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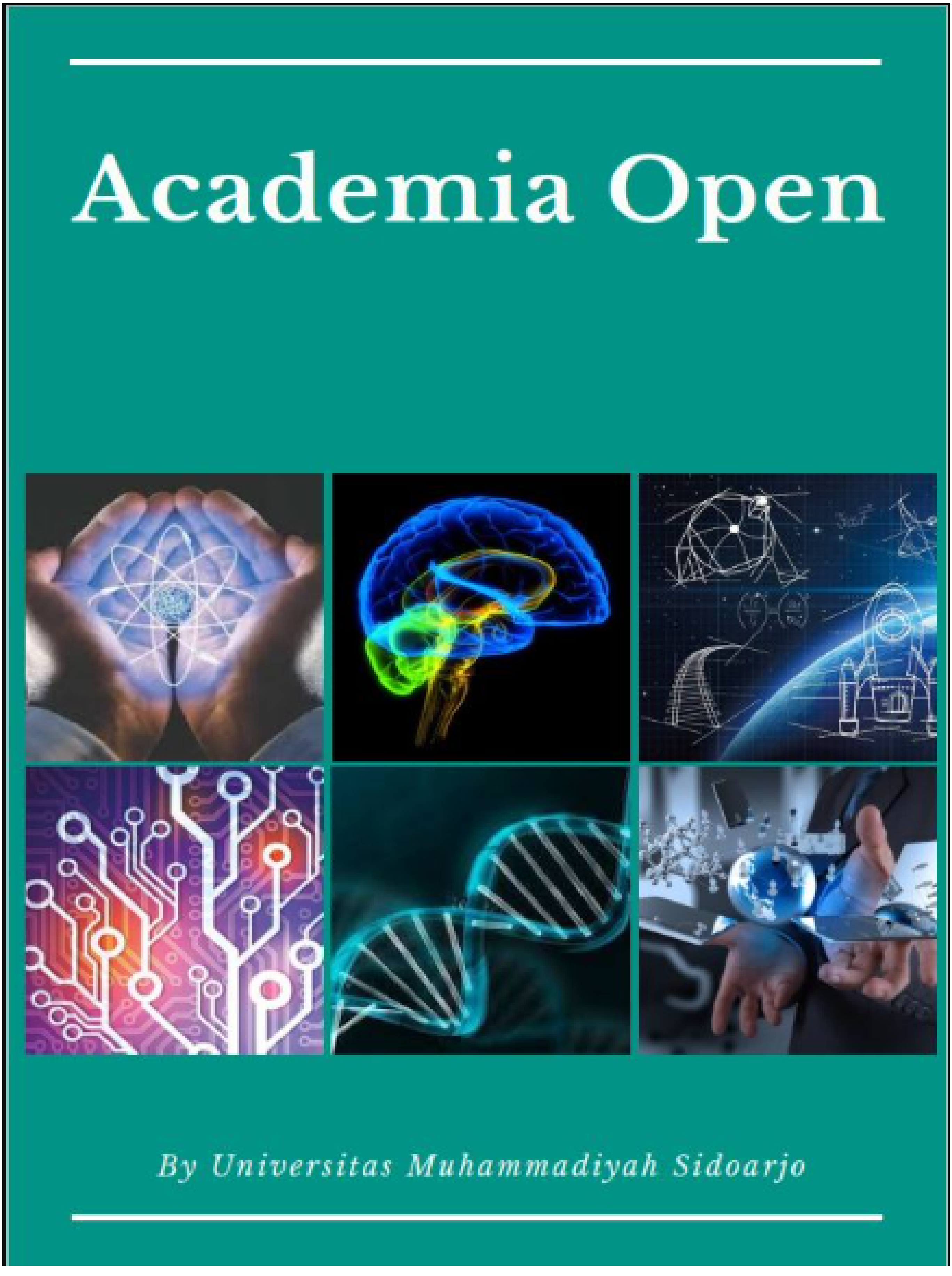

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The Role of Heat in Oxidation-Reduction Reactions: A Review: Peran Panas dalam Reaksi Oksidasi-Reduksi: Sebuah Tinjauan

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Abstract

General Background: Oxidation–reduction reactions are fundamental processes in chemistry and play essential roles in energy systems, biological processes, environmental chemistry, and metallurgical operations. **Specific Background:** Thermal energy is a critical factor that governs both thermodynamic feasibility and kinetic behavior in redox reactions, affecting reaction rates, equilibrium conditions, and electron transfer pathways. **Knowledge Gap:** Although the influence of temperature on chemical reactions has been widely recognized, a unified explanation connecting thermodynamic principles, kinetic theories, and practical redox applications across multiple scientific fields remains limited. **Aims:** This review summarizes how heat governs oxidation–reduction reactions by examining its effects on reaction thermodynamics, reaction kinetics, mechanistic pathways, and overall process performance. **Results:** The analysis of classical theories and published studies shows that temperature alters equilibrium constants, modifies activation energies, accelerates reaction rates, and affects electron transfer mechanisms. These thermal effects play significant roles in chemical systems including metallurgy, biological redox processes, environmental reactions, and emerging energy technologies. **Novelty:** The article synthesizes theoretical and applied perspectives to present an integrated view of thermal control in oxidation–reduction chemistry. **Implications:** Understanding the role of heat in redox reactions provides a conceptual foundation for improving chemical process design, optimizing reaction conditions, and guiding future research in electrochemistry, materials science, and energy conversion technologies.

Keywords: Oxidation Reduction Reactions, Reaction Kinetics, Electron Transfer, Thermodynamic Equilibrium, Thermal Energy

Key Findings Highlights

1. Temperature modifies equilibrium behavior and activation barriers in redox systems
2. Thermal conditions regulate electron exchange pathways during chemical transformations
3. Multiple scientific fields apply temperature-controlled redox chemistry principles

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Introduction

Oxidation-reduction reactions are amongst the most common and most vital systemic chemical transformations, involving the transfer of electrons between two chemical species [1, 2]. These reactions are present in almost every area of chemistry and biochemistry, from the cellular level in microbiological metabolism to bulk scale industrial production and geological transformations [3, 4]. It is more than merely some kind of simple kinetic acceleration due to a rise in temperature, and the thermodynamic concerns of the thermal energy of redox systems can actually cause changes in the possibility, selectivity of a reaction pathway, and the reaction efficiency [5, 6].

Thermal effects are of importance in redox systems and this aspect is particularly applicable in the world that we live in today. Challenges affecting sustainable production of energy, environmental remediation, and efficient production of chemicals in the society has directed more focus to research on redox processes alongside clever thermal management that streamline the maximization. Harnessing the growing interest in next generation battery technologies that can work at high temperatures, to solar thermochemical reactor to make fuels, heat and redox chemistry can be traced in its place of harmony in an ever-growing array of applications [7-10].

From a historical perspective, the acknowledgment of thermal effects as a factor in redox reactions could be traced back to the first studies of electrochemistry and chemical thermodynamics [11]. Some of the early foundations of our understanding of the effect of temperature on electron transfer reactions was through the illustrative work of Walther Nernst, Svante Arrhenius and the basic knowledge of redox outlined above has been altered and extended, by countless experimental and theoretical studies, over decades, into very complex models that describe, predict, and optimize the thermal properties of complex redox systems [14, 15].

These reviews have both the fundamental principles and some practical components, and it includes a comprehensive review of how heat can affect chemistry and redox chemistry in various systems. We have attempted to present sections on the thermodynamic grounds that allow for the temperature effect on redox transfer; address numerous kinetic factors such as activation energies and pathways, and present modern theories of electron transfer [16, 17] , examples that span from the high temperature metallurgically significant regions, to the biological redox processes that are operating at physiological conditions [18, 19] , and close with consideration of possible applications, and prospective research approaches to broaden our comprehension, representation, and application of thermal-based effects on redox chemistry [20, 21] .

2 . Thermodynamic Foundations of Temperature Dependent Redox Chemistry

2.1 Free Energy Relationships & Temperature Dependence

The thermodynamic feasibility of any redox reaction is determined fundamentally by the Gibbs free energy change (ΔG); and particularly this ΔG identifies if the reaction can actually occur spontaneously at the thermodynamic conditions that matter [21, 22]. The temperature dependent nature of ΔG is described by the Gibbs-Helmholtz relationship as follows:

$$\Delta G = \Delta H - T\Delta S$$

where ΔH is the change in enthalpy; T = absolute temperature; and ΔS is the entropy change associated with the reaction [22]. This relationship appears deceptively, simple, but has elegant consequences in redox chemistry; namely, that temperature can effectively negate the free energy or spontaneity of the electron transfer process [23].For redox reactions, the entropy change often represents considerable rearrangement of solvent molecules, changes to coordination spheres of metal centers, and change in the extent of ionic dissociation [24, 25]. Since these factors produce significant entropy changes, certain redox processes can exhibit a high sensitivity to temperature. Reactions that form or break metal-ligand bonds are an example of reactions that exhibit large entropy changes because of the reorganized coordination spheres and associated solvent molecules [26, 27] .

In real-world application, this thermodynamic relationship is particularly evident for some high-temperature metallurgical processes because reactions that are thermodynamically non-favorable at ambient temperature may become spontaneous at higher temperatures [28]. For example, the reduction of metal oxides by carbon (or hydrogen) is an example of this behavior, where the large positive entropy change due to gas formation drives the oxidation forward spontaneously at higher temperatures, even if the enthalpy change is expected to be non-favorable [28, 29] .

2.2 The Nernst Equation and Electrochemical Potentials

The Nernst equation elegantly expresses the quantitative relationship between temperature and electrochemical potentials. The Nernst equation provides a direct relationship between thermodynamic variables and measurable electrochemical values [11, 30]. The temperature dependence of standard electrode potentials is expressed by the relationship:

$$dE°/dT = \Delta S°/nF$$

Where E° is the relationship demonstrates that electrode potentials are fundamentally temperature-dependent, and the way that change occurs the magnitude and direction of change will depend on thermodynamic entropy [31, 32]

Experimental work has shown that the majority of common redox couples have negative temperature coefficients. This means that with increasing temperature the standard potentials are decreasing [31, 32]. It is consistent with the normal entropy changes expected with electron transfer reactions carried out in aqueous solutions. Typically, the reduction process involves a significant change in the hydration and coordination [31, 32]. However, there are exceptions in the case of gaseous species and reactions with large changes in molecular complexity [28, 29] .

The temperature dependence of electrode potentials has major consequences in practice such as in electrochemical energy storage systems (7,8). For example, high temperature batteries such as molten salt systems can exploit temperature dependence to produce favorable performance characteristics, such as higher energy densities and faster kinetics [8]. On the other hand, temperature sensitivity of electrode potentials must be controlled in applications where stable performance is required over broad temperature ranges [7, 8].

2.3 Equilibrium Thermodynamics and Le Chatelier's Principle

Le Chatelier's principle can be applied to redox equilibria to inform the thermal behavior of an electron transfer system [23]. For example, in an exothermic redox reaction ($\Delta H < 0$) increasing temperature shifts the equilibrium to the reactants, therefore shrinking the driving force of the forward reaction [23]. In contrast, endothermic redox processes ($\Delta H < 0$) are favored in high temperatures, which might help explain many high-temperature chemical processes involve endothermic redox processes [28, 29].

The behavior of redox equilibria as a function of temperature is determined by the relationship between enthalpy and entropy changes, which leads to complex thermal behavior in systems with competing enthalpy and entropy given that differences in entropy, and therefore temperature dependence, mostly depend on changes in the number of species involved [21, 22]. Temperature dependent equilibrium studies indicate some redox systems have temperature ranges where the equilibrium position is relatively immune to thermal changes, while other redox systems can exhibit relatively large changes in the equilibrium position over small temperature ranges [23].

Thermodynamic principles described can be directly applied to process design, and optimization in many different industries [36, 43]. The opportunity to change temperature is very valuable in chemical engineering, where manipulating reaction conditions can enhance yield, minimize favorable side reactions, and optimize energy efficiency of a redox process involving large quantities of products [43]. Relating complex chemical systems to fundamental thermodynamic relationships is critical in developing sustainable and economically favorable chemical manufacturing processes [36, 43].

3. Kinetic Considerations and Electron Transfer Mechanisms

3.1 Activation Energy and the Arrhenius Framework

Kinetic behaviour of redox reactions is essentially controlled by Arrhenius equation that measures the exponent relationship between the rate of the reaction and temperature [12, 33]:

$$k = A \exp(-Ea/RT)$$

The rate constant is denoted k, the pre-exponential factor is denoted by A, the activation energy is denoted Ea, the universal gas constant is denoted by R, and the absolute temperature is denoted by T [16]. This relation indicates that redox reactions are usually very temperature sensitive and the rate constant can increase two or three times with a increase of 10 o C in temperature [17, 33].

The redox activation energy involves a number of contributing factors in addition to the simple breaking and formation of bonds [17, 33]. The reorganization of solvent molecules and coordination spheres of the reacting species contribute a large fraction of the activation barrier in solution phase electron transfer reactions [24, 25]. This reorganization energy can be very significant especially in polar solvents, where the energetics of electron transfer are dominated by very strong solvation effects [32].

Recent calculations of computational methods have been used to clarify the molecular nature of activation barriers in redox reactions [34]. In particular, the simulations of the molecular dynamics indicate that thermal motions are essential in the process of optimizing reactant configurations to facilitate electron transfer, and temperature plays a fundamental role in the process [34]. The joint action of thermal energy and molecular motions leads to a complicated activation barrier topography that determines the general kinetic reaction in strong intensities in redox systems [17, 34].

3.2 Marcus theory and the modern theory of electron transfer

The seminal Marcus theory of electron transfer has provided great insight into the fundamental aspects of the kinetics of redox [5, 13]. The theory demonstrated that the rate constant for electron transfer is exponentially dependent on both reorganization energy and the driving force of the reaction, with both dependencies being highly temperature dependent [14, 24].

The rate constant for electron transfer can be described by the following equation:

$$k = (2\pi/\hbar)\ |HAB|^2\ (1/\sqrt{(4\pi\lambda kBT)})\ \exp\ [-(\Delta G° + \lambda)^2/(4\lambda kBT)]$$

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where, HAB is the electronic coupling matrix element, λ is the reorganization energy, ΔG° is the standard free energy change, kB is Boltzmann's constant, and ħ is the reduced Planck's constant [5, 24]. This expression-forcing a host of temperature dependence to each contribute to the overall thermal profile for electron transfer reactions [24, 25].

The molecular motion associated with λ, that is, reorganization energy, is also temperature dependent in its relationship with solvent dynamics [25]. Increased molecular motion contributes to reorganization at higher temperatures and can result in a decrease in the electron transfer barrier [25].For outer-sphere electron transfer processes where reactants are not bonded chemically to form a reaction intermediate [15, 35], the thermal activation of these processes is particularly important. Extensions of Marcus theory, with modern approaches, have included additional factors, include quantum mechanical tunneling distances and non-adiabatic transitions in order to better understand temperature effects in electron transfer processes [15, 24]. The nature of advanced treatments show that the relationship of temperature and reaction rate can often be more complex than simple Arrhenius behavior, especially in cases of very low temperatures where quantum effects can dominate the reaction [24, 25].

3.3 Inner-Sphere vs. Outer-Sphere Mechanisms

The role of temperature dependence in redox reactions are influenced first and foremost by the mechanism of electron transfer. Specifically, inner-sphere pathways and outer-sphere pathways will behave differently with respect to temperature dependence [26, 27]. The inner-sphere mechanism involves the creation of a bridged intermediate that has a direct bond between the electron donor and acceptor species [35]. These types of electron transfer processes have complex temperature relation due to the fact that either the thermal activation or coordination process is dominant [26, 27].

For inner-sphere electron transfer reactions, the temperature dependence (or thermal activation) is established from the kinetics of bridge formation as well as electron transfer [27]. Therefore, the overall activation energy is a composite from bridge formation and ligand substitution processes, which also have some differing temperature dependences [27]. Studies using experimental techniques have shown that most inner-sphere reactions show non-linear Arrhenius relationships that reflect the complexity of multi-step reactions [26, 27].

Outer-sphere electron transfer reactions, by contrast, are often seen to show simple Arrhenius behavior in accordance with their relatively simpler mechanisms [35].These processes occur without the need for the reactants to establish direct chemical bonds, and provide for through-space electron transfer by thermal movement in the solvent environment [35]. The temperature dependence of outer-sphere reactions is generally related to the reorganization energy and the degree to which thermal motion arranges the reactant molecule in a favored configuration for electron transfer [25, 35].

The difference between inner-sphere versus outer-sphere pathways is of considerable practical importance to process design and optimization [26, 27]. Improved understanding of the pathway clarifies the temperature dependence, and enables the determination of the best operating conditions for a particular application [36, 43]

4 . Generation and Consumption of Heat in Redox Processes

4.1 Exothermic Redox Reactions and Thermal Management

Many redox reactions are strongly exothermic reactions, generating hot fluids as a byproduct of redox activity involved with the reaction, which can create substantial thermal energy that may dramatically affect the reaction rates and performance of the redox process overall [17, 33]. Combustion reactions are the most common and commercially relevant exothermic redox process and are characterized by the rapid oxidation of organic compounds with the oxygen in the atmosphere resulting in the generation of heat [33]. The thermal energy is simply determined by the differences in the enthalpy of formation between the products and reactants, and gives good quantitative estimates of thermodynamic properties of particular redox systems [21, 22].

The exothermicity of many redox processes create considerable opportunities and challenges for practical applications [43, 44]. The heat generated can be useful by achieving useful ends, such as conducting other endothermic processes or providing thermal energy for heating [43]. Conversely, too much heat can produce thermal runaway situations where increasing temperature increase the reaction rate and thus generates more heat until reaching discrete degrees of danger [44, 45] .

Thermal management technology for exothermic redox processes (along with heat transfer technology and process control systems) has seen significant developments [43, 43]. For example, classic thermal management practices include heat exchangers to reclaim and utilize reaction heat, distributed reaction systems to avoid temperature hot spots, and modern control and algorithms to manage the best temperature [43]. Micro-reactor technologies are most appropriate and beneficial in very exothermic redox processes, where they improve heat transfer and safety [43, 44].

4.2 Endothermic Redox Processes and Energy Needs

Endothermic redox chemistry must have heat supplied continuously for setting reaction conditions and facilitating conversion rates [28,29]. Endothermic redox processes are more often thought to be in high-temperature metallurgical processes where thermodynamically stable compounds must be reduced by an outside energy source [18, 28]. The heat needed for the reaction must be supplied externally and which can be quite substantial and growing to be a considerable fraction of the process cost [18, 43] .

The metal smelting operations at high temperatures indicate the type of challenges and opportunities surrounding endothermic redox chemistry [18, 28].The reduction of iron ore in blast furnaces requires temperatures in excess of 1500°C, with the reducing agent of iron oxides being carbon monoxide [18, 28]. The enormous energy requirements of these processes has prompted the development of more efficient furnace designs and other alternative reduction technologies [18, 36].

Solar thermochemical processes are a new and emerging way of providing high-temperature energy for the thermal energy requirements of endothermic redox reactions [20, 37]. This is done through concentrated solar radiation, which can drive high-temperature chemical reactions, meaning that it could be a sustainable pathway for generating fuels and chemicals from renewable energy [20,37]. The design of efficient solar receivers and thermochemical reactors is still evolving as a field of research, with promising opportunities to help reduce the carbon footprint for energy-intensive redox processes [20, 47].

4.3 Autocatalytic Effects and Thermal Feedback

Some redox systems exhibit behavior that can essentially been viewed as autocatalysis, where heat released by a certain process, for instance oxidation, drive the reaction rate of the heat, produces a positive feedback loop and subsequently accelerates the process [33, 44]. Autocatalytic thermal effects are particularly significant in combustion systems where heat released from the initial oxidation reactions raises temperature; subsequently the reaction rates and other processes occur at a faster rate than expected. This may lead to exponential reactions, whose heat-release eventually results in potentially explosive behavior [44, 45] .

It is important to note that the mathematical description of autocatalytic thermal effects involves the coupling of heat and mass transfer equations with chemical kinetics, which results in a localized nonlinear system which can exhibit complex dynamic behavior [33, 44]. Perhaps the most significant safety consideration is recognizing the existence of the coupled effects for eventual safe design and operation, specifically safety during larger scale in-situ installations where thermal runaway can very quickly transition to controlled catastrophes [44, 45].

However, modern computational programs have dramatically increased the ability to predict and treat thermal autocatalytic effects [43, 44]. For example, computational fluid dynamics (CFD) simulations utilized in combination with a robust chemical kinetics model will result in estimated profile of concentration and temperature under recent operating conditions [43]. Computational programs like these promote safe design of processes and identification of the conditions to avoid destructive thermal runaway accidents [44, 45].

5. Metallurgical Applications and High-Temperature Redox Chemistry

5.1 Iron and Steel Production

Among the world's energy consumers, the iron and steel industry is among the largest, and throughout production, redox chemistry functions at virtually every step of production [28]. For example, in the blast furnace process, which has been around for longer than the other process for producing iron, all of the high-temperature redox reactions allow for the reduction of iron oxide to metallic iron [28]. The sintering, reduction, and melting involved within a blast furnace can occur at high temperatures between 1000°C and upwards of 1600°C presenting the chemistry of iron reduction is more complicated than typically described. Within a blast furnace, different reduction reactions will occur at different temperature zones of the furnace [28, 29].

The primary reduction reactions typically described in a blast furnace is when carbon monoxide is the reducing agent, however, the net reaction is only $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$ [28] and the chemistry is far more complex. Many intermediate oxide phases with several competing reactions will exist simultaneously, and vary based on temperature, gas concentration, and solid-state diffusion rates, for example [18,28]. Understanding the different thermal effects has been important to understanding concepts that improve operation and energy efficiency of a furnace [43].

Recently, new technologies have occurred for production of iron considering alternate reduction processes with lower temperature ranges for operation or use different reducing agents [18,36]. For example, direct reduction processes allow for the use of hydrogen or reformed natural gas at temperatures near 800-1000°C which may allow for potential savings in energy usage or lowering the environmental impact [18]. While these alternative technologies allow for different redox chemistries to be adopted, they encourage redox thermal management in a different way supporting the necessity of understanding temperature effects over the range of process conditions [18, 36].

5.2 Nonferrous Metal Extraction

As with other metals, the extraction of nonferrous metals (e.g., copper, zinc, lead, aluminum) proceeds through various redox processes and involves temperature variances that can range from room temperature to well over 1,200°C [18, 36]. Pyrometallurgy inherently involves high temperature processes (800°C to over 1,200°C). Hydrometallurgy can occur at much lower temperatures, often below 100°C [18, 36]. When to choose hydrometallurgical extraction over pyrometallurgical extraction (or vice versa) is a complex issue dependent on ore composition, relative energy costs, and other environmental concerns [18, 43 .

Copper smelting is a common and often cited example of high temperature redox chemistry in metal extraction [18, 28]. To form copper metal, copper ores undergo sequential steps including roasting, smelting and converting, each taking place at its own temperature [28]. In the case of roasting, the copper sulfide mineral is oxidized at temperatures of around 650-700°C to an oxide and sulfur dioxide [28]. In the smelting process, following roasting, the copper oxides are reduced back to metallic copper, utilizing carbon based reducing agents, at temperatures of around 1200°C [28, 29].

Aluminum is a unique example of a high-temperature environment, and one which undergoes electrochemical reduction in the Hall-Héroult process [7, 8]. The Hall-Héroult process is typically conducted at approximately 960 °C, and involves dissolving aluminum oxide in molten cryolite and subsequently reducing aluminum oxide to molten aluminum through electrolytic reduction [7, 8]. While the high temperature process allows both molten electrolyte and manageable current densities, the temperature usage must be weighed against energy consumption and the operational durability of the materials themselves [8, 18].

5.3 Advanced Materials Processing

The synthesis of advanced materials usually involves redox chemistry under controlled thermal conditions [18, 36]. An example of this is powder metallurgy where controlled reduction reactions are used to synthesize high purity metal powders with defined particle size and surface morphology [18]. These processes usually happen at intermediate temperatures (400-800°C) where the reaction rates are adequate for the production process to be practical but limits the amount of sintering or grain growth [18, 41] .

The synthesis of advanced performance ceramics and intermetallic also involves redox reactions of metal oxides and reducing agents at defined temperature sequences [41, 42]. The many redox processes from all of these materials also need controlled temperature profile management on either side to reach appropriate phase distributions and microstructures, while avoiding unexpected side reactions [41, 42]. A big part of this is carrying out a proper characterization, with no small amount of effort spent trying to define appropriate multi-level and multi-physics models in order to highlight the relationships that existed between temperature, reaction kinetics, and final properties of the material [41, 42].

With the rise of additive manufacturing technologies, there are also new features and opportunities to consider with the thermal management of these redox processes [41, 42]. Processes for selective laser melting and electron beam melting pathway a product through rapid heating and cooling cycles that can alter the redox chemistry in reactive metal powders [41]. Of course understanding the thermal component is important to obtain appropriate parts to be high quality and maintain certain properties [41, 42].

6 . Energy Conversion and Storage Systems

6.1 Battery Technologies with Thermal Impacts

It is fundamentally a controlled redox reaction for electrochemical energy storage systems. However, temperature is one of the most important factors that influences performance characteristics in terms of capacity, power capability, cycle life, and safety [7, 8]. Thus, the temperature dependence exhibit in batteries performance arises from many functional or physical phenomena including the kinetics of the electrode reactions, conductivity of the electrolytes, and the thermodynamics of the overall overall cell reaction [1, 7].

Lithium-ion batteries currently dominate the portable electronics and electrified vehicle markets, with performance that is characterized by complex temperature dependencies that need to be properly managed [8]. At low-temperatures, electrode kinetics have become sluggish and electrolyte conductivity has been reduced, impacting capacity and power capability to very low levels [8]. At elevated temperatures, side-reactions can become accelerated and thermal decomposition of electrolyte components can often lead to very rapid rate of capacity fade, presenting serious safety issue [8, 44].

High-temperature battery systems, such as sodium-sulfur and molten-salt batteries operating at temperatures of 300-600°C where the electrolyte and active materials are molten and work at high ionic conductivities and thus rapid kinetics [8]. This elevated state provides high energy density and power capability [8]. The downside is that there are additional concerns with respect to thermal insulation and corrosion resistance, and providing time for the system to start up [8, 41].

6.2 Fuel Cells and Electrochemical Energy Conversion

Fuel cells represent a direct conversion technology where the chemical energy of fuels is converted to electrical energy through controlled redox reactions [7, 32]. The temperature at which fuel cells operate significantly influences their efficiency, power density, and fuel flexibility [7, 32]. Low-temperature fuel cells, such as proton exchange membrane fuel cells, operate at temperatures below 100 °C and are well-suited for transportation applications [7].

High-temperature fuel cells, including solid oxide fuel cells and molten carbonate fuel cells, operate at temperatures ranging from 600°C to 1000°C [7, 38]. These elevated operating temperatures provide several advantages including rapid electrode kinetics, high efficiency, and the ability to internally reform hydrocarbon fuels [7,38]. The high temperature also enables the production of high-quality waste heat that can be utilized for cogeneration applications [7, 43].

The development of intermediate temperature fuel cells operating in the 400-600°C range has attracted significant research interest as a compromise between the advantages of high-temperature operation and the material challenges associated with extreme temperatures [7, 38]. These systems require advanced materials and careful thermal management to achieve acceptable performance and durability [7, 41].

6.3 Solar Energy Conversion and Thermochemical Processes

The solar thermochemical reactions are a new technology of transforming the high-temperature redox reactions of concentrated solar radiation to chemical fuels [20, 37]. Such reactions have the potential to be even more efficient than mainstream photovoltaic-electrolysis reaction chains since they can directly use the high temperature thermal energy found in concentrated solar systems [20, 47].

Metal oxide thermochemical cycles Splitting water to produce hydrogen: Splitting water by means of metal oxide thermochemical cycles has been highly examined as a route to solar hydrogen generation [20, 37]. Most of these processes occur in two step redox cycles; initially, a high temperature (1400-1600 ^{o}C) thermal reduction reaction of a metal oxide is carried out, followed by a lower temperature (800-1000 ^{o}C) reoxidation reaction of the reduced product with water vapor [37,47]. The high-temperature difference that is necessary to achieve these cycles is extremely difficult in terms of engineering yet has the possibility of producing solar fuels with high efficiency [20, 47].

The separation of carbon dioxide under similar thermochemical methods has also become a possible method of producing solar fuels out of carbon dioxide and water [37, 47]. These reactions consist of the same rudimentary two-step redox reaction except that carbon monoxide is the product of the initial step of splitting water into hydrogen [37]. The generated syngas ($CO + H_2$) may be further upgraded into liquid fuels by considering the known chemical synthesis technologies [47].

7. Biological Redox Systems and Biochemical Applications

7.1 Cellular Respiration and Metabolic Redox Chemistry

The biological domain has developed highly complex mechanisms to exploit redox chemistry over a relatively narrow temperature range determined by physiological conditions [19]. Cellular respiration, which is the universal means by which life extracts energy from food items, involves a complex set of redox reactions that are constrained to the temperature range that is safe for protein specification and pertains to cellular functioning [19].

The electron transport chain, which is the final step in cellular respiration, is one of the most effective redox system found in nature [19]. The electron transport chain consists of several protein used to transport electrons from NADH and $FADH_2$ to molecular O_2, allowing the unbridled energy to be captured as ATP [19]. Temperature dependence is managed by considerations of the protein’s structure, composition and stability [19]. Overall the redox processes are programmed to bring optimal performance within physiological temperature [19].

Biological redox adaptation to temperatures has been mostly examined in organisms that live under severe temperatures [19]. As an example, thermophilic bacteria that grow in a temperature of more than 60 ^{o}C altered the specificity of their proteins, membranes composition to also assist redox effort in high temperatures [19]. Instead, a psychrophilic organism was adapted to remain efficient at low temperatures in redox [19].

7.2 Photosynthetic Redox Processes

Photosynthesis is the most significant biological redox process on Earth, which transforms solar energy into chemical energy in a complicated system of light-dependent reactions of electron transfer [19]. The major photochemical reactions in photosynthesis are relatively temperature unaffected because they are directly linked to the absorption of photons and take place on timescales that are too short to allow thermal effects to play a role [19].

But later dark reactions of photosynthesis especially the Calvin cycle, in which carbon dioxide is trapped in organic products, are highly temperature dependent [19]. Ribulose-1,5-bisphosphate carboxylase/oxygenase (RuBisCO) that catalyzes the most important carbon fixation reaction has a complex temperature behavior that contributes greatly to the total photosynthetic efficiency [19].

Photosynthesis and temperature dependence has significant ramifications to plant productivity and global carbon cycle, especially in the climate change scenario [19]. The increase in temperatures of the world is likely to change the proportions between photosynthetic fixation and respiratory release of carbon, and the effects on carbon dioxide in the atmosphere may be quite drastic [19].

7.3 Enzymatic Redox Catalysis

Redox enzymes are catalysts undergoing rearrangement of electron transfer reactions under mild conditions with a high efficiency and selectivity [19]. The bell-shaped temperature dependence of these biological catalysts is a typical feature of the activity curves, and is a manifestation of the competing influences of elevated reaction rates at elevated temperatures and denaturation of the enzyme at temperatures higher than optimal temperatures [17, 19].

The temperature optima of redox enzymes are closely associated with the systems in which the source organisms evolved [19]. Enzymes from mesophilic organisms typically have optimal activity around 25-45°C, while thermophilic enzymes may have an optimal temperature in excess of 80°C [19]. These relationships between thermophiles and temperature have provided important information for developing industrial bio-catalytic processes [36].

Recent advances in protein engineering have made it possible to develop redox enzymes (used in biocatalytic processes) with increased thermal stability and modified temperature optima [19, 36]. Engineered redox processes will be widely used in industrial processes involving reacting at enhanced temperatures or involving process robustness [36].

8 . Environmental Redox Chemistry and Atmospheric Processes

8.1 Atmospheric Redox Reactions and Climate Chemistry

The atmosphere contains a highly complex series of redox reactions and these reactions are integral to determining global air quality, climate, and element cycling globally [33]. The chemistry of redox reactions in the atmosphere is highly temperature dependent and influences air quality and climate dramatically from determining the formation of local smogs to affecting climate feedbacks globally [33].

The oxidation of sulfur dioxide to sulfur trioxide in the atmosphere is one temperature-dependent process that affects the formation of acid rain [33]. Sulfur dioxide may have a number of atmospheric pathways of oxidation that may either be homogeneous gas-phase or heterogeneous processes involving aerosol particles or have contrasting temperature dependencies [33]. Understanding the thermal effects is important to predicting the environmental consequences of sulfur emissions from large industrial sources [33].

Both tropospheric and stratospheric ozone chemistry involves complex networks of redox chemistry that have temperature responses [33]. Tropospheric ozone is a photochemical smog component and shows strong temperature dependence where ozone concentrations are typically increasing with temperature during warmer summer months [33]. Stratospheric ozone depletion also involves the temperature imposed both on Cl and Br compound reactions, which affects ozone hole development severity [33].

8.2 Aquatic Redox Chemistry and Water Treatment

Biogeochemical redox chemistry in aquatic systems is heavily influenced by temperature variation that may affect the solubility of gases and the chemical and biological processes responsible for generating or degrading contaminants [31,32]. The temperature dependence of oxygen solubility in water contributes significantly to the health of aquatic ecosystems or the efficiency of biological treatment processes [31, 32].

Advanced oxidation processes (AOP's) used in water treatment are dependent on redox reactions that generate hydroxyl radicals which are highly reactive [31, 32]. The efficiency of an AOP process is mostly temperature dependent as a result of faster kinetics with increased temperature, but as with every operating process you must balance efficiency with energy costs [31, 43]. Ozone treatment, Fenton process, and photocatalytic oxidation are examples of AOP processes that may be significantly affected by temperature considerations [31, 32].

The growing number of electrochemical water treatment technologies use direct redox reactions at the electrode surfaces. The performance of an electrochemical treatment technology is influenced by the temperature influencing both the kinetics on the electrode surface but mass transfer phenomena within the process [31, 32]. Electrochemical processes that operate at high temperatures can have improved treatment efficiencies, but may alter the electrochemical process implementation requiring special electrode materials and system modifications [32, 41].

8.3 Soil Chemistry and Biogeochemical Cycling

Soil redox chemistry plays a fundamental role in nutrient cycling, contaminant fate and transport, and greenhouse gas emissions [19, 33]. The temperature dependence of soil redox processes influences everything from nitrogen mineralization rates to the mobility of heavy metals in contaminated soils [19, 33].

Redox activity in the soil by the microbes has a high temperature dependence that influences the rate of dissolution of organic matter and the generation of greenhouse gases like methane and nitrous oxide [19, 33]. Such relationships between temperatures are important in forecasting how the carbon stocks in the soil will react to climate change [19, 33].

The technology involves in situ chemical oxidation and reduction processes in soil and groundwater remediation, which are based on redox reactions to eliminate or fix the contaminants [31, 32]. The efficiency of these technologies is normally temperature dependent, however the temperature dependence can vary greatly depending on the specific redox chemistry under consideration [31,32].

9. Emerging Technologies and Future Applications

9.1 Solar Thermochemical Fuel Production

Concentrated solar energy can undergo solar thermochemical reactions on a promising pathway to the production of carbon-neutral energy through high temperature redox reactions [20, 37]. This can result in greater efficiencies than traditional photovoltaic-electrolysis schemes since these technologies can directly use the thermal energy at high temperature provided by concentrated solar collector systems [20, 47].

Splitting water and carbon dioxide Two-step metal oxide thermochemical cycles, which are known to split water and carbon dioxide, have been widely examined as pathways to solar fuels [37, 47]. They usually entail the reduction of metal oxides at high temperatures (1400-1600 ^{o}C) and reoxidation of the products at lower temperatures (800-1000 o C) with water vapor or carbon dioxide to obtain hydrogen or carbon monoxide [37,47]. The huge temperature difference to achieve efficient operation poses both serious engineering challenges and has the promise of high- efficiency in converting solar fuels [20, 47].

Recent research has focused on developing new materials and reactor designs that can operate efficiently under the extreme thermal conditions required for solar thermochemical processes [37, 47]. Advances in high-temperature materials, heat recovery systems, and reactor geometries have improved the prospects for practical implementation of these technologies [37, 48].

9.2 High-Temperature Electrochemical Systems

Solid oxide electrochemical systems function at elevated temperatures of 800-1000 °C, which can benefit energy conversion and chemical synthesis [38,39]. The benefits associated with high-temperature systems include fast kinetics of the electrode materials, high ionic conductivity, and the ability to recover waste heat produced in other processes [38, 39].

For example, solid oxide electrolysis cells (SOECs) require electrical and high-temperature heat to split water and carbon dioxide into hydrogen and carbon monoxide, respectively [38,39]. Because SOECs operate at high temperatures compared to low temperature electrolysis systems, SOECs utilize less electrical energy, resulting in potentially higher efficiencies overall, especially if waste heat from a prior process is utilized in the energy conversion proces [38,39] .

Furthermore, reversible solid oxide cells which encompass both fuel cell and electrolysis cell operations have been touted as a potential means of efficient, electrical energy storage systems [38, 39]. Reversible solid oxide cells could store electrical energy (owing to excess electricity) into hydrogen via electrolysis, and later convert hydrogen back into electricity through the operation of the device in fuel cell mode [38, 39].

9.3 Advanced materials and manufacture processes .

Pioneering additive manufacturing technologies are providing pathways for innovative design and manufacture of components utilized in high-temperature redox processes [41,42]. Selective laser melting and electron beam melting enable complex geometry designs to be manufactured with integrated cooling channels and optimized heat transfer characteristics [41, 42].

The rapid heating and cooling cycles that occur during additive manufacturing operations may have dramatic influences on redox chemistry of reactive metal powders leading to potential changes in composition, microstructure, or properties [41, 42]. Understanding and regulating thermal effects is paramount to develop and manufacture high-quality components that elicit repetitively high performances [41, 42].Nanostructured materials provide new prospects toward efficiencies in redox chemistry due to the benefits of surface area, mass-transfer, and electrical legacy [41, 42]. But, the materials and synthesis and processing of nanostructured materials typically activate temperature-dependent redox chemistry with a narrow range of temperature control (e.g., limited range if one wants to achieve desirable properties [41, 42].

10 . Challenges and Future Directions for Research

10.1 Materials Development and High-Temperature Stability

It continues to be a challenge to materialize materials that will withstand highly energetic environments correlated with high-temperature redox chemistry [41, 42]. The materials must withstand thermal stress, chemical and abrasive corrosion, and mechanical and tribological forms of physical degradation, while also maintaining functional limits to endure operations time [41, 42].

Advanced ceramics, and other structures, including oxide ceramics, carbides and nitrides will be more tolerant of thermal-temperature resistant high-temperature reliability than any structural metallic materials [41, 42]. However, these materials will very likely also not withstand a state of brittleness or thermally shock, which could lessen the appreciable usability of these materials. Engineers have recently begun addressing the toughness found in ceramic composites and functionally graded materials to provide materials with greater tolerances for thermal cycling [41, 42].

Computational materials science is becoming an increasingly plausible avenue towards prospecting and accelerating high-temperature materials development [41, 42]. Computational means allow for the development of material properties and possible compositions without foregoing laboratory testing in place of the research and laboratory environment. Engineering is also considering machine learning techniques for possible use as it could potentially accelerate high-temperature materials research and alternative discovery of new materials with properties for end use applications [41, 42].

10.2 Process Integration and Energy Efficiency

The design for the redox process will integrate the thermal management, which will be an important opportunity to optimize energy efficiency and facilitate distancing towards environmental impact [43,44]. Heat integration techniques can significantly diminish the total energy demands of industrial processes by recovering and reusing thermal energy from heat-producing reactions [43]. Factors of process intensification will be useful for heat and mass transfer improvements because they address redox processes, such as micro-reactor technologies and structured catalysts. These technologies would help improve temperature management, reduce equipment size, and alter the safety characteristics typically associated with redox processes [43,44] .

In addition, responsive and flexible process control systems will be necessary to optimize the thermal behavior of complex redox processes. As processes cross the complexity threshold and become more integrated, real-time optimization of performance will be essential [43,44] using advanced control algorithms which adapt to changing situations.

10.3 Environmental and Sustainability Considerations

Due to the operational characteristics of high-temperature redox processes, especially in relation to energy consumption, environmental considerations are increasingly important in the design & development of processes. Key facets of sustainable process design include: minimizing high-temperature energy consumption, minimizing waste heat generation, and utilizing renewable energy sources as alternatives for high-temperature energy sourcing [43,44] .

Life cycle assessment approaches are being implemented to assess the total environmental performance of redox processes, considering aspects such as energy consumption, raw material consumption/quantity, waste generation [43,44]. With these assessments, opportunities for improvement can be recognized, and more sustainable technologies can be developed [43,44].

The circular economy is driving new methods of process design that shift the redox process model from one that prioritizes the proper management of initial resources and waste, to the recovery of resources .These methods utilize fully closed loop procedures whereby waste material from one reaction can be used as a precursor for another reaction [43,44].

Conclusion

The effect of heat may be numerous in oxidation reduction reactions and can affect all aspects of the process including basic thermodynamics and the use of the process in the wide range of fields of sciences to engineering technology. Both thermodynamic and kinetic implications are concerned with the redox temperature dependence, and the correlations are complicated and multifaceted - they connect between the molecular scale of the electron transfer reactions and the macro-scale activity of industrial operations.

Examples of the thermodynamic principles of temperature dependent redox chemistry include the Gibbs-Helmholtz equation or Nernst equation showing how temperature can fundamentally change the thermodynamics of electron transfer reactions both in terms of whether they are feasible and in terms of driving force. These concepts are practiced in the high temperature metal processing through to fine-tuning electrochemical systems.

The kinetic effects, and those given in the context of Marcus theory or Arrhenius type processes, explain the effect of increasing thermal energy, that electron transfer can occur because pairing activation processes go together with molecular reorganization processes. Other important information on various contributions to the uncertainty is also the inner-sphere reactions and outer-sphere reactions unique molecular features.

The role of heat as reactants and products in redox processes is not only important in opportunities of energy recovery and process integration but also creates the challenge of thermal management and safety. The knowledge of thermal contributions to redox processes is essential to improving the existing processes and in designing new technologies which can find applications in the conversion of renewable energy into practical forms and in environmental remediation processes.

New directions in solar thermochemical fuel technology, high temperature electrochemical technology or the exploration of new processing materials, prompt us to re-examine our perspective on the effects of thermal effects on redox chemistry. These R&D operations will further increase the significance of redox processes and its significance in the development of solutions to the global issues of sustainable production of energy and environmental protection.

The research agendas in future should be aimed at co-designing materials and creating processing systems capable of becoming effective in the process of recovering heat to undergo redox transformations in sustainable and environmentally friendly approaches, the role of heat recovery in contributing positively to the societal social constructs should be taken into account. It will not be insignificant to capitalize on the integration of computational modeling to come up with enhanced materials science partnerships to exploit process systems engineering form of approaches to develop our comprehension and evaluate the potentials of maximizing thermal effects using redox systems in the future.

As a discipline, we will not cease to research, discover, and accumulate our knowledge at a molecular level of the underlying principles pertaining to thermal effects on redox chemistry. But this will only result in increasingly applicable applications, gradually more efficient processes, and will remain a demonstration of the importance of the central role heat plays in so many chemical reactions that are important to the society, and one upon which so much of nature depends.

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