Chemistry

Part II

Textbook for Class XI





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OFFICES OF THE PUBLICATION DIVISION, NCERT

NCERT Campus Sri Aurobindo Marg

New Delhi 110 016 108, 100 Feet Road

Hosdakere Halli Extension Banashankari III Stage Bengaluru 560 085

Navjivan Trust Building P.O.Navjivan

Ahmedabad 380 014

CWC Campus Opp. Dhankal Bus Stop

anihati Kolkata 700 114

CWC Complex Maligaon Guwahati 781 021 Phone: 011-26562708

Phone: 080-26725740

Phone: 079-27541446

Phone: 033-25530454

Phone: 0361-2674869

Publication Team

Head. Publication

Division

: M. Siraj Anwar

Chief Editor

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Production Assistant : Mukesh Gaur

Cover

Shweta Rao

Illustrations

Nidhi Wadhwa Anil Nayal

FOREWORD

The National Curriculum Framework (NCF), 2005 recommends that children's life at school must be linked to their life outside the school. This principle marks a departure from the legacy of bookish learning which continues to shape our system and causes a gap between the school, home and community. The syllabi and textbooks developed on the basis of NCF signify an attempt to implement this basic idea. They also attempt to discourage rote learning and the maintenance of sharp boundaries between different subject areas. We hope these measures will take us significantly further in the direction of a child-centred system of education outlined in the National Policy on Education (1986).

The success of this effort depends on the steps that school principals and teachers will take to encourage children to reflect on their own learning and to pursue imaginative activities and questions. We must recognise that, given space, time and freedom, children generate new knowledge by engaging with the information passed on to them by adults. Treating the prescribed textbook as the sole basis of examination is one of the key reasons why other resources and sites of learning are ignored. Inculcating creativity and initiative is possible if we perceive and treat children as participants in learning, not as receivers of a fixed body of knowledge.

These aims imply considerable change in school routines and mode of functioning. Flexibility in the daily time-table is as necessary as rigour in implementing the annual calender so that the required number of teaching days are actually devoted to teaching. The methods used for teaching and evaluation will also determine how effective this textbook proves for making children's life at school a happy experience, rather than a source of stress or boredom. Syllabus designers have tried to address the problem of curricular burden by restructuring and reorienting knowledge at different stages with greater consideration for child psychology and the time available for teaching. The textbook attempts to enhance this endeavour by giving higher priority and space to opportunities for contemplation and wondering, discussion in small groups, and activities requiring hands-on experience.

The National Council of Educational Research and Training (NCERT) appreciates the hard work done by the textbook development committee responsible for this book. We wish to thank the Chairperson of the advisory group in science and mathematics, *Professor J.V.* Narlikar and the Chief Advisor for this book, *Professor B. L.* Khandelwal for guiding the work of this committee. Several teachers contributed to the development of this textbook; we are grateful to their principals for making this possible. We are indebted to the institutions and organisations which have generously permitted us to draw upon their resources, material and personnel. We are especially grateful to the members of the National Monitoring Committee, appointed by the Department of Secondary and Higher Education, Ministry of Human Resource Development under the Chairpersonship of Professor Mrinal Miri and Professor G.P. Deshpande, for their valuable time and contribution. As an organisation committed to systemic reform and continuous improvement in the quality of its products, NCERT welcomes comments and suggestions which will enable us to undertake further revision and refinement.

New Delhi 20 December 2005 Director National Council of Educational Research and Training

TEXTROOK DEVELOPMENT COMMITTEE

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V.P. Gupta, Reader, Regional Institute of Education, NCERT, Bhopal

MEMBER-COORDINATOR

Alka Mehrotra, Reader, DESM, NCERT, New Delhi

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Unit 12 Organic Chemistry - Some Basic Principles and Techniques

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REDOX REACTIONS

Objectives

After studying this unit you will be able to

- identify redox reactions as a class of reactions in which oxidation and reduction reactions occur simultaneously;
- define the terms oxidation, reduction, oxidant (oxidising agent) and reductant (reducing agent);
- explain mechanism of redox reactions by electron transfer process;
- use the concept of oxidation number to identify oxidant and reductant in a reaction;
- classify redox reaction into combination (synthesis), decomposition, displacement and disproportionation reactions;
- suggest a comparative order among various reductants and oxidants;
- balance chemical equations using (i) oxidation number (ii) half reaction method;
- learn the concept of redox reactions in terms of electrode processes.

Where there is oxidation, there is always reduction – Chemistry is essentially a study of redox systems.

Chemistry deals with varieties of matter and change of one kind of matter into the other. Transformation of matter from one kind into another occurs through the various types of reactions. One important category of such reactions is **Redox Reactions**. A number of phenomena, both physical as well as biological, are concerned with redox reactions. These reactions find extensive use in pharmaceutical, biological, industrial, metallurgical and agricultural areas. The importance of these reactions is apparent from the fact that burning of different types of fuels for obtaining energy for domestic, transport and other commercial purposes. electrochemical processes for extraction of highly reactive metals and non-metals, manufacturing of chemical compounds like caustic soda, operation of dry and wet batteries and corrosion of metals fall within the purview of redox processes. Of late, environmental issues like Hydrogen Economy (use of liquid hydrogen as fuel) and development of 'Ozone Hole' have started figuring under redox phenomenon.

8.1 CLASSICAL IDEA OF REDOX REACTIONS - OXIDATION AND REDUCTION REACTIONS

Originally, the term **oxidation** was used to describe the addition of oxygen to an element or a compound. Because of the presence of dioxygen in the atmosphere (~20%), many elements combine with it and this is the principal reason why they commonly occur on the earth in the form of their oxides. The following reactions represent oxidation processes according to the limited definition of oxidation:

$$2 \text{ Mg (s)} + O_2 \text{ (g)} \rightarrow 2 \text{ MgO (s)}$$
 (8.1)

$$S(s) + O_2(g) \rightarrow SO_2(g)$$
 (8.2)

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In reactions (8.1) and (8.2), the elements magnesium and sulphur are oxidised on account of addition of oxygen to them. Similarly, methane is oxidised owing to the addition of oxygen to it.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$
 (8.3)

A careful examination of reaction (8.3) in which hydrogen has been replaced by oxygen prompted chemists to reinterpret oxidation in terms of removal of hydrogen from it and, therefore, the scope of term oxidation was broadened to include the removal of hydrogen from a substance. The following illustration is another reaction where removal of hydrogen can also be cited as an oxidation reaction.

$$2 H_2S(g) + O_2(g) \rightarrow 2 S(s) + 2 H_2O(l)$$
 (8.4)

As knowledge of chemists grew, it was natural to extend the term oxidation for reactions similar to (8.1 to 8.4), which do not involve oxygen but other electronegative elements. The oxidation of magnesium with fluorine, chlorine and sulphur etc. occurs according to the following reactions:

$$Mg(s) + F_2(g) \to MgF_2(s)$$
 (8.5)

$$Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$$
 (8.6)

$$Mg(s) + S(s) \rightarrow MgS(s)$$
 (8.7)

Incorporating the reactions (8.5 to 8.7) within the fold of oxidation reactions encouraged chemists to consider not only the removal of hydrogen as oxidation, but also the removal of electropositive elements as oxidation. Thus the reaction:

$$2K_4$$
 [Fe(CN)₆](aq) + H_2O_2 (aq) $\rightarrow 2K_3$ [Fe(CN)₆](aq) + 2 KOH (aq)

is interpreted as oxidation due to the removal of electropositive element potassium from potassium ferrocyanide before it changes to potassium ferricyanide. To summarise, the term "oxidation" is defined as the addition of oxygen/electronegative element to a substance or removal of hydrogen/electropositive element from a substance.

In the beginning, reduction was considered as removal of oxygen from a compound. However, the term **reduction** has been broadened these days to include **removal** of oxygen/electronegative element from a substance or addition of hydrogen/electropositive element to a substance.

According to the definition given above, the following are the examples of reduction processes:

$$2 \text{ HgO (s)} \xrightarrow{\Delta} 2 \text{ Hg (l)} + O_2(g)$$
(8.8)

(removal of oxygen from mercuric oxide)

2 FeCl
$$_3$$
 (aq) + H $_2$ (g) \rightarrow 2 FeCl $_2$ (aq) + 2 HCl(aq) (8.9)

(removal of electronegative element, chlorine from ferric chloride)

$$CH_2 = CH_2 (g) + H_2 (g) \rightarrow H_3C - CH_3 (g)$$
 (8.10) (addition of hydrogen)

$$2$$
HgCl₂ (aq) + SnCl₂ (aq) \rightarrow Hg₂Cl₂ (s)+SnCl₄ (aq) (8.11)

(addition of mercury to mercuric chloride)

In reaction (8.11) simultaneous oxidation of stannous chloride to stannic chloride is also occurring because of the addition of electronegative element chlorine to it. It was soon realised that oxidation and reduction always occur simultaneously (as will be apparent by re-examining all the equations given above), hence, the word "redox" was coined for this class of chemical reactions.

Problem 8.1

In the reactions given below, identify the species undergoing oxidation and reduction:

(i)
$$H_2S(g) + Cl_2(g) \rightarrow 2 HCl(g) + S(s)$$

(ii)
$$3\text{Fe}_3\text{O}_4$$
 (s) + 8 Al (s) \rightarrow 9 Fe (s)

 $+ 4Al_2O_3$ (s)

(iii) 2 Na (s) +
$$H_2$$
 (g) \rightarrow 2 NaH (s)

Solution

- (i) H_2S is oxidised because a more electronegative element, chlorine is added to hydrogen (or a more electropositive element, hydrogen has been removed from S). Chlorine is reduced due to addition of hydrogen to it.
- (ii) Aluminium is oxidised because oxygen is added to it. Ferrous ferric oxide

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(Fe₃O₄) is reduced because oxygen has been removed from it.

(iii) With the careful application of the concept of electronegativity only we may infer that sodium is oxidised and hydrogen is reduced.

Reaction (iii) chosen here prompts us to think in terms of another way to define redox reactions.

8.2 REDOX REACTIONS IN TERMS OF ELECTRON TRANSFER REACTIONS

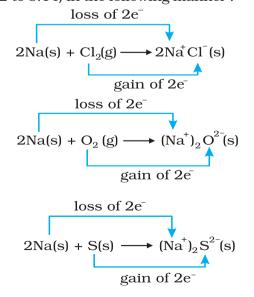
We have already learnt that the reactions

$$2Na(s) + Cl2(g) \rightarrow 2NaCl(s)$$
 (8.12)

$$4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$$
 (8.13)

$$2Na(s) + S(s) \rightarrow Na_2S(s)$$
 (8.14)

are redox reactions because in each of these reactions sodium is oxidised due to the addition of either oxygen or more electronegative element to sodium. Simultaneously, chlorine, oxygen and sulphur are reduced because to each of these, the electropositive element sodium has been added. From our knowledge of chemical bonding we also know that sodium chloride, sodium oxide and sodium sulphide are ionic compounds and perhaps better written as Na^+Cl^- (s), $(Na^+)_2O^2$ (s), and $(Na^+)_2$ S^2 (s). Development of charges on the species produced suggests us to rewrite the reactions (8.12 to 8.14) in the following manner:



For convenience, each of the above processes can be considered as two separate steps, one involving the loss of electrons and the other the gain of electrons. As an illustration, we may further elaborate one of these, say, the formation of sodium chloride.

$$2 \text{ Na(s)} \rightarrow 2 \text{ Na}^+(g) + 2e^-$$

$$Cl_2(g) + 2e^- \rightarrow 2 Cl^-(g)$$

Each of the above steps is called a half reaction, which explicitly shows involvement of electrons. Sum of the half reactions gives the overall reaction:

2 Na(s) + Cl₂ (g) \rightarrow 2 Na⁺ Cl⁻ (s) or 2 NaCl (s)

Reactions 8.12 to 8.14 suggest that half reactions that involve loss of electrons are called oxidation reactions. Similarly, the half reactions that involve gain of electrons are called reduction reactions. It may not be out of context to mention here that the new way of defining oxidation and reduction has been achieved only by establishing a correlation between the behaviour of species as per the classical idea and their interplay in electron-transfer change. In reactions (8.12 to 8.14) sodium, which is oxidised, acts as a reducing agent because it donates electron to each of the elements interacting with it and thus helps in reducing them. Chlorine, oxygen and sulphur are reduced and act as oxidising agents because these accept electrons from sodium. To summarise, we may mention that

Oxidation: Loss of electron(s) by any species. **Reduction:** Gain of electron(s) by any species.

Oxidising agent: Acceptor of electron(s).

Reducing agent: Donor of electron(s).

Problem 8.2 Justify that the reaction:

2 Na(s) + $H_2(g) \rightarrow 2$ NaH (s) is a redox change.

Solution

Since in the above reaction the compound formed is an ionic compound, which may also be represented as Na⁺H⁻ (s), this suggests that one half reaction in this process is:

$$2 \text{ Na (s)} \rightarrow 2 \text{ Na}^+(g) + 2e^-$$