436 کیم كيمياء السطوح والحفز

CHEM 436

Surface Chemistry And Catalysis

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Assessment Method

Exam	Points
Mid Exam	30
H.W	20
Flipped Learning and	10
Discussion	
Final Exam	40
Total	100

Textbook: There is no required textbook. Weekly class lectures will be posted on the course link on the blackboard. However, any physical chemistry book is recommended for further reading on topics covered in this class.



Surfaces – An Introduction

Surface Chemistry

Surface chemistry is referred to as the study of the phenomenon occurring on the surfaces of substances. This is very applicable in industries and day to day lives. In other words, surface chemistry deals with all types of surface phenomenon.

Many important phenomena that occur at interfaces:

- corrosion
- electrode processes
- heterogeneous catalysis
- painting
- water treatment
- dissolution
- crystallization
- removing dirt from surfaces such as the human skin, textiles, and other solids by soap and detergents.

The interface or surface is represented by separating the bulk phases by a hyphen (-) or a slash (/). For example, the interface between a solid and a gas may be represented by solid-gas

or

solid/gas.

Due to complete miscibility, there is no interface between the gases.

Miscibility

- is the property of two substances to mix in all proportions, forming a homogeneous mixture.
- The term is most often applied to liquids but also applies to solids and gases. For example, water and ethanol are miscible because they mix in all proportions.

Intermolecular Forces

Many physicochemical properties of liquids such as

- boiling point
- melting point
- vapor pressure
- evaporation
- viscosity
- surface tension
- solubility

Depend on the intermolecular forces.

The physicochemical properties differ from substance to another substance based on the type and strength of the intermolecular forces present in each substance.

The surface sciences depends of the surface tension.

And the surface tension depends mainly upon the forces of attraction (i.e.

intermolecular forces) between the particles within the given liquid and also

upon the gas, solid, or liquid in contact with it.

Therefore, it is of great importance to start this course by studying INTERMOLECULAR FORCES.

Intermolecular forces are the forces of attraction and repulsion between molecules.

- Generally, intermolecular forces are much weaker than intramolecular forces. It usually requires much less energy to evaporate a liquid than to break the bonds in the molecules of the liquid.
 - 41 kJ of energy are required to vaporize 1 mole of water at its boiling point.
 - 930 kJ of energy are necessary to break the two O-H bonds in 1 mole of water molecules.
- The boiling points of substances often reflect the strength of the intermolecular forces operating among the molecules.
- At the boiling point, enough energy must be supplied to overcome the attractive forces among molecules before they can enter the vapor phase.
- Boiling point and melting points of substances increase with the strength of the intermolecular forces.

Intramolecular forces are the forces that hold atoms together in a molecule. (Chemical bonding).



Intermolecular forces are much weaker than intramolecular forces

Types of Intermolecular Interactions

- **1. Van der Waals interactions**
 - A. Dipole–dipole interactions
 - **B**. Dipole–induced dipole interactions
 - C. Dispersion interactions
- 2. Hydrogen bonding
- 3. Ion-dipole interactions

A. Dipole-dipole interactions

Dipole-dipole interactions are the attractive forces between polar molecules.

A polar molecule is a chemical species in which the distribution of electrons between the covalently bonded atoms is not even due to the difference in electronegativity of the bonded atoms.

Electronegativity is the ability of an atom to attract toward itself the electrons in a chemical bond.

In a **polar bond** the electrons spend more time in the vicinity of one atom than the other.

Dipole-dipole forces cause polar molecules to cling to each other.

Dipole-dipole interactions





The arrows show the shift of electron density from the less electronegative hydrogen atom to the more electronegative chlorine atom. A polar molecule with two or more polar bonds must have a geometry which is asymmetric in at least one direction, so that the bond dipoles do not cancel each other.

 $\begin{array}{c} \longleftrightarrow \\ 0 = C = 0 \end{array}$



The linear geometry of the molecule results in the cancellation of the two bond dipoles. The symmetry of a trigonal planar shape means that the three bond dipoles exactly cancel one another:

B. Dipole-induced dipole interactions

A polar molecule can induce a dipole in a neighboring nonpolar molecule .The induced dipole interacts with the permanent dipole of the first molecule, and the two are attracted together.



C. Dispersion Interaction

- Nonpolar molecules attract one another even though neither has a permanent dipole moment.
- The abundant evidence for the existence of interactions between nonpolar molecules is their ability to exist as condensed phases, such as liquid hydrogen or argon and the fact that benzene is a liquid at normal temperatures.
- The interaction between nonpolar molecules arises from the transient dipoles which all molecules possess as a result of fluctuations in the instantaneous positions of electrons.
- The interaction results when the electrons in one molecule flicker into an arrangement that gives the molecule an instantaneous dipole. This dipole generates an electric field which polarizes the other molecule, and induces in that molecule an instantaneous dipole. And then the two dipoles attract each other and the potential energy of the pair is lowered.

- Although the first molecule will go on to change the size and direction of its instantaneous dipole, the electron distribution of the second molecule will follow; that is, the two dipoles are correlated in direction.
- This interaction is called either the **dispersion interaction** or the **London interaction**.

Two instantaneous dipoles



London dispersion force (I2 bond)

(a) An instantaneous
polarization can occur on atom
A, creating an instantaneous
dipole. This dipole creates an
induced dipole on neighboring atom B.



(b) Nonpolar molecules such as H_2 also can develop instantaneous and induced dipoles.

الجزيئات غير القطبية مثل جزيء الهيدروجين يمكنها أن تمتلك ثنائي قطب لحظي وثنائي قطب مستحث.





2. Hydrogen bonding

Hydrogen bonding is a strong intermolecular attraction which is a special type of dipoledipole interaction between the hydrogen atom in a polar bond, such as N-H, O-H, or F-H on one molecule, and a nitrogen, oxygen, or fluorine atom on another molecule.

The interaction is written as

 $A - H \cdot \cdot B$ or $A - H \cdot \cdot A$

A and B represent O, N, or F; A-H is one molecule or part of a molecule and B is a part of another molecule; and the dotted line represents the hydrogen bond.

□ The three atoms usually lie in a straight line, but the angle AHB (or AHA) can deviate as much as 30° from linearity.

□ Note that the O, N, and F atoms all possess at least one lone pair that can interact with the hydrogen atom in hydrogen bonding.

- □ If the molecules have O-H, N-H, or H-F bonds, they can form hydrogen bonds with themselves and with water.
- □ If the molecules contain O, N, or F atoms that are *not* bonded to hydrogen atoms, they may accept hydrogen bonds from water, even though they cannot form hydrogen bonds with themselves.



Image Source: Wikipedia.

Hydrogen bonding between water molecules.

Hydrogen bonding between formic acid and water molecules.

Solid lines represent covalent bonds, and dotted lines represent hydrogen bonds.

Hydrogen bonding and boiling point of molecules

Molecules that can form hydrogen bonds with themselves have a higher boiling point than similar molecules that cannot form hydrogen bonds with themselves.

Examples

Molecule	Formula	Molecular Weight (g/mol)	Boiling Point (°C)
Hydrogen sulfide	H ₂ S	34.10	-60
Water	H ₂ O	18.02	100
Ethanol	CH ₃ -CH ₂ -OH	46.07	78.5
Diethyl ether	CH ₃ -O-CH ₃	46.07	-24

Note:

- Water molecules can for hydrogen bonds with themselves, but hydrogen sulfide molecules cannot.
- > Ethanol molecules can form hydrogen bonds with themselves, but diethyl ether cannot.

3. Ion-dipole interactions

Ion-dipole interaction is the electrostatic attraction between an ion (either a cation or an anion) and a polar molecule to each other.



Two types of ion-dipole interaction.