NOTATION

c = local concentration
c_0 = inlet concentration
D = molecular diffusivity
f = Fanning friction factor
k = reaction rate constant
K = consistency index
m = reaction order
n = flow behavior index
r = radial coordinate
R = radius of the tube
Re = Reynolds number
Sc = Schmidt number
Sc_t = turbulent Schmidt number, ϵ/ϵ_D
u = time-averaged local axial velocity
u_* = friction velocity, $\sqrt{\tau_w/\rho}$
u^+ = dimensionless time averaged local axial velocity, u/u_*
U_4^+ = function defined by Equation (14)
U_5^+ = function defined by Equation (15)
$<u>$ = bulk average velocity
W = dimensionless concentration
x = axial coordinate
y = radial distance from the wall, $R - r$
z = dimensionless radial coordinate

Greek Letters

α = total diffusivity, $D + \epsilon_D$
β = reaction parameter, $kc_0^{m-1}R/<u>$
ϵ = eddy momentum diffusivity
ϵ_D = eddy mass diffusivity
ν = non-Newtonian viscosity
ρ = density
τ_w = wall shear stress
ψ = function defined by Equation (7)
ξ = dimensionless axial coordinate, $k\,c_0^{m-1}\,x/<u>$

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Kinetics of Solid Phase Reactions

The kinetics of isothermal transformations or decompositions of solids proceeding through nucleation and subsequent growth is treated in the spirit of Avrami, eliminating, however, some of the internal contradictions of his treatment. Universal solutions of the dimensionless integral equation are computed. The theory is extended to nonisothermal systems and the resulting integral equations are solved numerically for the adiabatic case. It is shown that two kinds of catastrophic behavior can occur: one is characterized by slopes approaching infinity in the conversion vs. time curve following a long period of quiescent behavior; the other is characterized by a very short time for total conversion and by milder slopes in the conversion vs. time curve throughout the course of reaction. In the first kind the nucleation is mainly responsible for the catastrophic behavior, while in the second kind the rate of growth is responsible.

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SCOPE

There is a tendency in the chemical engineering literature to treat solid phase reactions in the same manner as those taking place in fluids. In reality they are more complex because they are initiated by the activation of preexisting germ nuclei which under suitable conditions begin to grow, generating the solid product. As a result the rate of solid state reactions is influenced by the rate of nucleation as well as by the rate of growth of the nuclei. Since many solid state reactions, such as the decomposition of dolomite, magnesium hydroxide, nickel oxalate, mercury fulminate, heavy-metal styphnates, metallic azides, etc. are of importance, a study is undertaken here from the point of view of nucleus formation and growth. The transformation of a germ nucleus to a growth nucleus and the process of growth are activated processes (Young, 1966; Turnbull, 1956; Turnbull and Cohen, 1958). In the present paper it is assumed that nucleation occurs by first-order kinetic law and a growth rate introduced by Turnbull and Cohen (1958) is employed. Theoretical work concerning solid phase reactions has been carried out (Avrami, 1940; Young, 1966) under the assumption of isothermal conditions, using an approach which is not free of internal contradictions. Besides, the isothermal assumption is suitable only for reactions with a small heat effect. The scope of the present paper is to develop a theory free of interal contradictions for the isothermal case and to extend it to the nonisothermal conditions, in particular to those cases in which because of a large heat effect the reaction results in explosion.

CONCLUSIONS AND SIGNIFICANCE

The kinetics of solid state reactions are treated here taking into account the nucleation of the new phase and the growth of the nuclei. The resulting equation is solved numerically for the isothermal case. Universal curves of the fractional decomposition are presented as a function of a dimensionless time and a dimensionless group containing the growth rate and the rate constant for the nucleation process. For the nonisothermal case the same equation is modified to account for the heat effect and is coupled with the appropriate heat balance.

For all the values of the dimensionless group which are of physical interest, the kinetics of the isothermal case is described by a single curve (Figure 2) and a single equation [Equation (37)]. For the adiabatic case these equations are solved numerically and the effect of the parameters of physical interest (such as heat of reaction, energies of activation for nucleation and for growth, and the frequency factor for nucleation) on the kinetics is studied. Depending upon the values of various parameters, in particular upon the energies of activation and the heat of reaction, two kinds of explosion are identified. One is characterized by steep slopes in the decomposition vs. time curve following a long period of slow reaction, the other by milder slopes and very short times needed for total decomposition. For the first kind of explosion nucleation is mainly responsible, while for the second kind the rate of growth is mainly responsible. The main conclusion is that nucleation has significant effects on reactions in the solid state and therefore by controlling them by pretreatment procedures we can control the reaction kinetics.

The importance of phase change phenomena in engineering has prompted extensive experimental and theoretical studies of reactions of the type

$$A\ (\text{solid}) \rightarrow B\ (\text{solid})$$

The results of these studies apply equally well to solid decompositions of the type

$$A\ (\text{solid}) \rightarrow B\ (\text{solid}) + C\ (\text{gas})$$

provided the gas decomposition product is immediately removed from the site of reaction. Examples of reactions of the first kind are the various transformations in steels, such as the austenite-pearlite or the austenite-bainite transitions (Desch, 1934; Johnson and Mehl, 1939). Examples of reactions of the second kind are the decomposition of metallic azides, heavy-metal styphanates, oxalates, etc. (Young, 1966).

According to many theoretical and experimental studies (Avrami, 1941; Christian, 1965; Desch, 1934; Kolmogorov, 1937; Russell, 1970), the two kinds of reactions mentioned above are initiated by germ nuclei which preexist in the old solid phase. Such nuclei may consist of foreign particles, adsorbed layers of product, or embryos of the new solid phase. Under suitable conditions these germ nuclei give rise to macroscopically observable growth nuclei which are responsible for the appearance of the solid product.

The transformation of a germ nucleus to a growth nucleus is an activated process. In general, the macroscopic reaction can be considered as the combination of two basic processes, nucleus formation and subsequent growth. The phenomenon of formation of growth nuclei from the germ nuclei has been investigated by many workers. Young (1966) presents a comprehensive summary of the most important nucleation kinetic laws. In the present study it is assumed that nucleation occurs by a first-order kinetic law; however, the equations which are derived can be modified to accommodate any nucleation law of interest. Many investigators (Turnbull, 1956; Wischin, 1939; Young, 1966) consider the process of growth as an Arrhenius type activated process, while others (Göler and Sachs, 1932; Johnson and Mehl, 1939) simply consider the rate of growth to be a constant. In the present study a growth rate introduced by Turnbull and Cohen (1958) is employed.

Most of the work on solid phase reactions was carried out under the assumption of isothermal conditions. This assumption often is suitable for reactions with a small heat effect, for example, phase transformations in metals; however, the assumption is not valid for exothermic decompositions with large heat effects. The object of the present study is to develop a satisfactory theory for both the isothermal and the nonisothermal case. In particular, the results for the nonisothermal case will be extended to the case where, due to a large heat effect, the reaction results in an explosion.

The phenomenon of explosion in exothermic decompositions has been observed by numerous investigators.

Garner and Hailes (1933), in an experimental study of the thermal decomposition of mercury fulminate, found that the reacting system explodes if heated above a critical temperature. Tompkins and Young (1957) observed that the decomposition of the anhydride of barium styphnate monohydrate proceeds smoothly for temperatures in the range of 269 to 308°C, while for temperatures above this range explosion occurs after about 45% decomposition for whole crystals. The term *explosion* is used in the present calculations in a loose sense to denote catastrophic behavior of the reactions. This behavior is characterized either by nearly infinite slope in the V vs. t curve following a long period of slow reaction, or by very short times needed to accomplish total conversion.

DERIVATION OF THE GOVERNING EQUATIONS

Isothermal Case

According to Avrami (1939, 1940, 1941) the reacting system initially contains N_0' germ or *potential* nuclei per unit volume. As reaction takes place these potential nuclei are depleted in two different ways: (1) by activation and subsequent growth and (2) by incorporation into growth nuclei before activation occurs. Assuming the depletion in the first of the above mentioned ways obeys a simple first-order kinetic law and taking into account that the depletion by the second way is $(N'/(1-V))dV/dt$, the following balance on the potential nuclei N' can be written:

$$\frac{dN'}{dt} = -kN' - \frac{N'}{1-V}\frac{dV}{dt} \tag{1}$$

According to Avrami (1939) and others (Becker, 1938; Borelius, 1938), k is of the form

$$k = \mu \exp\left\{-\frac{Q + A(T)}{RT}\right\} \tag{2}$$

Even though theoretical calculations of $A(T)$ have been carried out (Becker, 1938; Borelius, 1938), it is more convenient to consider the sum $Q + A(T)$ as an activation energy.

Equation (1) can be integrated directly to obtain the number of potential nuclei present at time t. The result is

$$N' = N_0' \exp(-kt)(1-V) \tag{3}$$

The rate of appearance of growth nuclei at time t thus becomes

$$dN/dt = kN' \tag{4}$$

Substituting for N' from (3), Equation (4) becomes

$$dN/dt = kN_0' \exp(-kt)(1-V) \tag{5}$$

Assuming spherical growth nuclei and a constant growth rate expressed by

$$\frac{dr}{dt} = G \tag{6}$$

nuclei activated at some previous time z have at time t a radius

$$r = G(t-z) \tag{7}$$

and therefore a volume

$$v = \frac{4}{3}\pi G^3 (t-z)^3 \tag{8}$$

The volume of the new solid phase, considered as the sum of the volumes of all growth nuclei, can then be written in the form

$$V(t) = \int_0^t \left(\frac{dN}{dt}\right)_{t=z} v(z)\,dz \tag{9}$$

or, after substituting for dN/dt and $v(z)$ from Equations (5) and (8), respectively,

$$V(t) = K\int_0^t \exp(-kz)(t-z)^3[1-V(z)]\,dz \tag{10}$$

where

$$K = (4/3)\pi G^3 k N_0' \tag{11}$$

The assumption of spherical nuclei is not valid in the later stages of the reaction because the space formerly occupied by the initial phase cannot be filled completely with spheres. Nevertheless, it will be assumed that the equations apply to complete conversion.

Equation (10) is a Volterra integral equation of the second kind. To solve this equation, Avrami introduced the idea of an extended volume defined as the total volume of all nuclei, including overlapping regions and also including fictitious growth nuclei that would have been formed if the potential nuclei lost due to incorporation into growth nuclei were activated and allowed to grow. The expression for the extended volume V_{ex} derived in a similar manner as the one for V is

$$V_{ex}(t) = K\int_0^t \exp(-kz)(t-z)^3\,dz \tag{12}$$

where K is defined by Equation (11). Following an intuitive argument, Avrami related V and V_{ex} by the expression

$$dV/dV_{ex} = 1 - V \tag{13}$$

resulting, after some manipulation, in the following explicit expression for V:

$$-\ln[1-V(t)] = 6K\left[\exp(-kt) - 1 + kt - \frac{(kt)^2}{2!} + \frac{(kt)^3}{3!}\right] \tag{14}$$

However, differentiation of Equations (10) and (12) according to Leibnitz's rule of differentiation for integrals, produces the following results:

$$\frac{dV}{dt} = 3K\int_0^t \exp(-kz)(t-z)^2[1-V(z)]\,dz \tag{15}$$

and

$$\frac{dV_{ex}}{dt} = 3K\int_0^t \exp(-kz)(t-z)^2\,dz \tag{16}$$

Combining Equations (15) and (16) gives

$$\frac{dV}{dV_{ex}} = \frac{\int_0^t \exp(-kz)(t-z)^2[1-V(z)]\,dz}{\int_0^t \exp(-kz)(t-z)^2\,dz} \tag{17}$$

This result and the one given by Equation (13) are contradictory. A second contradiction between Avrami's model and Equation (14) can be also detected. Given that potential nuclei once activated grow at a constant rate, it is obvious that the depletion of the old solid phase will be completed in a finite time. Equation (14) predicts, however, that $V(t)$ will be unity at infinity, a result that contradicts the assumption of constant growth rate. Consequently only Equation (10) is consistent with Avrami's model and, in order to obtain $V(t)$, this equation must be solved.

Introducing a dimensionless time τ defined by

$$\tau = kt \tag{18}$$

Equation (10) can be written as

$$V(\tau) = \psi(\tau) + \lambda \int_0^\tau \exp(-w)(\tau - w)^3 V(w)\, dw \tag{19}$$

with

$$\psi(\tau) = -\lambda [6\exp(-\tau) + \tau^3 - 3\tau^2 + 6\tau - 6] \tag{20}$$

and

$$\lambda = -\frac{4\pi G^3 N_0'}{3k^3} \tag{21}$$

Even though the possibility of solving such equations analytically cannot be ruled out (Tricomi, 1970), the complexity of the operations involved makes a numerical solution preferable. The numerical solution is given in the section on Results and Discussion.

The Nonisothermal Case

To keep the equations to be derived as simple as possible, the reacting system is assumed to be a perfect thermal conductor so that its temperature is always uniform. In addition, some of the more weakly temperature-dependent quantities are replaced with suitable average values over the range of temperatures of interest. The heat balance then becomes

$$\Delta H \frac{\rho}{M} \frac{dV}{dt} = \rho' c \frac{dT}{dt} + \frac{S}{V_s} h(T - T_a) \tag{22}$$

This equation is to be solved subject to the initial condition

$$T = T_0 \quad \text{at} \quad t = 0 \tag{23}$$

Equation (1) is still valid as the balance on potential nuclei. However, k must now be replaced by an expression of the form

$$k(t) = \nu \exp\left[-\frac{E}{RT(t)}\right] \tag{24}$$

Equation (1) can then be rewritten in the form

$$\frac{dN'}{dt} = -\nu \exp\left[-\frac{E}{RT(t)}\right] N' - \frac{N'}{1-V}\frac{dV}{dt} \tag{25}$$

which, after integration, becomes

$$N' = N_0' \exp\left\{-\nu \int_0^t \exp\left[-\frac{E}{RT(w)}\right] dw\right\} (1 - V) \tag{26}$$

When Equations (24) and (26) are substituted into Equation (4), the following expression for the rate of appearance of growth nuclei is obtained:

$$\frac{dN}{dt} = \nu N_0' \exp\left[-\frac{E}{RT(t)}\right] \exp\left\{-\nu \int_0^t \exp\left[-\frac{E}{RT(w)}\right] dw\right\} (1 - V) \tag{27}$$

Because the temperature no longer is constant, the assumption of constant growth rate can no longer be made. A more satisfactory expression for the growth rate which accounts for the temperature effect has been presented by Turnbull and Cohen (1958). This expression is

$$\frac{dr}{dt} = u(t)$$

$$= a_0 \nu_0 \exp\left[-\frac{\Delta G'}{RT(t)}\right] \left\{1 - \exp\left[\frac{\Delta G}{RT(t)}\right]\right\} \tag{28}$$

According to Turnbull and Cohen, the linear velocity of growth $u(t)$ just after nucleation depends strongly on the free energy of activation per mole $\Delta G'$ for the jumping of a particle across the new-old solid phase interface. The authors emphasize that the kinetic barrier $\Delta G'$ is not necessarily equal to or even of the same order of magnitude as the energy of activation for nucleus formation. The free energy of activation for growth may be much smaller than the kinetic barrier to nucleation because of the disorganization at the interface between the two phases or because of secondary processes which facilitate growth at the interface.

Applying Equation (28), the radius of a growth nucleus formed at time z is

$$r = \int_z^t u(x)\, dx \tag{29}$$

and therefore its volume (the assumption of spherical nuclei still being retained) is

$$v = (4/3)\pi \left[\int_z^t u(x)\, dx\right]^3 \tag{30}$$

Upon substituting Equation (28), this expression becomes

$$v = (4/3)\pi a_0^3 \nu_0^3 \left\{\int_z^t \exp\left[-\frac{\Delta G'}{RT(x)}\right] \left[1 - \exp\left(\frac{\Delta G}{RT(x)}\right)\right] dx\right\}^3 \tag{31}$$

When the expressions for dN/dt and v from Equations (27) and (31) are substituted into Equation (9), the following expression for $V(t)$ is obtained:

$$V(t) = \frac{4}{3}\pi \nu N_0' a_0^3 \nu_0^3 \int_0^t \exp\left[-\frac{E}{RT(z)}\right] [1 - V(z)] \times \left[\int_z^t \exp\left[-\frac{\Delta G'}{RT(x)}\right] \left\{1 - \exp\left[\frac{\Delta G}{RT(x)}\right]\right\} dx\right]^3 \times \exp\left\{-\nu \int_0^z \exp\left[-\frac{E}{RT(x)}\right] dx\right\} dz \tag{32}$$

Equation (32) and the previously derived heat balance, Equation (22), are the equations describing the nonisothermal case. In order to have both equations in integral form, Equation (22) can be integrated to give

$$\Delta H \frac{\rho}{M} V = \rho c (T - T_0) - \frac{S}{V_s} h T_a t + \frac{S}{V_s} h \int_0^t T dt \tag{22a}$$

where use was made of condition (23) and of the simplifying assumption $\rho' = \rho$. Finally, introducing the dimensionless quantities

$$\nu t = \tau \tag{33a}$$

$$\theta = \frac{T - T_0}{T_0} \tag{33b}$$

$$\theta_a = \frac{T_a - T_0}{T_0} \tag{33c}$$

$$E^* = \frac{E}{RT_0} \tag{33d}$$

$$\Delta G^* = \frac{\Delta G}{RT_0} \tag{33e}$$

$$\Delta G'^* = \frac{\Delta G'}{RT_0} \tag{33f}$$

and the dimensionless groups

$$\alpha = \frac{cT_0M}{\Delta H} \tag{34a}$$

$$\beta = \frac{ST_0hM}{V_s\nu\Delta H\rho} \tag{34b}$$

and

$$\gamma = \frac{4\pi a_0^3\nu_0^3N_0'}{3\nu^3} \tag{34c}$$

the system of Equations (32) and (22a) reduces to the following dimensionless form:

$$V(\tau) = \gamma \int_0^\tau \exp\left[-\frac{E^*}{1+\theta(s)}\right][1-V(s)] \times \left[\int_s^\tau \exp\left[-\frac{\Delta G'^*}{1+\theta(x)}\right] \left\{1-\exp\left[\frac{\Delta G^*}{1+\theta(x)}\right]\right\} dx\right]^3 \times \exp\left\{-\int_0^s \exp\left[-\frac{E^*}{1+\theta(x)}\right] dx\right\} ds \tag{35}$$

$$V(\tau) = \alpha\theta(\tau) - \beta\theta_a\tau + \beta\int_0^\tau \theta(s)\, ds \tag{36}$$

Equations (35) and (36) describing the nonisothermal case, form a system of coupled integral equations. Because of its complexity this system can be solved by numerical methods only. The numerical results are discussed in the next section.

RESULTS AND DISCUSSION

Isothermal Case

Equation (19) was solved numerically by successive approximations. The results are plotted in Figure 1. The computations show that as the absolute value of λ increases, the curves of dimensionless volume vs. the normalized dimensionless time τ/τ_{max} become very close to each other and, for large enough absolute values of λ, superimpose. Figure 2 demonstrates that the values of λ for which the curves of Figure 1 have been computed lie entirely within the region of asymptotic behavior. The same is true for all values of λ consistent with reported values (Russell, 1970; Young, 1966) of the parameters k, N_0', and G that appear in the definition of λ, Equation (21). In the region of asymptotic behavior the maximum dimensionless time τ_{max}, that is, the dimensionless time that is required for completion of the reaction, plotted against λ leads to the simple linear expression

$$\log_{10}\tau_{max} = 0.1525 - 0.25\log_{10}(-\lambda) \tag{37}$$

This expression is valid in the range $-10^{15} \leqq \lambda \leqq -10^9$ where computations have been performed, but it is expected to hold for all values of λ below -10^9.

Nonisothermal Case

The system of Equations (35) and (36) was solved numerically by successive approximations. The values of the parameters were taken as $c = 0.235$ cal/g°K, $T_0 = T_a = 500$°K, $M = 221.38$, $\rho = 2.936$ g/cm^3, $N_0' = 10^{17}$ cm^{-3}, $a_0 = 5 \times 10^{-8}$ cm, $\nu_0 = 10^{12}$ s^{-1}. The last two values were reported (Turnbull and Cohen, 1958); the density ρ and the molecular weight M are the values for barium azide. In the computations only the adiabatic case ($h = 0$) was considered. This leads to a significant simplification of an otherwise complex computation. The simplification is valid only when the heat losses are negligibly small compared with the heat effect due to the reaction, however.

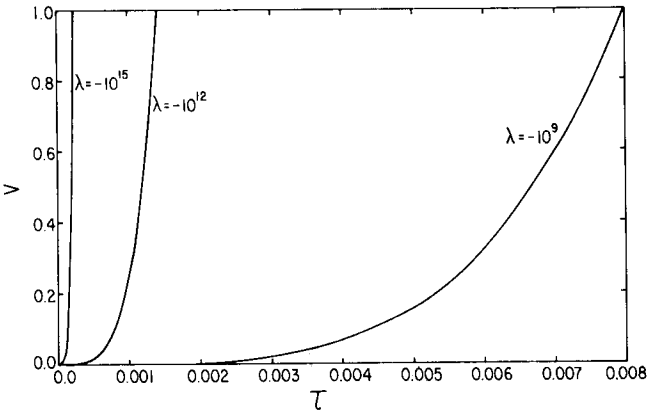

Fig. 1. The dimensionless volume V as a function of the dimensionless time τ for various values of λ.

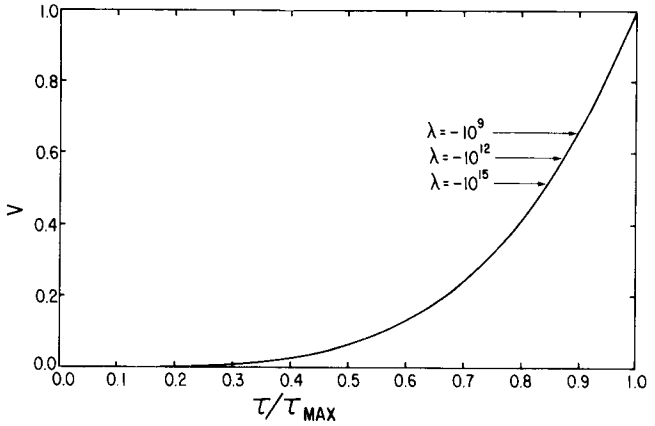

Fig. 2. The dimensionless volume V as a function of the normalized dimensionless time τ/τ_{max} for various values of λ.

Under the assumption of adiabatic conditions Equation (36) reduces to the form

$$V(\tau) = \alpha\theta(\tau) \tag{38}$$

which indicates that, in the adiabatic case, the dimensionless temperature θ behaves like the dimensionless volume V. Therefore, all observations made on V apply equally well to θ.

The effect of heat of the reaction ΔH is shown in Figure 3. The very large slopes close to the endpoints of the curves corresponding to $\Delta H = 5$ and 10 kcal/mol indicate catastrophic behavior. The presence of a period of slow reaction prior to explosion is characteristic. The length of this period depends on the choice of the initial temperature T_0. The curves in Figure 3 show that a relatively substantial increase in the value of ΔH only moderately shortens the time needed for total conversion. However, the larger the value of ΔH, the larger is the part of the total decomposition that takes place instantaneously.

The results obtained from the numerical solution of the system of Equations (35) and (36) are supported by the experimental observations of Garner and Hailes (1933) in their study of the decomposition of mercury fulminate. They reported that the reaction is characterized by an

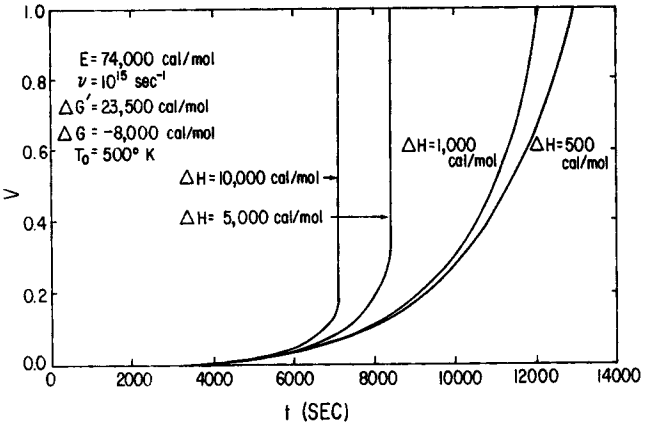

Fig. 3. Dependence of dimensionless volume V on time t for various values of heat of reaction ΔH. Curves for $\Delta H = 5000$ and 10000 cal/mol exhibit high slopes characteristic of explosive behavior.

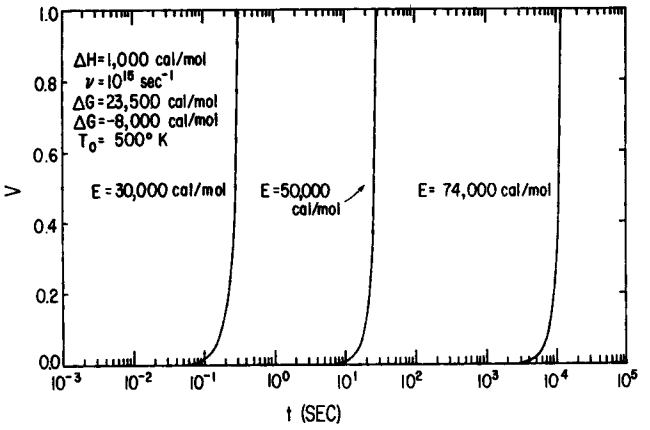

Fig. 4. The dimensionless volume V as a function of time t for various activation energies of nucleation E.

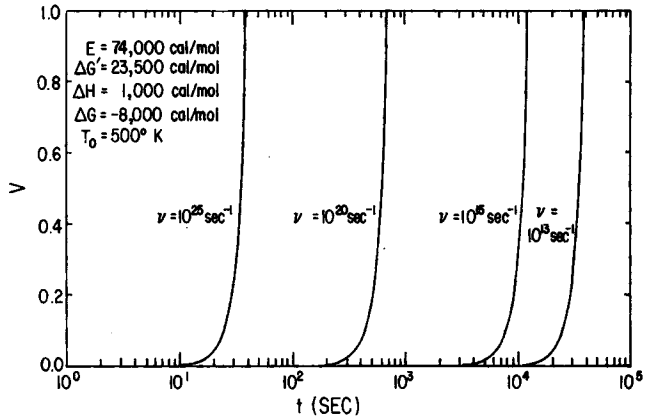

Fig. 5. The dimensionless volume V as a function of time t for various frequency factors ν.

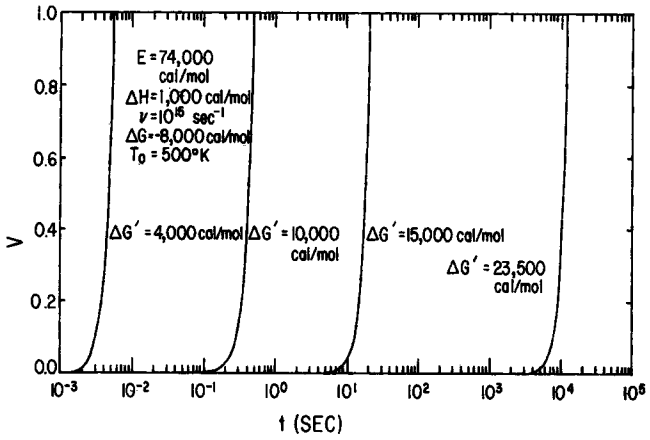

Fig. 6. The dimensionless volume V as a function of time t for various free energies of activation for growth $\Delta G'$.

initial quiescent period followed by a rapid acceleration of the decomposition. If heated above a critical temperature (228°C), the reacting system explodes shortly after the end of the quiescent period. By plotting the pressure of the released gas (mainly CO_2) versus time they obtained curves which are very similar to those in Figure 3.

The growth rate is affected by the heat effect ΔH because the temperature is increased. It is important to observe that the growth rate is low and nearly constant during the entire course of reaction for the conditions considered here. The highest value 0.104×10^{-3} cm/s was reached for $\Delta H = 10{,}000$ cal/mol. Thus the main factor which accounts for the particular behavior observed here is the nucleation process. The very high value of the activation energy for nucleation (74,000 cal/mol) provides additional support for this argument. It appears, therefore, that after an initial long slow period the nucleation rate suddenly reaches catastrophically large values.

The importance of nucleation related effects on reaction kinetics for solids suggests the use of various pretreatments. For example, such pretreatments as annealing or pre-irradiation, which affect the nucleation process, can alter the kinetic behavior of the reacting material.

The dimensionless forms of Equations (35) and (36) and the assumption of adiabatic conditions indicate that the effect of ΔH on the reaction kinetics is expressed through the dimensionless group α defined by Equation (34a). Thus the observations made in this section concerning the effect of ΔH on the reaction kinetics can be re-expressed in terms of each of the parameters appearing in Equation (34a). The fact that catastrophic behavior does not occur for low values of ΔH suggests that there exists a critical value for the dimensionless group α above which this kind of behavior is impossible. Based on the limited number of computations carried out, the critical value is about $\alpha = 20$. For values of α below this critical value, catastrophic behavior always occurs. Furthermore, the greater the departure from 20 the more violent is the behavior.

The effect of the activation energy for nucleation E on the reaction kinetics is shown in Figure 4. It is worth noting that as the value of E decreases the time needed for completion of the reaction decreases dramatically. Thus for $E = 74{,}000$ cal/mol, $t_{max} = 0.12 \times 10^5$ s, while for $E = 30{,}000$ cal/mol, $t_{max} = 0.32$ s.

The effect of the frequency factor ν is shown in Figure 5. Figure 6 shows the effect of the activation energy for growth, $\Delta G'$. The slopes become smaller as $\Delta G'$ decreases from 23,500 cal/mol to 4,000 cal/mol, and at the same time the growth rate increases drastically from 0.64×10^{-5} cm/s maximum growth rate for $\Delta G' = 23{,}500$ cal/mol to 1035.47 cm/s for $\Delta G' = 4{,}000$ cal/mol. As a result the reaction time is drastically reduced. In the previous computations, the value of 23,500 cal/mol for $\Delta G'$ corresponds to the value reported for barium azide by Wischin (1939), while the value of 4,000 cal/mol is typical for a growth process controlled by diffusion in the solid state.

Figure 7 shows the result of a computation carried out for the following values of nucleation and growth parameters: $E = 30{,}000$ cal/mol, $\nu = 10^{25}$ s^{-1}, $\Delta G' = 4{,}000$ cal/mol. The milder slopes along the computed curve suggest

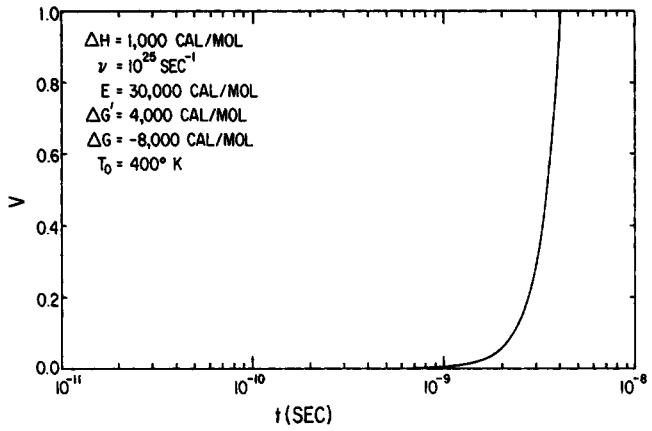

Fig. 7. The dimensionless volume V as a function of time t during explosions of the second type.

departure from the explosive character of the curves shown in Figure 3. However, according to Figure 7, the maximum time needed for completion of the reaction is very small (0.4×10^{-8} s) and this suggests explosive behavior. It follows that a second kind of explosion is possible for the reactions under consideration. This second kind of explosion is characterized by a very short time needed for completion and by the absence of very steep slopes along the V vs. t curve. The large value of the computed growth rate (410.85 cm/s at completion) suggests that growth phenomena dominate during this second kind of explosion.

CONCLUSIONS

Isothermal Case

The existence of an asymptotic solution, valid for all values of λ of physical interest, allows the kinetics to be adequately described for the isothermal case by Figure 2 and Equation (37) only.

Nonisothermal Case

The heat effect accompanying most reactions has a pronounced effect on their kinetics. Under certain circumstances the heat released results in an explosion. Two kinds of explosion are identified: the first is characterized by the appearance of near infinite slopes in the V vs. t curve after an initial period of slow reaction; the second is characterized by a very short time required for total decomposition without the appearance of very steep slopes in the V vs. t curve. The rate of nucleation is mainly responsible for the first type of explosion while the rate of growth is mainly responsible for the second type.

Note added in proof: A recent treatment by the authors of the non-adiabatic case has shown that, for the values of the parameters used in the present paper, the adiabatic approximation is valid for particles larger than about 0.1 cm.

NOTATION

$A(T)$ = work per mole required to form a growth nucleus at temperature T
a_0 = interatomic spacing
c = heat capacity
E = activation energy for nucleus formation
E^* = dimensionless activation energy for nucleus formation defined by Equation (33d)
G = constant growth rate of the isothermal case
h = heat transfer coefficient
k = first-order rate constant for potential nucleus activation
K = constant defined by Equation (11)
M = molecular weight of the new solid phase
N' = number of potential nuclei per unit volume of the old phase at time t
N_0' = number of potential nuclei per unit volume of the old phase at time $t = 0$
N = number of growth nuclei per unit volume of the old phase at time t
Q = constant energy of activation for nucleus formation
R = gas constant
r = radius of a growth nucleus at time t
S = external surface of the reacting system
t = time
t_m = maximum time required for the completion of the reaction
T = absolute temperature
T_a = ambient temperature
T_0 = initial temperature of reactant
u = temperature dependent growth rate
V = volume of the new phase per unit volume of the old phase
v = volume of a growth nucleus
V_{ex} = extended volume
V_s = total volume of reacting system
z = time

Greek Letters

α = dimensionless group defined by Equation (34a)
β = dimensionless group defined by Equation (34b)
γ = dimensionless group defined by Equation (34c)
ΔH = heat of reaction per mole of the new phase
$\Delta G'$ = free energy of activation per mole for nucleus growth
$\Delta G'^*$ = dimensionless free energy of activation for growth defined by Equation (33f)
ΔG = change in chemical potential per mole of new phase accompanying the macroscopic transformation
ΔG^* = dimensionless form of the chemical potential change accompanying the macroscopic transformation defined by Equation (33e)
θ = dimensionless temperature defined by Equation (33b)
θ_a = dimensionless ambient temperature defined by Equation (33c)
λ = dimensionless group defined by Equation (21)
ν = frequency factor
ν_0 = vibrational frequency at the interface of the new-old phase
ρ = density of the new phase
ρ' = density of the reacting mixture
τ = dimensionless time defined by Equations (18) and (33a) for the isothermal and nonisothermal cases, respectively
τ_{max} = maximum dimensionless time required for completion of the reaction
ψ = dimensionless function defined by Equation (20)

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Oxygen Reduction at an Anodically Activated Platinum Rotating Disk Electrode

The reduction of oxygen in neutral saline solution and in seawater was studied using the rotating disk electrode (RDE). The objective was to test the applicability of the RDE as a primary reference standard for the measurement of oxygen concentrations below 0.1 ppm in seawater. Limited success was achieved with an activated platinum electrode. A gold electrode was less effective. If one postulates that the 2-electron reduction of oxygen at an activated RDE is rapid, it appears that little or no 4-electron reduction occurs and that the subsequent 2-electron reduction or catalytic decomposition of hydrogen peroxide is relatively slow. The anodic activation procedure developed appears to impart a transient catalytic activity to the electrode surface for the peroxide reaction(s).

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SCOPE

Dissolved oxygen is responsible for much of the corrosion experienced in desalination plants and must be substantially removed to prolong equipment life. Oxygen sensors are required to monitor this operation. Most sensors require calibration initially and recalibration at irregular intervals because of drift. A stable sensor needing no calibration and having high sensitivity would be of considerable practical value. A rotating disk electrode (RDE) operating at limiting current is in theory capable of serving as a primary reference standard, failing only if competing electrode reactions can occur or if the kinetics of one of the steps of the desired electrode reaction is insufficiently fast. In this work the reduction of oxygen at concentrations down to 0.07 ppm in neutral saline solutions and in seawater was studied using an RDE device with platinum and gold as electrode materials.

CONCLUSIONS AND SIGNIFICANCE

An aged platinum RDE does not exhibit a well-defined limiting-current plateau when oxygen is reduced in neutral saline solution or seawater. Instead, the voltage-current curve has an indistinct inflection point in the potential range for oxygen reduction (see Figure 1). The current at that point is irreproducible, varies with time, and is less than predicted for the 4-electron reduction of oxygen. An empirical activation procedure was developed which yields good limiting-current behavior for oxygen reduction in air-saturated neutral saline solution and seawater. Currents were within ±2% of calculated values at a rotational speed of 600 rev./min. However, at oxygen concentrations of about 0.1 ppm an inflection point, rather than a true plateau, was observed. In neutral saline solution this inflection point was quite close to the calculated value of the limiting current (see Figure 2). In seawater it was about 25% high. Further work to determine long-term stability would be required before this system could be used as a primary standard.

A reaction model was developed to interpret the variation of limiting current with rotational speed for an activated RDE. It was postulated that the 2-electron reduction of oxygen to peroxide is rapid. Analysis of the data in terms of this model indicates that little or no 4-electron reduction of oxygen occurs and that either 2-electron reduction or catalytic decomposition of hydrogen peroxide is the second, relatively slow step. The activation procedure appears to impart a transient catalytic activity to the electrode surface for this second step. The value of the reaction-rate constant for H_2O_2 reduction at an activated electrode was calculated from limiting current-vs.-rotational speed data. The value found for neutral saline solutions is reproducible and within about a factor of three of constants found in the literature for acidic and basic solutions.

Gold was found to be less satisfactory than platinum as an electrode material.