MULTICOLOUR EDITION

ESSENTIALS OF Physical Chemistry

Arun Bahl
B.S. Bahl
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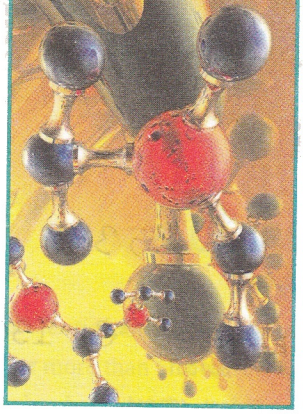
Essentials of
PHYSICAL CHEMISTRY



Essentials of
PHYSICAL CHEMISTRY

(A Textbook for B.Sc. Classes as per UGC Model Syllabus)

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Preface

The *Essentials of Physical Chemistry* has been written for BSc students. It has been national best-seller for more than 65 years. It has been used by more than 2 million students. It is 26 editions old. It really has been that long. A lot of things have changed since then. We also changed with every edition so that you could get the best. In this new edition we have retained all those features that made it a classic. Recent reviews from some teachers are reproduced. These sum up book's high-quality and study-approach :

> The Essentials of Physical Chemistry is best summarised by "classic text, modern presentation". This simple phrase underlines its strong emphasis on fundamental skills and concepts. As in previous editions, clearly explained step-by-step problem-solving strategies continue to be the strength of this student-friendly text. This revision builds on its highly praised style that has earned this text a reputation as the *voice of authority* in Physical Chemistry. The authors have built four colour art program that has yet to be seen in India !

> The acknowledged leader and standard in Physical Chemistry, this book maintains its effective and proven features – clear and friendly writing style, scientific accuracy, strong exercises, step-by-step solved problems, modern approach and design. The organisation and presentation are done with marvelous clarity. The book is visually beautiful and the authors communicate their enthusiasm and enjoyment of the subject in every chapter.

> This textbook is currently in use at hundreds of colleges and universities throughout the country and is a national best-seller. In this edition, the authors continue to do what they do best, focus on the important material of the course and explain it in a concise, clear way. I have found this book to be very easy to follow. There are hundreds of computer-generated coloured diagrams, graphs, photos and tables which aid in understanding the text. The book goes step-by-step, so you don't get lost. No wonder it is a market-leader !

STUDENT FRIENDLY

Many BSc students do not have a good background in Physical Chemistry. This examination-oriented text is written with these students in mind. The language is simple, explanations clear, and presentation very systematic. Our commitment to simplicity is total !

Concept-density per page has been kept low. We feel that this is a big time saver and essential to quick-learning and retention of the subject matter.

STRESS IS ON UNDERSTANDING

This book will help you overcome the fear of Physical Chemistry. Stress is on understanding and not on memorisation. Topics which usually confuse the students are explained in greater detail than commonly done. This text will help you learn Physical Chemistry faster and enjoy it more !

USEFUL FOR ENTRANCE TESTS

This is an important textbook for the Medical and Engineering College Entrance Exams. Your choice of a book can mean success or failure. Because today you need a book that can help you streak ahead of competition and succeed. No-one knows more about your needs than us. It is a tall claim, but it is true !

NEW IN THIS EDITION

The new edition of *Essentials of Physical Chemistry* contains numerous discussions, illustrations, and exercises aimed at overcoming common misconceptions. It has become increasingly clear from our own teaching experience that students often struggle with Physical Chemistry because they misunderstand many of the fundamental concepts. In this text, we have gone to great lengths to provide illustrations and explanations aimed at giving students more accurate pictures of the fundamental ideas of chemistry.

In this New Edition we have retained all that was judged good in the previous edition. However, a number of changes have been made in this new edition. Subject matter has been updated. This edition provides quick access to the important facts and concepts. It includes every important principle, equation, theorem, and concept.

The new syllabus recommended by the University Grants Commission has been our model. This edition now includes two new chapters : Mathematical Concepts (Chapter 32), and Introduction to Computers (Chapter 33).

VALUE ADDITION

1. **Problem-Solving.** To a great extent, a student's understanding of chemistry depends on his or her ability to solve and analyse problems. We have structured this book with the idea of weaving the techniques of problem-solving throughout the content, so that the student is systematically guided and challenged to view chemistry as a series of solvable problems.

   Question-style has changed over the years. Latest university questions are given at the end of each chapter to show these trends. Step-by-step answers are provided for the in-chapter problems. This book contains more than 1600 latest university questions. It also contains more than 1600 multiple-choice questions. By solving these problems you can precisely know your own success-level. This is the book which the examiners use !

2. **Four-Colour Art Program.** One of the distinctive features of the text is its visual impact. This is the first Indian Physical Chemistry textbook to be completely done in four-colour and on computer. Colour graphics, illustrations, and real pictures have been extensively used to

highlight and reinforce the important points. Colour has also been used to highlight change and concepts.

3. **Guidelines** are provided to help you understand concepts that are considered difficult and catch careless mistakes before exams.

4. **Scientific Accuracy** has been checked and rechecked. Subject matter is modern and error-free.

5. **Extensive** Index has been provided for quick cross-reference.

WE WISH YOU SUCCESS !

Yes, we think you will appreciate the thought and care that has gone into the making of this text. If you have the will, this book will show the way. We urge you to study regularly, and hope that this error-free book will make it easier for you to do so. You can depend on this book !

The book has everything you want to have in your Physical Chemistry text. In case you find something missing, please write at the following address :

Mail : # 590, Sector 18-B, Chandigarh - 160018

e-mail : arunbahl2000@gmail.com

We would be glad to receive suggestions and comments for further improvements.

Authors

Highlights of 4 Colour Edition

Chapter openers include a half-page photograph related to the chapter material.

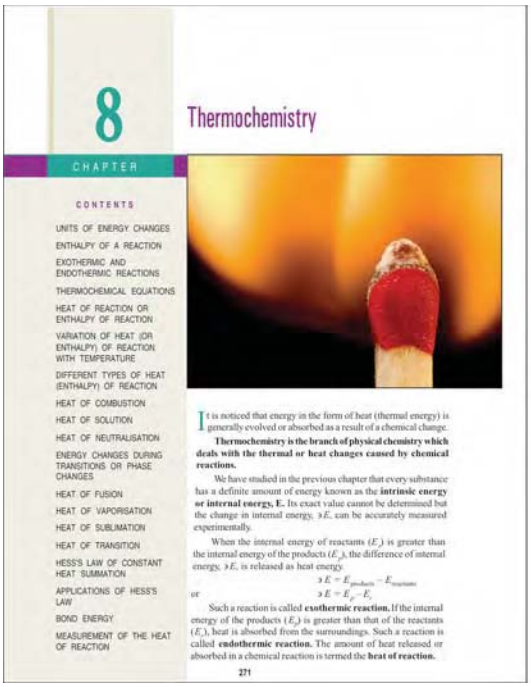
The **Contents** give students an overview of the topics to come.

The **Artwork** has been completely revised. This has made the subject come alive !

New colour drawings and photographs make the artwork more realistic and easier to understand. Flowcharts, important rules walk students through chemical processes in a simple, straight forward manner.

Special-interest boxes describe current applications of the subject.

Solved problems are located throughout the text. These solved problems emphasise step-by-step approach to solving problems.



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Thermochemistry

CHAPTER

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UNITS OF ENERGY CHANGES
ENTHALPY OF A REACTION
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VARIATION OF HEAT (OR ENTHALPY) OF REACTION WITH TEMPERATURE
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HESS'S LAW OF CONSTANT HEAT SUMMATION
APPLICATIONS OF HESS'S LAW
BOND ENERGY
MEASUREMENT OF THE HEAT OF REACTION

It is noticed that energy in the form of heat (thermal energy) is generally evolved or absorbed as a result of a chemical change.

Thermochemistry is the branch of physical chemistry which deals with the thermal or heat changes caused by chemical reactions.

We have studied in the previous chapter that every substance has a definite amount of energy known as the **intrinsic energy or internal energy, E.** Its exact value cannot be determined but the change in internal energy, ΔE, can be accurately measured experimentally.

When the internal energy of reactants (E_r) is greater than the internal energy of the products (E_p), the difference of internal energy, ΔE, is released as heat energy.

$$\Delta E = E_{products} - E_{reactants}$$

or

$$\Delta E = E_p - E_r$$

Such a reaction is called **exothermic reaction.** If the internal energy of the products (E_p) is greater than that of the reactants (E_r), heat is absorbed from the surroundings. Such a reaction is called **endothermic reaction.** The amount of heat released or absorbed in a chemical reaction is termed the **heat of reaction.**

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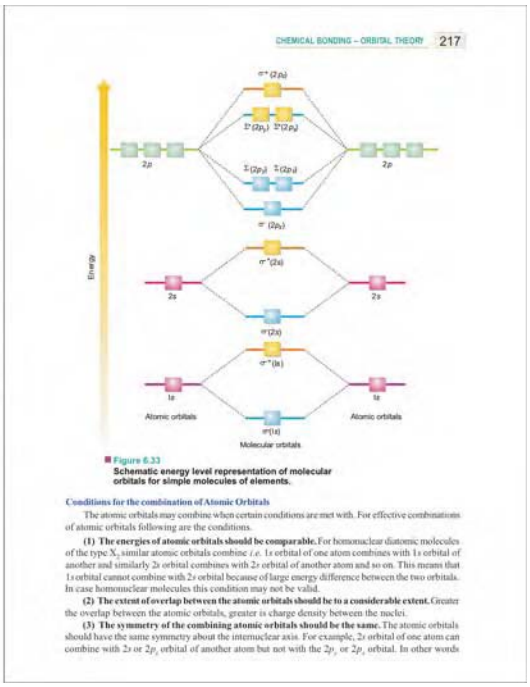

Energy

Atomic orbitals

Atomic orbitals

Molecular orbitals

Figure 6.33
Schematic energy level representation of molecular orbitals for simple molecules of elements.

Conditions for the combination of Atomic Orbitals

The atomic orbitals may combine when certain conditions are met with. For effective combinations of atomic orbitals following are the conditions.

(1) The energies of atomic orbitals should be comparable. For homonuclear diatomic molecules of the type X_2 similar atomic orbitals combine *i.e.* 1s orbital of one atom combines with 1s orbital of another and similarly 2s orbital combines with 2s orbital of another atom and so on. This means that 1s orbital cannot combine with 2s orbital because of large energy difference between the two orbitals. In case homonuclear molecules this condition may not be valid.

(2) The extent of overlap between the atomic orbitals should be to a considerable extent. Greater the overlap between the atomic orbitals, greater is charge density between the nuclei.

(3) The symmetry of the combining atomic orbitals should be the same. The atomic orbitals should have the same symmetry about the internuclear axis. For example, 2s orbital of one atom can combine with 2s or $2p_y$ orbital of another atom but not with the $2p_z$ or $2p_x$ orbital. In other words

SURFACE TENSION

Surface tension helps dew drops stick to the grass and prevents them from spreading.

Surface tension prevents this flower from sinking.

Surface tension prevents a paper clip from sinking.

Surface tension helps insects to walk on water.

Surface tension is an effect within the surface layer of a liquid that causes the layer to behave as an elastic sheet. It is the effect that allows insects (such as the water strider) to walk on water, and causes capillary action.

Surface tension is caused by the attraction between the molecules of the liquid, due to various intermolecular forces. In the bulk of the liquid each molecule is pulled equally in all directions by neighbouring liquid molecules, resulting in a net force of zero. At the surface of the liquid, the molecules are pulled inwards by other molecules deeper inside the liquid, but there are no liquid molecules on the outside to balance these forces.

All of the molecules at the surface are therefore subject to an inward force of molecular attraction which can be balanced only by the resistance of the liquid to compression. Thus the liquid squeezes itself together until it has the lowest surface area possible.

Determination of Surface Tension

The methods commonly employed for the determination of surface tension are :

(1) Capillary-rise Method

A capillary tube of radius r is vertically inserted into a liquid. The liquid rises to a height h and forms a concave meniscus. The surface tension (θ) acting along the inner circumference of the tube exactly supports the weight of the liquid column.

By definition, surface tension is force per 1 cm acting at a tangent to the meniscus surface. If the angle between the tangent and the tube wall is T, the vertical component of surface tension is $\theta\cos$

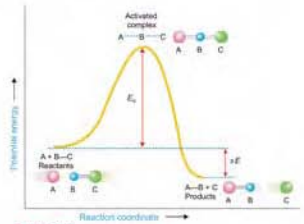

Figure 20.13
Change of potential energy during a collision between the reactant molecules for an exothermic reaction.

Here the potential energy of the system undergoing reaction is plotted against the **reaction coordinate** (the progress of the reaction). The difference in the potential energy between the reactants and the activated complex is the **activation energy,** E_a. The reactants must have this minimum energy to undergo the reaction through the transition state.

As evident from the energy diagram, energy is required by the reactants to reach the transition state. Also, the energy is obtained in passing from the transition state to the products. If the potential energy of the products is less than that of the reactants (Fig. 20.14) the energy obtained in going from the activated complex to products will be more than the activation energy (E_a). Thus such a reaction will be **exothermic.**

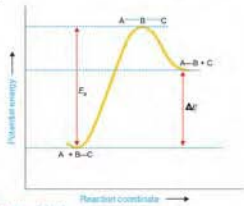

Figure 20.14
A potential energy diagram for an endothermic reaction.

$$Al^{3+} + 3H_2O \rightleftharpoons Al(OH)_3 + 3H^+$$
$$Al(OH)_3 + 4H_2O + H^+ \rightleftharpoons Al(OH)_4(H_2O)_2^+$$

The positively charged *floc* attracts to it negative sol particles which are coagulated. The *floc* along with the suspended matter comes down, leaving the water clear.

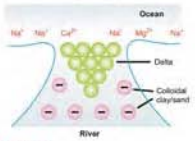

Figure 22.31
Formation of Delta.

(6) Formation of Delta

The river water contains colloidal particles of sand and clay which carry negative charge. The sea water, on the other hand, contains positive ions such as Na^+, Mg^{2+}, Ca^{2+}. As the river water meets sea water, these ions discharge the sand or clay particles which are precipitated as **delta.**

(7) Artificial Kidney machine

The human kidneys purify the blood by dialysis through natural membranes. The toxic waste products such as urea and uric acid pass through the membranes, while colloidal-sized particles of blood proteins (haemoglobin) are retained. Kidney failure, therefore, leads to death due to accumulation of poisonous waste products in blood . Now-a-days, the patient's blood can be cleansed by shunting it into an 'artificial kidney machine'. Here the impure blood is made to pass through a series of *cellophane tubes* surrounded by a washing solution in water. The toxic waste chemicals (urea, uric acid) diffuse across the tube walls into the washing solution. The purified blood is returned to the patient. The use of artificial kidney machine saves the life of thousands of persons each year.

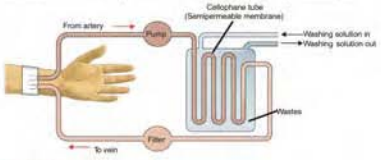

Figure 22.32
An artificial kidney machine for purification of blood by dialysis.

HOW TO DRAW STRUCTURE OF NaCl ?

Draw a perfect square.

Now draw an identical square behind this one and offset a bit. You might have to practice a bit to get the placement of the two squares right. If you get it wrong, the ions get all tangled up with each other in your final diagram.

Turn this into a perfect cube by joining the squares together.

Now the tricky bit! Subdivide this big cube into 8 small cubes by joining the mid point of each edge to the mid point of the edge opposite it. To complete the process you will also have to join the mid point of each face (easily found once you've joined the edges) to the mid point of the opposite face.

Now all you have to do is put the ions in. Use different colours or different sizes for the two different ions, and don't forget a key. It doesn't matter whether you end up with a sodium ion or a chloride ion in the centre of the cube – all that matters is that they alternate in all three dimensions.

You should be able to draw a perfectly adequate free-hand sketch of this in under two minutes – less than one minute if you're not too fussy!

If the pressure is written as force per unit area and volume as area times length, from (1)

$$R = \frac{(\text{force/area}) \times \text{area} \times \text{length}}{n \times T} = \frac{\text{force} \times \text{length}}{n \times T}$$

$$= \frac{\text{work}}{n\,T}$$

Hence R can be expressed in units of work or energy per degree per mole. The actual value of R depends on the units of P and V used in calculating it. The more important values of R are listed in Table 10.1.

TABLE 10.1. VALUE OF R IN DIFFERENT UNITS

0.0821	litre-atm K^{-1} mol^{-1}	8.314×10^7	erg K^{-1} mol^{-1}
82.1	ml-atm K^{-1} mol^{-1}	8.314	Joule K^{-1} mol^{-1}
62.3	litre-mm Hg K^{-1} mol^{-1}	1.987	cal K^{-1} mol^{-1}

DALTON'S LAW OF PARTIAL PRESSURES

John Dalton visualised that in a mixture of gases, each component gas exerted a pressure as if it were alone in the container. The individual pressure of each gas in the mixture is defined as its **Partial Pressure.** Based on experimental evidence, in 1807, Dalton enunciated what is commonly known as the **Dalton's Law of Partial Pressures.** It states that : **the total pressure of a mixture of gases is equal to the sum of the partial pressures of all the gases present (Fig. 10.10).**

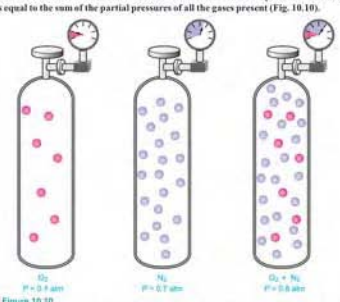

Figure 10.10
Dalton's law of partial pressures states that the total pressure of a mixture of gases is equal to the sum of the partial pressures exerted by each gas. The pressure of the mixture of O_2 and N_2 (Tanks) is the sum of the pressures in O₂ and N ₂anks.

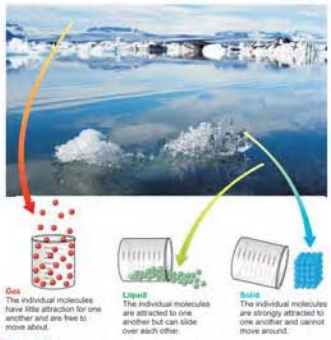

Figure 10.1
Molecular representation of the gaseous, liquid and solid states.

3. **Diffusibility**
Gases can diffuse rapidly through each other to form a homogeneous mixture.
4. **Pressure**
Gases exert pressure on the walls of the container in all directions.
5. **Effect of Heat**
When a gas, confined in a vessel is heated, its pressure increases. Upon heating in a vessel fitted with a piston, volume of the gas increases.

The above properties of gases can be easily explained by the Kinetic Molecular Theory which will be considered later in the chapter.

PARAMETERS OF A GAS

A gas sample can be described in terms of four parameters (measurable properties):
(1) the volume, V of the gas
(2) its pressure, P
(3) its temperature, T
(4) the number of moles, n, of gas in the container

van't Hoff theory holds only for dilute solutions and if there is no dissociation or association of the solute molecules.

CALCULATION OF OSMOTIC PRESSURE

As shown above, all gas laws may be considered to apply to dilute solutions rigidly. This gives an easy solution to problems on osmotic pressure.

SOLVED PROBLEM 1. Calculate the osmotic pressure of a 5% solution of glucose (mol wt = 180) at 18°C.

SOLUTION

$$\Sigma V = nRT \quad \text{...van't Hoff Equation}$$

where Σ = osmotic pressure in atmospheres; V = volume in litres; n = number of moles of solute (w/M), w being the weight in grams and M its molecular weight; R = gas constant.

In this case :

$$\Sigma = ?$$
$$V = 100\text{ ml} = \frac{1}{10}\text{ litre}$$
$$n = \frac{5}{M} = \frac{5}{180}$$
$$R = 0.0821 \text{ litre-atmosphere deg}^{-1} \text{ mole}^{-1}$$
$$T = 273 + 18 = 291\text{ K}$$

Substituting the values in van't Hoff Equation

$$\Sigma \times \frac{1}{10} = \frac{5}{180} \times 0.0821 \times 291$$
$$\Sigma = \mathbf{6.64\ atm}$$

SOLVED PROBLEM 2. Find the osmotic pressure in millimetres of mercury at 15°C of a solution of naphthalene ($C_{10}H_8$) in benzene containing 14 g of naphthalene per litre of solution.

SOLUTION

$$\Sigma V = nRT \quad \text{...vant Hoff equation}$$

Here,
$$\Sigma = ? \text{ atmosphere}$$
$$V = 1\text{ litre}$$
$$n = \frac{14}{128} \text{ (mol mass of naphthalene = 128)}$$
$$R = 0.0821 \text{ litre-atmosphere } K^{-1} \text{ mol}^{-1}$$
$$T = 15 + 273 = 288\text{ K}$$

Substituting values in van't Hoff equation,

$$\Sigma \times 1 = \frac{14}{128} \times 0.0821 \times 288$$
$$\Sigma = 2.586 \text{ atm}$$
$$= 2.586 \times 760 = \mathbf{1965\ mm}$$

SOLVED PROBLEM 3. Calculate the osmotic pressure of solution obtained by mixing (a) 100 ml of 3.4 per cent solution of urea (mol mass = 60) and (b) 100 ml of 1.6 per cent solution of cane sugar (mol mass = 342) at 20°C.

SOLUTION

Osmotic pressure of urea

$$\Sigma V = nRT$$

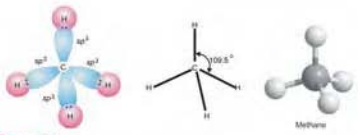

Figure 6.14
Shape and formation of methane molecule.

(b) sp^2 Hybridization of Carbon

When three out of the four valence orbitals hybridize, we have three sp^2 hybrid orbitals lying in a plane and inclined at an angle of 120°. If $2s$, $2p_x$ and $2p_y$ orbitals of the excited carbon atoms are hybridized, the new orbitals lie in the x-y plane while the fourth pure $2p_z$ orbital lies at right angles to the hybridized orbitals with its two lobes disposed above and below the plane of hybrid orbitals. Two such carbon atoms are involved in the formation of alkenes (compounds having double bonds). In the formation of ethene two carbon atoms (in sp^2 hybridization state) form one sigma bond by 'head-on' overlap of two sp^2 orbitals contributed one each by the two atoms. The remaining two sp^2

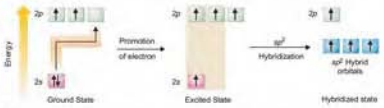

Figure 6.15
Excited carbon atom undergoing sp^2 hybridization leaves a pure $2p_z$ orbital.

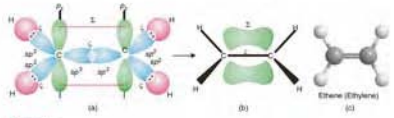

Figure 6.16
Orbital model of ethene molecule. (a shows scheme of overlaps; (b shows the bonds, sigma bonds indicated by straight lines; and (c shows ball-and-stick model of ethene (ethylene).

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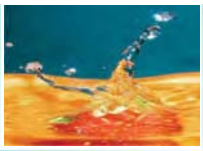

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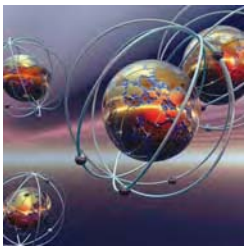

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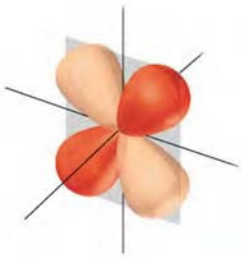

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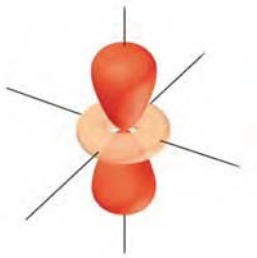

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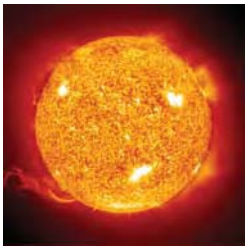

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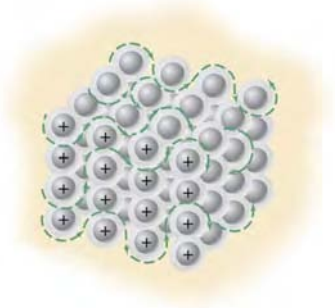

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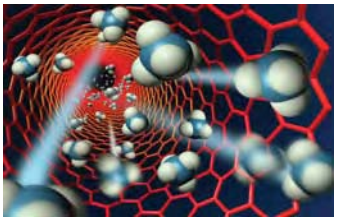

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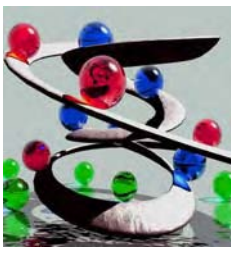

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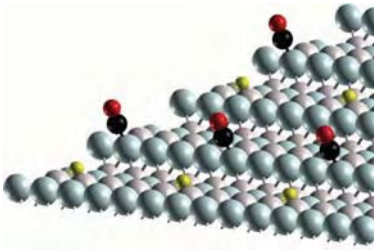

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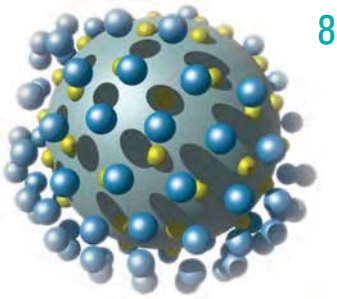

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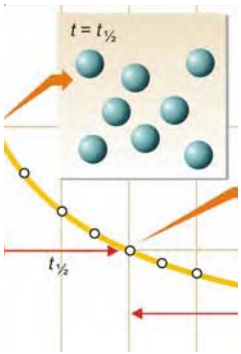

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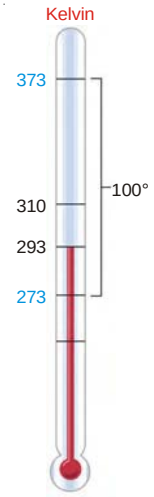

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