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Chemical Kinetics or Reaction Kinetics

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ABSTRACT: Chemical kinetics, also known as reaction kinetics, is the branch of physical chemistry that is concerned with understanding the rates of chemical reactions. It is to be contrasted with chemical thermodynamics, which deals with the direction in which a reaction occurs but in itself tells nothing about its rate. Chemical kinetics includes investigations of how experimental conditions influence the speed of a chemical reaction and yield information about the reaction's mechanism and transition states, as well as the construction of mathematical models that also can describe the characteristics of a chemical reaction. In 1864, Peter Waage and Cato Guldberg pioneered the development of chemical kinetics by formulating the law of mass action, which states that the speed of a chemical reaction is proportional to the quantity of the reacting substances. Van 't Hoff studied chemical dynamics and in 1884 published his famous "Études de dynamique chimique". In 1901 he was awarded by the first Nobel Prize in Chemistry "in recognition of the extraordinary services he has rendered by the discovery of the laws of chemical dynamics and osmotic pressure in solutions

KEYWORDS: chemical, reaction, kinetics, physical, rate, laws, activation, energy, temperature, catalysts

I. INTRODUCTION

"After van 't Hoff, chemical kinetics deals with the experimental determination of reaction rates from which rate laws and rate constants are derived. Relatively simple rate laws exist for zero order reactions¹(for which reaction rates are independent of concentration), first order reactions, and second order reactions, and can be derived for others. Elementary reactions follow the law of mass action, but the rate law of stepwise reactions has to be derived by combining the rate laws of the various elementary steps, and can become rather complex. In consecutive reactions, the rate-determining step often determines the kinetics. In consecutive first order reactions, a steady state approximation can simplify the rate law. The activation energy for a reaction is experimentally determined through the Arrhenius equation and the Eyring equation. The main factors that influence the reaction rate include: the physical state of the reactants, the concentrations of the reactants², the temperature at which the reaction occurs, and whether or not any catalysts are present in the reaction. Gorban and Yablonsky have suggested that the history of chemical dynamics can be divided into three eras. The first is the van 't Hoff wave searching for the general laws of chemical reactions and relating kinetics to thermodynamics. The second may be called the Semenov--Hinshelwood wave with emphasis on reaction mechanisms, especially for chain reactions. The third is associated with Aris and the detailed mathematical description of chemical reaction networks.³

Factors affecting reaction rate

Nature of the reactants

The reaction rate varies depending upon what substances are reacting. Acid/base reactions, the formation of salts, and ion exchange are usually fast reactions. When covalent bond formation takes place between the molecules and when large molecules are formed, the reactions tend to be slower. The nature and strength of bonds in reactant molecules greatly influence the rate of their transformation into products.⁴

Physical state

The physical state (solid, liquid, or gas) of a reactant is also an important factor of the rate of change. When reactants are in the same phase, as in aqueous solution, thermal motion brings them into contact. However, when they are in separate phases, the reaction is limited to the interface between the reactants. Reaction can occur only at their area of contact; in the case of a liquid and a gas, at the surface of the liquid. Vigorous shaking and stirring may be needed to bring the reaction to completion. This means that the more finely divided a solid or liquid reactant the greater its surface area per unit volume and the more contact it with the other reactant, thus the faster the reaction. To make an analogy, for example, when one starts a fire, one uses wood chips and small branches — one does not start with large logs right away. In organic chemistry, on water reactions are the exception to the rule that homogeneous reactions take place faster than heterogeneous reactions (are those reactions in which solute and solvent not mix properly)⁵

Surface area of solid state

In a solid, only those particles that are at the surface can be involved in a reaction. Crushing a solid into smaller parts means that more particles are present at the surface, and the frequency of collisions between these and reactant particles increases, and so reaction occurs more rapidly. For example, Sherbet (powder) is a mixture of very fine powder of malic acid (a weak organic acid) and sodium hydrogen carbonate. On contact with the saliva in the mouth, these chemicals quickly dissolve and react, releasing carbon dioxide and providing for the fizzy sensation. Also, fireworks manufacturers modify the surface area of solid reactants to control the rate at which the fuels in fireworks are oxidised, using this to create diverse effects. For example, finely divided aluminium confined in a shell explodes violently. If larger pieces of aluminium are used, the reaction is slower and sparks are seen as pieces of burning metal are ejected.⁶

Concentration

The reactions are due to collisions of reactant species. The frequency with which the molecules or ions collide depends upon their concentrations. The more crowded the molecules are, the more likely they are to collide and react with one another. Thus, an increase in the concentrations of the reactants will usually result in the corresponding increase in the reaction rate, while a decrease in the concentrations will usually have a reverse effect. For example, combustion will occur more rapidly in pure oxygen than in air (21% oxygen).

The rate equation shows the detailed dependence of the reaction rate on the concentrations of reactants and other species present. The mathematical forms depend on the reaction mechanism. The actual rate equation for a given reaction is determined experimentally and provides information about the reaction mechanism⁷

Temperature

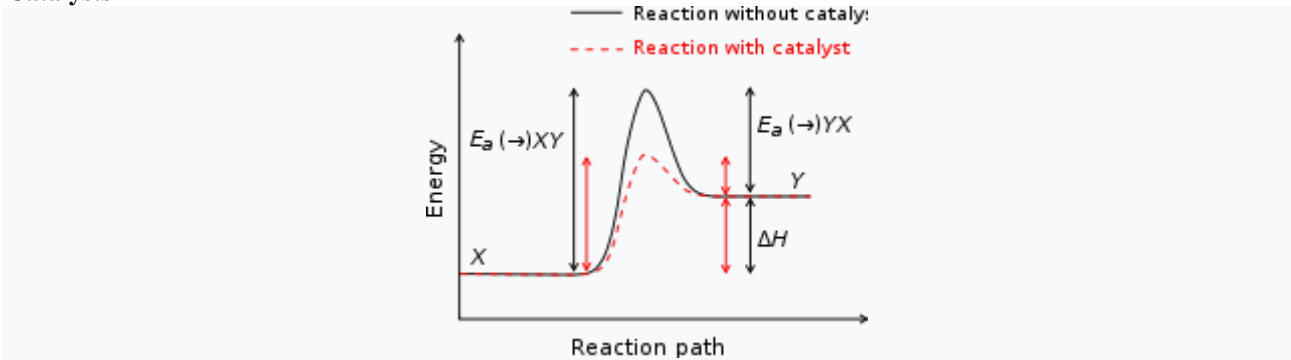
Temperature usually has a major effect on the rate of a chemical reaction. Molecules at a higher temperature have more thermal energy. Although collision frequency is greater at higher temperatures, this alone contributes only a very small proportion to the increase in rate of reaction. Much more important is the fact that the proportion of reactant molecules with sufficient energy to react (energy greater than activation energy: $E > E_a$) is significantly higher and is explained in detail by the Maxwell–Boltzmann distribution of molecular energies.

At a given temperature, the chemical rate of a reaction depends on the value of the A-factor, the magnitude of the activation energy, and the concentrations of the reactants. Usually, rapid reactions require relatively small activation energies.

The 'rule of thumb' that the rate of chemical reactions doubles for every 10 °C temperature rise is a common misconception. This may have been generalized from the special case of biological systems, where the α (temperature coefficient) is often between 1.5 and 2.5.⁷

The kinetics of rapid reactions can be studied with the temperature jump method. This involves using a sharp rise in temperature and observing the relaxation time of the return to equilibrium. A particularly useful form of temperature jump apparatus is a shock tube, which can rapidly increase a gas's temperature by more than 1000 degrees.

Catalysts



Generic potential energy diagram showing the effect of a catalyst in a hypothetical endothermic chemical reaction. The presence of the catalyst opens a new reaction pathway (shown in red) with a lower activation energy. The final result and the overall thermodynamics are the same.



A catalyst is a substance that alters the rate of a chemical reaction but it remains chemically unchanged afterwards. The catalyst increases the rate of the reaction by providing a new reaction mechanism to occur with in a lower activation energy. In autocatalysis a reaction product is itself a catalyst for that reaction leading to positive feedback. Proteins that act as catalysts in biochemical reactions are called enzymes. Michaelis–Menten kinetics describe the rate of enzyme mediated reactions. A catalyst does not affect the position of the equilibrium, as the catalyst speeds up the backward and forward reactions equally.

In certain organic molecules, specific substituents can have an influence on reaction rate in neighbouring group participation.⁸

Pressure

Increasing the pressure in a gaseous reaction will increase the number of collisions between reactants, increasing the rate of reaction. This is because the activity of a gas is directly proportional to the partial pressure of the gas. This is similar to the effect of increasing the concentration of a solution.

In addition to this straightforward mass-action effect, the rate coefficients themselves can change due to pressure. The rate coefficients and products of many high-temperature gas-phase reactions change if an inert gas is added to the mixture; variations on this effect are called fall-off and chemical activation. These phenomena are due to exothermic or endothermic reactions occurring faster than heat transfer, causing the reacting molecules to have non-thermal energy distributions (non-Boltzmann distribution). Increasing the pressure increases the heat transfer rate between the reacting molecules and the rest of the system, reducing this effect. Condensed-phase rate coefficients can also be affected by pressure, although rather high pressures are required for a measurable effect because ions and molecules are not very compressible. This effect is often studied using diamond anvils. A reaction's kinetics can also be studied with a pressure jump approach. This involves making fast changes in pressure and observing the relaxation time of the return to equilibrium.⁹

Absorption of light

The activation energy for a chemical reaction can be provided when one reactant molecule absorbs light of suitable wavelength and is promoted to an excited state. The study of reactions initiated by light is photochemistry, one prominent example being photosynthesis.

III. DISCUSSION

The experimental determination of reaction rates involves measuring how the concentrations of reactants or products change over time. For example, the concentration of a reactant can be measured by spectrophotometry at a wavelength where no other reactant or product in the system absorbs light. For reactions which take at least several minutes, it is possible to start the observations after the reactants have been mixed at the temperature of interest.

Fast reactions

For faster reactions, the time required to mix the reactants and bring them to a specified temperature may be comparable or longer than the half-life of the reaction.^[8] Special methods to start fast reactions without slow mixing step include

- Stopped flow methods, which can reduce the mixing time to the order of a millisecond. The stopped flow methods have limitation, for example, we need to consider the time it takes to mix gases or solutions and are not suitable if the half-life is less than about a hundredth of a second.
- Chemical relaxation methods such as temperature jump and pressure jump, in which a pre-mixed system initially at equilibrium is perturbed by rapid heating or depressurization so that it is no longer at equilibrium, and the relaxation back to equilibrium is observed. For example, this method has been used to study the neutralization $\text{H}_3\text{O}^+ + \text{OH}^-$ with a half-life of 1 μs or less under ordinary conditions.¹⁰
- Flash photolysis, in which a laser pulse produces highly excited species such as free radicals, whose reactions are then studied

While chemical kinetics is concerned with the rate of a chemical reaction, thermodynamics determines the extent to which reactions occur. In a reversible reaction, chemical equilibrium is reached when the rates of the forward and reverse reactions are equal (the principle of dynamic equilibrium) and the concentrations of the reactants and products no longer change. This is demonstrated by, for example, the Haber–Bosch process for combining nitrogen and hydrogen to produce ammonia. Chemical clock reactions such as the Belousov–Zhabotinsky reaction demonstrate that component concentrations can oscillate for a long time before finally attaining the equilibrium.¹¹



In general terms, the free energy change (ΔG) of a reaction determines whether a chemical change will take place, but kinetics describes how fast the reaction is. A reaction can be very exothermic and have a very positive entropy change but will not happen in practice if the reaction is too slow. If a reactant can produce two products, the thermodynamically most stable one will form in general, except in special circumstances when the reaction is said to be under kinetic reaction control. The Curtin–Hammett principle applies when determining the product ratio for two reactants interconverting rapidly, each going to a distinct product. It is possible to make predictions about reaction rate constants for a reaction from free-energy relationships.

The kinetic isotope effect is the difference in the rate of a chemical reaction when an atom in one of the reactants is replaced by one of its isotopes.

Chemical kinetics provides information on residence time and heat transfer in a chemical reactor in chemical engineering and the molar mass distribution in polymer chemistry. It also provides information in corrosion engineering.

The mathematical models that describe chemical reaction kinetics provide chemists and chemical engineers with tools to better understand and describe chemical processes such as food decomposition, microorganism growth, stratospheric ozone decomposition, and the chemistry of biological systems. These models can also be used in the design or modification of chemical reactors to optimize product yield, more efficiently separate products, and eliminate environmentally harmful by-products. When performing catalytic cracking of heavy hydrocarbons into gasoline and light gas, for example, kinetic models can be used to find the temperature and pressure at which the highest yield of heavy hydrocarbons into gasoline will occur.¹²

Chemical Kinetics is frequently validated and explored through modeling in specialized packages as a function of ordinary differential equation-solving (ODE-solving) and curve-fitting.

In some cases, equations are unsolvable analytically, but can be solved using numerical methods if data values are given. There are two different ways to do this, by either using software programmes or mathematical methods such as the Euler method. Examples of software for chemical kinetics are i) Tenua, a Java app which simulates chemical reactions numerically and allows comparison of the simulation to real data, ii) Python coding for calculations and estimates and iii) the Kintecus software compiler to model, regress, fit and optimize reactions.

IV. RESULTS

Electrochemical kinetics is the field of electrochemistry that studies the rate of electrochemical processes. This includes the study of how process conditions, such as concentration and electric potential, influence the rate of oxidation and reduction (redox) reactions that occur at the surface of an electrode, as well as an investigation into electrochemical reaction mechanisms. Two accompanying processes are involved in the electrochemical reaction and influence the overall reaction rate:

- electron transfer at the interface between the electrode and the electrolyte
- transport of the redox species from the interior of the solution to the surface of the electrode; the transport can occur by diffusion, convection and migration.

Contributors to this field include Alexander Frumkin, John Alfred Valentine Butler, Max Volmer, and Julius Tafel. A single chemical reaction is said to be autocatalytic if one of the reaction products is also a catalyst for the same or a coupled reaction. Such a reaction is called an autocatalytic reaction. A set of chemical reactions can be said to be "collectively autocatalytic" if a number of those reactions produce, as reaction products, catalysts for enough of the other reactions that the entire set of chemical reactions is self-sustaining given an input of energy and food molecules (see autocatalytic set). These chemical reactions proceed slowly at the start (the induction period) because there is little catalyst present, the rate of reaction increases progressively as the reaction proceeds as the amount of catalyst increases and then it again slows down as the reactant concentration decreases. If the concentration of a reactant or product in an experiment follows a sigmoid curve, the reaction may be autocatalytic. These kinetic equations apply for example to the acid-catalyzed hydrolysis of some esters to carboxylic acids and alcohols. There must be at least some acid present initially to start the catalyzed mechanism; if not the reaction must start by an alternate uncatalyzed path which is usually slower. The above equations for the catalyzed mechanism would imply that the concentration of acid product remains zero forever. An example of autocatalytic reaction is the formose reaction, in which formaldehyde condensates into glycolaldehyde and, after some intermediates, two molecules of glycolaldehyde are formed thus creating an autocatalytic cycle. The second law of thermodynamics states that the disorder (entropy) of a physical or chemical system and its surroundings (a closed system) must increase with time. Systems left to themselves become

increasingly random, and orderly energy of a system like uniform motion degrades eventually to the random motion of particles in a heat bath.¹³

There are, however, many instances in which physical systems spontaneously become emergent or orderly. For example, despite the destruction they cause, hurricanes have a very orderly vortex motion when compared to the random motion of the air molecules in a closed room. Even more spectacular is the order created by chemical systems; the most dramatic being the order associated with life. This is consistent with the Second Law, which requires that the total disorder of a system and its surroundings must increase with time. Order can be created in a system by an even greater decrease in order of the system's surroundings. In the hurricane example, hurricanes are formed from unequal heating within the atmosphere. The Earth's atmosphere is then far from thermal equilibrium. The order of the Earth's atmosphere increases, but at the expense of the order of the sun. The sun is becoming more disorderly as it ages and throws off light and material to the rest of the universe. The total disorder of the sun and the earth increases despite the fact that orderly hurricanes are generated on earth.

A similar example exists for living chemical systems. The sun provides energy to green plants. The green plants are food for other living chemical systems. The energy absorbed by plants and converted into chemical energy generates a system on earth that is orderly and far from chemical equilibrium. Here, the difference from chemical equilibrium is determined by an excess of reactants over the equilibrium amount. Once again, order on earth is generated at the expense of entropy increase of the sun. The total entropy of the earth and the rest of the universe increases, consistent with the Second Law. Some autocatalytic reactions also generate order in a system at the expense of its surroundings. For example, (clock reactions) have intermediates whose concentrations oscillate in time, corresponding to temporal order.¹⁴ Other reactions generate spatial separation of chemical species corresponding to spatial order. More complex reactions are involved in metabolic pathways and metabolic networks in biological systems. The transition to order as the distance from equilibrium increases is not usually continuous. Order typically appears abruptly. The threshold between the disorder of chemical equilibrium and order is known as a phase transition. The conditions for a phase transition can be determined with the mathematical machinery of non-equilibrium thermodynamics. The initial amounts of reactants determine the distance from a chemical equilibrium of the system. The greater the initial concentrations the further the system is from equilibrium. As the initial concentration increases, an abrupt change in order occurs. This abrupt change is known as phase transition. At the phase transition, fluctuations in macroscopic quantities, such as chemical concentrations, increase as the system oscillates between the more ordered state (lower entropy, such as ice) and the more disordered state (higher entropy, such as liquid water). Also, at the phase transition, macroscopic equations, such as the rate equations, fail. Rate equations can be derived from microscopic considerations.¹⁵ The derivations typically rely on a mean field theory approximation to microscopic dynamical equations. Mean field theory breaks down in the presence of large fluctuations (see Mean field theory article for a discussion). Therefore, since large fluctuations occur in the neighborhood of a phase transition, macroscopic equations, such as rate equations, fail. As the initial concentration increases further, the system settles into an ordered state in which fluctuations are again small. In chemistry, heterogeneous catalysis is catalysis where the phase of catalysts differs from that of the reactants or products. The process contrasts with homogeneous catalysis where the reactants, products and catalyst exist in the same phase. Phase distinguishes between not only solid, liquid, and gas components, but also immiscible mixtures (e.g. oil and water), or anywhere an interface is present.¹⁶

Heterogeneous catalysis typically involves solid phase catalysts and gas phase reactants. In this case, there is a cycle of molecular adsorption, reaction, and desorption occurring at the catalyst surface. Thermodynamics, mass transfer, and heat transfer influence the rate (kinetics) of reaction. Heterogeneous catalysis is very important because it enables faster, large-scale production and the selective product formation. Approximately 35% of the world's GDP is influenced by catalysis. The production of 90% of chemicals (by volume) is assisted by solid catalysts. The chemical and energy industries rely heavily on heterogeneous catalysis. For example, the Haber–Bosch process uses metal-based catalysts in the synthesis of ammonia, an important component in fertilizer; 144 million tons of ammonia were produced in 2016.¹⁷

V. CONCLUSIONS

Most metal surface reactions occur by chain propagation in which catalytic intermediates are cyclically produced and consumed. Two main mechanisms for surface reactions can be described for $A + B \rightarrow C$.

- Langmuir–Hinshelwood mechanism: The reactant molecules, A and B, both adsorb to the catalytic surface. While adsorbed to the surface, they combine to form product C, which then desorbs.
- Eley–Rideal mechanism: One reactant molecule, A, adsorbs to the catalytic surface. Without adsorbing, B reacts with adsorbed A to form C, that then desorbs from the surface.



Most heterogeneously catalyzed reactions are described by the Langmuir–Hinshelwood model.

In heterogeneous catalysis, reactants diffuse from the bulk fluid phase to adsorb to the catalyst surface. The adsorption site is not always an active catalyst site, so reactant molecules must migrate across the surface to an active site. At the active site, reactant molecules will react to form product molecule(s) by following a more energetically facile path through catalytic intermediates (see figure to the right). The product molecules then desorb from the surface and diffuse away. The catalyst itself remains intact and free to mediate further reactions. Transport phenomena such as heat and mass transfer, also play a role in the observed reaction rate¹⁷.

REFERENCES

1. C.M. Guldberg and P. Waage, "Studies Concerning Affinity" Forhandling i Videnskabs-Selskabet i Christiania (1864), 35
2. ^ P. Waage, "Experiments for Determining the Affinity Law" ,Forhandling i Videnskabs-Selskabet i Christiania, (1864) 92.
3. ^ C.M. Guldberg, "Concerning the Laws of Chemical Affinity", Forhandling i Videnskabs-Selskabet i Christiania (1864) 111
4. ^ Hoff, J. H. van't (Jacobus Henricus van't); Cohen, Ernst; Ewan, Thomas (1896-01-01). Studies in chemical dynamics. Amsterdam : F. Muller; London : Williams & Norgate.
5. ^ The Nobel Prize in Chemistry 1901, Nobel Prizes and Laureates, official website.
6. ^ A.N. Gorban, G.S. Yablonsky Three Waves of Chemical Dynamics, Mathematical Modelling of Natural Phenomena 10(5) (2015), p. 1–5.
7. ^ Laidler, K. J. Chemical Kinetics (3rd ed., Harper and Row 1987) p.42 ISBN 0-06-043862-2
8. ^ Laidler, K. J. Chemical Kinetics (3rd ed., Harper and Row 1987) p.33-39 ISBN 0-06-043862-2
9. ^ Espenson, J.H. Chemical Kinetics and Reaction Mechanisms (2nd ed., McGraw-Hill 2002), p.254-256 ISBN 0-07-288362-6
10. ^ Atkins P. and de Paula J., Physical Chemistry (8th ed., W.H. Freeman 2006) p.793 ISBN 0-7167-8759-8
11. ^ Espenson, J.H. Chemical Kinetics and Reaction Mechanisms (2nd ed., McGraw-Hill 2002), p.256-8 ISBN 0-07-288362-6
12. ^ Steinfeld J.I., Francisco J.S. and Hase W.L. Chemical Kinetics and Dynamics (2nd ed., Prentice-Hall 1999) p.140-3 ISBN 0-13-737123-3
13. ^ Atkins P. and de Paula J., Physical Chemistry (8th ed., W.H. Freeman 2006) pp.805-7 ISBN 0-7167-8759-8
14. ^ Laidler, K.J. Chemical Kinetics (3rd ed., Harper and Row 1987) p.359-360 ISBN 0-06-043862-2
15. ^ Espenson, J.H. Chemical Kinetics and Reaction Mechanisms (2nd ed., McGraw-Hill 2002), p.264-6 ISBN 0-07-288362-6
16. ^ Steinfeld J.I., Francisco J.S. and Hase W.L. Chemical Kinetics and Dynamics (2nd ed., Prentice-Hall 1999) p.94-97 ISBN 0-13-737123-3
17. ^ "Chemical Kinetics: Simple Binding: $F + G \rightleftharpoons B$ " (PDF). Civilized Software, Inc. Retrieved 2015-09-01.



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