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Chlorination Kinetics of Zirconia in an RF Chlorine Plasma Tail Flame

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The chlorination kinetics of zirconia were studied in a single stationary particle reactor system. A plasma of pure chlorine generated by an induction torch provided both the high enthalpy field and the reacting gas. The influence on the rate of conversion of such parameters as temperature, chlorine concentration (in the presence of argon) and particle diameter and porosity were investigated. Based on experimental and theoretical studies, rate equations were developed under different rate controlling mechanisms.

The chlorination of zirconia in the particle temperature range of 1 540° to 2 480°K obeyed a shrinking core reaction model. The reaction was chemically controlled below 1 950°K, and above this temperature both chemical and mass transfer resistances were important. The experimental results confirmed the theoretical analysis.

SCOPE

The chlorination of zirconium oxide may be considered as an integral part of the overall process for the production of nuclear grade zirconium. The latter's commercial production is currently based on the Kroll process (Miller, 1954; Shelton et al., 1956; Starrat, 1959; Elger, 1962; Babu et al., 1969; Chintamani et al., 1972; Spink, 1977) which uses hafnium free, pure zirconium tetrachloride as the feed material. Newer processes which have been proposed to replace the conventional commercial method of production also use zirconium tetrachloride as the starting material. These include plasma decomposition of zirconium tetrachloride (Chizhikov, Deineka and Makarova, 1969; Chizhikov et al., 1971; Semenenko et al., 1975; Gragg, 1973; Little and Wentzell, 1965; CIBA, 1966) and electrowinning of the metal from fused salts containing zirconium tetrachloride (Martinez and Couch, 1972; Martinez et al., 1976).

For the production of nuclear grade zirconium, the near complete separation of hafnium, which is always associated with zirconium in the ore, is necessary owing to hafnium's high neutron absorption cross section. In the present conventional process, hafnium separation is effected by means of solvent extraction, to yield purified $Zr(OH)_4$. The latter is then calcined to yield dehafniated zirconia. The subsequent chlorination of the dioxide to produce the tetrachloride feed for the Kroll process is thus an essential processing step in the overall complex production scheme.

Zircon, the main source of the metal, may be either chlorinated directly (Manieh and Spink, 1973; Manieh, Scott and Spink, 1974) or through a two-step process, namely, the carburization of zircon followed by the chlorination of zirconium carbide or carbonitride (Kroll, Carmody and Schlechton, 1952; Stephens and Gilbert, 1952; Shelton et al., 1956). The former requires a larger reactor volume, extra chlorine and carbon for the silica constituent of the ore, for the same throughput of zirconium tetrachloride. Furthermore, it necessitates the separation, handling and disposal of silicon tetrachloride. On the other hand, the two-step process has been shown to be less efficient than zircon chlorination (Stephens and Gilbert, 1952). The recent development of a plasma process for the dissociation of zircon into its two constituent oxides zirconia and silica (Wilks et al., 1972, 1974; Bayliss, Bryant and Sayce, 1977) followed by leaching of the silica may lead in future to the direct chlorination of the impure zirconia thus produced rather than that of zircon.

The kinetics of the chlorination of zirconium oxide have not received much attention. The available publications in the field are limited to those of O'Reilly et al. (1972), Landsberg et al. (1972) for the kinetic study; to those of Stephen and Gilbert (1952) and Sehra (1974) for vertical shaft furnace and fluidized bed chlorination operation, respectively, and to that of Vasilenko and Volskii (1958) for thermodynamic analysis. All of these studies are concerned with temperatures below 1 400°K, under which conditions the reaction rates are too low for a viable industrial process.

In the present work, it was intended to study the kinetics of zirconium oxide chlorination at high temperatures (1 400° to 2 480°K). A chlorine induction plasma reactor system was used to provide both the high temperature field and the reactant gas. To the authors' knowledge, the generation of a plasma of pure chlorine has never been attempted before, nor has the use of a plasma system for chlorination kinetic studies.

To achieve the objectives of the study, a special reactor system had to be designed and developed to handle hot chlorine and control and measure all parameters affecting the rate of the heterogeneous zirconia chlorination. A theoretical analysis was carried out along with the experimental work.

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The results indicate that the direct high temperature chlorination of zirconia to produce the tetrachloride may offer distinct advantages in the elaboration of future, more efficient production processes. This possibility is further enhanced if the use of a plasma flame is considered to generate the high temperature field necessary.

CONCLUSIONS AND SIGNIFICANCE

The kinetics of the reaction between zirconium dioxide and chlorine in the temperature range of 1 540° to 2 480°K in a radio frequency chlorine plasma tail flame were studied. The influences of such parameters as time, temperature, porosity, diameters and chlorine concentration on the rate were determined experimentally, using a single stationary spherical pellet. The range of particle Reynolds number extended from 150 to 850.

The microscopic examinations of partially reacted pellets revealed that the reaction was confined to a very thin layer near the external surface. This was confirmed by the experimental conversion-time data which fitted the shrinking core model.

The Arrhenius plots of the experimental data indicated the existence of a gas film diffusion resistance above about 1 950°K, below which the rate was controlled by chemical reaction. The activation energy of 101.2 kJ/g mole (24.2 kcal/mole) obtained for the latter region did not change with the pellet porosity, thus supporting the conclusion with respect to the surface reaction.

The overall rate constant, however, showed a higher porosity dependence [proportional to $(1 - \epsilon)^{-2}$] than could be accounted for by the change of solid density [proportional to $(1 - \epsilon)^{-1}$]. This was attributed to the existence of a thin fluffy layer near the external surfaces, resulting in a higher actual reacting area than the geometrical surface area on which the shrinking core model is based.

The rate was found to be inversely proportional to the pellet diameter, in agreement with the theoretical formulation, Equation (9), again confirming the conclusion of chemical reaction resistance.

The rate was first order with respect to the gaseous reactant concentration when it was expressed in terms of molecular chlorine, or in terms of atomic chlorine in the form of $y_{Cl}/(2 - y_{Cl})$.

At temperatures below 1 950°K, where the rate was controlled by chemical reaction, the following expression, derived from the theoretical formulation and the regression analysis of the experimental data, represented the latter reasonably well:

$$1-(1-X)^{1/3} = 3.313 \exp(-12\,162/T) y_{Cl_2} (1-\epsilon)^{-2} D^{-1} t, \quad (33)$$

This expression includes the effects of all parameters affecting the rate of the reaction (temperature, diameter of particle, porosity and chlorine concentration) and should therefore be useful for industrial design purposes.

For the region of $T > 1\,950$°K, where both the chemical and mass transfer resistances were important, the theoretical analysis showed that the total reaction time could be approximated by the summation of two terms: the time required to reach the same conversion in the absence of diffusional resistance and that for pure mass transfer control. Theoretically calculated mass transfer resistance confirmed the experimental findings with respect to the controlling mechanisms. Furthermore, the predicted reaction time compared reasonably well with the experimental values.

INTRODUCTION

The chlorination of zirconium dioxides, in the absence of a reducing agent, has been studied experimentally in a preliminary way by Landsberg et al. (1972) and by Pogonina and Ivashentsev (1974) at temperatures not exceeding 1 420°K. In both cases, the rate of conversion was quite slow.

In plasma systems, the temperature difference between the reacting particle and the ambient gas is usually quite large. In the present study, it was of the order of 2 000° to 3 000°K, with the ambient gas temperature in the range 3 500° to 6 000°K. The equilibrium concentrations of molecular and atomic chlorine, as calculated from the data in the JANAF tables at different temperatures, indicate that, at the experimental gas temperature levels (3 500° to 6 000°K) used in this work, the chlorine gas will be in the atomic form (dissociation is 98.94% complete at 3 000°K). Thus, the following reactions may take place on the zirconium dioxide surface:

$$4\,Cl = 2\,Cl_2 \quad (1)$$

$$ZrO_2 + 2\,Cl_2 = ZrCl_4 + O_2 \quad (2)$$

$$ZrO_2 + 4\,Cl = ZrCl_4 + O_2 \quad (3)$$

The free energy data shown in Figure 1 for these three reactions were extracted from the JANAF thermochemical tables (1967).*

Reaction (2) is possible, depending upon whether atomic chlorine associates to form molecular chlorine at the oxide surface. Although the reaction temperature of zirconia pellets is lower than the bulk gas temperature and permits the formation of molecular chlorine, the extent of reaction (1) may not be large owing to very short residence times. In any event, reaction (3) represents both the summation of reactions (1) and (2) and also the direct action of atomic chlorine on zirconium dioxide. Hence, regardless of what happens on the pellet surface, reaction (3) may be considered as representing the chlorination of

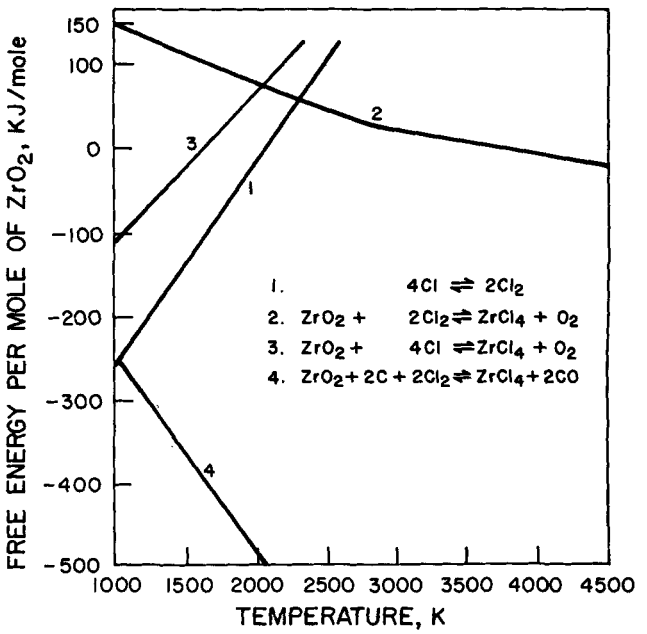


Figure 1. Free energies of zirconia chlorination reactions.

*The chlorination of zirconia in the presence of carbon is included in Figure 1 for comparison purposes. A study of the kinetics of this system will be published in a subsequent paper.

zirconia in the absence of a reducing agent in the chlorine plasma. This reaction is also a reversible one, and it is thermodynamically more favorable than that with molecular chlorine below about 2 050°K (dissociation less than 50%), as indicated in Figure 1.

The purpose of this study was to investigate fully the possibility of direct chlorination of zirconia with chlorine alone and to study its kinetics. A theoretical analysis was carried out along with the experimental work in order to obtain a time-conversion relationship and to compare the experimental data with those of theoretical predictions of this work when gas film diffusion becomes important.

THEORETICAL ANALYSIS

A review of the mathematical treatments of gas-solid reactions shows that every conceptual picture or model for the progress of a heterogeneous reaction is accompanied by its specific mathematical representation. The published treatments either assume a surface reaction which is expressed by a shrinking core model (Yagi and Kunii, 1953, 1955*a*, 1955*b*); Shen and Smith, 1965; Levenspiel, 1972; Szekely et al., 1976), or a diffuse zone reaction model. The latter either views the reacting pellet as a homogenous matrix-volumetric reaction model (Ishida and Wen, 1968; Wen, 1968; Calvelo and Cunningham, 1970; Williams et al., 1972), considers a pore structure (Peterson, 1957; Ramachandran and Smith, 1977) or envisages a grain structure (Szekely and Evans, 1970, 1971; Sohn and Szekely, 1972; Sampath et al., 1975). The uniform reacting pellet model is treated as a special case of diffuse zone reaction models. The shrinking core model was found useful in analyzing many solid-gas, reactions including porous solids, owing to its mathematical simplicity (Costa and Smith, 1971; Wang and Wen, 1972; Munz and Gauvin, 1975; Morris and Jensen, 1976; Fahim and Ford, 1976).

In the light of the experimental observations, the theoretical analysis of the reaction between zirconia and atomic chlorine will be based on surface reaction of the shrinking pellet, and it will be carried out for chemical reaction and for gas film diffusion controlling mechanisms, separately. Then an approximate solution will be obtained for the intermediate case, where both the chemical reaction and the gas film diffusion resistances contribute.

Chemical Reaction Control

For the reaction

$$ZrO_2 + 4\ Cl = ZrCl_4 + O_2 \tag{3}$$

in the absence of mass transfer effects, and neglecting porosity, sintering and structural changes, we can write the following rate equations:

$$-N = k_s f(y) = -(4/4\pi r^2)(4\pi r^2 \rho_s)(dr/dt) \tag{4}$$

or

$$-(dr/dt) = (k_s/4\rho_s) f(y) \tag{5}$$

Integrating between R and r, and between $t = 0$ and $t = t$, we get

$$1-(r/R) = (k_s/4\rho_s R) f(y) t \tag{6}$$

In terms of the fractional conversion X of solid reactant, and noting that $r/R = (1-X)^{1/3}$, we can write this as

$$1 - (1 - X)^{1/3} = (k_s/4\rho_s R) f(y) t \tag{7}$$

The reaction rate dependence on the concentration $f(y)$ is usually expressed as an exponent of the gaseous reactant concentration. In accordance with the experimental data, $f(y)$ can be written as

$$f(y) = (y_{Cl} - y_{Cl_e})/(2 - y_{Cl}) \tag{8}$$

where y_{Cl} is the atomic chlorine concentration at the surface (which, in absence of diffusional mass transfer resistance, is also equal to the bulk gas concentration), and y_{Cl_e} is the concentration of atomic chlorine in equilibrium with the concentration of the product gases at the reaction surface. The final form of Equation (7) for the conversion time relationship thus becomes

$$1-(1-X)^{1/3} = (t_r)(k_s/4\rho_s R)(y_{Cl} - y_{Cl_e})/(2 - y_{Cl})$$

or

$$t_r = 4\rho_s R[1-(r/R)]/[k_s(y_{Cl} - y_{Cl_e})/(2 - y_{Cl})] \tag{9}$$

Mass Transfer Control

Equation (3) involves multicomponent nonequimolar counter-diffusion. Bird, Stewart and Lightfoot (1960) have shown that mass transfer rates through a gas film in multicomponent systems can be predicted by using analogous binary formulas if an effective binary diffusivity D_{im} for the diffusion of the i^{th} component in a mixture can be defined so that species i behaves as if it were in a binary mixture of diffusivity D_{AB} equal to the prevailing D_{im}. The requirements for such a treatment are that the mass transfer rates should be low and the physical properties, including the effective diffusivities, should be constant. It is obvious that the physical properties generally vary from point to point, and this variation is more significant in the case of plasma systems, owing to the large temperature gradients. For an approximate calculation, average fluid properties and film composition will be evaluated at the mean of the reaction surface and plasma gas temperatures.

The molar flux of component i (N_i) by analogy with the binary formulas, is the sum of the diffusional contribution and of the bulk flow contribution; that is

$$N_i = k_{mi}(y_{is} - y_{io}) + y_{is} \sum_{j=1}^{n} N_j \tag{10}$$

Starting with this basic equation, a detailed generalized derivation is given in Biceroglu's work (1978). The following is a summary of the major steps. For chlorine, this equation reduces to

$$N = 2k_m(y_{Cl_s} - y_{Cl})/(2 - y_{Cl_s}) \tag{11}$$

Also, for the disappearance of zirconia

$$N = -(dr/dt) = k_m(y_{Cl_s} - y_{Cl})/2(2 - y_{Cl_s})\rho_s \tag{12}$$

For a spherical pellet, the mass transfer coefficient for chlorine, k_m, may be calculated from the Ranz and Marshall (1952) correlation as

$$N_{Sh} = 2 + 0.6\ N_{Sc}^{1/3} N_{Re}^{1/2}$$

or

$$2k_m r/cD_m = 2 + 0.6\ (\mu/\rho D_m)^{1/3}(2U\rho r/\mu)^{1/2} \tag{13}$$

Inserting the value of k_m from Equation (13) into Equation (12) and integrating the latter between $t=0$ and $t=t_m$, we get

$$t_m = -[(y_{Cl_s} - y_{Cl})cD_m/2R^2\rho_s(2 - y_{Cl_s})]i^{-1}$$
$$\{(2/3\alpha)[1-(r/R)^{3/2}] - \alpha i^{-2}(1-r/R) +$$
$$2\alpha^{-3}[1-(r/R)^{1/2}] - 2\alpha^{-3}[1-(r/R)^{1/2}] - 2\alpha^{-4}$$
$$\ln[(1+\alpha)/1+\alpha(r/R)^{1/2}]\} \tag{14}$$

where

$$\alpha = 0.3\ N_{Sc}^{1/3} N_{Re}^{1/2} \tag{15}$$

As noted before

$$r/R = (1-X)^{1/3} \tag{16}$$

The concentration driving force in the treatment up to now was taken to be the difference between that at the reaction

surface and that in the bulk gas. For a purely gas-film diffusion controlled reaction, a good approximation to the reaction surface gas concentration may be obtained by assuming that chemical equilibrium exists at the reaction surface. Then, the chemical equilibrium relationship may be written as

$$K_E = (y_{O_{2_s}})(y_{ZrCl_{4_s}})/y_{Cl_s}{}^4 \tag{17}$$

Also

$$y_{Cl_s} + y_{ZrCl_{4_s}} + y_{O_{2_s}} = 1 \tag{18}$$

and

$$N_{O_2} = N_{ZrCl_4} \tag{19}$$

Expressions similar to (12) can now be written for N_{O_2} and N_{ZrCl_4}. Since the fluid density, viscosity and effective diffusion coefficient are all functions of the gas film composition, the mass transfer coefficient k_m is also composition dependent. Hence, to calculate y_{Cl_s}, an iteration technique must be used to simultaneously solve Equations (10), (17), (18) and (19).

Combined Mass Transfer and Chemical Reaction Control

When chemical reaction and mass transport present comparable resistances to the progress of a reaction, the contribution of these processes must be considered simultaneoulsy. A pseudo steady state assumption, stating that the rate of movement of the reaction surface $-dr/dt$ is small with respect to the velocity of the gaseous components through the gas film, has been shown to be a good approximation for most of the gas-solid reaction systems, except for those under extremely high pressures and very low solid reactant concentration (Bischoff, 1965; Bowen, 1965; Luss, 1968). Then, the overall rate is identical to the rate of interfacial chemical reaction and also to that of mass transport.

For the chemical reaction, Equation (5) can be rewritten as

$$-dr/dt = (k_s/4\rho_s)\quad (y_{Cl_s} - y_{Cl_e})/(2 - y_{Cl_s}) \tag{20}$$

where surface, instead of bulk, concentration is used, since these are no longer the same. Similarly, for mass transfer control, Equation (12) still applies:

$$-dr/dt = k_m(y_{Cl_s} - y_{Cl})/\ 2\rho_s(2 - y_{Cl_s}) \tag{21}$$

Here the surface concentration is no longer at equilibrium.

Combining Equations (20) and (21), we get

$$(y_{Cl} - y_{Cl_e})/(2 - y_{Cl_s}) = -(4\rho_s/k_s)dr/dt - (2\rho_s/k_m)drdt \tag{22}$$

Replacing k_m by its value from Equation (13) and integrating, we obtain

$$t = 4\rho_s R[1-(r/R)]/[k_s(y_{Cl} - y_{Cl_e})/(2 - y_{Cl_s})] + (2R^2\rho_s/cD_m)/[y_{Cl} - y_{Cl_e}/\ (2 - y_{Cl_s})]\{(2/3\alpha)[1-(r/R)^{2/3} - \alpha^{-2}(1-r/R) + 2\alpha^{-3}(1 - r/R^{1/2} + 2\alpha^{-4}\ln[(1+\alpha)/[1+\alpha(r/R)^{1/2}]] \tag{23}$$

In this final equation, if the surface concentration y_{Cl_s} is approximated by y_{Cl} in the chemical reaction term and by y_{Cl_e} in the mass transfer term, it can be seen that the first term is the time required to reach a given conversion under chemical control alone, and the second is that required to reach the same conversion under mass transfer control alone. The total time is thus the sum of the two; hence, $t = t_r + t_m$.

Prediction of Transport Properties

To allow the calculation of t_m for mass transfer control in Equations (14) and (23), there remains the problem of estimating the effective diffusivisity coefficients and viscosities of the gas mixture. Based on the theoretical treatment of Hsu and Bird (1960) and Bird, Stewart and Lightfoot (1960) which, in turn, used the concept of using binary formulas for multicomponent diffusion, the effective binary diffusivity D_{im} for the diffusion of i in a mixture is given by

$$D_{im} = \left(N_i - y_i \sum_{j=1}^{n} N_j\right) \Big/ \sum_{j=1}^{n} (1/D_{ij})(y_j N_i - y_i N_j) \tag{24}$$

For D_{ij}, Reid and Sherwood (1966) recommend the expression

$$D_{ij} = 0.001858\ T^{3/2}[(M_i + M_j)/M_i M_j]^{1/2}/P\sigma_{ij}^2\Omega_D \tag{25}$$

To estimate the collision integral Ω_D, it is convenient, for computerized work, to use the correlation of Hattikudur and Thodos (1970):

$$\Omega_D = 1.069/T^{*0.1580} + 0.3445/\exp(0.6537T^*) + 1.556/\exp(2.099T^*) + 1.976/\exp(6.488T^*) \tag{26}$$

For the calculation of the effective viscosities of the mixture, the semiempirical formula of Wilke (1950*b*) was used:

$$\mu_{mix} = \sum_{i=1}^{n} \left(y_i\mu_i \Big/ \sum_{j=1}^{n} y_j\psi_{ij}\right) \tag{27}$$

in which

$$\psi_{ij} = (1/\sqrt{8})(1 + M_i/M_j)^{-1/2}[1 + (\mu_i/\mu_j)^{1/2}(M_j/M_i)^{1/4}]^2 \tag{28}$$

$$\mu_i = 2.669 \times 10^{-5}\ \sqrt{M_i\ T}/(\sigma^2{}_i\Omega_r) \quad \text{(poise)}$$

and from Hattikudur and Thodos (1970)

$$\Omega_r = 1.155/T^{*0.1462} + 0.3945/\exp(0.6672T^*) + 2.05/\exp(2.168T^*)$$

To use the above expressions, a knowledge of the Lennard-Jones potential parameters σ and (ϵ/k) is required. For chlorine and oxygen, these values were readily available (Svehla, 1962), but not for zirconium tetrachloride vapors. Using experimental viscosity data for the latter at two temperatures given by Tsirel'nikov et al. (1961), Biceroglu showed that use of the critical properties to estimate the Lennard-Jones parameters gave excellent agreement, while the method based on the second virial coefficients gave erroneous results. Thus, for zirconium tetrachloride vapor, the calculated parameters were

$$\epsilon/k = 528.4°K$$

and

$$\sigma = 5.616\ \text{Å}$$

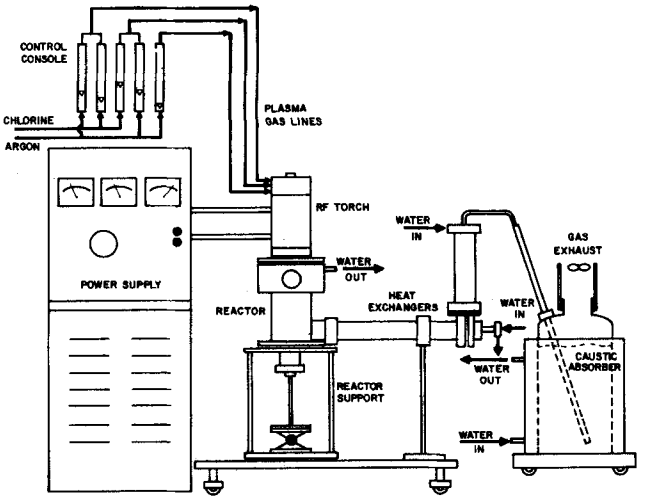


Figure 2. Schematic drawing of equipment.

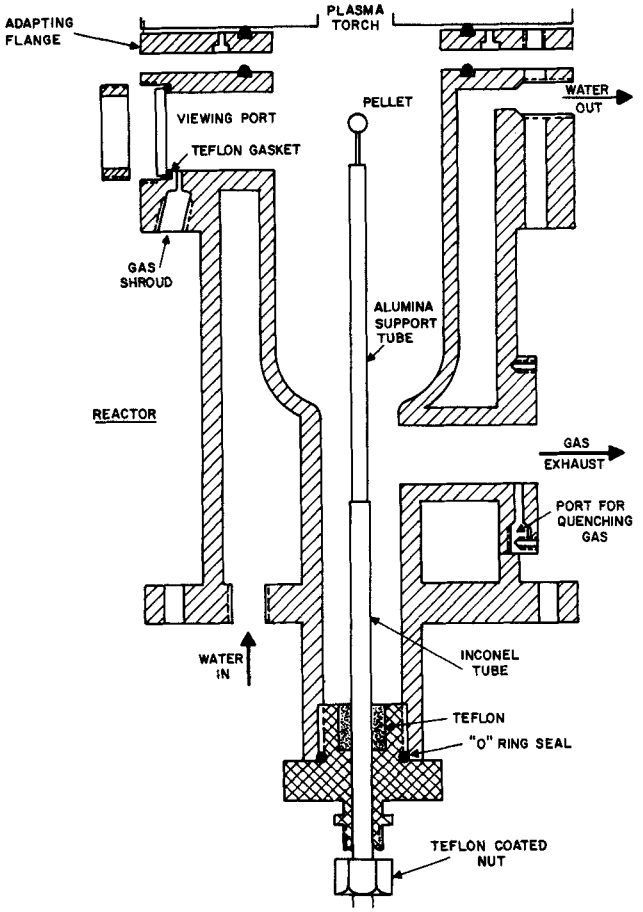


Figure 3. Schematic drawing of reactor.

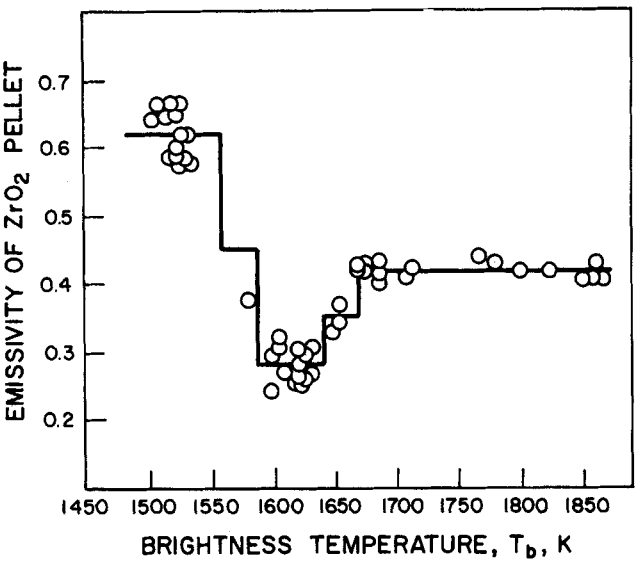


Figure 4. Spectral emissivity of reacting zirconium dioxide pellet.

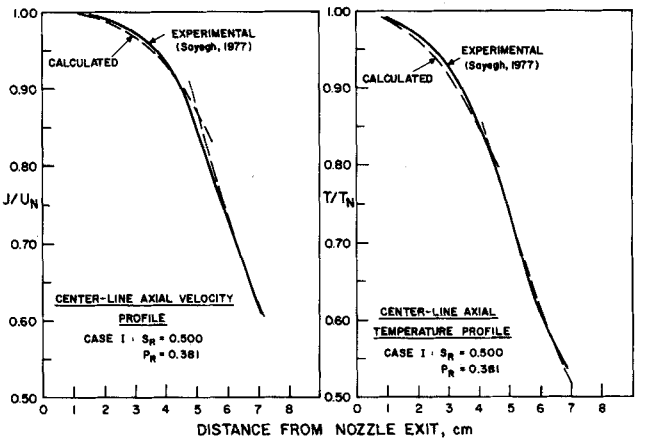


Figure 5. Decay of chlorine velocity and temperature along the center line (condition 1).

EXPERIMENTAL

Apparatus

A schematic diagram of the apparatus is shown in Figure 2. The plasma was generated in a radio frequency (4.3 M Hz) induction torch. The torch was started with pure argon, and chlorine was then added until the plasma consisted of pure chlorine alone. The power ranged between 7 and 25 kW. The plasma left the torch through a monel nozzle, 25.4 mm in diameter, and entered the reactor system shown in Figure 3, machined out of monel. The upper section, or reaction chamber, was 5.08 cm in diameter and 11.4 cm long. The lower section (2.54 cm in diameter and 11.4 cm long) housed the particle support system and provided a nonreactive area for the particle while steady plasma conditions were established. It also accommodated the reactor outlet (1.9 cm ID), without disturbing the symmetry of the flow in the reaction chamber.

The particle was mounted on an alumina sting, 0.08 cm in diameter and 1.0 cm in length, connected to a larger alumina rod 0.48 cm in diameter and 30.5 cm in length. Provisions were made in the design of the reactor and of the heat exchangers for calorimetric measurements in order to predict the gas velocity and the temperature at the reactor inlet.

Particle Preparation

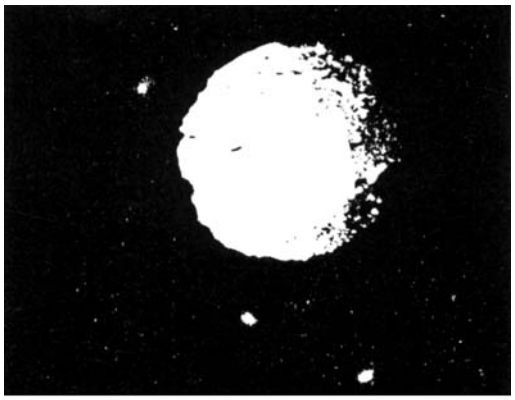
The zirconium dioxide was optical grade with a minimum purity of 99.8%. Impurities were Al <0.01%, Fe <0.01%, Hf <0.03%, Mg<0.01%, Mn <0.01% and Si <0.1%. Presence of other impurities could not be detected. About 96 mass % of the fine powder had an equivalent diameter less than 44 μm, with a mass median diameter of 6.6 μm. Spherical pellets in the range of 0.494 to 1 cm in diameter and 0.485 to 0.59% in porosity were formed by a die compacting method, followed by sintering in air at 1 400°K for 4 hr. The pellets thus formed were not strictly spherical, as they exhibited a small disk portion around the equator.

Measurement Techniques

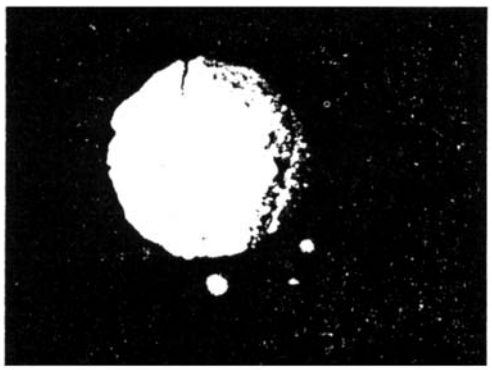
Particle Temperature: The temperature of the particles was measured with a high resolution pyrometer capable of measuring the temperature of objects as small as 0.1 mm in the range 1 000° to 3 500°K. As chlorination proceeded, the microscale surface roughness changed and so did the emissivity of the pellet. A large number of blackbody experiments had to be made, using a blackbody hole on the pellet, and the observed dependence of the spectral emissivity on temperature is summarized in Figure 4.

Plasma Velocity and Temperature: Predictions of the axial velocity and temperature of the chlorine plasma were based on previous careful experimental measurements on argon reported by Sayegh (1977) on the same equipment. Details of the analysis can be found in Biceroglu's work (1978). Typical results are shown in Figure 5 for a given condition of S_R (the ratio of swirl to radial gas flow rates to the torch) and P_R (the ratio of power at the nozzle exit to the inlet plate power). Use of these relationships require a knowledge of U_N, the nozzle exit gas velocity, and T_N, the corresponding nozzle exit temperature. The temperature at the nozzle exit was obtained from calorimetric measurements on the reactor cooling water, working back from a similar determination of the exhaust gas temperature from a calorimetric measurement on the exit heat exchange. U_N varied between 17 and 51 m/s and T_N between 3 000° and 6 500°K. The range of particle Reynolds number covered in this work was from 150 to 850. For the purpose of computer calculations on the exit heat exchanger, the following expression was developed for the enthalpy of molecular chlorine in the temperature range of 298° to 1 000°K by curve fitting the tabular data of JANAF tables:

$$H_{Cl_2} = -2\,323.9 + 7.332\,T + 17.436 \times 10^{-4}\,T^2 - 636.27 \times 10^{-9}\,T^3 \quad (29)$$



(a)



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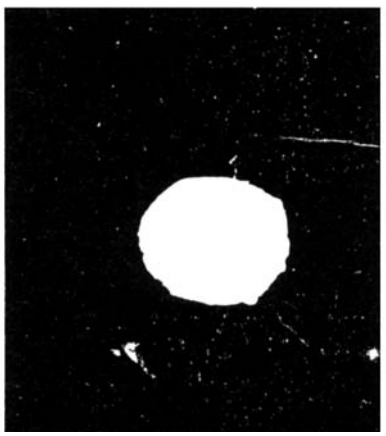

(c)

Figure 6. Micrographs (x6.4) od partially reacted pellets of the same initial diameter (0.671 cm).

Having determined the mean enthalpy at the nozzle exit, and using the atomic chlorine density at the corresponding temperature, we could calculate the mean plasma gas velocity at the nozzle exit from the mass flow rate of the gas fed to the torch through calibrated rotameters.

Extent of Reaction: This was simply measured through weight loss with an accuracy of ±0.0001 g. At the completion of an experiment, the reacted pellet was micrographed. Typical micrographs are shown in Figure 6. The reduction in pellet diameter during an experiment ranged from 5 to 6%.

RESULTS AND DISCUSSION

Conversion-Time Relationship: Based on the microscopic examinations of partially reacted pellets (which showed that the reaction was confined to the external surfaces), the conversion-

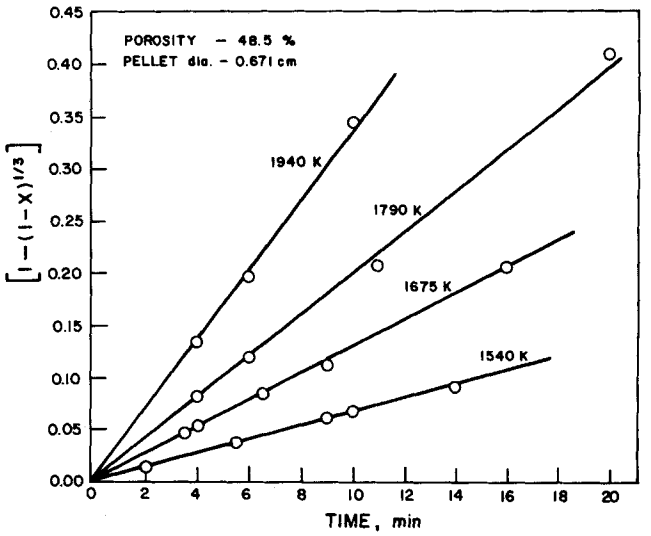

Figure 7. Conversion vs. reaction time. Void fraction = 0.485, pellet diameter = 0.671 cm.

time relationship can be expressed by the shrinking core model of changing particle size. Thus, when the chlorination of zirconium dioxide is purely chemical reaction controlled, the overall consumption of zirconia with time [as developed previously, Equation (7)] can be written as

$$1 - (1 - X)^{1/3} = K\,t \tag{30}$$

The validity of this expression was confirmed by the experimental results (showing linear relationship between the conver-

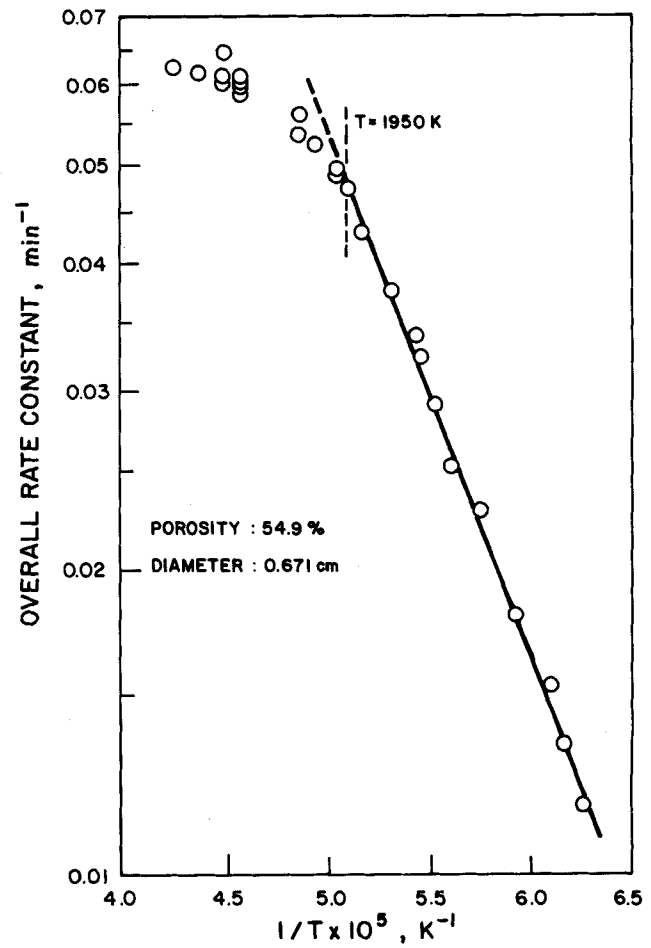

Figure 8. Arrhenius plot of reaction between zirconium dioxide and chlorine.

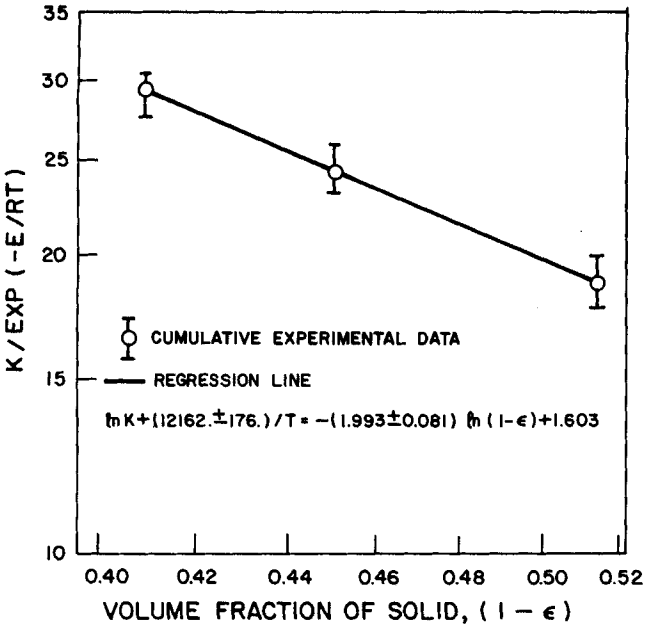

Figure 9. Effect of porosity on overall rate constant.

sion expression and time), typical of which is Figure 7, for a 0.671 cm pellet with a void fraction of 0.481. Similar straight lines were obtained for porosity of 54.9 and 59.0%.

Influence of Temperature: The effect of pellet temperature on the reaction rate was studied in the range 1 540° to 2 480°K. The results were plotted in the form of an Arrhenius type of relationship, that is, plots of K, the overall rate constant, vs. $1/T$, typical of which is Figure 8. One hundred twenty-three experiments were performed for different pellet diameters and three void fractions, 0.485, 0.549 and 0.590, respectively. In all cases, these plots indicated that above 1 950°K, independently of the porosity, chemical reaction was no longer the sole controlling mechanism, but that an additional resistance (gas film diffusion) began to slow down the rate at the higher temperature.

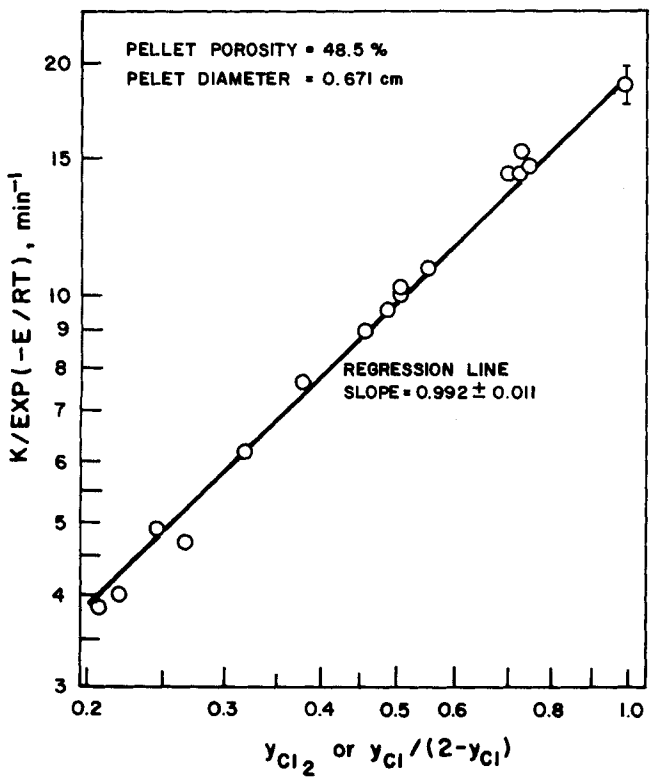

Figure 11. Effect of chlorine concentration.

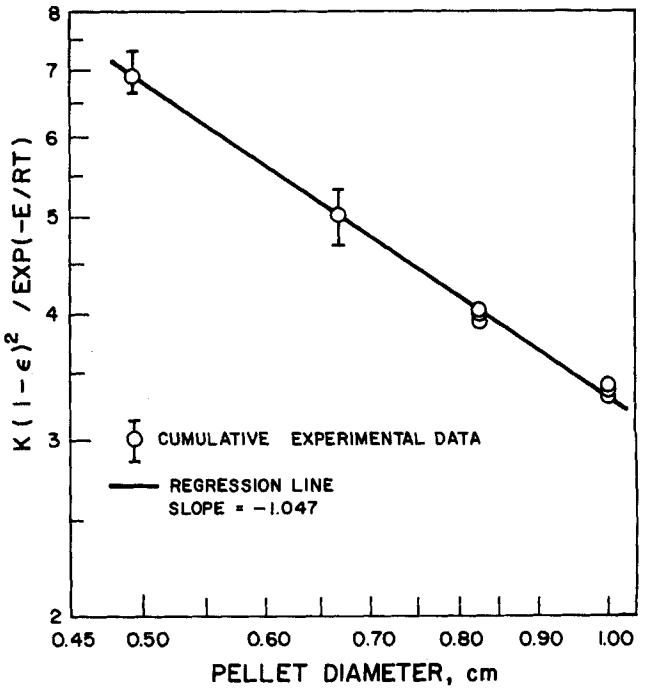

Figure 10. Effect of pellet diameter on overall rate constant.

From a multiple regression analysis of these data, the following expression was obtained:

$$\ln K = 1.603 - (12\,162 \pm 176)/T - (1.993 \pm 0.081)\ln(1 - \epsilon) \quad (31)$$

with a multiple correlation coefficient of 0.998 and with a probability associated with F of unity. From this equation, an activation energy of 101.18 ± 1.46 kJ/g mole (24.166 ± 0.350 kcal/mole) was calculated. The partial correlation coefficient of activation energy was 0.997.

Influence of Pellet Porosity: The experimental data are plotted in Figure 9, where each point represents the cumulative data of a large number of experiments. The straight line is the result of

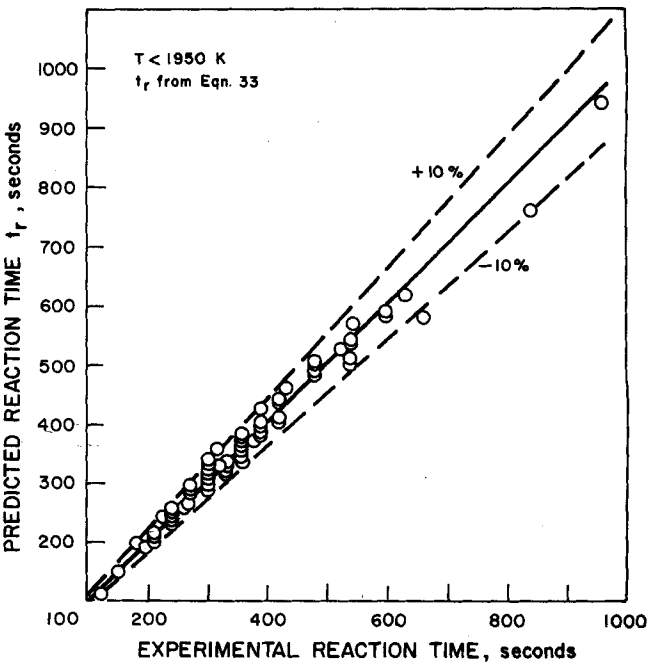

Figure 12. Comparison of experimental reaction time with values predicted by Equation (33). (Chemical controlled region, T<1 950K).

the regression analysis as given by Equation (31), which yields an exponent of nearly −2 on the solid volume fraction $(1 - \epsilon)$. On the other hand, Equation (7) predicts that the overall rate constant should be inversely proportional to the porous solid density ρ_s, that is, inversely proportional to $(1 - \epsilon)$, since ρ_s = (density of dense solid) $(1 - \epsilon)$.

This contradictory conclusion may be explained by the fact that the reaction between a zirconium dioxide pellet and chlorine is not taking place truly on the geometrical surface area but in a very thin layer on the exterior of the pellet, as observed from the microscopic examination of a partially reacted pellet. Therefore, depending upon the void fraction of a pellet (probably also on the pore size and structure) the thickness of this layer and, consequently, the actual reacting area, changed in such a way as to result in a higher overall rate constant than could be accounted for by the simple dependence on the solid density, as given in Equation (7). It should be mentioned that Fruehan and Martonik (1973) in the chlorination of iron and nickel oxides, and also Costa and Smith (1971) in the hydrofluorination of uranium dioxide, reported similar behavior but with a higher porosity dependence than in the present case. It should also be pointed out that the value of the activation energy did not change with the void fraction in the range studied here, indicating, therefore, that it should be representing an intrinsic activation energy. In this respect, Fahim and Ford (1976), in the reduction of cobalt sulfide in nonporous powder and porous pellet forms, also found the same activation energy for both cases, although in the latter a diffuse reaction front was observed and consequently a higher rate constant was obtained.

Influence of Pellet Diameter: All of the previous results were based on a pellet diameter of 0.671 cm. To evaluate the influence of the diameter on the overall rate constant, three other diameters were studied, giving a range diameter from 0.494 to 1 cm. The porosity varied somewhat but could be corrected for by plotting the results as shown in Figure 10, in which K in the ordinate is multiplied by $(1 - \epsilon)^2$, as derived from Equation (31). The particle temperature was in every case lower than 1 950°K. As indicated by the slope of nearly unity, the overall rate constant was inversely proportional to the diameter, as predicted by the theoretical analysis, Equation (7), for chemical reaction control.

Influence of Chlorine Concentration: The effect of chlorine partial pressure on the overall rate constant was studied on pellets of two different porosities (48.5 and 54.9%) and the same diameter (0.671 cm) by diluting the chlorine plasma with argon over a temperature range of 1 680° to 1 950°K. Typical results are shown in Figure 11. The slope is nearly unity. As previously noted, it can be shown that y_{Cl_2} and y_{Cl} are related by

$$y_{Cl_2} = y_{Cl}/(2 - y_{Cl}) \tag{32}$$

Rate Expression for Chemical Reaction Control (T<1 950°K): From the theoretical formation and the regression analysis of the experimental data, the following empirical expression for chemical control of the chlorination reaction is obtained:

$$1-(1-X)^{1/3} = 3.313 \exp(-12\,162/T) y_{Cl_2} (1-\epsilon)^{-2} D^{-1} t_r \tag{33}$$

Figure 12 compares the predictions of Equation (33) with the experimental values of t_r, including the effects of all the individual parameters discussed previously. The agreement is reasonable in view of the experimental complexities of the study.

Combined Chemical Reaction and Mass Transfer Control (T>1 950°K): As illustrated in Figure 8, Arrhenius plots of the experimental data indicate that above 1 950°K, gas film diffusion began to contribute some resistance. The theoretically derived Equation (23) predicts that

$$t = t_r + t_m \tag{34}$$

where t_r is the time required to reach a conversion X in the absence of mass transfer resistances as calculated from Equation (33), and t_m is the time required to reach the same conversion when the reaction is controlled purely by mass transfer as given by Equation (14).

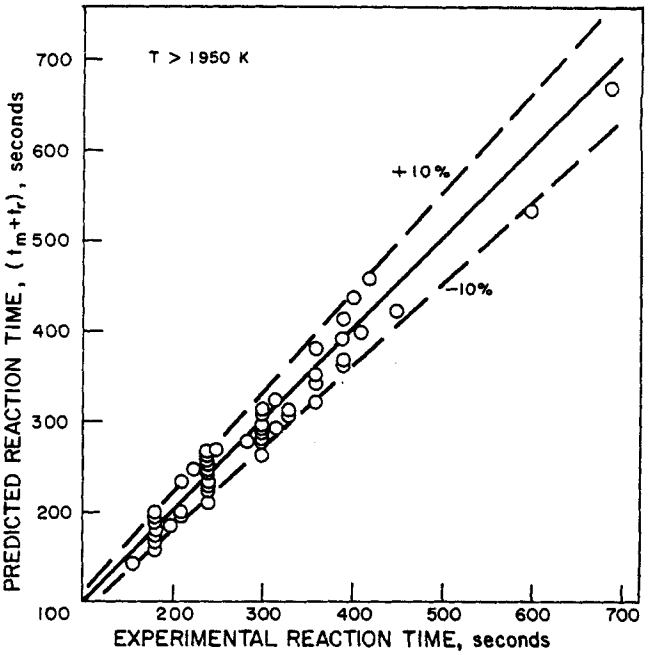

Figure 13. Comparison of experimental reaction time with values predicted by Equations (33) and (23). (Combined chemical reaction and mass transfer controlled region T>1 950K).

Biceroglu (1978) has carried out numerical calculations with the aid of a computer program described in detail in his thesis to predict the contribution of mass transfer according to Equation (14). Figure 13, in which the values of the experimental reaction time are plotted against the ones predicted for the same conversions in the region of the combined resistances, shows that the theoretical formulation agrees reasonably well with the experimental results.

ACKNOWLEDGMENT

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NOTATION

c	= total gas concentration (moles per unit volume)
D	= diameter of spherical reacting particle
D_{AB}	= binary diffusion coefficient of mixture of two components A and B
D_{ij}	= binary diffusion coefficient for the components i and j
D_{im}	= effective binary diffusion coefficient of component i in mixture
D_m	= effective diffusion coefficient of chlorine
E	= activation energy
f	= concentration function
H_{Cl_2}	= molar enthalpy of gaseous chlorine (calories per mole)
K	= overall rate constant
k	= Boltzmann's constant
K_E	= equilibrium constant
k_m	= mass transfer coefficient for chlorine
k_{mi}	= mass transfer coefficient of component i [Equation (10)]
k_s	= surface reaction rate constant
M	= molecular weight
N	= rate of reaction (moles of chlorine per unit time, per unit surface area)
n	= total number of gaseous components
N_i	= molar flux of component i

N_{Re} = Reynolds number
N_{Sc} = Schmidt number
N_{Sh} = Sherwood number
P = pressure
P_R = ratio of power at the nozzle exit to the inlet (plate) power
R = initial radius of spherical particle
r = radius of shrinking spherical particle
S_R = ratio of swirl to radial gas in RF torch
T = temperature
t = reaction time
T^* = dimensionless temperature, $T/(\epsilon/k)$, Equation (26)
t_m = reaction time under mass transfer control
T_N = nozzle exit gas temperature
t_r = reaction time under chemical reaction control
U = gas velocity
U_N = nozzle exit gas velocity
X = fraction of solid reactant reacted at time t
y = mole fraction of gaseous component
y_{Cl_2} = mole fraction of molecular chlorine
y_{Cl} = atomic chlorine concentration in bulk gas
y_{Cl_e} = atomic chlorine concentration in equilibrium at surface
y_{Cl_s} = atomic chlorine concentration at surface
y_{is} = mole fraction for component i at surface [Equation (10)]
y_{io} = mole fraction for component i in bulk gas [Equation (10)]

Greek Letters

α = constant defined by Equation (15)
ϵ = void fraction; also Lennard-Jones parameter
ψ = mixture viscosity parameter as defined by Equation (28)
Ω_D = collision integral for diffusion
Ω_v = collision integral for viscosity
ρ = density of fluid
ρ_s = molar density of reacting solid
σ = Lennard-Jones parameter
μ = viscosity

Subscripts

e = equilibrium
i, j = components i, j
mix = mixture
0 = bulk fluid
s = surface

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Simultaneous Melting and Freezing in the Impingement Region of a Liquid Jet

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An experimental investigation of an impinging water jet freezing on a melting solid surface has been carried out. Attention was focused on the stagnation region of an axisymmetric jet. In the experiment, a water jet was directed upward against the lower end of a meltable rod, having a diameter about twice that of the jet orifice. Solid octane (m.p.—56.5°C) and solid mercury (m.p.—38.9°C) served as the meltable materials. A laminar-axisymmetric flow model was developed to describe melting heat transfer in the presence of jet solidification within the impingement region. Measurements of the melting rate and conditions for the onset of jet solidification were found to agree quite well with the values predicted with this model.

SCOPE

There is extensive literature on fluid convection problems involving phase changes that pertain to either a warm liquid flowing over a melting surface or the solidification of a molten stream on a cooled wall. However, this mutually exclusive situation is not always the case. If the molten stream and the wall are different materials of immiscible liquids, with the fusion temperature of the hot flowing material exceeding that of the wall material, melting of the wall and freezing of the flow can take place simultaneously. An example, which is important to fast reactor safety research, is the melting of solid steel (m.p. 1 410°C) immersed in a flow of molten ceramic UO_2 (m.p. 2 850°C). An important conclusion arising out of past theoretical and experimental work on this problem is that the steel melting rate is controlled by a frozen layer (or crust) of UO_2 which floats on the steel melt.

An investigation of frozen crust behavior which yielded results of qualitative interest for our present purposes is that of Epstein (1977). In this work, a linear stability analysis was employed to study the mechanical behavior of a growing crust on an underlying lighter melt layer in a gravity field. The analysis compared well with experimental observations for low melting material pairs. A notable result was that a ceramic UO_2 crust growing on melting steel was predicted to be stable against buoyancy forces. Further evidence for the existence of a protective crust has been found by injecting hot Freon 112A

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