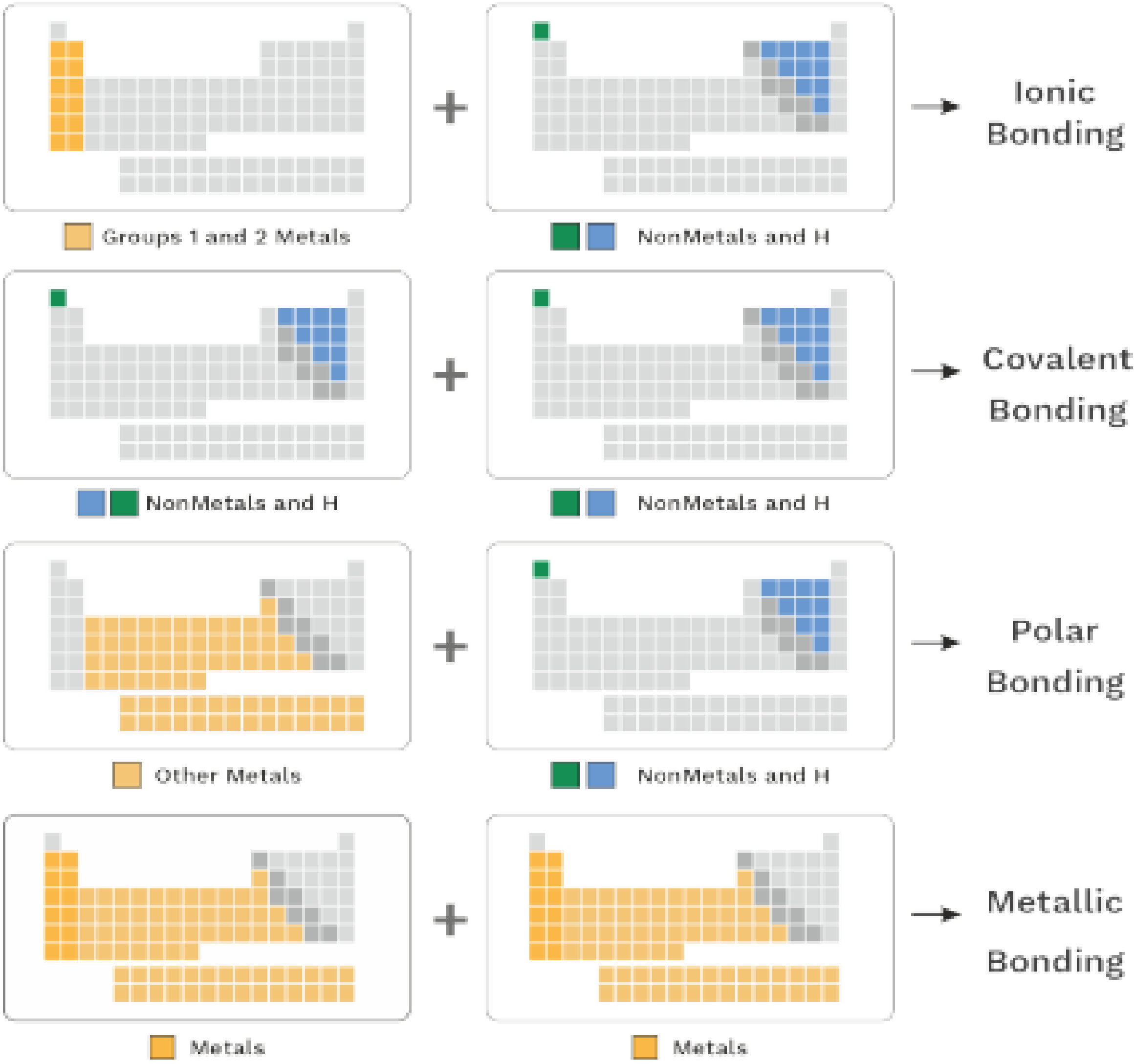
Bond Type	Electronegativity Difference
pure covalent	< 0.4
polar covalent	between 0.4 and 1.8
ionic	> 1.8

Figure V.3: As the electronegativity difference increases between two atoms, the bond becomes more ionic.

A rough approximation of the electronegativity differences associated with covalent, polar covalent, and ionic bonds is shown in Figure V.3. This table is just a general guide, however, with many exceptions. For example, the H and F atoms in HF have an electronegativity difference of 1.9, and the N and H atoms in NH3 a difference of 0.9, yet both of these compounds form bonds that are considered polar covalent. Likewise, the Na and Cl atoms in NaCl have an electronegativity difference of 2.1, and the Mn and I atoms in MnI2 have a difference of 1.0, yet both of these substances form ionic compounds. The best guide to the covalent or ionic character of a bond is to consider the types of atoms involved and their relative positions in the periodic table. Bonds between two nonmetals are generally covalent; bonding between a metal and a nonmetal is often ionic. Some compounds contain both covalent and ionic bonds. The atoms in polyatomic ions, such as OH– , NO3 −, and NH4 +, are held together by polar covalent bonds. However, these polyatomic ions form ionic compounds by combining with ions of opposite charge. For example, potassium nitrate, KNO3, contains the K+ cation and the polyatomic NO3 − anion. Thus, bonding in potassium nitrate is ionic, resulting from the electrostatic attraction between the ions K+ and NO3 −, as well as covalent between the nitrogen and oxygen atoms in NO3 −.

Summary


Hydrogen
Metals
Metalloids
Nonmetals
Group 18


Groups 1 and 2 Metals
+
NonMetals and H
Ionic Bonding
NonMetals and H
+
NonMetals and H
Covalent Bonding
Other Metals
+
NonMetals and H
Polar Bonding
Metals
+
Metals
Metallic Bonding

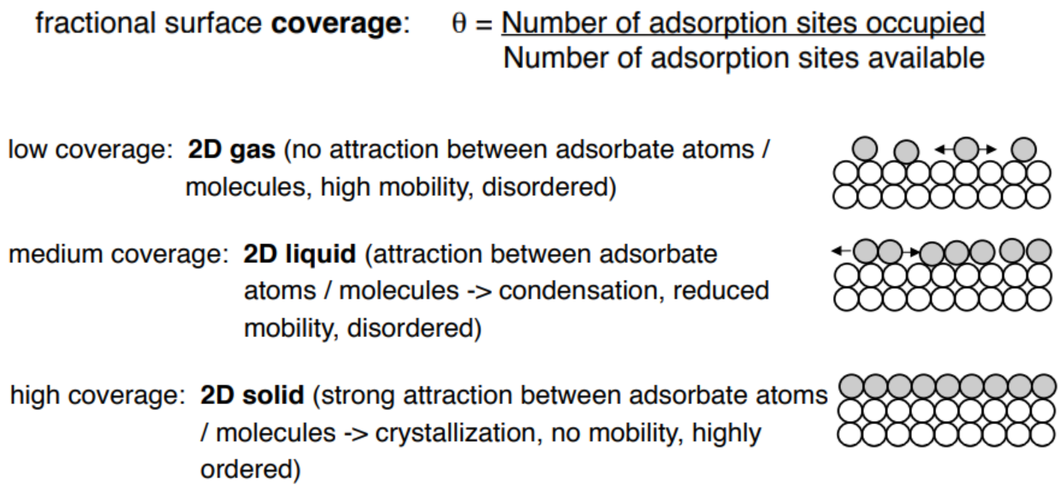
Chapter VI: Adsorption on solid surfaces

VI.1 Introduction

Adsorption is the process where component 'A' preferentially accumulates on the surface of material 'B', where 'A' is the adsorbate and 'B' is the adsorbent. The surfaces include both external and internal surfaces due to pores, with a much larger internal surface area for highly porous materials. In the bulk of the adsorbent, molecules are balanced in all directions, but at the adsorbent surface, unbalanced molecular forces create an attraction for adsorbate molecules. These forces, known as van der Waals attraction forces, are weak and facilitate adsorption of adsorbate molecules.

VI. 2 Definition of adsorption

Adsorption is the accumulation of particles (adsorbate) at a surface (adsorbent or substrate). The reverse process is called desorption.



fractional surface **coverage**: $$\theta = \frac{\text{Number of adsorption sites occupied}}{\text{Number of adsorption sites available}}$$

low coverage: **2D gas** (no attraction between adsorbate atoms / molecules, high mobility, disordered)

medium coverage: **2D liquid** (attraction between adsorbate atoms / molecules -> condensation, reduced mobility, disordered)

high coverage: **2D solid** (strong attraction between adsorbate atoms / molecules -> crystallization, no mobility, highly ordered)

The main difference between adsorption and absorption lies in the process and location of the interaction between substances:

- **Adsorption:** In adsorption, atoms, ions, or molecules from a substance adhere to the surface of another substance. It is a surface phenomenon where particles accumulate on the surface of a solid or liquid substance. This process involves the adhesion of particles onto the surface of a substance.

- **Absorption:** On the other hand, absorption involves the mass transfer of particles into another material, where one substance is absorbed by another. It is a bulk phenomenon where molecules pass into a bulky material, diffusing or dissolving into another substance to form a solution. Once absorbed, the molecules are not easily separated from the absorbent.

ABSORPTION	ADSORPTION
It is a bulk phenomenon.	It is a surface phenomenon.
It is a slow process.	It is a fast process.
Substance uniformly distributed throughout the surface.	Higher concentration of molecular species in the surface than in the bulk.
Attainment of equilibrium takes more time.	Equilibrium attained easily.
Eg.: Ammonia adsorbed in Charcoal.	Eg.: Ammonia adsorbed in water.

VI.2.1 Types of adsorption

The process where adsorbate molecules adhere to an adsorbent surface due to van der Waals forces is termed physisorption or physical adsorption. Van der Waals forces primarily involve dipole-dipole interactions, resulting in an exothermic process with a low enthalpy change known as the heat of adsorption. This process, akin to liquefaction, is also referred to as the heat of liquefaction in physisorption. At higher temperatures, adsorbed molecules can undergo electronic rearrangement with surface molecules, known as chemisorption, involving the formation and breaking of chemical bonds. Chemisorption is selective, with adsorbate molecules chemisorbing only on specific adsorbent surfaces where significant interaction occurs. This process is depicted in Figure VI.1, illustrating the different scenarios of adsorption, including physisorption and chemisorption.

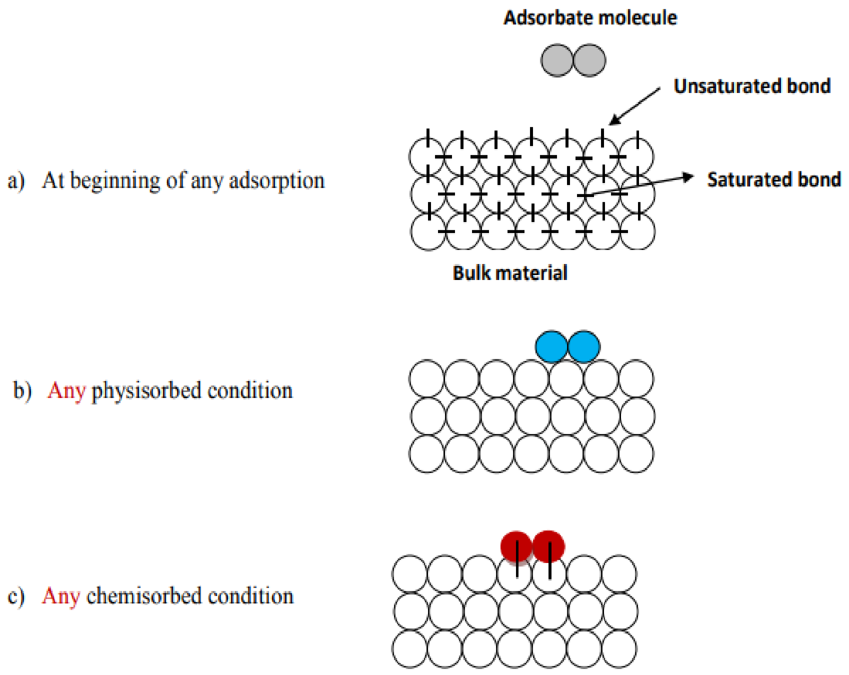


Figure VI.1: Schematic representation of different adsorption processes.

Differences between physisorption and chemisorption

Physical Adsorption	Chemical adsorption
It is due to weak Vander Waals force.	It is due to the formation of strong chemical bond.
It is a fast and reversible process.	It is a slow and irreversible process.
Heat of adsorption is low.	Heat of adsorption is high.
Distance between the adsorbate and adsorbent is more than 5 A°.	Distance between the adsorbate and adsorbent is between 1-2 A°.
Multimolecular layer is formed.	Unimolecular layer is formed.
No activation energy is needed.	Activation energy is needed.
Not specific in nature	Highly specific in nature.
Occurs at low temperature.	Increases with the increase in temperature.
As pressure increases, Physisorption increases, but at high pressure desorption occurs.	High pressure is favorable. No desorption occurs at high pressure.

VI.2.1.1 Physical adsorption or physisorption

This phenomenon is due to weak forces, of the Van der Waals type, between the adsorbed species and the surface. It is a reversible phenomenon that does not involve an activation energy. The heat of adsorption does not exceed 50 kJ mol , which is −1 comparable to that for the condensation of a gas. Figure 3.9 schematically shows the potential energy of a physisorbed atom or molecule as a function of its distance from the surface. The equilibrium position corresponds to the energy minimum. The adsorbed species must receive energy at least equal to the value of Qads in order to escape from this position. During physisorption, several layers of adsorbed atoms may form on top of each other

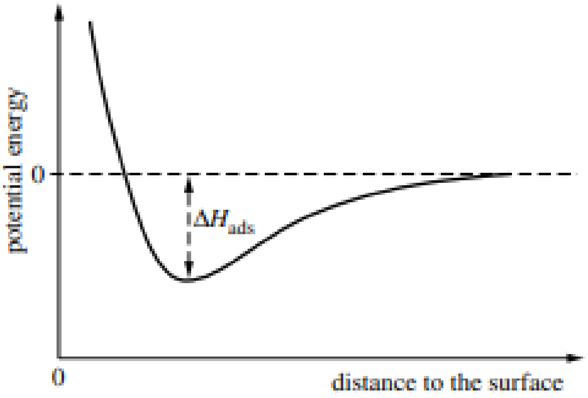


Figure VI.2: Variation of the potential energy with distance in physisorption.

VI.2.1.2 Chemical adsorption or chemisorption

The higher heat of adsorption (ranging from 100 to 500 kJ/mol) characterizes chemical adsorption, indicating the presence of strong chemical bonds. This process often involves overcoming an activation energy and typically results in the adsorption of a single layer of atoms or molecules. Chemisorption, a type of chemical adsorption, involves the dissociation of diatomic gas molecules like hydrogen or oxygen into adsorbed atoms, forming strong chemical bonds with the adsorbent. surface.

$$O_2 \rightleftharpoons 2\,O_{ads}$$

$$H_2 \rightleftharpoons 2\,H_{ads}$$

The type of reaction described is dissociative chemical adsorption. In Figure VI.3, the potential energy variation with distance from the surface is depicted. The first minimum represents the precursor state, indicating the physical adsorption of molecule X. The second, significantly lower minimum signifies the stable state of chemical adsorption. While the energy between the minima can be positive (curve b), the transition state energy is typically negative (curve a). Therefore, the activation energy for desorption is equal to Qads.

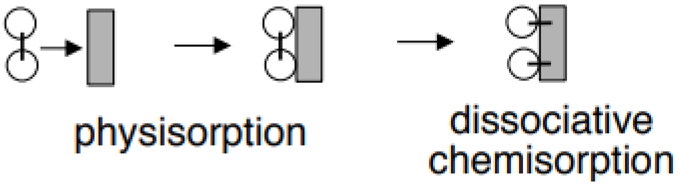


Figure VI.3: dissociative adsorption: upon chemisorption the molecules can dissociate into individual atoms / fragments.

The potential energy variation of a molecular system approaching a solid surface is illustrated by a potential energy diagram (Figure VI.4), where the potential energy is plotted against the distance of the molecule from the adsorbent surface. Initially, the molecule experiences a weak attractive force, leading to a relatively flat potential minimum, indicating non-dissociative physical adsorption. Depending on the level of interaction, the molecule can transition to a non-dissociative chemisorbed state and eventually to a stable dissociated state. When the interaction is weak, the adsorbate molecules undergo physical adsorption or non-dissociative chemisorption. In the presence of only van der Waals interactions, the adsorbates remain in a physisorbed state. Stronger electronic interactions can lead directly to dissociative chemisorption. If the crossing points on the potential energy diagram are below the line of zero potential energy, the process is non-activated; if they are above, activation is required for the overall process.

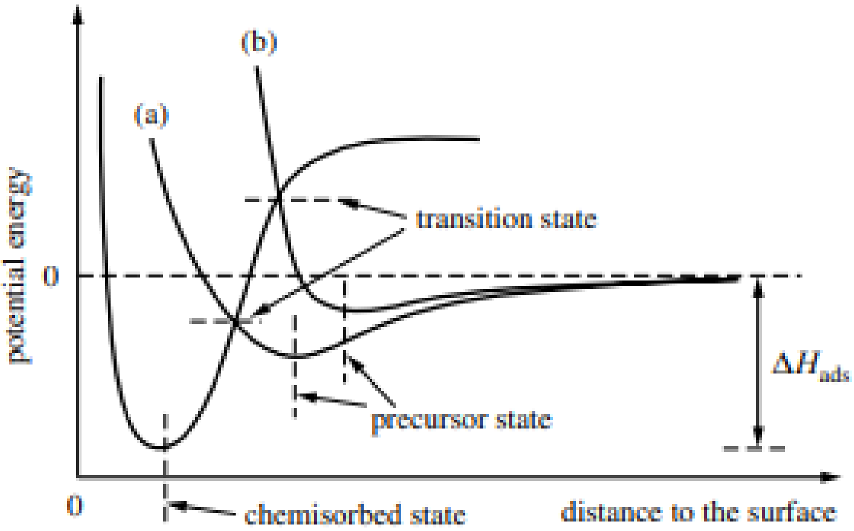


Figure VI.4: Variation of the potential energy with distance during chemisorption. The energy of the transistion state can be either negative (a) or positive (b).

VI.3 Adsorption of gases on solids

In adsorption of gases on solid surface, the solid surface is called the adsorbent and the gas adsorbed is called adsorbate. The extent of adsorption depends on many factors.

- **Factors affecting the adsorption of gases on solids**

(i) Nature of Adsorbent

- If the adsorbent is highly porous the rate of adsorption is high.
- Activated carbon, metal oxides like aluminum oxide, silica gel and clay are commonly used adsorbents.
- The rate of adsorption can be increased by activation process. It helps in increasing the pores in the adsorbent.

(ii) Surface area of adsorbent

- Greater the surface area greater is the adsorption.
- Increase in surface area increases the number of adsorbing sites.
- Finely divided and highly porous materials act as good adsorbents. Eg. Charcoal and silica gel (excellent adsorbents).

(iii) Nature of Gases

- Easily liquefiable gases like HI, NH_3, Cl_2, SO_2 etc., are adsorbed more easily than the permanent gases like H_2, N_2, and O_2 etc.

(iv) Effect of temperature Increase in temperature increases the kinetic energy of the gas molecules and hence adsorption increases.

(v) Effect of pressure:

VI.3.1 Adsorption isotherms

When an adsorbate molecule in the gas phase interacts with the surface of an adsorbent, an equilibrium distribution of adsorbate molecules occurs between the surface and the gas phase. This equilibrium distribution is influenced by factors such as the partial pressure of the adsorbate, temperature, the nature of the adsorbate, and the surface area and characteristics of the adsorbent. The adsorption isotherm illustrates the quantity of molecules adsorbed on the solid surface concerning the equilibrium partial pressure at a constant temperature. In contrast, the adsorption isobar demonstrates how the adsorbed species vary with temperature at a constant pressure. The adsorption-desorption isotherm provides insights into the adsorbent's characteristics, revealing the nature of the adsorption-desorption process and the pore structure of the adsorbent. Typically, the isotherm is represented as the standard volume adsorbed relative to the relative pressure, which is the ratio of the actual gas partial pressure to the saturated vapor pressure of the adsorbate at a constant temperature. The Brunauer empirical classification identifies five types of isotherms for solid adsorbents, each reflecting distinct characteristics and behaviors in adsorption processes.

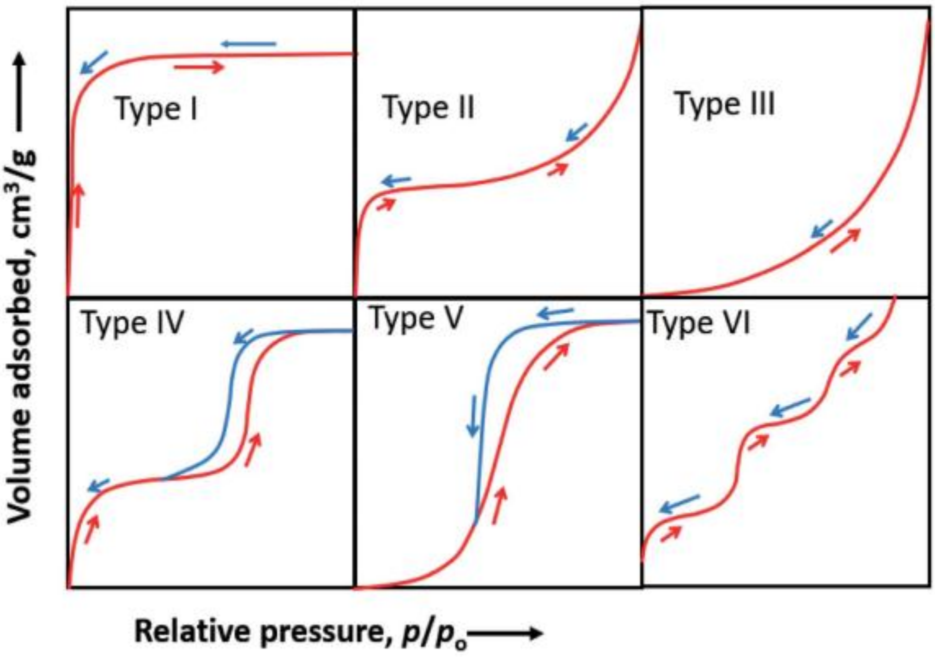


Figure VI.6: Different types of adsorption isotherms as classified by IUPAC.

The different types of adsorption isotherms provide insights into the pore structure and surface characteristics of adsorbents:

Type I isotherms are observed for microporous adsorbents with small pore sizes. Adsorption occurs by filling the micropores, with the uptake rate depending on the accessible micropore volume rather than the total internal surface area. Examples include the adsorption of nitrogen or hydrogen on charcoal at temperatures near -180°C.

Type II and IV isotherms are characteristic of non-porous or macroporous adsorbents, exhibiting unrestricted monolayer-multilayer adsorption. At low relative pressures (< 0.01), adsorption rapidly increases due to interactions with high-energy regions, followed by interactions with lower-energy regions. Once monolayer formation is complete, multilayer formation begins, corresponding to the sharp knee in the isotherms. As relative pressure approaches unity, an abrupt rise indicates bulk condensation of the adsorbate gas to liquid. Examples include the adsorption of nitrogen on iron catalysts or silica gel at -195°C.

Type III and V isotherms lack the sharp knee shape, implying stronger adsorbate-adsorbate interactions than adsorbate-adsorbent interactions. Type III isotherms, such as bromine or iodine adsorption on silica gel at 790°C, show large deviations from the Langmuir model and indicate multilayer formation without a distinct monolayer. Type V isotherms, like water vapor adsorption on charcoal at 100°C, are similar to Type IV and exhibit capillary condensation of gases.

Type VI isotherms, representing layer-by-layer adsorption, are less common and more complex to analyze. Fitting the first adsorption step to a theoretical model can provide insights into adsorbent-adsorbate interactions.In summary, the different isotherm types reveal the pore structure, surface heterogeneity, and adsorption mechanisms of adsorbents, with Type I indicating microporous materials, Types II and IV representing non-porous or macroporous adsorbents, and Types III and V suggesting stronger adsorbate-adsorbate interactions.

VI.3.1.1 Hysteresis loop

The hysteresis loop in adsorption isotherms for nonporous materials typically shows the desorption curve retracing the adsorption curve. In contrast, for mesoporous and macroporous materials, the desorption curve does not retrace the adsorption curve, resulting in a wide loop. This phenomenon, known as hysteresis loop, corresponds to capillary condensation of the adsorbate in the multilayer region, reflecting the pore filling and emptying mechanism. The nature of the hysteresis loop is linked to different pore shapes, as illustrated in Figure VI.7. Type A hysteresis is associated with cylindrical or tubular pores with a narrow distribution, characterized by steep and narrow parallel adsorption and desorption curves. Type B exhibits a long flat plateau in adsorption and a steep desorption curve, indicating a complex structure with interconnected networks or ink bottle-shaped pores. Type C represents aggregates of adsorbent with parallel plates, slit-shaped pores, or wide capillaries (>500 Å). Type D is linked to slit-shaped pores primarily in the micropore region.

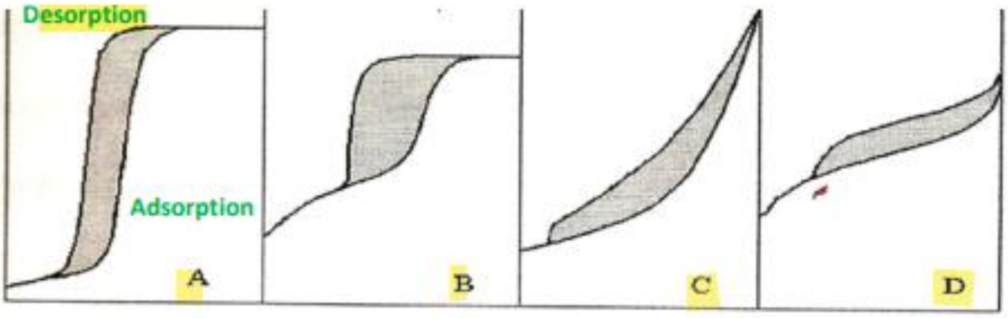


Figure VI.7: Different hysteresis loops as represented by IUPAC.

VI.3.1.2 Henry's isotherm

The Henry's Isotherm Model, named after Henry's adsorption constant, is a fundamental concept in adsorption science. In this model, the partial pressure of the adsorptive fluid is directly proportional to the amount of adsorbate, making it one of the simplest adsorption isotherms. It is derived from Gibbs adsorption and is used to determine the equilibrium state of adsorption for adsorbates at low and constant temperatures. The equilibrium amount of adsorbate in the fluid is related to the partial pressure of the adsorptive fluid by Equation 1:

$$Qe = KHCe,$$

where Qe is the amount of adsorbate at equilibrium, KH is Henry's adsorption constant, and Ce is the equilibrium concentration of the adsorbate on the adsorbent. It is worth noting that Henry's isotherm is not recommended for high-temperature and high-pressure experiments due to the intense molecular motion caused by significant interaction forces and potential energy.

VI.3.1.3 Langmuir adsorption isotherm

Langmuir isotherm is derived based on the following assumptions:

- Surface is energetically uniform, that is all the surface sites have the same activity for adsorption.
- Adsorbed molecules do not interact with the other adsorbed molecules on the surface.
- Heat of adsorption is therefore constant throughout the fractional surface coverage of 0 to 1.
- Adsorption of all molecules occurs by the same mechanism and results in the same adsorbed structure.

- Extent of adsorption is less than one complete monolayer coverage.

When a gas is in contact with a solid surface, the gas molecules continuously strike the surface and a fraction of these adhere. However, the more energetic molecules also continuously leave the surface. Eventually, the equilibrium is established so that the rate of adsorption equals the rate at which the molecules leave the surface.

$$\mathrm{M_{gas} + A_s \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M_{ads}}$$

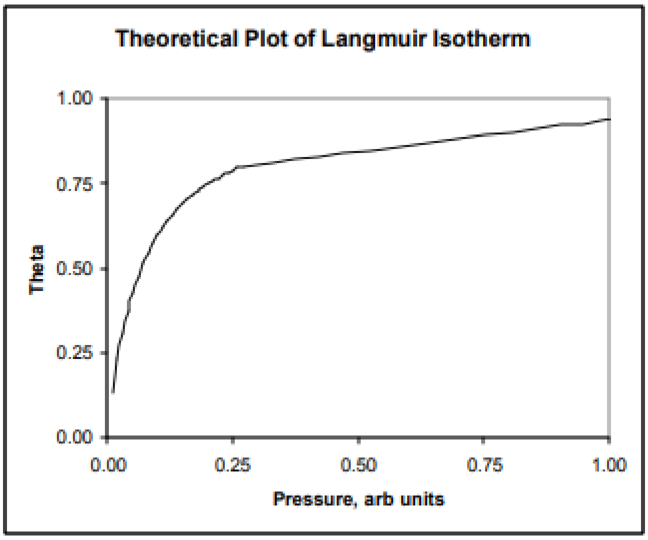
Rate of adsorption related to the fractional number of sites available. Rads µ P(1 - q).

Rate of desorption related to the coverage: Rdes µ q.

Simplified derivation of Langmuir isotherm.

– At steady state:

$$\begin{aligned} R_{ads} &= R_{des} \\ k_1 p(1-\theta) &= k_{-1}\theta \\ \frac{\theta}{1-\theta} &= \frac{k_1}{k_{-1}} \cdot p = bp \\ \theta &= bp(1-\theta) \\ &= bp - bp\theta \\ \theta &= \frac{bp}{1+bp} \end{aligned}$$



and θ can be written as $\theta = \frac{V}{V_m}$

In the limit of low pressure, the Langmuir isotherm is equivalent to Henry's law:

$$\lim_{P\to 0} \frac{KP}{1+KP} = \frac{KP}{1} = KP$$

The separation factor (Rl) is another key parameter that is often used to determine the nature of the adsorption process described in the Langmuir model. The separation factor is defined by equation :

$$R_l = \frac{1}{(1+K_L C_0)}$$

Where C0 is the starting concentration of the absorbate (mg/L).

Dissociative chemical adsorption of the molecule X requires two sites:

$$X_2 + 2 \text{ sites} \rightleftharpoons 2\, X_{\text{ads}}$$

As a result, the equilibrium is written as:

$$k_{\text{ads}}\, P_{\text{i}}\, (1-\theta)^2 = k_{\text{des}} \cdot \theta^2$$

Which gives

$$\theta_{\text{i}} = \frac{(b_{\text{L}} P_{\text{i}})^{1/2}}{1+(b_{\text{L}} P_{\text{i}})^{1/2}}$$

Extended Langmuir model for adsorption in a multi-adsorbate system

The Langmuir model, a fundamental concept in adsorption theory, can be extended to multi-component systems, known as the extended Langmuir model. This model is widely employed to analyze adsorption equilibrium data, particularly in binary systems. Butler and Ockrent first proposed the extended Langmuir model, which relies on the same assumptions as the Langmuir model for single adsorbates:

- The surface is homogeneous concerning adsorption energy.
- There are no interactions between adsorbed species.
- All adsorption sites are equally accessible to all adsorbed species.

By assuming that the adsorption and desorption rates of a species at equilibrium are equal, the extended Langmuir model derives equations that describe the adsorption behavior in multi-component systems. This model is valuable for predicting mixture adsorption and correlating adsorption equilibrium data.

$$X_1 = \frac{X_{m1} b_1 C_1}{1 + b_1 C_1 + b_2 C_2}$$

$$X_2 = \frac{X_{m2} b_2 C_2}{1 + b_1 C_1 + b_2 C_2}$$

Where, the X_1 and X_2 are the amount of solute 1 and solute 2 respectively, which are absorbed per unit weight or per unit surface area of absorbent at equilibrium concentrations C1 and C2, respectively. The X_{m1} and X_{m2} are the maximum values of X_1 and X_2, respectively, that can be obtained in single solute system and correspond to monolayer coverage of the adsorbent. The b1 and b2 are constants and function of the energy of adsorption of solutes 1 and 2, respectively, in a single solute system.

When some of the adsorption sites are inaccessible or unavailable to one type of solute in a bisolute system then, a fraction of the adsorption occurs without competition that is Xm1 ≠ Xm2

$$X_1 = \frac{(X_{m1} - X_{m2})b_1C_1}{1 + b_1C_1} + \frac{X_{m2}b_1C_1}{1 + b_1C_1 + b_2C_2} \qquad \because (X_{m1} > X_{m2})$$

$$X_2 = \frac{X_{m2}b_2C_2}{1 + b_1C_1 + b_2C_2}$$

The first term on the right hand side of Eq. 9 is the number of molecules of solute 1 that adsorb without competition on the surface area proportional to (Xm1-Xm2). The second term represents the number of solute 1 adsorbed on the surface area proportional to Xm2 under competition with solute 2 and is based on the Langmuir model for competitive adsorption.

For heterogeneous surfaces with a distribution of adsorption sites of different characteristic energies, one possibility is to superimpose a set of Langmuir equations, each corresponding to a different type of site. This generalized-Langmuir equation can be written as:

$$\theta = \sum_i \alpha_i \left(\frac{K_i P}{1 + K_i P}\right)$$

$$\sum_i \alpha_i = 1$$

The weight of each component isotherm, αi, corresponds to the fraction of sites with the energy Ei. This form of Langmuir's equation is applicable across a wide range of experimental systems, and can lend insight into the heterogeneity of the adsorbent surface and the range of its characteristic binging energies. Its treatment of adsorption sites as belonging to a two-dimensional "monolayer" can be made completely general; the adsorption layer can be understood as any set of equally accessible sites within the adsorption volume, assuming the volume of gas remains constant as site occupancy increases (an assumption that is valid when ρa >> ρg).

VI.3.1.4 Freundlich adsorption isotherm

The Freundlich adsorption isotherm model is a widely used empirical equation that describes the adsorption equilibrium between a fluid (liquid or gas) and a solid material. Unlike the Langmuir model, which assumes monolayer adsorption, the Freundlich model can be applied to multilayer adsorption. The Freundlich model expression accounts for the heterogeneity of the adsorbent surface and the exponential distribution of active sites and their energies.The non-linearized form of the Freundlich isotherm model is given by:

$$Q_e = K_F C_e{}^{1/n}$$
$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e$$

where K_F is the Freundlich constant or maximum absorption capacity (L/mg), n is the adsorption intensity or surface heterogeneity, which indicates the energy distribution and the absorbate site’s heterogeneity.

The Freundlich model is widely used due to its simplicity and ability to fit a wide range of adsorption data. However, it has some limitations. At high pressures, it fails to predict the saturation point where adsorption becomes independent of pressure. The model also does not reduce to Henry's law at low concentrations. Despite these limitations, the Freundlich model remains a valuable tool for understanding and predicting adsorption phenomena.

VI.3.1.5 Temkin Isotherm Model

The Temkin isotherm model ignores extremely low and high concentrations and assumes that the heat of adsorption of all molecules in the layer decreases linearly rather than logarithmically. This distinguishes the Temkin isotherm from models that exhibit logarithmic decreases in heat of adsorption. The Temkin isotherm can be described by the following equation:

$$Q_e = \frac{RT}{b} \ln K_T + \left(\frac{RT}{b}\right) \ln C_e$$

where KT is the maximum binding energy or the Temkin isotherm equilibrium-biding constant (Lmol^{-1}), b is the Tempkin isotherm constant related to the adsorption heat.

VI.3.1.6 Brunauer-Emmett-Teller (BET) isotherm

Brunauer, Emmett & Teller developed a model for type II isotherms, which considers that gas molecules are adsorbed in monolayers, i.e. monomolecular layers. In the specific relative pressure range from 0.05 to 0.30 each monolayer evenly covers the previous one. By applying Langmuir theory to those monolayers they obtained the following BET equation:

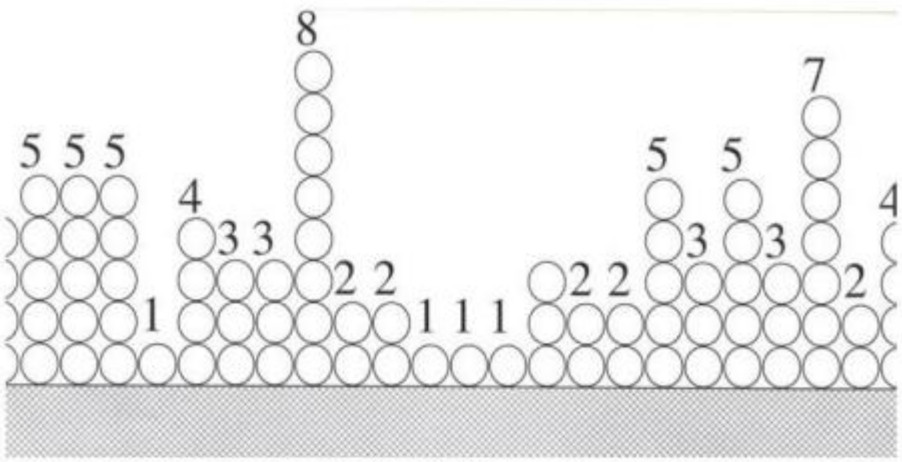


Figure VI.8: modelling of adsorption according to bet theory.

ASSUMPTIONS OF BET THEORY

- The gas molecules undergo multilayer adsorption on solid surface.
- The principle of Langmuir theory can be applied to each layer.
- A dynamic equilibrium exists between successive layers. The rate of evaporation from a particular layer is equal to the rate of condensation of the preceding layer.
- The enthalpy of adsorption of the first layer (E1) is a constant, whereas that of any layer above the first layer is the energy of liquefaction of the adsorbate (EL)

S0 , S0 , S2 , S3 ......Si represent the surface area of the adsorbent covered by 0, 1, 2, 3 .....i layers of adsorbates. Rate of condensation on the bare surface = a1 PS0

Rate of evaporation from the first layer=

$$b_1S_1e^{-E_1/RT}$$

$$a_2PS_1 = b_2S_2e^{-E_2/RT}$$

$$a_3PS_2 = b_3S_3e^{-E_3/RT}$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$a_iPS_{i-1} = b_iS_ie^{-E_i/RT}$$

Total surface area of the adsorbent:

$$A = \sum_{i=0}^{\propto} S_i$$

Total volume of the adsorbed gas:

$$V = V_0 \sum_{i=0}^{\propto} iS_i$$

V0 is the volume of the gas adsorbed on 1 cm2 of the adsorbent surface monolayer coverage.

$$\frac{V}{A} = \frac{V_0 \sum_{i=0}^{\propto} iS_i}{\sum_{i=0}^{\propto} S_i} \longrightarrow \frac{V}{AV_0} = \frac{\sum_{i=0}^{\propto} iS_i}{\sum_{i=0}^{\propto} S_i} \longrightarrow \frac{V}{V_m} = \frac{\sum_{i=0}^{\propto} iS_i}{\sum_{i=0}^{\propto} S_i}$$

Vm is the volume of the gas for monolayer coverage.

Approximations by Stephen Brunauer, Paul Emmett and Edward Teller made a couple of approximations:

$$S_1 = \left(\frac{a_1}{b_1}\right) \cdot Pe^{E_1/RT} \cdot S_0$$

$$S_1 = yS_0 \qquad y = \left(\frac{a_1}{b_1}\right) \cdot Pe^{E_1/RT}$$

$$S_2 = \left(\frac{a_2}{b_2}\right) \cdot Pe^{E_2/RT} \cdot S_1$$

$$S_2 = \left(\frac{P}{g}\right) \cdot e^{E_L/RT} \cdot S_1$$

$$S_2 = x \cdot S_1 \qquad x = \left(\frac{P}{g}\right) \cdot e^{E_L/RT}$$

$$S_2 = x \cdot yS_0$$

$$S_3 = x \cdot S_2$$

$$S_3 = x \cdot x \cdot S_1 = x^2 \cdot S_1$$ by putting $S_2 = x \cdot yS_0$

$$S_3 = x^2 \cdot yS_0$$ by putting $S_1 = yS_0$

$$S_4 = x^3 \cdot yS_0$$

$$\boxed{S_i = x^{i-1} \cdot yS_0}$$

$$S_i = x^i \cdot c \cdot S_0$$

$$c = \frac{y}{x} = \frac{\left(\frac{a_1}{b_1}\right) \cdot Pe^{E_1/RT}}{\left(\frac{P}{g}\right) \cdot e^{E_L/RT}} = \left(\frac{a_1}{b_1}\right) \cdot ge^{(E_1-E_L)/RT}$$

$$\frac{V}{V_m} = \frac{\sum_{i=0}^{\infty} iS_i}{\sum_{i=0}^{\infty} S_i}$$

$$\frac{V}{V_m} = \frac{\sum_{i=0}^{\infty} iS_i}{\sum_{i=0}^{\infty} S_i} = \frac{0 + \sum_{i=1}^{\infty} iS_i}{S_0 + \sum_{i=1}^{\infty} S_i}$$

$$S_i = x^i \cdot c \cdot S_0$$

$$\frac{V}{V_m} = \frac{\sum_{i=1}^{\infty} i \cdot x^i cS_0}{S_0 + \sum_{i=1}^{\infty} x^i cS_0} = \frac{cS_0 \sum_{i=1}^{\infty} i \cdot x^i}{S_0 + cS_0 \sum_{i=1}^{\infty} x^i}$$

$$\frac{V}{V_m} = \frac{c \sum_{i=1}^{\infty} i \cdot x^i}{1 + c \sum_{i=1}^{\infty} x^i}$$

Applying the expressions for summations $\sum_{i=1}^{\infty} i \cdot x^i = \frac{x}{(1-x)^2}$ and $\sum_{i=1}^{\infty} x^i = \frac{x}{(1-x)}$

$$\frac{V}{V_m} = \frac{c\frac{x}{(1-x)^2}}{1 + c\frac{x}{(1-x)}} = \frac{\frac{cx}{(1-x)}}{(1-x) + cx} = \frac{\frac{cx}{(1-x)}}{1 + (c-1)x}$$

$$\frac{V}{V_m} = \frac{cx}{(1-x)\left[1 + (c-1)x\right]}$$

$$\frac{x}{(1-x)V}=\frac{[1+(c-1)x]}{cV_m}$$

$$\frac{x}{(1-x)V}=\frac{1}{cV_m}+\frac{(c-1)}{cV_m}x$$

$$\frac{p}{(p^0-p)V}=\frac{1}{cV_m}+\frac{(c-1)}{cV_m}\frac{p}{p^0}$$

The BET equation was specifically developed to characterize adsorption in gas-solid systems near the saturation point of the adsorptive gas, primarily for determining the surface area of the solid adsorbent. Despite its narrow set of assumptions, the BET equation is widely applicable in experimental systems, making it the most commonly used adsorption model even in cases where the assumptions are not fully met. Nitrogen adsorption at 77 K up to P0 = 101 kPa has become a crucial technique for characterizing porous materials, with the BET model frequently used to calculate the BET surface area. Even for microporous adsorbents where the BET assumptions are not ideal, this method remains the standard for determining specific surface area, with any deficiencies assumed to be similar across comparable materials.

The BET surface area of a material can be determined by fitting experimental adsorption data to previous equation and determining the monolayer capacity, nsites. Typically, N2 adsorption data are plotted in the form of the linearized-BET equation, a rearrangement of Equation:

$$\frac{n_a}{n_{sites}}=\frac{c_{BET}\,\frac{P}{P_0}}{\left(1-\frac{P}{P_0}\right)\left(1-\frac{P}{P_0}+c_{BET}\,\frac{P}{P_0}\right)}$$

$$B_{BET}=\frac{\frac{P}{P_0}}{n_a\left(1-\frac{P}{P_0}\right)}=\frac{\left(1-\frac{P}{P_0}-c_{BET}\,\frac{P}{P_0}\right)}{c_{BET}\,n_{sites}}=\frac{1}{c_{BET}\,n_{sites}}+\frac{c_{BET}-1}{c_{BET}\,n_{sites}}\frac{P}{P_0}$$

VI.3.1.5.1 VPore-Filling Models

The Dubinin-Radushkevich (DR) equation is a significant contribution to adsorption science, particularly in the context of microporous materials. Developed by Dubinin and collaborators, this equation describes the fractional pore occupancy θpore and is based on the concept of pore-filling rather than layer-by-layer surface coverage. The DR equation is widely used for linearizing gas adsorption isotherms and obtaining micropore volumes from the intercept of the DR plots. It is given by:

$$\theta_{pore} = \frac{\mathrm{W}}{\mathrm{W}_0} = \mathrm{e}^{\left(-B\left(\frac{T}{\beta}\right)^2 \log^2\left(\frac{P}{P_0}\right)\right)}$$

The DR equation can be used for determining DR micropore volume, W0, in an analogous way as the Langmuir or BET equation for determining surface area.

VI.3.1.5.2 Gibbs surface excess

The measurement of adsorption near or above the critical point, using either volumetric (successive gas expansions into an accurately known volume containing the adsorbent) or gravimetric (gas expansions into an enclosed microbalance containing the adsorbent) methods, has a simple shortcoming: it cannot directly determine the adsorbed amount. This becomes readily apparent at high pressures, where the measured uptake amount is observed to increase up to a maximum and then decrease with increasing pressure. This behavior is fundamentally inconsistent with the Langmuir model of adsorption, which predicts a monotonically increasing adsorption quantity as a function of pressure.

The reason for this discrepancy can be traced to the finite volume of the adsorbed phase. The "free gas" volume displaced by the adsorbed phase would have contained an amount of gas given by the bulk gas density even in the absence of adsorption. Therefore, this amount is necessarily excluded from the measured adsorption amount since the gas density, measured remotely, must be subtracted from the entire void volume, such that adsorption is zero in the "reference state" which does not have any adsorption surface.

The Gibbs definition of excess adsorption, ne, as a function of absolute adsorption, na , is:

$$n_e = n_a - V_{ads}\,\rho(P,T)$$

The measurement of gas density far from the surface does not consider the presence of reference molecules near the surface, which would be part of the reference system. The excess quantity, representing the amount in the densified layer exceeding the bulk gas density, is the experimentally accessible value. At low pressures, the excess uptake is approximately equal to the absolute quantity. However, as the bulk gas density rises, the difference between excess and absolute adsorption increases. At high pressures, a state may be reached where the increase in adsorption density matches the increase in bulk gas density, leading to the excess quantity reaching a maximum.

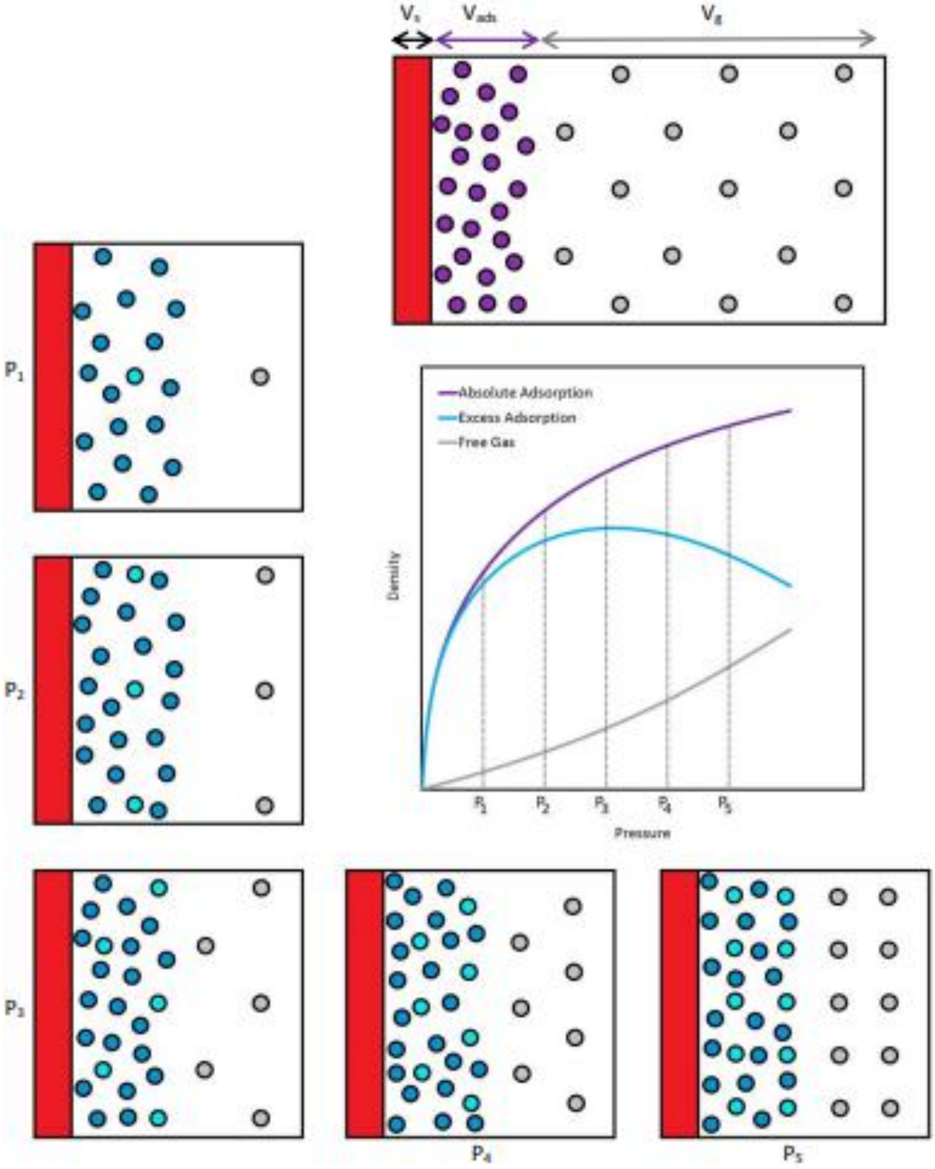


Figure VI.9: The Gibbs excess adsorption is plotted as a function of pressure (center). A microscopic representation of the excess (light blue), reference (dark blue), and absolute (combined) quantities is shown at five pressures, P1-P5. The bulk gas density (gray) is a function of the pressure and depicted as a regular pattern for clarity. The volume of the adsorbed phase, unknown experimentally, is shown in purple.

VI. 4 Adsorption thermodynamics

VI.4.1 Gibbs free energy

Adsorption, as a spontaneous process, necessitates a reduction in the total free energy of the system. When a gas molecule or atom is adsorbed onto a surface, it transitions from the free gas phase, characterized by three degrees of translational freedom, to the adsorbed film, where it has only two degrees of translational freedom. This transition results in a loss of translational entropy. Unless the adsorbed state exhibits a substantial additional entropy contribution, such as from vibrational modes, adsorption is inherently exothermic (ΔHads < 0). The decrease in translational entropy is typically not offset by a significant increase in vibrational entropy. This thermodynamic principle aligns with the observation that adsorption tends to be favored at lower temperatures, as indicated by the decrease in the adsorption constant (K) with increasing temperature. The Freundlich isotherm model, an empirical formula for gaseous adsorbates, also reflects this behavior, with its constants adjusting with temperature to show that higher pressures are needed to saturate the surface at elevated temperatures. Unless the adsorbed state is characterized by a very large additional entropy (perhaps from vibrations), it follows that adsorption must always be exothermic (ΔHads < 0) since:

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} < 0$$

$$\Delta H_{ads} = H_a - H_g$$

The chemical potential in each phase is defined as:

$$\mu_a = \left(\frac{\partial G_a}{\partial n_a}\right)_{T,P}$$

$$\mu_g = \left(\frac{\partial G_g}{\partial n_g}\right)_{T,P}$$

When equilibrium is reached, the chemical potential of the gas phase and the adsorbed phase are equal, since:

$$dG = (\mu_a - \mu_g)dn_a = 0$$

$$\mu_a = \mu_g$$

Determining the change in chemical potential, or the Gibbs free energy, of the adsorptive species as the system evolves toward equilibrium is essential to a fundamental understanding of adsorptive systems for energy storage or other engineering applications. We develop this understanding through the experimentally accessible components of the Gibbs free energy: ΔHads and ΔSads.

VI.4.2 Entropy of adsorption

The total derivative of both sides of Equation 2.24, and rearrange to arrive at the classic Clausius-Clapeyron relation:

$$-s_a dT + v_a dP = -s_g dT + v_g dP$$

$$\frac{dP}{dT} = \frac{(s_g - s_a)}{(v_g - v_a)}$$

where:

$$s_i = \left(\frac{\partial S}{\partial n_i}\right)_{T,P} \quad v_i = \left(\frac{\partial V}{\partial n_i}\right)_{T,P}$$

The specific volume of the free gas is usually much greater than that of the adsorbed gas, and a robust approximation simplifies the relation:

$$v_g - v_a \approx v_g$$

$$\frac{dP}{dT} = \frac{(s_g - s_a)}{v_g} = -(s_a - s_g)\,\rho_g$$

We rearrange to derive the common equation for change in entropy upon adsorption:

$$\Delta S_{ads}(n_a) = -\left(\frac{dP}{dT}\right)_{n_a} \rho_g{}^{-1}$$

VI.4.3 Enthalpy of adsorption

At equilibrium, the corresponding change in enthalpy upon adsorption is:

$$\Delta H_{ads}(n_a) = T\,\Delta S_{ads} = -T\left(\frac{dP}{dT}\right)_{n_a} \rho_g{}^{-1}$$

For an ideal gas:

$$\rho_g = \frac{n_g}{V_g} = \frac{P}{R\,T}$$

$$\Delta H_{ads}(n_a) = -T\left(\frac{dP}{dT}\right)_{n_a}\frac{R\,T}{P} = -\frac{R\,T^2}{P}\left(\frac{dP}{dT}\right)_{n_a}$$

This is often rearranged in the van’t Hoff form:

$$\Delta H_{ads}(n_a) = R\left(\frac{d\ln P}{d\left(\frac{1}{T}\right)}\right)_{n_a}$$

The isosteric heat of adsorption, a commonly reported thermodynamic quantity, is given a positive value:

$$q_{st}(n_a) = -\Delta H_{ads}(n_a) = -R\left(\frac{d\ln P}{d\left(\frac{1}{T}\right)}\right)_{n_a} > 0$$

For adsorption at temperatures or pressures outside the ideal gas regime, the density of the bulk gas phase is not easily simplified, and we use the more general relationship:

$$q_{st}(n_a) = T\left(\frac{dP}{dT}\right)_{n_a} \rho_g{}^{-1}$$

If the excess adsorption, ne, is substituted for the absolute quantity in the equations above, the result is called the “isoexcess heat of adsorption.

It is common to include the ideal gas assumption in the isoexcess method since the assumptions are valid in similar regimes of temperature and pressure, giving:

$$q_{st}(n_e) = -R\left(\frac{d\ln P}{d\left(\frac{1}{T}\right)}\right)_{n_e}$$

This gives the following equations for the isosteric and isoexcess heat of adsorption:

$$q_{st}(n_e) = T\left(\frac{dP}{dT}\right)_{n_e} (v_g - v_{liq})$$

In summary:

Assumptions:	Isosteric Method	Isoexcess Method ($n_a \approx n_e$)
Ideal Gas $v_g \gg v_a$	$\Delta S_{ads}(n_a) = \frac{R}{T}\left(\frac{d\ln P}{d\left(\frac{1}{T}\right)}\right)_{n_a}$ $q_{st}(n_a) = -R\left(\frac{d\ln P}{d\left(\frac{1}{T}\right)}\right)_{n_a}$ Eq. 2.31	$\Delta S_{ads}(n_e) = \frac{R}{T}\left(\frac{d\ln P}{d\left(\frac{1}{T}\right)}\right)_{n_e}$ $q_{st}(n_e) = -R\left(\frac{d\ln P}{d\left(\frac{1}{T}\right)}\right)_{n_e}$ Eq. 2.34
Non-ideal Gas $v_g \gg v_a$	$\Delta S_{ads}(n_a) = -\left(\frac{dP}{dT}\right)_{n_a} \rho_g{}^{-1}$ $q_{st}(n_a) = T\left(\frac{dP}{dT}\right)_{n_a} \rho_g{}^{-1}$ Eq. 2.32	$\Delta S_{ads}(n_e) = -\left(\frac{dP}{dT}\right)_{n_e} \rho_g{}^{-1}$ $q_{st}(n_e) = T\left(\frac{dP}{dT}\right)_{n_e} \rho_g{}^{-1}$ Eq. 2.33
Non-ideal Gas $v_a \approx v_{liq}$	$\Delta S_{ads}(n_a) = -\left(\frac{dP}{dT}\right)_{n_a} (v_g - v_{liq})$ $q_{st}(n_a) = T\left(\frac{dP}{dT}\right)_{n_a} (v_g - v_{liq})$ Eq. 2.36	$\Delta S_{ads}(n_e) = -\left(\frac{dP}{dT}\right)_{n_e} (v_g - v_{liq})$ $q_{st}(n_e) = T\left(\frac{dP}{dT}\right)_{n_e} (v_g - v_{liq})$ Eq. 2.37

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