Oxidation – Reduction Reactions

- Practical applications of oxidation reduction reactions can be traced back thousands of years to the period in human culture when metal tools were first made.

- The metal needed to make tools was obtained by heating copper or iron ores, such as cuprite Cu_2O or hematite Fe_2O_3, in the presence of carbon.

- Since that time, iron has become the most widely used of all metals and it is produced in essentially the same way: by heating Fe_2O_3 in the presence of carbon in a blast furnace.

- An ore is a mineral from which a metal can be extracted. Many metal ores are oxides and the metals are obtained from their oxides by the removal of oxygen.

$$Fe_2O_3(s) + 3\,CO(g) \xrightarrow{\Delta} 2\,Fe(l) + 3\,CO_2(g)$$

- In this reaction, we can think of the CO as taking O atoms away from Fe_2O_3 to produce CO_2 and the free element iron.

- A commonly used term to describe a reaction in which a substance gains O atoms is oxidation, and a reaction in which a substance loses O atoms is reduction.

- In reaction, CO is oxidized and Fe_2O_3 is reduced. Oxidation and reduction must always occur together, and such a reaction is called an oxidation reduction, or redox, reaction.

- Definitions of oxidation and reduction based solely on the transfer of O atoms are too restrictive.

- By using broader definitions, many reactions in aqueous solution can be described as oxidation reduction reactions, even when no oxygen is involved.

- Suppose we rewrite the equation and indicate the oxidation states (O.S.) of the elements on both sides of the equation.

$$\overset{+3\ -2}{Fe_2O_3} + 3\,\overset{+2-2}{CO} \longrightarrow 2\,\overset{0}{Fe} + 3\,\overset{+4-2}{CO_2}$$

- The O.S. of oxygen is 2- everywhere it appears in this equation.

- That of iron changes. It decreases from 3+ to 0 in the free element, Fe.

- The O.S. of carbon also changes. It increases from 2+ in CO to 4+ in CO_2 .

- In terms of oxidation state changes, in an oxidation process, the O.S. of some element increases; in a reduction process, the O.S. of some element decreases.

- Chemists frequently use the terms oxidizing agent and reducing agent to describe certain of the reactants in redox reactions, as in statements like fluorine gas is a powerful oxidizing agent, or calcium metal is a good reducing agent.

- In a redox reaction, the substance that makes it possible for some other substance to be oxidized is called the oxidizing agent, or oxidant.

- In doing so, the oxidizing agent is itself reduced.

- Similarly, the substance that causes some other substance to be reduced is called the reducing agent, or reductant.

- In the reaction, the reducing agent is itself oxidized.

Stated in other ways,

- An oxidizing agent (oxidant)
  - causes another substance to be oxidized
  - contains an element whose oxidation state decreases in a redox reaction
  - gains electrons (electrons are found on the left side of its half-equation)
  - is reduced
- A reducing agent (reductant)
  - causes another substance to be reduced
  - contains an element whose oxidation state increases in a redox reaction
  - loses electrons (electrons are found on the right side of its half-equation)
  - is oxidized

Chaos in the Belousov-Zhabotinsky Reaction

- Since its discovery 60 years ago, the Belousov-Zhabotinsky (BZ) Reaction has been the subject of intensive investigation as an example of a chemical oscillator.

- The reaction was discovered by Boris Pavlovitch Belousov around 1950 while he was trying to model the Krebs cycle using a metallic catalyst instead of proteins.

- He noticed that a solution of aqueous malonic acid with acidified bromate with a catalyst would oscillate between clear and colored for up to an hour.

- The original reaction used a cerium catalyst, which was later replaced by iron phenanthroline.

- However, Belousov's efforts to publish were frustrated by the disbelief of those who thought that the reaction was impossible, as it seemingly violated the second law of thermodynamics by reversing its state.

- The four laws of thermodynamics define fundamental physical quantities (temperature, energy, and entropy) that characterize thermodynamic systems.

- The laws describe how these quantities behave under various circumstances, and forbid certain phenomena (such as perpetual motion).

- The four laws of thermodynamics are:

  - Zeroth law of thermodynamics: If two systems are in thermal equilibrium respectively with a third system, they must be in thermal equilibrium with each other.

  - First law of thermodynamics: When energy passes, as work, as heat, or with matter, into or out from a system, its internal energy changes in accord with the law of conservation of energy.

- Second law of thermodynamics: In a natural thermodynamic process, the sum of the entropies of the participating thermodynamic systems increases.

- Third law of thermodynamics: The entropy of a system approaches a constant value as the temperature approaches absolute zero.

- After the recipe for the reaction circulated through Moscow State University, and the Biophysics Institute of the USSR Academy of Sciences at Puschino, Belousov was eventually identified as the discoverer, and was persuaded to write an abstract which appeared in a Soviet radiology journal in 1959.

- In 1961, while a graduate student at Moscow State University, Anatol M. Zhabotinsky was assigned by his advisor to investigate the reaction, which resulted in publication of a manuscript which was the first serious investigation describing the reaction.

➢In the 1970s, chaotic limit cycles of the BZ reaction were observed, but whether the chaos was the result of the chemical mechanism or uncontrolled fluctuations in experimental parameters was debated.

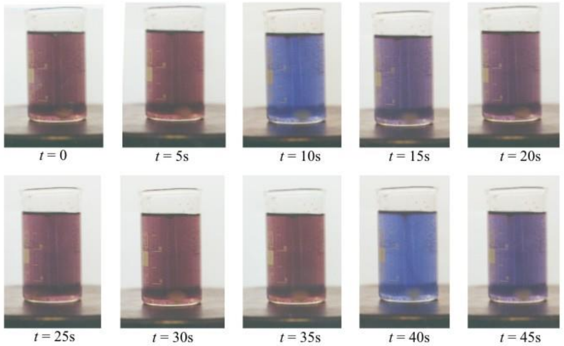
➢By using a Continuous Flow Stirred Tank Reactor (CSTR), in which reactants are pumped into a system at a constant rate to keep the system far from equilibrium to control these possible fluctuations.

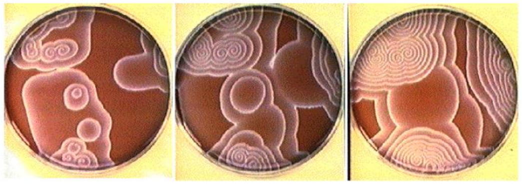
➢The system was shown to be chaotic in the early 1980s by using the time delay reconstruction technique on experimental data from a CSTR reactor.

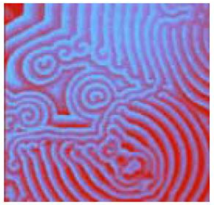
➢The reactions are theoretically important in that they show that chemical reactions do not have to be dominated by equilibrium thermodynamic behavior.

➢These reactions are far from equilibrium and remain so for a significant length of time.

➢In this sense, they provide an interesting chemical model of nonequilibrium biological phenomena, and the mathematical models of the BZ reactions themselves are of theoretical interest.







➢The mechanism of the BZ reaction is very complicated: a recent improved model for the Ce(IV)/Ce(III)-catalyzed reaction contains 80 elementary steps and 26 variable species concentrations.

➢However, in a sequence of landmark papers, Field, Koros, and Noyes formulated a model for the most important parts of the kinetic mechanism that gives rise to oscillations in the BZ reaction.

➢This is often referred to as the FKN mechanism. The FKN mechanism for the BZ reaction can be described as three concurrent (and at times competing) processes.

➢Process A: The three step reduction of bromate to bromine.
➢Process B: The introduction of hypobromous acid to compete as a reducing agent for bromate.
➢Process C: The reduction of the catalyst formed from Processes A and B.

Table 2: Abbreviated FKN mechanism governing the BZ reaction.

	Reaction	Rate constant
(R1)	$Br^- + HOBr + H^+ \rightarrow Br_2 + H_2O$	$k_{R1} = 8 \times 10^9\, M^{-2}\, s^{-1}$
(R2)	$HBrO_2 + Br^- + H^+ \rightarrow 2HOBr$	$k_{R2} = 10^6\, M^{-2}\, s^{-1}$
(R3)	$BrO_3^- + Br^- + 2H^+ \rightarrow HBrO_2 + HOBr$	$k_{R3} = 2\, M^{-3}\, s^{-1}$
(R4)	$2HBrO_2 \rightarrow BrO_3^-$	$k_{R4} = 2 \times 10^3\, M^{-1}\, s^{-1}$
(R5)	$BrO_3^- + HBrO_2 + H^+ \rightarrow 2BrO_2 \cdot + H_2O$	$k_{R5} = 10\, M^{-2}\, s^{-1}$
(R6)	$BrO_2 \cdot + Ce(III) + H^+ \rightarrow HBrO_2 + Ce(IV)$	$k_{R6} = 6 \times 10^5\, M^{-2}\, s^{-1}$
(C1)	$CH_2(COOH)_2 \rightleftharpoons (HO)_2C = CHCOOH$	see [7]
(C2)	$(HO)_2C = CHCOOH + Br_2$ $\rightarrow BrCH(COOH)_2 + H^+ + Br^-$	see [7]
(C3)	$2Ce(IV) + CH_2(COOH)_2 + BrCH(COOH)_2$ $\rightarrow fBr^- +$ other products	see [7]

➢The seventies developed some important works about non linear phenomenon's.

➢One of the most great conclusion of these studies is that some dynamic systems belonging to various parts of physic have unexpected behaviour although they are described by determinist rules.

➢These systems have a large sensitivity to the initial conditions, and are named "determinist chaos".

➢It's logical to wonder if the BZ reaction, which dynamic behaviour is described by non linear equations, can have a chaotic behaviour.

➢ Some experiments, done by Schmitz and Hudson in 1977, showed the appearance of chaos in the BZ reaction.

➢Chaos theory is a field of study in mathematics, with applications in several disciplines including meteorology, sociology, physics, engineering, economics, biology, and philosophy.

➢Chaos theory studies the behavior of dynamical systems that are highly sensitive to initial conditions—a response popularly referred to as the butterfly effect.

➢Small differences in initial conditions (such as those due to rounding errors in numerical computation) yield widely diverging outcomes for such dynamical systems, rendering long-term prediction difficult in general.

➢This happens even though these systems are deterministic, meaning that their future behavior is fully determined by their initial conditions, with no random elements involved.

➢In other words, the deterministic nature of these systems does not make them predictable.