



## Chemical kinetics: A Discipline and a Mechanistic Tool

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### ABSTRACT

The purpose of this review is to introduce young researchers, advance undergraduate and graduate students of inorganic chemistry to the field of chemical kinetics both as a discipline and as a tool in mechanistic diagnosis of inorganic chemical reactions. Inorganic reaction mechanism is an important aspect of inorganic chemistry that deals with the study of the detailed step by step processes through which reactants in chemical reactions are converted to products. The overall equation of a reaction tell us what happens in a chemical reaction, whereas the mechanism explains how it happens –the steps involved and the effect of reaction conditions and catalyst, if employed. The review will deal with concepts and well established principles within the broad field of chemical kinetics, which can be employed in determining the stoichiometry, kinetics and ultimately the mechanisms of chemical reactions.

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### INTRODUCTION

The review begins with a look at the relevance and application of chemical kinetics before delving into discussion on reaction rate and the techniques for its measurement and interpretations. The results of such measurements show that reaction rates depend on the concentrations of reactants, products and in some cases even intermediates in characteristic manners that can be expressed in terms of differential equations known as rate laws (Wilkins, 2002). The rate law describes the effect of concentration on the rate of a reaction and its solutions can be used to predict the concentration of specie at any time after the start of the reaction (Atkins and de Paula, 2010). The study of reaction rates ultimately leads to an understanding of the mechanisms of reactions (Ghosh and Rajput, 2012). An insight into the elementary steps through which a reaction occurs can be gotten from the form of the rate law (Wilkins, 2002). Therefore the main task in kinetics is the construction of a rate law from a proposed mechanism and its comparison with the experimentally determined one (Atkins and de Paula, 2010). The concepts of the rate determining step of a reaction, the steady-state concentration of a reaction intermediate, and the existence of a pre-equilibrium are all employed in deriving the rate law from the proposed mechanism (Jordan, 2007).

The word kinetics has its origin in the Greek word 'kinesis' which means 'to move' or 'moving' (Rescigno and Boccbialini, 1991; Ferner and Aronson,

2016). It is a general term referring to time-dependent phenomena that involves change in a parameter (Hammes, 1978). The principles of kinetics are used in different aspects of sciences (Rescigno and Boccbialini, 1991; Qin, 2013; Ferner and Aronson, 2016) and chemical engineering (Levenspiel, 1999; Coker, 2001). Knowledge about chemical kinetics is also required for the understanding, design, and control of the chemical reactor, to explain enzyme actions and polymerisation (Coker, 2001), as well as to describe drug degradation and absorption (Ferner and Aronson, 2016). In fact, nothing will be more important in chemistry than the understanding of the mechanism through which chemical reactions occur and this explains the significance of kinetics as an important field of chemistry (Houston, 2001).

Chemical kinetics also involves the construction of models that can facilitate the prediction and calculations of experimental results. Modeling and simulation of chemical system can be achieved by mathematical approach (Bellouquid & Delitala, 2006), with the experimental kinetic data collected used to obtain parameters such as rate constant and rate order of a system theoretically (Atkins & de Paula, 2005). The correlation between the theoretically and experimentally determined constants confirms the plausibility of a mechanism (Chinake & Simoyi, 1998; Bellouquid & Delitala, 2006; Jordan, 2007). Software packages which are based on mathematical models have been designed to simulate reactions and validate the plausibility of

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a proposed mechanism (Svir *et al.*, 2004). Recent progress in reaction kinetics can be attributed to the availability of supercomputers and software of quantum chemical methods (Wright, 2004; Groenhof, 2013) and the development of methods for monitoring very fast reactions (Espenson, 1995; Atkins & Jones, 1999; Houston, 2001).

The significance and importance of kinetics as a field of chemistry is emphasized by the fact that it has produced several Nobel Laureates including Jacobus Henricus van't Hoff, Irvin Langmuir, Manfred Eigen, Henry Taube, Rudolph A. Marcus and Ahmed Zewail (Leroy *et al.*, 2003; Daintith, 2008).

Chemistry is an aspect of science that deals with the transformation of matter from one form to another (Ivanovic'-Burmazovic, 2011). These transformations which are mainly chemical reactions can occur in the gas phase, in solution of varying solvents, in solid state and at gas-solid or liquid-solid interfaces (House, 2008; Froment *et al.*, 2011). This review is devoted mainly to solution phase chemical kinetics, with emphasis on homogenous reactions taking place in water. The study of homogenous reactions is very important to kineticists since most reactions; from the simple laboratory experiments to the very complex reactions occurring in living systems are homogenous in nature (Svir *et al.*, 2004). Water is the solvent of choice for most solutes and reactions because of its structure, large polarity and the fact that it interact strongly with ions/molecules of solutes (Silberberg, 2007; House, 2008; Burgess, 2011). It is also readily available, easily purifiable and plays a unique role in physiological and chemical processes (Snoeyink & Jenkin, 1980).

A thorough study of any chemical reaction should include the study of structures, equilibria and rates (Arnaut *et al.*, 2007). The study of rates of a reaction is under the domain of kinetics. Kinetics can be sub-divided into physical and chemical kinetics. Physical kinetics is concerned with physical phenomena such as diffusion, viscosity and adsorption, while chemical kinetics deals with the study of rates of chemical reactions (Connors, 1990). Chemical kinetics is a branch of physical chemistry concerned with measuring and studying the rates of chemical reactions (Atkins and Jones, 1999). It is a blend of chemistry, physical theory and mathematics, which explains why for a chemistry student/researcher to do well in kinetics, he/she must have a good background in mathematics and a sound understanding of physical theories (Houston,

2001; Atkins and de Paula, 2010). Physical theories, such as the collision theory and the transition state theory provide a guide to the understanding and interpretation of reaction kinetic results (Atkins and Jones, 1999). The importance of mathematics in kinetics is emphasized by the fact that the law of mass action, which can be said to be the foundation of the modern day rate law, was formulated by a mathematician, Cato Maximilian Guldberg, in collaboration with a chemist, Peter Waage (Denisov *et al.*, 2003; Ferner and Aronson, 2016). Waage and Guldberg, unaware of Wilhelmy's work, published papers, in 1864 and 1867, which looked at the influence of time on chemical reactions and led to the acceptance of the expression (Denisov *et al.*, 2003). Also the first Nobel Prize winner in chemistry, van't Hoff, was trained as a Mathematician (Bo & Bertil, 2013).

The reaction that is under study in chemical kinetics is referred to as a system (Jordan, 2007; De Oliveira *et al.*, 2016), while everything that is not part of the system is called the surrounding (Krenos and Potenza, 2013). Quite often the surrounding is thermostated water bath that is used to maintain the system at constant temperature (Atkins and de Paula, 2010).

#### KINETIC STUDY OF A CHEMICAL REACTION

The more the kinetics and non-kinetic information that can be obtained about the chemistry of a reaction, the better the conclusions that can be drawn about its mechanisms. Therefore effective interpretation of kinetic data depends on accurate knowledge of the behaviour and occurrence of the reactant species in the solvents in which the reaction is carried out, the establishment of the stoichiometry of the reaction, the determination and characterisation of the products and if possible, intermediate(s) that will be formed during the course of the reaction, and the identification of side reaction(s) (Wilkins, 2002; Wright, 2004; Mandal *et al.*, 2009). Physical observation, chemical analysis (Bhattacharyya and Mukhopadhyay, 2005), chromatography (Bhattacharyya, *et al.*, 2004; Gao *et al.*, 2008) and spectroscopy (Deepa and Chandramohan, 2012) can all be used in characterising the reactants, intermediates and products of a reaction. The method to be employed is determined by the nature of the species under consideration.

The stoichiometry of a reaction is the chemical equation that shows the relative amounts

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of reactants that take part and the products formed in a chemical reaction (Ramirez and Garcia-Sosa, 2012). Of the several methods that have been proposed for the determination of the stoichiometry of reactions (Dave and Shah, 2008; Nimse *et al.*, 2012), the Job's method of continuous variation and the Yoe-Jones molar ratio methods are the most widely used (Gadkariem *et al.*, 2009; Ugye *et al.*, 2013). This is due to their simplicity and easy experimental application. A modification of the Yoe-Jones method which is known as the slope ratio method involves the addition of measured deficient quantities of one reactant, which is the limiting reagent, to a known excess of the other whose concentration is held constant (Kundu *et al.*, 1996; Gadkariem *et al.*, 2009) is also employed by some researchers.

After establishing the stoichiometry of the reaction, characterising the reactants, intermediates and products of the reaction and identifying any side reactions, the next thing is the determination of the empirical rate law (Jordan, 2007). Rate law is an equation that links the reaction rate with the concentrations of the reactants in the overall reaction and they are determined empirically (Upadhyay, 2006). Differential equations, which can be simple or complex in form, express rates as functions of concentrations and are therefore used to describe systems undergoing changes (Pyun, 1971). A simple rate equation can be solved analytically using calculus (Hammes, 1978). Complex rate laws can be simplified using the steady state and equilibrium approximations (De Levie, 2002; Arnaut *et al.*, 2007). They can also be solved numerically using Euler's methods, the midpoint methods, Laplace transform method, Gear method, Matrix method or Runge-Kutta method (Viossat and Ben-Aim, 1993; Olcese and Toselli, 1998) or stochastically using Monte Carlo (Dixon and Shafer, 1973) or Markov chains (Arnaud *et al.*, 2007). It is often observed that the rate of reaction is proportional to the product of the individual concentrations of the reactants raised to a simple power, known as order of the reaction with respect to those reactants (Upadhyay, 2006).

Since the amounts of products and reactants are related by stoichiometry, any substance in the reaction can be monitored and used to express the rate of reaction (Espenson, 1995; Upadhyay, 2006). Therefore the basic data of chemical kinetics that is required to obtain the rate law is the concentration of reactant at intervals after

the reaction has been initiated (Atkins and de Paula, 2006; Jordan, 2007). The method used to monitor the change in concentrations depends on the substance being followed and how rapidly its change in concentration (Wright, 2004). The spectral regions have been employed for monitoring the progress of a chemical reaction, with the visible region being the most useful since most reactions of interest involved coloured species (Bhattacharyya and Mukhopadhyay, 2005; Busari *et al.*, 2016). Properties, such as pH or ionic conductivity of the system can also be used to monitor the rate of a reaction (Atkins and de Paula, 2010).

Reaction orders and subsequently rate coefficients can be established with methods that use either concentration-time or rate-concentration data. These include the use of differential or integrated equation, isolation (pseudo order) techniques, initial rate method or half-life method (Atkins and de Paula, 2010). Whatever the experimental method used the reaction must be maintained at a constant temperature throughout (Thabaj *et al.*, 2006), except for situations where the experiment is repeated systematically at different temperatures to obtain information on the activation parameters using the Arrhenius (Jonnalagadda and Gollapalli, 1999) or Eyring equation (Rangappa *et al.*, 1998).

Once the rate law of a reaction is known and the value of the rate constant determined, the rate of a reaction for any values of reactant concentrations can be calculated (Atkins and de Paula, 2010). The rate constant for a particular reaction has a fixed value at a particular temperature (Silberberg, 2007). The effect of temperature on reaction rate varies considerably from one reaction to another, with collision theory and the transition state theory used for the theoretical explanation of the strong dependence of reaction rates on temperature (Atkins and de Paula, 2010). According to the transition state theory, the activation energy for a reaction can be lowered by the use of a catalyst (Silberberg, 2007).

It is generally observed that the rate of reaction can be altered by the nature of the solvent employed (Wilkins, 2002; Arnaut *et al.*, 2007) and by the presence of non-reacting ionic species in the solution (House, 2007). Therefore, since the rate constants for many reactions are affected by the ionic strength of the medium it is necessary either to maintain a constant ionic strength with added electrolyte (Bhattacharyya *et al.*, 2007; Busari *et al.*,

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2016), or to carry out a series of measurements at different ionic strengths and extrapolate to infinite dilution (Wilkins, 2002; Wright, 2004).

#### INTERPRETATION OF KINETICS DATA

The basic mechanisms of all fundamental elementary reactions include substitution, electron-transfer, insertion, oxidative addition and reductive elimination (Jordan, 2007). Electron-transfer (oxidation-reduction) reactions are perhaps the most important class of inorganic reactions (Jordan, 2007; Silberberg, 2007). The study of oxidation-reduction (redox reaction) is important to kineticist because most reactions whether simple or complex, organic or inorganic, chemical or biological, in vitro or in vivo, involve the transfer of at least one electron from a reducing agent to an oxidizing agent (Sabou, 2011). These reactions have been widely studied in an effort to understand the details of their mechanisms (Bhattacharyya *et al.*, 2007; Busari *et al.*, 2016). Based on their stoichiometry redox reactions can be classified as complementary or non-complementary, with no direct mechanistic implications (Jordan, 2007). But classification of electron transfer processes as inner-sphere or outer-sphere reactions are based on their mechanisms (Upadhyay, 2006; Busari *et al.*, 2016).

A reaction mechanism is a sequence of individual reaction steps, known as elementary reactions or elementary steps, which sum to the overall reaction equation. It is the step-by-step pathway by which a reaction occurs (Morrison and Boyd, 1992). Mechanisms are the means by which chemical reactions are rationalized and optimized. They represent the framework that enables the proper understanding of chemical reactions. A mechanism is an explanation of how reactants are transformed into products under certain conditions. General guidelines for proposing plausible reaction mechanism include:

- i. The determination of the stoichiometry of the reaction as well as the complete identification of all the reactants and products of the reaction (Bhattacharyya *et al.*, 2004).
- ii. Accumulated data in the chemical kinetics of a related system can be used in comparing, interpreting and analyzing the new experimental data. Therefore the mechanism of a reaction can be developed by analogy to previous study on related systems (Shezi & Jonnalagadda, 2012).

- iii. A unimolecular or bimolecular reactions are usually proposed as reasonable steps in a mechanism (Connors, 1990; De Oliveira *et al.*, 2016). Termolecular elementary steps are extremely rare while higher molecularities than three are not known (Espenson, 1995).
- iv. For a mechanism to be plausible, the elementary steps must be reasonable, and must all add up to the overall balance equation of the reaction (Espenson, 1995; Arnaut *et al.*, 2007; Silberberg, 2007). Also a mechanism must account for all the kinetic, spectroscopic and theoretical information available on the reaction (Espenson, 1995).
- v. Intermediate is an unstable species that is formed during the course of a reaction. It provides valuable clues to the mechanism of a reaction and is consumed immediately it is formed (Winterton, 1999; Coker, 2001). Therefore, an intermediate will not appear in the overall equation of the reaction, although some intermediates are stable enough to be isolated and characterised (Espenson, 1995; Wilkins, 2002).
- vi. The form of the experimental rate law provides an insight into the nature of the mechanism of the reaction (Espenson, 1995; Jordan, 2007).
- vii. For reactions in which the magnitude of the stoichiometric coefficient of a reactant is greater than the order of the reaction with respect to that reactant, it means there are intermediate(s) and reactions after the rate determining step. Therefore, for any mechanism, only the rate determining step and the steps preceding it contribute to the rate law (Coker, 2001).
- viii. If the rate of the reaction is proportional to the concentration of a product raised to a positive exponent, it means the reaction is autocatalytic (Espenson, 1995).
- ix. Once the outline of the mechanism is established, it is necessary to show that the proposed mechanism gives the experimental rate law (Bakac, 2010).
- x. The polarity and ionic strength of the medium in which a reaction is taking place can both affect the rate of the reaction in a way that can give an idea of the nature of the interactions taking place in the reaction





- or at the activated complex (Arnaut *et al.*, 2007; House, 2007).
- xi. Interpretation of kinetic data can be made more meaningful by non-kinetic investigations such as the detection of intermediates (Chinake and Simoyi, 1998; Winterton, 1999; Coker, 2001) or radicals (Mehrotra and Mehrotra, 2003), or the formation of isosbestic points (Bhattacharyya *et al.*, 2007), or the quantitative analysis of a product (Rangappa *et al.*, 1998), which can support or disprove a proposed mechanism.
- xii. The slight difference in chemical behaviour between isotopes of elements such as hydrogen and deuterium can be used to investigate the detailed mechanisms of chemical reactions involving hydrogen. This is referred to as kinetic isotopic effects and it gives significant information as to the structures of transition states and intermediates and as to the position of bond breakage in the course of a reaction (Espenson, 1995; Rangappa *et al.*, 1998; Winterton, 1999). Other isotopic elements such as B, C, N, O, Mg, Si, S, Cl, Ge, Se, and Br can also be employed for this investigation (Edwards and Fleischauer, 1968).
- xiii. The correlation that exist in the form of linear free energy relationship (LFER) between rate constants and the reactivity of structurally related compounds can be used to diagnose mechanism by determining the extent of bond formation or breakage in the transition state or by assessing the importance of electronic, polar, or steric effects on the rate (Karunakaran *et al.*, 1999).
- xiv. The effect of added anions and cations on the rate of a reaction are used to find out if the reactant species are linked together or not in the activated complex. This gives an indication of whether a reaction is occurring via the outer-sphere or inner-sphere mechanism (Rangappa *et al.*, 1998; Busari *et al.*, 2016).
- xv. Specialised programs based upon density functional theory (DFT), as well as multiconfigurational self-consistent field (MCSCF) and perturbation theories such as ChemCAD, Chemkin, Kinsim, Acuchem, CKS

etc., (Sandu and Miehe, 2010; Manafov, 2015) and general purpose programs such as Mathematica, Maple, and MathCAD can be used to simulate and validate the kinetics and mechanisms of a system (De Levie, 2002). These programs are helpful in evaluating the plausibility of proposed mechanisms. Simulation generates model curves of concentrations of all the species in the system with which experimental data can be compared, and possibly fitted (Rabai *et al.*, 1993; De Levie, 2002).

- xvi. If the proposed rate law from the plausible mechanism does not agree with the experimental rate law even after much modification of the reaction conditions then the proposed reaction mechanism is rejected and another one proposed.

## CONCLUSION

No single review, monograph or textbook can fully cover the broad and important field of chemical kinetics. But we hope our aim of writing a review that can serve as an expository on the principles and methodologies that are employed in kinetics studies and spur researchers' interest in the field by providing a readable introduction to the subject is fulfilled. Elaborate explanations can be found in more advanced and specialized materials on chemical kinetics (Hammes, 1978; Basolo and Johnson, 1986; Levenspiel, 1999; Froment *et al.*, 2011; Upadhyay, 2006).

## REFERENCES

- Arnaut, L., Formosinho, S. and Burrows, H (2007): *Chemical Kinetics from Molecular Structure to Chemical Reactivity*, Elsevier B.V., Amsterdam, pp 1, 4, 31, 49 and 83.
- Atkins, P., & Jones, L. (1999). *Chemical principles: the quest for insight*, New York, W. H. Freeman, pp 595–600, 613–627.
- Atkins, P. W. and de Paula. J. (2010): *Physical Chemistry*, Ninth Edition, W. H. Freeman Publisher, New York, pp 1, 770, 771, 782–810 and 878–880.
- Bakac, A. (2010): *Physical inorganic chemistry: Principles, methods, and models*. John Wiley and Sons, Inc., New Jersey, pp 67–78.
- Basolo F. and Johnson, R. C. (1986): *Coordination Chemistry*, Second Edition, pp 97–119.
- Bellouquid A. and Delitala M. (2006): *Mathematical Modeling of Complex Biological*



- Systems: A Kinetic Theory Approach*, Birkhauser, Boston, USA, pp 1–56.
- Bhattacharyya, J., Das, S. and Mukhopadhyay, S. (2007): Mechanistic Studies on Oxidation of L-Ascorbic Acid by a  $\mu$ -Oxo-bridged Diiron Complex in Aqueous Acidic Media, *Dalton Transaction*, 12: 1214–1220.
- Bhattacharyya, J., Dutta, K. and Mukhopadhyay, S. (2004): Mechanistic studies on oxidation of hydrazine by a  $\mu$ -oxo diiron(III,III) complex in aqueous acidic media–proton coupled electron transfer, *Dalton Transaction*, 18: 2910–2917.
- Bhattacharyya, J. and Mukhopadhyay, S. (2005): Mechanistic Studies on the Oxidation of Nitrite by a  $\mu$ -Oxodiiron(III, III) Complex in Aqueous Acidic Media, *Helvetica Chimica Acta*, 88: 2661–2674.
- Bo G. M. and Bertil A. (2103): *The Nobel Prize in Chemistry: The Development of Modern Chemistry*, Retrieved from [http://www.nobelprize.org/nobel\\_prizes/chemistry/articles/malmstrom/](http://www.nobelprize.org/nobel_prizes/chemistry/articles/malmstrom/).
- Busari A., Iyun J. F., and Idris S. O. (2016): Kinetics and mechanism of the oxidation of 3,7-bis(dimethylamino)phenothionium chloride (methylene blue) by bromate ion in aqueous hydrochloric acid medium. *International Journal of Science for Global Sustainability*, 2(3): 13–20.
- Chinake, C. R. and Simoyi, R. H. (1998): Oxyhalogen-Sulfur Chemistry: Kinetics and Mechanism of the Formation of Bromamines from the Reaction between Acidic Bromate and Aminomethanesulfonic Acid, *Journal of Physical Chemistry B*, 102: 10490–10497.
- Coker, K. A. (2001): *Modeling of Chemical Kinetics and Reactor Design*, Gulf Publishing Company, Houston, Texas, U. S. A., pp xvii, xviii and 1–36.
- Connors, K. A. (1990): *Chemical Kinetics: The Study of Reaction Rates in Solution*, VCH Publisher, Inc., New York, pp 1.
- Daintith, J. (ed.) (2008): *Oxford Dictionary of Chemistry*, Appendix 7: Nobel Prizes in Chemistry, Sixth Edition, Oxford University Press, UK, Pp 576–582.
- Dave, J. A., & Shah, S. S. (2008). 2–Hydroxy–3–iodo–4–n–butoxy–5–bromopropiophenone oxime as an analytical reagent for copper(II). *Asian Journal of Chemistry*, 20(6), 4185–4190.
- Deepa, D. and Chandramohan, G. (2012): Kinetic and Mechanistic Study on the Oxidation of Indole-3-Propionic Acid in Acetic Acid Medium, *Research Journal of Chemical Sciences*, 2(10): 70–74.
- De Levie, R. (2002): Spreadsheet Simulation of Chemical Kinetics, *Critical Reviews in Analytical Chemistry*, 32(1):97–107
- De Oliveira, L. P., Hudebine, D., Guillaume, D. and Verstraete, J. J. (2016): A Review of Kinetic Modeling Methodologies for Complex Processes, *Oil & Gas Science and Technology – Review IFP Energies nouvelles*, 71(45): 1–49.
- Denisov, E. T, Sarkisov, O. M, and Likhtenshtien, G. I. (2003): *Chemical Kinetics: Fundamentals and New Developments*, Elsevier Science BV., Amsterdam, Pp v, 1.
- Dixon D. A. and Shafer, R. H. (1973): Computer Simulation of Kinetics by the Monte Carlo Technique, *Journal of Chemical Education*, 50(9): 648 – 650.
- Edwards, J. O., & Fleischauer, P. D. (1968). The double-isotope-label technique and inorganic reaction mechanisms. *Inorganica Chimica Acta*, 53–63.
- Espenson, J. H. (1995): *Chemical Kinetics and Reaction Mechanisms*, Second Edition, New York, McGraw-Hill, pp 3, 125–132 and 253–269.
- Ferner, R. E. and Aronson, J. K. (2016): *Cato Guldberg and Peter Wage: The History of the Law of Mass Action and its Relevance to Clinical Pharmacology*, 81(1): 52–55.
- Froment, G. F., Bischoff, K. B. and De Wilde, J. (2011): *Chemical Reactor Analysis and Design*, Third Edition, John Wiley & Sons, Inc. pp 11–13 and 21–23.
- Gadkariem, E. A., Ibrahim, K. E. E., Kamil, N. A. A., Haga, M. E. M. and El-Obeid, H. A. (2009): A new spectrophotometric method for the determination of methyl dopa, *Saudi Pharmaceutical Journal*, 17: 289–293.
- Gao, Q., Wang, G., Sun, Y., & Epstein, I.R. (2008). Simultaneous tracking of sulphur species in the oxidation of thiourea by hydrogen peroxide, *Journal of Physical Chemistry A*, 112, 5771–5773.
- Ghosh, M. K. and Rajput, S. K. (2012): Kinetics and Mechanism of Rhodium(III) Catalyzed Oxidation of Dextrose by Cerium(IV) in



- Aqueous Acidic Medium, *Chemical Sciences Journal*, Vol.77: 1–10.
- Groenhof, G. (2013). Solving chemical problems with a mixture of quantum-mechanical and molecular mechanics calculations: Nobel Prize in chemistry 2013, *Angewandte Chemie, International Edition*, 52(48): 2–5.
- Hammes, G. G. (1978): *Principles of Chemical Kinetics*, Academic Press, Inc., New York, pp 1–8.
- House J. E. (2007): *Principles of Chemical Kinetics*, Second Edition, Elsevier Inc., USA, pp 167 – 169 and 182–185.
- House, J. E., (2008). *Inorganic Chemistry*, USA, Elsevier, pp 229–232, 255–283, 309–313, 331 - 494, 523, 673 and 755, 807–808.
- Houston, P. L. (2001): *Chemical Kinetics and Reaction Dynamics*, Dover Publications, Inc.
- Mineola, New York, pp xii–xv.
- Ivanovic´-Burmazovic, I. (2011): New era of reaction mechanisms in inorganic and bioinorganic chemistry, *Bioinorganic Reaction Mechanism*, 7(1-4): 3–4.
- Jonnalagadda, S. B. and Gollapalli, N. R. (1999): Studies on Toluidine Blue Reaction with Sulfite in Aqueous Solution and Role of Cu(II) as Promoter, *International Journal of Chemical Kinetics*, 31(5): 539–549.
- Jordan R. B. (2007): *Reaction Mechanisms of Inorganic and Organometallic Systems*, Third Edition, Oxford University Press, UK, Pp 1–42, 253–285.
- Karunakaran, C., Ramachandran, V. and Palanisamy, P. N. (1999): Linear Free Energy Relationship in Complex Reaction: Tungsten(VI) Catalyzed Perborate Oxidation of S-Phenylmercaptoacetic Acids, *International Journal of Chemical Kinetics*, 31(9): 675–681.
- Krenos, J. and Potenza, J. (2013): *Study Guide to Accompany Chemical Principles – The Quest for Insight*, Sixth Edition, W.H. Freeman and Company, USA, pp 94, 95.
- Kundu, S., Bhattacharya, A. K., & Banerjee, R. (1996). Kinetics of oxidation of nitrogen(III) by an oxo-bridged dinuclear manganese(III, IV) complex in weakly acidic media, *Journal of Chemical Society: Dalton Transactions*, 3951–3957.
- Leroy, F., Ronneau, C. and Demortier, G. (2003): *A Century of Nobel Prizes Recipients– Chemistry, Physics and Medicine*, Marcel Dekker, Inc. Spain, pp 13–111.
- Levenspiel O. (1999): *Chemical Reaction Engineering*, Third Edition, John Wiley & Sons, Inc, USA, p 1.
- Manafov, M. R. (2015). Development of a software application for solving of problems of chemical kinetics and its implementation in a C#. *International Journal of Engineering and Applied Sciences*, 2(10), 33–37.
- Mandal, P. C., Bhattacharyya, J., Das S. Mukhopadhyay, S. and Kirschenbaum, L. J. (2009): Mechanistic studies on the oxidation of pyruvic acid by an oxo-bridged diiron(III,III) complex in aqueous acidic media, *Polyhedron*, 28: 3162–3168.
- Mehrotra, M. and Mehrotra, R. N. (2003): The kinetics of the oxidation of thiourea by 12-tungstocobaltate(III) ion: evidence for anionic, neutral and protonated thiourea species in acetic acid–acetate buffer and perchloric acid solution, *Dalton Transaction*, 3606–3611.
- Morrison, R. T. and Boyd, R. N. (1992): *Organic Chemistry*, Sixth Edition, Prentice Hall, New Jersey, pp 45, 46.
- Nimse, S. B., Song, K-S and Kim, T. (2012): Water-Soluble Calix[4]arene Derivatives: Binding Stoichiometry and Spectroscopic Evaluation of the Host-Guest Recognition Mechanism, In: *Stoichiometry and Research–The Importance of Quantity in Biomedicine*, 28–46.
- Olcese, L. E. and Toselli, B. M. (1998): Fast and Reliable Numerical Methods to Simulate Complex Chemical Kinetic Mechanisms, *International Journal of Chemical Kinetics*, 30: 349–358.
- Pyun, C. W. (1971). Steady-state and equilibrium approximations in chemical kinetics, *Journal of Chemical Education*, 48(3), 194–196.
- Qin Q. (2013): Dynamics of a Discrete Lotka–Volterra Model, *Advances in Difference Equation*, 95: 1–13.
- Rabai, G. Wang, R. T., & Kustin, K. (1993). Kinetics and mechanism of the oxidation of thiourea by chlorine dioxide, *International Journal of Chemical Kinetics*, 25, 53–62.
- Ramirez, F. de M. and Garcia-Sosa, I. (2012): Stoichiometric Ratio in Calixarene Complexes,

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- In: Alessio Innocenti (Ed.) *Stoichiometry and Research— The Importance of Quantity in Biomedicine*, pp 1–26.
- Rangappa, K. S., Chandrāju, S. and Gowda, N. M. M. (1998): Oxidation of L-Glutamine by Manganese(III) in Aqueous Sulfuric Acid, Acetic Acid, and Pyrophosphate Media: A Kinetic and Mechanistic Study, Inc., *International Journal of Chemical Kinetics*, 30: 7–19.
- Rescigno, A. and Bocchialini, B. M. (1991): New Trends in Pharmacokinetics (NATO advanced science institutes series. In: Rescigno A. and Thakur. A. K. (Eds.) *Series A. Life sciences: Pharmacokinetics: Unfolding of a Concept*, Plenum Press, New York, pp 1–26.
- Sabou, D. M. (2011): *A Kinetic Study on the Oxidation of Thiols and Mercaptoacids by Several Transition Metal Ions*, Ph D. Thesis, Faculty of Chemistry and Chemical Engineering, University of Cluj–Napoca, Romania.
- Sandu, A., & Miehe, P. (2010). Forward, tangent linear, and adjoint Runge–Kutta methods for stiff chemical kinetic simulations, *International Journal of Computer Mathematics*, 87(11), 2458–2479.
- Shezi, M. N. and Jonnalagadda, S. B. (2012): Easy to use program “simkine3” for simulating kinetic profiles of multi-step chemical systems and optimization of predictable rate coefficients therein, *Bulletin Chemical Society of Ethiopia*, 26(2): 267–277.
- Silberberg, M. L. (2007): *Principles of General Chemistry*, McGraw-Hill Higher Education. Pp 498–533.
- Snoeyink, V. L., & Jenkin, D. (1980). *Water Chemistry*, USA, Wiley, pp 1–3.
- Svir I. B., Klymenko O. V., Oleinick A. I. and Platz M. S. (2004): *KINFITSIM (Version 2.1) – A Powerful Tool for Kinetic Simulation of Any Reaction Mechanism and Fitting of Any Number of Pairs of Theoretical and Experimental Data Sets*, pp 22–25.
- Thabaj, K. A., Chimatadar, S. A. and Nandibewoor, S. T. (2006): Mechanistic study of oxidation of palladium(II) by cerium(IV) in aqueous acid, *Transition Metal Chemistry*, 31: 186–193.
- Ugye, T. J., Uzairu, A., Idris, S. O. and Kwanashie, H. O. (2013): Spectrophotometric Measurement of the Stoichiometry of Formaldehyde and Plasma Albumin Reaction in Water Solution Using the Method of Continuous Variation (Job’s Method) and the Mole Ratio Method, *Journal of Environmental Science, Toxicology and Food Technology*, 5(6): 42–45.
- Upadhyay, S. K. (2006): *Chemical Kinetics and Reaction Dynamics*, Anamaya Publishers, India, pp 30–39 and 139–141.
- Viossat, V. and Ben-Aim, R. I. (1993): A Test of the Validity of Steady State and Equilibrium Approximations in Chemical Kinetics, *Journal of Chemical Education*, 70(9): 732–738.
- Wilkins, R. G. (2002): *Kinetics and Mechanisms of Reactions of Transition Metal Complexes*, Second Edition, Wiley-VCH Verlag GmbH & Co. p 131–134.
- Winterton, N. (1999): Mechanisms of Reactions in Solution, *Annual Report Progress in Chemistry, Section A*, 95: 535–591.
- Wright, M. R. (2004): *An Introduction to Chemical Kinetics*, John Wiley & Sons, Ltd. Pp 1–39.