KINETICS OF IRON OXIDE DIRECT REDUCTION BY COAL

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Abstract - A new interpretation to the kinetics of iron oxide direct reduction, based on the influence of probability of activation of the reaction on the “flux of transformation”, is presented in this paper. This interpretation is applied to justify a new process of direct reduction of iron oxides, by using carbon as the only reactant.

Keywords - Direct reduction; kinetics of chemical reactions; activated complex; flux of reaction; carbon activity

I. INTRODUCTION

In order to analyze the direct reduction of iron oxides, a new kinetic interpretation, based on concepts similar to those of Eyring activated complex theory (Glasston et al., 1941 and Darken and Gurry 1953), is applied. This new interpretation does not relate to a thermodynamic equilibrium condition but to a probabilistic approach.

The interpretation was developed by Abril (1978) and improved by Abril (1997). Additional innovations are included in this paper, mainly to explain the reason why the empirical "specific rate of reaction" is generally constant, at a given temperature.

II. CHARACTERISTICS OF THE NEW INTERPRETATION

A "flux of transformation" will be defined -for a given reaction- as the number of moles of reactants which are transformed into products, at a unit time.

This flux is assumed to depend on an average "probability of activation" of a reaction, related to a constant frequency for the interchange of energy.

A group of reactants may be defined as the minimum amount of reactants, grouped near enough among themselves, as to be able to be transformed into an activated complex, when all the components of the group are simultaneously activated.

The number of groups of reactants to be considered is assumed to be proportional to the number of deficient components of reactants, from an estequiometric point of view.

The probability of activation of a reaction is considered as a compound probability, which means that its value is equal to the product of probabilities corresponding to each one of the reactants of a group.

The flux of transformation, \( J \), is defined by the following formula:

\[
J = f \cdot n \cdot W \cdot K_i, \tag{1}
\]

where \( f \) is the assumed constant number of energy changes of the components per second; \( n \) the number of deficient components of the reactants; \( W \) the probability of activation of the reaction and \( K_i \) a factor of proportionality between the number of deficient reactants and the total number of reactant groups of the system.

With homogeneous reactions, to any activated complex formed, a group of products will be produced in the system. When dealing with heterogeneous reaction- as the one to be analyzed in this paper- only the activated complexes formed in a small volume, facing the interface can be transformed into products. The reason for this will be later analyzed.

From the value of \( J \) given by formula (1), corresponding values of rate of reaction, and of specific rate of reaction, may be obtained, as explained by Abril (1997)\(^2\)

III. PROBABILITY OF ACTIVATION OF A SINGLE COMPONENT

In order to obtain the \( W \) value of formula (1) the meaning of the probability of a single component will be defined.

Based on statistical concepts, the following expression will be accepted to be proportional to the probability of activation of a component \( i \).

\(^2\)J and the reaction rate are considered equivalent but \( J \) is not necessarily related to a unit volume of a system, as happens with reaction rates.
where $E_i$ and $G_i$ relate respectively to internal energies, and Gibbs free energies, of a mole of component $i$, both in the system and when $i$ forms part of an activated complex.

According to the definition of internal energy $E$, the value $\Delta E'_i$ becomes:

$$\Delta E'_i = \Delta[TS_i] - \Delta[PV_i],$$  \hspace{1cm} (3)$$

where $T$ is the absolute temperature (assumed constant in a given reaction), $P$ the external pressure (also assumed constant), $S_i$ relates to molar entropies of $i$, and $V_i$ to molar volumes of $i$.

In both formulae (2) and (3), the symbol $\Delta$ represents differences of molar energy -related to component $i$- between those corresponding to the activated complexes and those corresponding to component $i$ alone in the system.

At a given temperature and pressure, the molar values of $E_i$ and $G_i$ may be considered constant when analyzed in an activated complex.

The expression $e^{-\Delta G_i/RT}$ represents a particular value of the activity of component $i$, which is proportional to any other value of the activity of the same component, particularly to the activity related to a pure component $i$.

This last activity may be related to the concentration of component $i$ alone in the system.

It will be postulated that, in many cases, the value of $\Delta E'_i$ -given by (3)- is practically constant, if the process is performed at constant temperature and pressure.

This constancy is assumed to be related to the fact that, generally, every change of the thermoeconomic energy of a component of a system is practically compensated by a corresponding change of thermodynamic work.

If the values of $TS_i$ and $PV_i$ are considered constant in the activated complexes, at a given temperature and pressure, the value of $\Delta E'_i$ may be considered constant at this condition.

The reason why $\Delta E'_i$ does not always appear as constant, may be related to an important change of the molar entropy of a component of the system, which may not be compensated by a corresponding change of the molar volume of the component.

As it was said before, expression (2) is proportional to corresponding probability of activation. If the constant of proportionality is considered included in the value of $f_i$ of formulae (1), this probability may be considered defined by:

$$W'_i = e^{-\Delta G_i/RT} \cdot e^{-\Delta E_i/RT},$$ \hspace{1cm} (4)$$

From this expression, the corresponding values of $W$ may be obtained by applying the compound probability concept.

IV. CONSTANCY OF THE SPECIFIC RATE OF REACTION

From the value of $\Delta E'_i$, for any reactant, a corresponding value, to be called $\Delta E_i$, may be obtained in relation to all components of a reaction, by applying the concept of compound probability mentioned above.

If the value of $\Delta E'_i$ is assumed constant for any component of a group of reactants, $\Delta E'_i$ will also be constant.

The constancy of $\Delta E'_i$ explains why, in many cases, the experimental specific rate of reaction appears to be constant, for a given temperature and pressure. It is so if we consider that $\Delta E'_i$ defines the exponential of the specific rate of a reaction.

When temperature increases, the value of $TS_i - PV_i$ also increases both in the activated complexes and in the system. It appears logical to assume that similar increases will be produced in both cases, at any temperature, and so values of $\Delta E'_i$ (and corresponding values of $\Delta E'_i$) may be independent of temperature, as found in the experimental values of specific rates of many reactions.

V. STOPPAGE OF HETEROGENEOUS REACTIONS IN SOLIDS

It will be accepted that any reaction between a gaseous reactant and a solid component is produced when the gas reactant is previously incorporated to the solid, through its external vacancies.

Any obstacle which avoids this incorporation, acts as stoppage of the reaction.

When a metal is in contact with a gas containing oxygen, an oxidation of the metal will be produced. This may be stopped by the products of the reaction, if they are fixed to the external vacancies of the metal.

This is what happens in the oxidation of aluminum at normal temperature, but not in the oxidation of iron.

What is assumed to happen is that the aluminum oxide is greatly fixed to the external vacancies of the metal, while this does not happen with the iron oxide.

In the reduction of iron oxide by hydrogen, the product of the reaction is water vapor. If this water reacts with some foreign component of the iron ore, the reduction may be stopped.

This is assumed to happen with some types of iron ore pellets, which appear difficult to be reduced with actual processes of direct reduction, which employ hydrogen.

In relation to the process to be analyzed in this paper, the only component that may stop the reaction is the carbon powder that may appear over the surface of the iron oxide pellets.

This phenomenon is produced when the activity of carbon,
related to pure carbon, is equal or greater than one. The reasons for this stoppage are later analyzed.

VI. CARBON ACTIVITY

The chemical reaction between \( CO \) and \( CO_2 \) in a solid vessel is normally assumed to be given by:

\[
2CO_{(in\ gas)} = CO_2_{(in\ gas)} + C_{(in\ solid)}.
\]  

(5)

According to this, the reaction constant is related to the activity of carbon in solid.

By accepting the activity equivalence principle, stated by Abril (1978), the activity of carbon will be considered to be, at equilibrium, equal in solid and in gas, if the same system of reference is used.

It will be assumed that atoms of carbon exist in the gas, what defines its activity. The number of such atoms may be very small, if the corresponding coefficient of activity is quite large.

According to the above, the precipitation of carbon powder comes from the gas, when the activity of carbon, related to pure carbon, becomes equal or larger than one.

VII. CHARACTERISTICS OF IRON ORE

DIRECT REDUCTION BY A CO AND CO₂ ATMOSPHERE

If only the reduction of FeO iron oxide is analyzed, the following two types of reactions may be considered to apply, when using a gas formed by CO and CO₂:

\[
FeO + CO = CO_2 + Fe
\]  

(6)

and

\[
FeO + C = CO + Fe
\]  

(7)

In any case the reactive component is considered to be previously fixed on the superficial vacancies of the pellets.

It will be assumed that, due to the size of carbon atoms, reaction (7) is mainly produced.

The two above reactions are additive so, if we apply reaction (7), reaction (6) effect may be considered included by affecting the value of \( J \), of formula (1), by an additional constant factor. This is so, as the same parameters will affect the obtained formula, as it will be later seen.

The carbon will be the deficient reactant of reaction (7) and, due to that, the \( n \) value of formula (1), may be accepted to depend on the amount of vacancies of the iron oxide, where the carbon atoms may be introduced.

Not all such carbon atoms may be able -after being activated- to produce products of the reaction, as the corresponding activated complexes have to be formed near the interface between gas and iron oxide, in order for the CO formed to pass from solid to gas.

It will be accepted that only the atoms of carbon located in a small volume, near the interface, should be considered in the value of \( n \).

The above mentioned volume will be considered defined by the interface surface \( \Omega \), times a normal distance, which is assumed to be a constant, at a given temperature.

The relationship between this distance -to be called \( \Delta \lambda \)- and the temperature, is assumed to be such, that the volume \( \Omega \Delta \lambda \) remains constant when temperature changes but the interface surface is the same.

The number of carbon atoms which defines de value of \( n \) of formula (1) is considered proportional to the number of vacancies in the volume \( \Omega \Delta \lambda \).

In order to obtain this number, a factor that relates -in a crystalline system- the number of lattice atoms to corresponding vacancies will be established.

This factor is, according to Reed Hill (1966), defined by:

\[
e^{-Q/RT}
\]  

(8)

where \( Q \) is a constant.

In relation to our problem, the lattice atoms are the oxygen atoms of the iron oxide, as the iron behaves as an interstitial component.

The number of oxygen atoms of the volume \( \Omega \Delta \lambda \) is related to corresponding number of vacancies (on the iron oxide phase) by means of factor (8).

As not all such vacancies may be filled with carbon atoms, it will be accepted that a constant percentage will always be occupied by carbon atoms.

From all the above, the number \( n \) of formula (1) may be defined by:

\[
N = \beta \cdot \Omega \cdot e^{-Q/RT}
\]  

(9)

where \( \beta \) is a constant independent of \( T \), which depends on the constant percentage of carbon filled vacancies and, also, on the constant number of oxygen atoms in the volume \( \Omega \Delta \lambda \), which, as stated above, is the same for any value of \( \Omega \).

The value of \( n \) given by (9), has to be introduced in formula (1) where only \( W \) has to be obtained, as \( f \) and \( K \) are considered as unknown constants.

According to what was said before, the value of \( W \) may be found by multiplying the probabilities of activation of carbon and that of FeO.
The probability of activation of carbon may be written, according to formula (4) as:

\[ W_c = \delta \cdot a_c \cdot e^{-\Delta E_c/RT} \]  

(10)

if subscript \( c \) represents carbon, \( a_c \) defines the activity of carbon related to pure carbon, and \( \delta \) is a constant factor which relates \( a_c \) to \( e^{-\Delta G_c/RT} \).

A similar expression may be obtained for the probability of activation of the \( FeO \).

The activity of \( FeO \), related to pure \( FeO \), is equal to one, if no solute exists in the iron oxide phase.

By multiplying the probability of activation of carbon by that of iron oxide, and incorporating the value of \( n_c \), given by (9), on formula (1), the following definition of the flux \( J \) may be obtained:

\[ J = d \cdot S_n \cdot a_c \cdot e^{-\Delta E'/(RT)} \]  

(11)

where \( d \) relates to the product of all factors so far considered constant (or practically constant), \( S_n \) is the nominal interface surface (considered proportional to \( \Omega \)), \( a_c \) is the activity of carbon, and \( \Delta E' \) has the meaning assigned before to any reaction.

It may be proved that if reaction (6) is considered a similar expression to (11) will be obtained, as \( a_c \) is directly related to the activity of reactant \( CO \). According to that, only the values of \( d \) and \( \Delta E' \) have to be changed, to apply expression (11), when the two reactions are considered.

A formula similar to (11) was obtained in Abril (1987), for the reduction of iron oxide by using hydrogen as reactant. In this case partial pressure of hydrogen was used instead of the activity of carbon.

In the mentioned reference, experimental results, taken from the literature, were analyzed. It was observed that the value of \( \Delta E' + Q_v \) was constant, independent of \( T \), and that \( d \) changed slightly with the percentage of reduction.

It may be assumed that similar situations will appear when formula (11) is applied to the reaction being analyzed here.

The reason why \( d \) changes with reduction percentage was analyzed in the mentioned reference. Similar considerations may apply to our case.

**VIII. INFLUENCE OF THE ACTIVITY OF CARBON**

According to equation (11) the activity of carbon affects directly the reduction of iron oxide in the process being analyzed.

The larger this activity, the faster the reduction will be but, if this activity becomes equal to or larger than one, the presence of carbon powder may stop the reaction.

The reason why the reaction is stopped when \( a_c \) is one, or larger than one, is related to the structure of carbon powder, which reduces drastically the entropy of carbon introduced into the vacancies.

According to what was said before, this change of entropy affects the value of \( \Delta E' \) and so the probability of activation of the reaction.

After many trials performed at our laboratories, it was found that the carbon powder may be avoided from the process if iron pellets were heated, to the reaction temperature, in contact to the required carbon, and if the gases are recirculated by passing them trough a cooling area.

These findings are reported mainly in Valdez (1999).

**IX. INFLUENCE OF CIRCULATION OF GASES**

If the gases are recirculated, and they pass through cooling areas, the activity of carbon –at the process temperature- will be increased, due to the increase of the amount of carbon atoms in the atmosphere, originated by the reduction of temperature, and affected by the gas velocity.

This increase of activity may allow to reduce the time required for the reaction to be completed, but, if the gases are in contact with coal, the process has to be regulated, in order to allow the reaction to be finished, before the appearance of carbon powder.

**X. CONCLUSIONS**

According to test performed at our laboratories, a method may be established to economically reduce iron oxide pellets, by using an atmosphere formed by heating coal, in presence of oxygen.

It was found that the process could be applied to any type of pellets, what does not happen with actual direct reduction methods. The reason is assumed to be related to the presence of hydrogen in actual methods, which according to what was said before may stop the reaction with some types of pellets.

As hydrogen is not used in the proposed method, this phenomenon is not produced.

**REFERENCES**


