

KINETIC ANALYSES OF METALLURGICAL SYSTEMS

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INTRODUCTION

Two questions about a chemical reaction are of paramount importance to engineers engaged in research, design or operation involving chemical reactions:

1. Under what conditions a chemical reaction will be feasible and how far can the reaction proceed.
2. How fast a reaction would take place under some desired operating conditions.

Proper answers to the above are rather complex since many properties and condition of a chemical system affect both the feasibility and speed of reaction. Though the questions are related, yet no unified quantitative approach exists and to a large extent they are handled separately by the science of thermodynamics and reaction kinetic. In this presentation, we will be dealing with the second aspect of a chemical reaction.

In general, the subject which deals with the measurement of reaction rate is turned as "Reaction Kinetics".

In addition to the feasibility of a reaction, thermodynamics can predict the compositions of co-existing phases under certain pressure and temperature. However, merely feasibility assessment through thermodynamics does not ensure that the reaction will even proceed at a measurable rate. For example, thoroughly dry oxygen and hydrogen mixture would stay indefinitely without undergoing any chemical reaction, if not intervened. Carbon does not reach with appreciably, even though both the reactions are thermodynamically feasible. Therefore, finding the conditions under which thermodynamically feasible reaction will proceed at a sufficient speed is one of the main tasks of the science and art of reaction kinetics.

Thermodynamics is interested only in the initial and final states of a transformation process without considering the reaction path, mechanism of conversion and the time required. What path a reaction takes, would again depend over number of details as well as properties of the system that are structure-sensitive. Therefore, kinetic predictions are mostly either qualitative or quantitative with some uncertainty.

CLASSIFICATION OF CHEMICAL REACTION

There are several ways of classifying chemical reactions. For example- The basis of mechanism, with respect to the number of molecules actually participation in the reaction, with respect to the operating conditions. However, the most useful scheme is possibly according to the number and types of phases involved in a chemical reaction.

A reaction is homogeneous if it takes place in one phase along. Most of the gas phase reactions are example of homogeneous if it required the presence of two phases to proceed at a rate that it does. Burning of coal, roasting of ores, dissolution of solids in acid fall in the category of heterogeneous reaction.

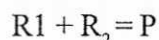
It is to be rated that these classifications are not mutually exclusive. Thus a reaction may be irreversible- second order, Taking place under adiabatic and approximately constant pressure conditions in a continuous type reactor.

They may be irreversible, reversible, simultaneous or consecutive type with respect to the number of molecules actually participating in the reaction, it may unimolecular or bimolecular. Considering the operating conditions, a chemical reaction may be isothermal at constant volume, isothermal at constant pressure, adiabatic or non-adiabatic and non-isothermal.

The Rate of a Chemical Reaction

When a chemical reaction takes place, the atoms of the reactants undergo rearrangement to produce the product molecules and speed at which this occurs depends on the natures of the participants and circumstances. Quantitatively, the rate of a chemical reaction is expressed as the number of units of mass of some participant that may be consumed or produced per unit time per unit volume or surface area.

Thus, for a generalized reaction



Where R_1 & R_2 are reactants and P is the product, the rate in terms of a reactant may be expressed as

$$P = -\frac{1}{V} \frac{dn_{Ri}}{dt} \frac{\text{moles } i \text{ consumed}}{(\text{Volume})(\text{time})} \quad (1)$$

$$= -\frac{dc_{Ri}}{dt} \quad \text{At constant volume} \quad (2)$$

$$= -\frac{1}{w} \frac{dn_{Ri}}{dt} \frac{\text{moles } i \text{ consumed}}{(\text{mass})(\text{time})} \quad (3)$$

$$= -\frac{1}{s} \frac{dn_{Ri}}{dt} \frac{\text{moles } i \text{ consumed}}{(\text{surface})(\text{time})} \quad (4)$$

Similar expressions can also be written in terms of the product.

Molecularity and order of reaction

The molecularity of an elementary reaction is the number of molecules involved in the reaction and has been found to have the values of one, two and occasionally three. The manner in which the rate of a reaction changes with concentrations of the reacting substances say $A, B, \dots, D$ can be expressed as

$$\text{Rate} = k C_A^a C_B^b \quad (5)$$

Then the overall order of the overall reaction(n) is

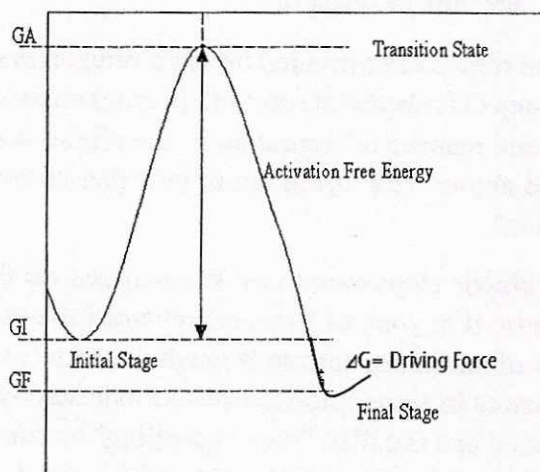
$$n = a+b+\dots\dots (6)$$

Such a reaction would be having ath order with respect to reactant A, bth order with respect to reactant B etc. It should be noted that power to which the concentrations are raised do not necessarily relate to the stoichiometric co-efficient. Order of reaction is found experimentally and may have a fractional value. However, molecularity of a reaction must be integer since it refers to the mechanism of reaction and can only apply to an elementary reaction.

Activation energy

In accordance with the law of Mass Action, the rate of a chemical reaction is proportional to the active masses of the reacting substance. This implies the fact that all the molecules in a system do not undergo transformation at one and the same time. Reactants and products co-exist throughout the transformation and at any instant only a fraction of the available mass can be in the process of transformation for the simple reason that only a fraction of the mass have free energy in excess of the mean and therefore, energetically suitable for transformation. It always possible to find more than one set of configuration changes capable

of providing a given transformation, called "reaction path" and each such reaction path and each such reaction path is associated with a free energy curve. The free energy of an atom or group of atoms during transformation first increases to a maximum and then decreases to the final value.



Thus, the deriving force

$$\Delta G = E_A - TS_A (7)$$

Where EA is the "activation energy", the difference in internal energies of the system in the transition state to that in the initial state and SA is activation entropy change.

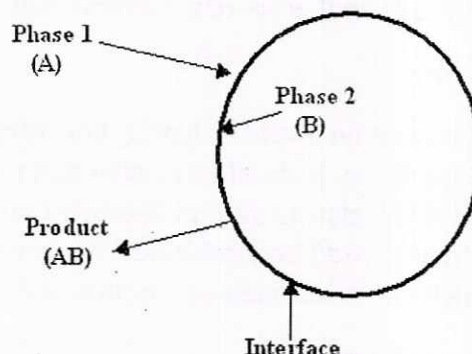
Kinetic steps

Let us consider a generalized chemical reaction



It is assumed that there are two phases 1 and 2 and the reactant A is dissolved in phase 1, reactant 2 in phase 2 and the product AB in phase 1. Noting that A does not dissolve in phase 2 and B does not dissolve in phase 1. Their only plausible meeting place is the interface, dividing the two phases. The kinetic steps involved in progress of the reaction are

- Transfer of A from bulk of phase 1 to the interface.
- Transfer of B from bulk of phase 2 to the interface.
- Chemical reaction at the interface.
- Transfer of AB away from the interface into the bulk of phase 1.



These steps can be divided into two categories step a), b) and d) are "mass transfer processes" and step c) is chemical reaction. In cases either of the phases was non-existent to start with, the rate and manner of formation of the phases are part of the overall kinetics besides the steps noted above. The formation of new phases takes place by processes called "nucleation and growth".

The kinetic steps mentioned summarized for the generalized chemical reaction are in series, because if anyone of them is prevented the overall reaction would not occur. Analogous to flow of minimum current through the path containing largest resistor in an electronic circuit (resistors in series), the slowest kinetic step would determine the overall rate of a chemical reaction and is called "rate controlling" or rate "limiting step".

For simplicity, let us assume that only one of the kinetic steps is rate controlling and other steps are infinitely fast, so that they are equilibrium. Under this desired situation, the rate of the slowest step would be maximum and the rate of the overall reaction calculated is termed as "virtual maximum rate".

A comparison of calculated virtual maximum rate of the various kinetic steps is one good way to tell which the slowest one is. It is apparent from the above discussion that chemical reaction rate is influenced by mass transfer, chemical kinetic and also heat transfer so as to maintain steady supply of at the reaction site. A thorough knowledge of all these three areas along with nucleation and growth is essential for proper understanding of metallurgical kinetics in the following section, a brief account of various important issues related to mass transfer, chemical reaction and the heat transfer would be discussed.

Mass transfer

In a metallurgical system, most of reactions are heterogeneous in nature, implying that more than one phase participate in the chemical reaction. Hence mass transfer involving multiple phases is of primary interest to a metallurgist. However, system involving a single phase is also not uncommon and needs attention. Accordingly mass transfer can broadly be classified under four categories.

- Mass transfer in solid.
- Mass transfer in fluid.
- Mass transfer between a fluid and a solid.
- Mass transfer between two fluids.

In the preceding discussion, the underline features and the governing equation of each of the above category of mass transfer will be presented.

Diffusion

Mass transfer in solids takes place by a mechanism, known as "diffusion". It involves movement of items and molecules along a down hill (negative) concentration gradient. In fluids (liquid and gases), diffusion takes place just as in solids. However, fluids being deformable, there are other modes of mass transfer in fluids as well. There are two aspects of diffusion, namely, phenomenological and atomistic. The former starts with the phenomenological equation of diffusion and it are concerned with the macroscopic aspect of it. The later is concerned with the atomistic mechanism of diffusion. The subsequent discussion will deal phenomenological aspects only.

Laws of diffusion

It was proposed by Adolf Fick in 1855 and is stated as follows

$$J_{i,x} = -D_i \frac{\partial C_i}{\partial x} \quad (9)$$

Where, $J_{i,x}$ ($\text{Kmol m}^{-2} \text{s}^{-1}$) is the diffusion flux of the i th species in the x direction, C_i (Kmol m^{-3}) is the concentration of species i per unit volume. The constant of proportionality ' D_i ' ($\text{m}^2 \text{s}^{-1}$) is known as "diffusivity coefficient" of the i th species. Fick's first law is applicable to an isothermal, isobaric, binary system of well define state, consisting of single-phase region. The first law of diffusion is applicable in steady state that is when the system is independent of time.

In unsteady state (transient) transport, the concentration of species is a function of time as a result of a sudden change in the environment. Unsteady state analysis may be used to describe conditions in the body of interest between the time of the sudden environmental changes and the time at which steady state is again reached.

The law of conservation for any species in a system can be written as
Input + Generation = Output + accumulation.

Thus, the generalized form of the unsteady state of the state of diffusion equation for an isotropic system may be presented as

$$D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right) + R = \frac{\partial c}{\partial t} \quad (10)$$

In vector form

$$D\nabla^2 c + R = \frac{\partial c}{\partial t} \quad (11)$$

Where R is the generation term.

Application : Diffusion through a Slab

A slab may be considered finite along the thickness (x-direction) and infinite along the length and width (y-axis and z-direction). There fore

$$\frac{\partial c}{\partial y} = 0 \text{ and } \frac{\partial c}{\partial z} = 0 \quad (12)$$

At steady state and in absence of a chemical reaction

$$\frac{\partial c}{\partial t} = 0, R = 0 \quad (13)$$

Hence Eq (1) transforms to

$$\frac{\partial^2 c}{\partial x^2} = 0 \quad (14)$$

Since, C is a function of x only, the partial derivative can be replaced by exact derivatives. On integration

$$C = mx + n \quad (15)$$

The two constants m and n are to be evaluated from two boundary conditions like

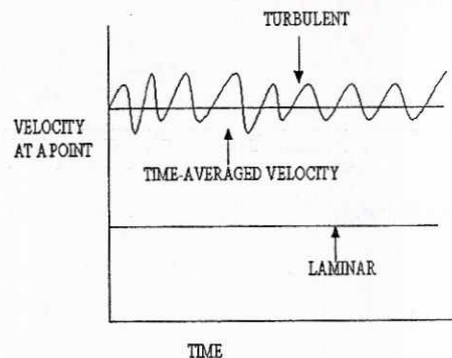
$$\begin{array}{ll} \text{At } X=0 & C=C_1 \\ \text{At } X=L & C=C_2 \end{array}$$

$$\text{Hence } J_x = \frac{D}{L}(C_1 - C_2) \quad (16)$$

where L is the thickness of the slab. The concentration terms can be calculated considering chemical equilibrium at the two surfaces.

Mass transfer in fluid

In fluid, both diffusion and convection contributes to mass transfer. Convection means flow of fluid. Convection is either free (natural) or forced. In free convection flow is not caused by any external agent, but is a result of non-uniformity of temperature or concentration. On the contrary, forced convection is said to be present when an external agent such as a fan, a stirrer or a pump in devices a fluid motion. Free or forced convection can be categorized in one of the three types, namely



- (a) laminar
- (b) turbulent, and
- (c) transitional.

The laminar flow is observed at low fluid velocity and is characterized by stable streamline. If the velocity of flow is increased; a stage would come when the streamlines would start oscillating. This is transitional flow. At velocity, further higher than the transitional flow, streamline would cease to exist and the fluid body would intimately mix together to cause movement. This is called turbulent flow.

Mass transfer under Laminar flow

As mentioned laminar flow can take place both for free and forced convection. Mass transfer through convection thought is much faster than diffusion; The diffusion may have contribution in the overall flux of a species, accordingly for movement of a species I in X direction.

$$\text{Total Flux} = J_{ix} = C_i V_{ix} = J_{ix} (\text{diffusive flux}) + J_{ix} (\text{Convective flux})$$

Where V_{ix} = Velocity of the i^{th} species in X-direction across a stationary plane.

$$\text{Now, } J_{ix} (\text{Convection}) = C_i \bar{V}_x$$

$$\text{Where } \bar{V}_x = \frac{\sum_i C_i v_{ix}}{\sum_i C_i} = \frac{\sum_i j_{ix}}{\sum_i C_i} \quad (17)$$

$$\text{Where } \bar{V}_x \text{ is the convective velocity in x direction } \bar{V}_x = \frac{J_{Ar}}{C_{Ar}} + \frac{J_{Fe}}{C_{Fe}}$$

$$\text{Thus } j_{ix} (\text{total}) = j_{ix} (\text{diffusion}) + C_i \frac{\sum_i j_{ix}}{\sum_i C_i} \quad (18)$$

Application:

Consider absorption of Fe vapor by platinum foil. Fe vapor is moving from liquid surface to the foil through Ar filled space. Since Ar is not getting absorbed either by liquid iron or by platinum foil,

$$J_{Ar} = 0$$

The convective velocity

$$= \frac{J_{Fe}}{C_{Ar} + C_{Fe}} \quad (19)$$

So, total flux of the moving species (iron)

$$\begin{aligned} J_{Fe} &= J_{ix} (\text{diffusion}) + J_{ix} (\text{convection}) \\ &= -D \frac{\partial C_{Fe}}{\partial x} + C_{Fe} \frac{J_{Fe}}{C_{Ar} + C_{Fe}} \end{aligned} \quad (20)$$

If P_T is the total pressure in the gas phase, then

$$J_{Fe} = -\frac{D}{RT} \frac{\partial P_{Fe}}{\partial x} + J_{Fe} \frac{P_{Fe}}{P_T} \quad (21)$$

Considering steady state and suitable rearrangement of the above equation

$$J_{Fe} = -\frac{D}{RT} \frac{P_T}{L} \ln \frac{P_T - P_{Fe}}{P_T} \quad (22)$$

Knowing every thing else, the value of D can be calculated

Mass transfer under turbulent flow

When a fluid is under turbulent motions, the velocity of a fluid element (i.e, an infinitesimally small volume of fluid) at a point exhibits random fluctuation and may be different from the surroundings. This makes the element to change its position with respect to the surrounding and go to a new position. A new fluid element comes and fills up the void left by the first element. The exchanging fluid element are called "eddy elements" or 'eddies' and exchange of eddies would lead to a net mass transfer from higher to lower concentration. This is what is called "eddy diffusion".

Similar to molecular diffusion, the rate of mass transfer by eddy diffusion may be expressed as

$$\bar{J}_{ix} = -E_D \frac{\partial \bar{c}_i}{\partial x} \quad (23)$$

Where ED is eddy diffusivity.

Therefore, the rate of mass transfer under turbulent flow can be written as

$$\bar{J}_{ix} = -D \frac{\partial \bar{c}_i}{\partial x} + \bar{c}_i \cdot \bar{v}_x - E_D \cdot \frac{\partial \bar{c}_i}{\partial x} \quad (24)$$

Where $\bar{J}_{ix}$ and $\bar{c}_i$ denote "time-smoothed value of J_{ix} and C_i .

In general, $ED \gg D$, because a fluid element contains billions of molecules and its jump distance is much larger than atomic distance. In some system ED/D is found to be as high as 105. Such high value of ED leads to rapid mass transfer and mixing in turbulent flow and, therefore, of interest for engineering application.

Mass transfer between a fluid and a solid

Many important metallurgical systems such as roasting of sulfides, reduction of oxides, dissolution of graphite in liquid view both involve multiple phases where one of them is a fluid (gas or liquid). The mass transfer in the bulk fluid phase being fast, the same at the phase boundary is often rate limiting in a metallurgical/chemical reaction.

It is to be noted that the fluid at the solid fluid interface would have different characteristics compared to the bulk fluid. It is expected that the layer of fluid just at the solid-fluid interface

cannot slip past the solid, as it would require an unduly large shear stress, which the fluid is unable to sustain. Therefore, the relative velocity of fluid with respect to solid is zero at the interface. There will be a gradual velocity gradient in the fluid layer adjacent to the solid surface, towards the bulk. This fluid layer is called the "velocity boundary layer" and thickness is determined by the distance, where the velocity attains 99 percent of that of the bulk. The flow in velocity boundary layer is laminar even when the bulk flow is turbulent.

Similar to velocity boundary layer, a concentration gradient of the transferring species develops in the liquid layer adjacent to the solid-liquid interface. The layer where this concentration gradient exists is called the 'Concentration boundary layer' and the thickness of the layer is determined by the distance where the concentration of the transferring species is 99 percent of the bulk.

Let us examine the mass transfer situation at the interface ($X=0$), It may be noted that

$[V_x]_{x=0} = 0$ and $[E_D]_{x=0} = 0$ as the flow is laminar.

$$\text{Hence } [J_x]_{x=0} = -[D \cdot \frac{\partial c}{\partial x}]_{x=0} \quad (25)$$

Assigning D to be a constant

$$[J_x]_{x=0} = D \cdot \frac{c_s - c_0}{\delta} \quad (26)$$

Where C_s and C_0 are concentration at the interface and bulk fluid and δ is the effective concentration boundary layer thickness.

Mass transfer is a first order process, and is typically denoted by the equation

$$[J]_{x=0} = K(c_s - c_0) \quad (27)$$

Where K is called the mass transfer co-efficient and can be presented as $K = \frac{D}{\delta}$

Mass transfer between two fluids

Reaction between two fluids is very commonly encountered in extraction and refining of metals and is exemplified by slag-metal, salt-metal and gas-metal reaction. These are three theories of mass transfer between two fluids viz film theory, boundary layer theory and surface renewal theory.

It has already been discussed that in a solid-fluid system, a stagnant fluid layer sticks to the solid surface and the thickness of the layer or film is determined by the hydrodynamic condition of the fluid. Attempts were made to extend the same to the two- fluid situation by assuming existence of concentration boundary layer on both sides of interface. Many a times, this concept is not application in fluid - fluid system, as the boundary layer is assumed to be stagnant and turbulent cannot reach the interface.

Boundary layer theory in turbulent flow was modified by assuming that eddy diffusion, rather than molecular diffusion to be responsible for mass transfer. However, the boundary layer

approach is incapable of taking into account surface renewal. This led to the development of "Surface Renewal Theories" of mass transfer between two fluids.

Let us consider that flow at the interface is laminar. If the viscosity of one fluid is much larger than that of the other, and then the forms can be considered as a rigid body. For example in a gas liquid system, the liquid being much viscous compared to gas would behave like a rigid body near the interface. In such situation mass transfer at and near the interface of high viscosity fluid would be by diffusion. Since the surface gets renewed continuously at the interface, the diffusion would be unsteady.

However, in engineering systems the flow is turbulent and the mass transfer at the interface is not realistically represented by the rigid body concept. In such situation, it is assumed that an eddy element when thrown on to the interface stays there for a while. During this period, it participates in mass transfer and again is thrown back into the bulk. Fresh eddy elements reprocess it thus causing surface renewal. The mathematical treatment of the surface renewal theory is little involved and needs prior knowledge of dimensionless groups. Hence no mathematical derivation for this mode of mass transfer has been presented.

Theory of reaction rate

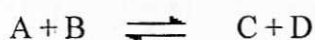
It has already been stated that chemical reactions in a metallurgical system can take place either in a single phase or in multi-phases. In general, laws and theories of chemical reaction rates were first proposed, developed and tested for homogeneous chemical reactions and were subsequently extrapolated to heterogeneous chemical reactions (i.e. reaction taking place at phase boundaries).

In kinetic laws give the relationship between the velocity of a chemical reaction and various factors such as concentration, temperature and pressure. Chemical reactions are specific in nature and hence, the coefficients are determined experimentally. In the following discussion, a brief account of various aspects of homogeneous reaction will be presented first and then the concepts will be extrapolated to heterogeneous systems.

The basic concept of rate of reaction, order of reaction and rate constant has already been described in the previous section. The rate of a chemical reaction depends on the mechanism (i.e., path) of the reaction. It has been established that the formation of the final products from the initial reactants always takes place by one or more relatively simple steps, called elementary processes. The overall chemical reaction is controlled by the slowest elementary process in series and the order of the overall reaction is nothing but the order of the rate controlling step.

Concept of equilibrium

Let us consider the reaction



Rate of forward reaction = $k_f C_A C_B$

Rate of backward reaction = $k_b C_C C_D$

Net rate (r) = $k_f C_A C_B - k_b C_C C_D$ (28)

When the rate of forward reaction and the backward reaction become equal, the net rate becomes zero. Under the reversible reaction condition

$$k_f C_A C_B = k_b C_C C_D \quad (29)$$

$$\frac{k_f}{k_b} = \frac{C_C C_D}{C_A C_B} = K_e \quad (30)$$

Where K_e is the equilibrium constant under a particular set of temperature and pressure values. If the reaction takes place far away from the equilibrium, the rate of backward reaction can be ignored and the rate can be written as

$$r = k_f C_A C_B \quad (31)$$

The concept of equilibrium can be viewed in the following ways from three different approaches

- In thermodynamics: at equilibrium $(\Delta G)_{PT} = 0$
- In statistical mechanics: Equilibrium is the state of system consisting of the greatest number of equally likely molecular configurations, which are macroscopically indistinguishable and can be considered identical.
- In chemical kinetics: Equilibrium means rate of all the forward and backward reactions are same.

The Arrhenius Equation :

It has been empirically found that the rate of a reaction vis-à-vis. The rate constant increases with rise in temperature. The temperature dependence of the rate constant is expressed by the following equation, known as Arrhenius equation.

$$K = A \exp (-E/RT) \quad (32)$$

where A is a constant, E is the activation energy and R is the gas constant. The following important information can be derived from the above co-relation.

- It gives the temperature dependence of rate constant
- Enthalpy change of a reaction is nothing but this difference in activation energies of forward and backward reaction of reversible process.
- $\ln k$ vs $\frac{1}{T}$ plot yields a straight line with negative slope. Steeper the slope, larger is the activation energy.
- Reaction with high activation energy is more temperature sensitive.
- A reaction is more temperature sensitive at lower temperature.

The success of the concept of activation energy of a reaction and Arrhenius part to explain dependence of rate constant on temperature, several attempts have been made to explain the observation through fundamental concept like breaking and formation of bond due to atomic

rearrangement, collision of atoms and molecules etc. However, due to complexity in mathematical treatment of these concepts, further discussion on the subject is avoided.

Heterogeneous reaction:

It has been mentioned earlier that there is heterogeneity in most of the metallurgical processes and many examples of even more than 3 phase systems exist. The chemical reaction in the heterogeneous system can take place only at the interface. The common boundary of three-phases is a line and for four-phases is a point. Because of such extremely small interfacial areas, the extent of reaction at three-phase and four-phases boundaries are negligible. On the other hand, the overall reaction can proceed at a much faster rate as a combination of several two-phase reactions. The rate of chemical reaction at an interface is proportional to the interfacial area. This is in contrast to the homogeneous reaction where rates are proportional to the volume. In a heterogeneous reaction, the steps involved are

- a) Adsorption of reactant into the interfacial layer
- b) Chemical reaction amongst the adsorbed species, and
- c) Desorption of products into the bulk.

It may be noted that no adsorption or desorption of species is involved in the progress of a homogeneous reaction.

Adsorption refers to incorporation of species into the interfacial layer, which may be a few atomic layers thick only. Adsorption is of two kinds viz. Physical and Chemical.

In physical adsorption, the attractive force resulting in adsorption is physical and weak van der Waals type force is active. Physical adsorption is predominant at low (especially sub-zero) temperature and is reversible. Adsorption of various gases by charcoal at liquid nitrogen temperature and their desorption on heating is an example of physical adsorption.

At high temperature, we are concerned with chemical adsorption or chemisorption, where specific chemical force (i.e. bond formation) exists between adsorbed species and the substrate. Unlike physical adsorption, chemisorption is an irreversible process. For example, if oxygen is chemisorbed on charcoal, desorption yields CO.

The relation between the equilibrium amount of adsorption and pressure (or concentration) at a constant temperature is called "Adsorption Isotherm". The simplest isotherm for a perfectly uniform surface with no interaction between the adsorbed molecules is known as Langmuir Isotherm and is described in brief as below.

Assuming the gas (C_1) gets adsorbed undissociated on a substrate surface site (S), the adsorption and desorption may be represented as



$$\text{At equilibrium, } k_f P (1-\theta) = k_b \theta \text{ or } K_e P = \theta / (1-\theta) \quad (33)$$

where P is the pressure of the gas, θ is the fraction of surface site covered, k_f & k_b have their usual significance.

The concept of interfacial reaction, has been successfully applied to evaluate the kinetics of many high temperature metallurgical reactions such as nitriding, carburising, gasification of carbon, dissolution of gas in liquid bath etc.

Details of assumptions and mathematical treatments are available in standard textbooks and hence not presented here.

Identification of rate controlling step

It is apparent from the discussion presented so far that a chemical reaction is primarily affected by the rate of mass transfer and chemical reaction when supply of heat is unlimited. Appropriate analysis of the rate data and its dependence of process variable like temperature, composition (catalyst) gives a fair idea about the rate limiting step.

If a reaction rate exhibits little dependence on temperature, negligible influence of catalyst or inhibitor and low activation energy, it is likely to be controlled by mass transfer. Mass transfer control of a reaction is predominant at high temperature.

On the contrary, when temperature has strong influence on the rate, catalyst or inhibitors effect in significant and the activation energy is high, the reaction is likely to be controlled by chemical reaction. A reaction is likely to be chemically controlled at low temperature.

It has to be borne in mind that in case of transport of multiple species or multiple chemical reactions, the above analysis does not specify transport of which species or which chemical reaction is rate limiting, except indication the slowest phenomena under certain operating condition. Both the mass transfer and chemical reaction may have comparable contribution and the reaction may be mixed controlled. A detailed analysis is needed to evaluate which specific elementary step is the slowest to identify the rate controlling step.

Summary

Kinetic analysis of a metallurgical system forms the basis for understanding the progress of a reaction and factors influencing the rate. A through understanding of the underlying principle helps to design, and control an industrial operation for optimal performance. In this paper, a brief outline has been presented on the concepts of the two major phenomena namely mass transfer and chemical reaction without much detail of mathematical treatment. It is expected that an exposure to the overall scope of the subject would help in analyzing an industrial operation in more meaningful way.