NOTATION

B = bottom product volume
D = downflow internal stream volume in continuous systems
F = feed stream volume
g_i = solid phase concentration of species i in equilibrium with fluid; if not subscripted, then it refers to species 1
$h(y_D)$ = function, Equation (7), relating concentrations before and after temperature change
i, j = names of solutes
$K_j^i(\theta)$ = binary selectivity coefficient between species i and j at temperature θ, see Equation (8)
n = number of components in a multicomponent system
R = reflux stream volume in continuous system
T = top product volume
TM_i = total moles of species i in a batch system; if not subscripted, it refers to species 1
U = upflow stream volume in continuous system
x = axial position in sorbent bed with $x = 0$ at the bottom and $x = 1.0$ at the top
y_i = fluid phase concentration of species i; if not subscripted, it refers to species 1
$\bar{y}_i$ = solid phase concentration of species i; if not subscripted, it refers to species 1

Greek Letters

α = number of column void volumes displaced per half cycle
γ = number of column void volumes in reservoirs not displaced
δ_i = fraction of sorbent bed length; if not subscripted, it refers to species 1
θ = temperature
ν = ratio of molar capacity of sorbent to molar capacity of fluid on an equal basis, for example, per unit volume of bed
σ = slope of a characteristic in $x - \tau$ plane
τ = time

Subscripts and Superscripts

B = bottom reservoir or product
D = downflow or stream D
F = feed stream
R = reflux stream
s = shock
T = top reservoir or product
U = upflow or stream U
1,2,... = component number
$*$ = leading edge of expansive wave

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Manuscript received June 24, 1975; revision received November 19 and accepted November 21, 1975.

Solid Phase Reactions Under Nonadiabatic Conditions

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The kinetics of solid phase reactions proceeding through nucleation and subsequent nucleus growth is treated by taking into account heat losses by convection and radiation from the reacting solid. A critical initial reaction temperature dependent upon particle size is identified below which the reaction decays and above which explosion can occur.

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SCOPE

Preexisting theoretical treatments of chemical reactions in solids accompanied by heat effects and losses (Frank-Kamenetskii, 1969) have put the primary emphasis on heat transfer, while the role of chemical kinetics has received minor attention. As a result, simplified zeroth- or first-order rate expressions, valid only for reaction in fluids, have been used to describe the chemical kinetics of reactions occurring in the solid phase. In reality, solid phase reactions are much more complex than reactions in fluids because they are initiated by the activation of preexisting germ nuclei which, under suitable conditions, begin to grow, generating the solid product.

The scope of the present paper is to develop a theory of solid phase reactions which accounts for the effects of nucleation, nucleus growth, and heat transfer on the course of the reaction. This is accomplished by extending the theory of nonisothermal solid phase reactions occurring under adiabatic conditions [Ruckenstein and Vavanellos (1975)] to account for radiative and convectional heat losses from the reacting solid. The incorporation of the heat loss terms in the fundamental equations makes it possible to interpret the experimentally observed effect of particle size on thermal explosions (Bowden and Singh, 1954; Bowden and Yoffe, 1958; Groocock, 1958; Young, 1966; Chaudhri and Field, 1975) in such important reactions as the thermal decomposition of metallic azides, fulminates, oxalates, styphnates, etc. Explosion means that the largest part of the conversion occurs in a very short time.

CONCLUSIONS AND SIGNIFICANCE

The kinetics of solid phase reactions occurring in combination with heat transfer is treated here, taking into account the effects of nucleation, nucleus growth, and reactant depletion on the reaction course. The theory predicts the existence of a critical initial reaction temperature, which depends on reacting particle size, below which the reaction decays and above which explosion can occur. It is further established that variations in the initial temperature and size of the reacting particle cause variations in reaction behavior between two limiting regimes: the adiabatic regime, characterized by independence of reaction kinetics on reacting particle size, and the nonadiabatic regime, characterized by pronounced size effects.

The fundamental equations are solved numerically for single crystals of parallelopiped shape. The computed dependence of the critical initial reaction temperature on crystal size proves that the incorporation of rate expressions accounting for nucleation and growth leads to a better agreement with experimental observations than the theories based upon zeroth-order kinetics. A study of the onset of explosion for reactions occurring in the regime of pronounced size effects establishes a critical value of the dimensionless group α below which explosion always takes place. This critical value, along with the corresponding value for explosion in the adiabatic regime (Ruckenstein and Vavanellos, 1975), allows the formulation of a criterion for thermal explosion in solid phase reactions.

In conclusion, the present theory represents an improvement over existing theories of solid phase reactions and thermal explosions (Frank-Kamenetskii, 1969) because of the incorporation of rate expressions corresponding to more realistic conditions under which a solid phase reaction occurs, that is, nucleation and subsequent nucleus growth. The rate of the overall process can be improved through modification (by various pretreatments such as irradiation, annealing, aging, etc.) of the rate of nucleation.

Reactions occurring in the solid state which evolve large amounts of heat have always been of engineering importance. In particular, the decomposition and resulting explosion of such compounds as metallic azides and fulminates, commercially used as primary solid explosives, have been the subject of numerous theoretical and experimental investigations. It is, therefore, important to develop an understanding of the kinetics of such reactions.

When a solid such as a metallic azide is heated to a high enough temperature it begins to decompose and eventually explodes. Although several mechanisms of explosion have been proposed (Bowden and Yoffe, 1952), it is believed that the explosion is usually thermal in its origin (Bowden and Singh, 1954). Furthermore, it has been observed (Bowden and Curton, 1949; Bowden and Williams, 1951; Chaudhri and Field, 1975) that the size of the decomposing crystal has a definite effect on the kinetics of decomposition, and that a critical size exists for explosion to occur at a particular temperature. It also has been observed (Bowden and Curton, 1949; Bowden and Williams, 1951; Groocock, 1958) that when such reactions are carried out in vacuum instead of air, the kinetic behavior is altered to the extent that size effects become insignificant.

The theory of thermal explosion in solids has been developed (Frank-Kamenetskii, 1969) by placing primary emphasis on the heat transfer, while the chemical kinetics has received little attention. Thus, the rate of reaction in the solid state has been described by simplified expressions valid for reactions in fluids. In reality, solid phase reactions are more complex because they are initiated by the activation, under suitable conditions, of preexisting germ nuclei which begin to grow generating the new phase (Young, 1966). Thus, the rate of solid state reactions depends on both the nucleation rate and the rate of growth of active nuclei.

In the present paper, a theory involving kinetic expressions accounting for the processes of nucleus activation and growth is developed by incorporating the heat losses from the reacting solid by convection and radiation in the treatment previously proposed by Ruckenstein and Vavanellos (1975) for the adiabatic case. It is then shown that the experimental facts described above can be explained and that quantitative results regarding critical conditions for reaction occurrence, and criteria for explosion, can be computed.

DERIVATION OF THE GOVERNING EQUATIONS

In order to account for heat losses due to radiation as well as convection, the heat balance for the whole system must be written in the form

$$\frac{\Delta H}{M}\rho\frac{dV}{dt} = \rho' c\frac{dT}{dt} + \frac{S}{V_s}h(T - T_a) + \frac{S}{V_s}\epsilon\sigma(T^4 - T_a^4) \tag{1}$$

Except for the last term which represents the heat losses due to radiation, the equation is the same as that given by Ruckenstein and Vavanellos (1975). The assumptions underlying the validity of Equation (1) can be summarized as follows:

1. During the reaction, the temperature of the reacting solid is uniform throughout, and its density and specific heat remain constant.
2. During the reaction, and up to the point of explosion, particle dimensions do not change significantly.

In what follows, the reacting solid is considered to be a single crystal placed on a supporting specimen boat and brought into a furnace of controlled temperature. Reaction is assumed to start after the temperature of the crystal becomes equal to the temperature of the furnace. The temperature of the furnace is assumed low enough and the heating time of the small crystal short enough that the reaction during this period of heating can be neglected. At the relatively high temperatures required for decomposition of the reacting crystal the gas released is assumed to produce a film between the crystal and the supporting specimen boat so that the crystal is effectively suspended (Groocock, 1958).

For the sake of simplicity, the crystals are assumed to be parallelopipeds of uniform length and width l and thickness a. In addition, the thickness is assumed to be much smaller than the crystal length and width. For the cases of interest, it can be shown (Chaudhri and Field, 1975) that the product of Grashof and Prandtl numbers is less than 10^{-5}. Under these conditions the heat transfer coefficient h is given by the expression $(hL/k) = 0.4$, with k being the thermal conductivity of air and L a characteristic length defined as $(1/L) = (1/L_v) + (1/L_h)$, with L_v and L_h being the appropriate pair of edge lengths of the convecting surface (Jakob, 1949). For the crystal shape considered here, two of the convecting surfaces have $L_v = L_h = l$ giving $L = l/2$, while the remaining four have $L_v = a$ and $L_h = l$ giving, under the assumption $a << l$, $L = a$. Thus the product hS in Equation (1) referring to all six convecting crystal surfaces of total area $4al + 2l^2$ becomes $hS = 4alh_1 + 2l^2h_2$. With $h_1 = 0.4k/a$ and $h_2 = 0.8k/l$, the expression for hS simplifies to $hS = 3.2lk$. This allows Equation (1) to be rewritten in the form

$$\frac{\Delta H}{M}\rho\frac{dV}{dt} = \rho'c\frac{dT}{dt} + \frac{3.2k}{al}(T - T_a) + \frac{2(l + 2a)}{al}\epsilon\sigma(T^4 - T_a^4) \quad (2)$$

where the expressions $4al + 2l^2$ and al^2 have been substituted for the area S and the volume V_s.

Equation (2) can now be integrated by using the initial condition

$$T = T_o \quad \text{at} \quad t = 0 \quad (3)$$

and the simplifying assumption $\rho = \rho'$ to give

$$\frac{\Delta H}{M}\rho V = \rho c(T - T_o) + \frac{3.2k}{al}\int_o^t (T - T_a)dt + \frac{2(l + 2a)\epsilon\sigma}{al}\int_o^t (T^4 - T_a^4)dt \quad (4)$$

By introducing the dimensionless quantities

$$\tau = \nu t \quad (5a)$$

and

$$\theta = \frac{T - T_o}{T_o} \quad (5b)$$

Equation (4) can be rewritten, after some algebraic manipulation, in the following dimensionless form

$$V(\tau) = \alpha\theta(\tau) + \beta\int_o^\tau [\theta(s) - \theta_a]ds + \delta\int_o^\tau \{4[\theta(s) - \theta_a] + 6[\theta^2(s) - \theta_a^2] + 4[\theta^3(s) - \theta_a^3] + [\theta^4(s) - \theta_a^4]\}ds \quad (6)$$

where the resulting dimensionless groups α, β, and δ are given by the expressions

$$\alpha = \frac{cT_oM}{\Delta H} \quad (7a)$$

$$\beta = \frac{3.2kT_oM}{\rho\Delta H al\nu} \quad (7b)$$

$$\delta = \frac{2(l + 2a)M\epsilon\sigma T_o^4}{\rho\Delta H al\nu} \quad (7c)$$

and the dimensionless constant θ_a by

$$\theta_a = \frac{T_a - T_o}{T_o} \quad (7d)$$

The volume V of the new solid phase per unit volume of the old phase is given by (Ruckenstein and Vavanellos, 1975)

$$V(\tau) = \gamma\int_o^\tau \exp\left[-\frac{E^*}{1 + \theta(s)}\right][1 - V(s)] \times \left\{\int_s^\tau \exp\left[-\frac{\Delta G'^*}{1 + \theta(x)}\right] \left\{1 - \exp\left[\frac{\Delta G^*}{1 + \theta(x)}\right]\right\} dx\right\}^3 \times \exp\left\{-\int_o^s \exp\left[-\frac{E^*}{1 + \theta(x)}\right]dx\right\} ds \quad (8)$$

where

$$\gamma = \frac{4\pi a_o^3\nu_o^3N_o'}{3\nu^3} \quad (9a)$$

$$E^* = \frac{E}{RT_o} \quad (9b)$$

$$\Delta G^* = \frac{\Delta G}{RT_o} \quad (9c)$$

and

$$\Delta G'^* = \frac{\Delta G'}{RT_o} \quad (9d)$$

Equations (6) and (8) describe the kinetics of a nonisothermal reaction in the solid state when heat losses due to both convection and radiation are taken into account. These equations form a system of coupled integral equations which, because of its complexity, can be solved by numerical methods only. In the present paper this system of equations was solved by the following successive approximation technique: initial functions $V_o(\tau)$ and $\theta_o(\tau)$ were chosen, then the sequence $\{V_n(\tau), \theta_n(\tau)\}$ was determined from the recurrence relations

$$V_n(\tau) = \gamma\int_o^\tau \exp\left[-\frac{E^*}{1 + \theta_{n-1}(s)}\right][1 - V_{n-1}(s)] \times \left\{\int_s^\tau \exp\left[-\frac{\Delta G'^*}{1 + \theta_{n-1}(x)}\right]\right.$$

$$\left\{ 1 - \exp\left[\frac{\Delta G^*}{1 + \theta_{n-1}(x)} \right] \right\} dx \Bigg\}^3$$

$$\times \exp\left\{ - \int_o^s \exp\left[- \frac{E^*}{1 + \theta_{n-1}(x)} \right] dx \right\} ds, \qquad n = 1, 2, 3, \ldots \qquad (10a)$$

and

$$\theta_n(\tau) = \frac{1}{\alpha} V_{n-1}(\tau) - \frac{\beta}{\alpha} \int_o^\tau [\theta_{n-1}(s) - \theta_a] ds$$

$$- \frac{\delta}{\alpha} \int_o^\tau \{4[\theta_{n-1}(s) - \theta_a] + 6[\theta^2{}_{n-1}(s) - \theta_a{}^2]$$

$$+ 4[\theta^3{}_{n-1}(s) - \theta_a{}^3] + [\theta^4{}_{n-1}(s) - \theta_a{}^4]\} ds \qquad n = 1, 2, 3, \ldots \qquad (10b)$$

The iterative scheme described above was continued until a certain (arbitrary) convergence criterion was met. The numerical results obtained in this manner are discussed in a later section.

QUALITATIVE ANALYSIS OF THE GOVERNING EQUATIONS

The first term on the right-hand side of Equation (10*b*) represents the adiabatic temperature of the system, and the next two terms account for heat losses due to convection and radiation, respectively. Considering, for the time being, heat losses by convection only, and writing the corresponding term in the form

$$L_c = \frac{\beta}{\alpha} I_c \qquad (11a)$$

with

$$I_c = \int_o^\tau [\theta(s) - \theta_a] ds \qquad (11b)$$

we can rewrite Equation (10*b*) in the form

$$\theta = \theta_{ad} - L_c \qquad (12a)$$

where

$$\theta_{ad}(\tau) = \frac{1}{\alpha} V(\tau) \qquad (12b)$$

Since $V \leq 1$, one can write

$$\theta_{ad} \leq \frac{1}{\alpha} \qquad (13)$$

Therefore, replacing $\theta - \theta_a$ by $1/\alpha$ in Equation (11*b*) provides an upper bound for I_c; that is

$$I_c < \frac{\nu t}{\alpha} \qquad (14)$$

Combining Equations (11*a*), (14), (7*a*), and (7*b*), we get

$$L_c < \frac{3.2kt}{al\rho c\alpha} \qquad (15)$$

The process is close to adiabatic conditions when

$$L_c << \theta_{ad} \qquad (16a)$$

By approximating θ_{ad} by $1/\alpha$ and L_c by $kt/al\rho c\alpha$, this inequality can be rewritten as

$$\frac{kt}{al\rho c} << 1 \qquad (16b)$$

In the event that L_c is of the same order as θ_{ad}, the transformation will proceed relatively slowly because the heat losses are comparable to the heat generated by reaction. If $L_c > \theta_{ad}$, cooling will occur, and the reaction will decay in time. Thus, the longest reaction time for nondecaying reaction will be obtained for $L_c = \theta_{ad}$. In view of Equations (16*a*) and (16*b*), this will happen when $kt/al\rho c$, which compares the heat losses to the heat accumulated in the particle, is sufficiently large. Thus, a critical time t_c can be evaluated as

$$\frac{kt_c}{al\rho c} \sim 1 \qquad (17)$$

corresponding to conditions of maximum deviation from adiabatic behavior. Because of the numerous approximations involved, Equation (17) provides only the order of magnitude of t_c.

A critical reaction temperature T_{o_c} can be defined as the temperature below which reaction decays due to the fact that $L_c > \theta_{ad}$. Because of the complexity of the fundamental equations, no simple algebraic relation for T_{o_c} can be derived. Its value can only be determined numerically by trial and error.

By introducing the reaction time $t_{\max}$, defined as the time needed for reaction to reach completion, a criterion of adiabatic behavior can be formulated as follows: if $t_{\max} << t_c$, the reaction takes place under nearly adiabatic conditions and the adiabatic solution presented earlier (Ruckenstein and Vavanellos, 1975) is valid; if, however, the inequality $t_{\max} << t_c$ is not satisfied, heat losses become significant and the adiabatic solution is no longer applicable.

In terms of the critical reaction temperature T_{o_c}, if the initial temperature T_o of the reacting solid satisfies $T_o >> T_{o_c}$, adiabatic behavior is obtained, otherwise significant deviations from adiabatic behavior occur.

In the case that only radiative heat losses are present, the following relations, derived from Equation (10*b*), are valid:

$$L_R = \frac{\delta}{\alpha} I_R \qquad (18a)$$

with

$$I_R = \int_o^\tau \{4[\theta(s) - \theta_a] + 6[\theta^2(s) - \theta_a{}^2]$$

$$+ 4[\theta^3(s) - \theta_a{}^3] + [\theta^4(s) - \theta_a{}^4]\} ds \qquad (18b)$$

and

$$\theta = \theta_{ad} - L_R \qquad (19)$$

Thus, by following the same procedure, a new expression for t_c, valid when heat is lost owing to radiation only, can be obtained.

When heat losses due to both convection and radiation are present, it can be seen that since $\alpha > 1$ for most cases of physical interest, I_c and I_R are of the same order. Furthermore, the ratio

$$\frac{\delta}{\beta} = \frac{2(l + 2a)\epsilon\sigma T_o{}^4}{3.2k} \qquad (20)$$

for most cases of interest has a small value (typically $\delta/\beta \simeq 0.07$). It is then apparent that the term L_R is small compared to L_c. Consequently, the qualitative results obtained earlier under the assumption of heat losses occurring by convection only are valid, even if heat losses by radiation are also present.

It follows directly from Equation (17) that since for a given reaction the values of the parameters ρ, c, and k are fixed, the value of t_c will depend solely on the values of a and l, that is, the size of the crystal.

In order to study the effect of crystal size on the reaction kinetics, it becomes clear from the previous arguments that

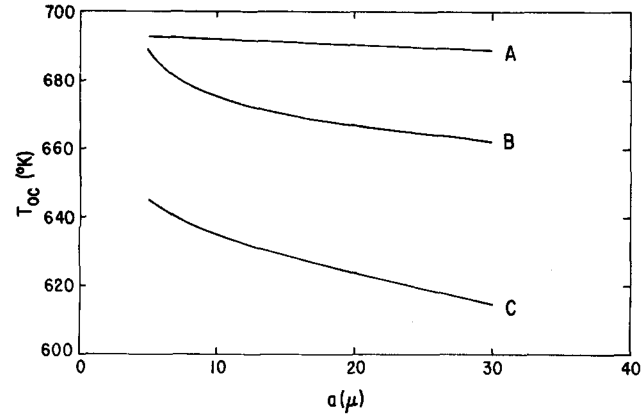

Fig. 1. Dependence of critical reaction temperature T_{o_c} on crystal thickness a. Curve A corresponds to zeroth-order kinetics and curve B to the experimental results of Chaudhri and Field (1975). Curve C was computed according to the present theory by using for the parameters the values $\Delta H = 1\,000$ cal/mole, $E = 74\,000$ cal/mole, $\Delta G' = 23\,500$ cal/mole, $\Delta G = -8\,000$ cal/mole, and $\nu = 10^{20}$ s^{-1}. See text for explanation of the difference between curves B and C.

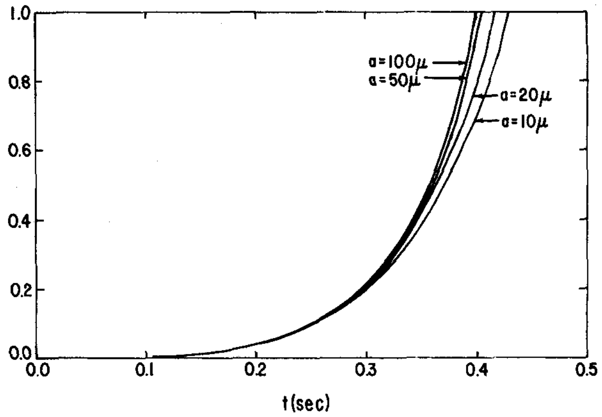

Fig. 2. The dimensionless volume V as a function of time t for various crystal thicknesses a and for reaction occurring in the regime of pronounced size effects accompanied by convectional and radiative heat losses. The values of the parameters are as in Figure 1, $T_o = 635$°K.

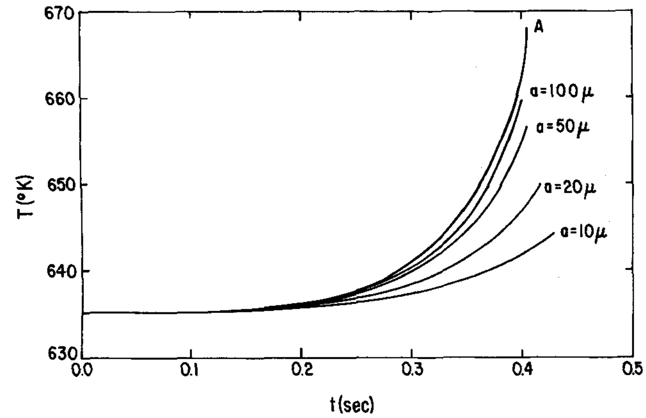

Fig. 3. The temperature T as a function of time t for various crystal thicknesses a and for reaction occurring in the regime of pronounced size effects accompanied by convectional and radiative heat losses. Curve A is for the adiabatic regime. The values of the parameters are as in Figure 2.

reaction conditions must be selected in such a way that the resulting $t_{\max}$ lies very close to t_c. It can be shown by using Equation (17) that for small crystal sizes ($a < 100\mu$, $l = 200\mu$) adiabatic behavior is rather unusual. This is so because the predicted values of t_c are small (0.1 to 5 s), and the time $t_{\max}$ is normally of the same order or larger. On the other hand, for much larger crystals ($a > 500\mu$), the predicted values of t_c are relatively large ($t_c > 10$ s), and the time $t_{\max}$ can be much shorter than t_c.

In accordance with the previous observations, two different limiting reaction regimes are possible: an adiabatic regime, corresponding to $t_{\max} << t_c$, or equivalently, $T_o >> T_{o_c}$; a regime of pronounced size effects, corresponding to $t_{\max} \sim t_c$, or equivalently, $T_o \sim T_{o_c}$. In the present paper, computations have been carried out for reactions occurring in the latter regime.

The predictions made in this section concerning the existence of a size effect and of critical conditions are supported by the observations of various investigators. Bowden and Singh (1954), studying the effect of crystal size on the explosion of α lead azide, have observed that the crystal dimensions determine the explosion temperature and that the latter decreases with increasing crystal dimensions. This behavior is in agreement with Equation (17) which predicts that for increasing crystal thickness a, the corresponding value of t_c increases, which implies a smaller value of the critical temperature T_{o_c}. Additional data in support of such behavior have been presented by Bowden and Yoffe (1958) for a number of solid explosives.

The experimental results of Groocock (1958) on the decomposition of batches of crystals of α lead azide in vacuum (radiative heat losses only) showing no significant size effect can be explained by the present theory; the experiments were carried out under conditions lying closer to the adiabatic reaction regime (that is, $t_{\max} << t_c$ or $T_o >> T_{o_c}$) than to the regime of pronounced size effects (that is, $t_{\max} \sim t_c$ or $T_o \sim T_{o_c}$).

RESULTS AND DISCUSSION

The system of Equations (10*a*) and (10*b*) was solved numerically by employing the successive approximation scheme described earlier. The values of the parameters were taken as $c = 0.1169$ cal/g°K, $k = 0.58 \times 10^{-4}$ cal/cm s °K, $M = 291.23$, $\rho = 4.7$ g/cm^3, $N_o' = 10^{17}$ cm^{-3}, $a_o = 5 \times 10^{-8}$ cm, $\nu_o = 10^{12}$ s^{-1}, $E = 74\,000$ cal/mole, $\Delta G' = 23\,500$ cal/mole, $\nu = 10^{20}$ s^{-1}. The majority of these values correspond to the properties of α lead azide for which there exist extensive experimental data concerning its thermal decomposition.

The decomposing crystal was assumed to have a uniform width and length of $l = 200\mu$ and a thickness a. The value of a was varied between 5 and 100μ in order to study the effect of crystal size on reaction kinetics. The qualitative results obtained in this manner are not only valid for α lead azide but also for a large number of metal azides and fulminates since, according to Bowden and Williams (1951), lithium azide, calcium azide, thallous azide, silver azide, thallous fulminate, silver fulminate, cadmium fulminate, and cuprous fulminate all behave similarly to α lead azide when in the form of thin films.

The first series of computations were carried out to determine the dependence of the critical temperature T_{o_c} on crystal thickness a. By considering the remaining parameters representing the physical properties of the reactant as fixed, Equations (10*a*) and (10*b*) can be written in the form

$$V = f(V, \theta, t, T_o, a) \tag{21a}$$

$$\theta = g(V, \theta, t, T_o, a) \tag{21b}$$

The critical temperature is defined by the condition

$$\theta_{ad} = L_c + L_R \tag{22}$$

and, since $\theta = \theta_{ad} - L_c - L_R$, Equations (21) become

$$V = f(V, t, T_{o_c}, a) \tag{23a}$$

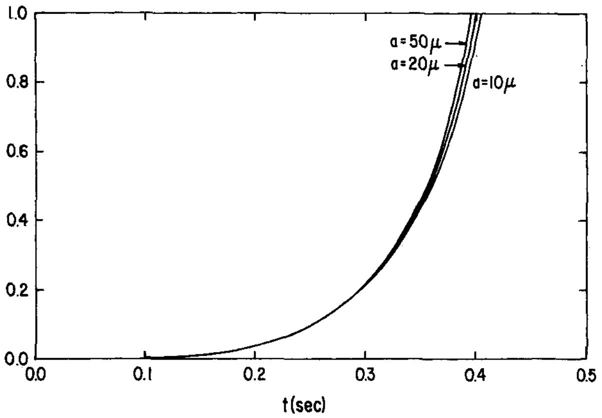

Fig. 4. The dimensionless volume V as a function of time t under the same conditions as in Figure 2 but with only radiative heat losses present. The values of the parameters are as in Figure 2.

and

$$0 = g(V, t, T_{0c}, a) \qquad (23b)$$

Because T_{0c} is a constant, its value can be obtained by setting $V = 1$ and, consequently, $t = t_{\max}$. The following system of equations is obtained for T_{0c} and the corresponding $t_{\max}$:

$$f(t_{\max}, T_{0c}, a) = 1 \qquad (24a)$$

and

$$g(t_{\max}, T_{0c}, a) = 0 \qquad (24b)$$

The actual solution of this system was carried out by a computer trial-and-error procedure by using for $t_{\max}$ the value of t_c calculated from Equation (17) as a first estimate. It was found that the true value of $t_{\max}$ was higher than the value evaluated from Equation (17) [for example, for $a = 10\mu$, Equation (17) predicts $t_c = 0.19$ s, while the computed value is $t_{\max} = 0.43$ s]. It was also found that this computational scheme suffered from an apparent oscillatory behavior which became particularly noticeable for estimates of $t_{\max}$ very close to its true value. This limited, to a certain degree, the accuracy of the results obtained.

Computations for $a = 5$, 10, 20, and 30μ gave values of 645, 635, 624, and 615°K, respectively, for T_{0c}. Owing to the previously stated limitations on the accuracy of these computations, the true values of T_{0c} are expected to be slightly smaller, that is, smaller by 2°K at the most.

Figure 1 shows the results of these computations (curve C) plotted along with the experimental results of Chaudhri and Field (1975) (curve B) and with their theoretical curve based upon zeroth-order kinetics for the decomposition of α azide. The lower values of T_{0c} obtained by the present method are due to the too low value of ΔH employed in these computations ($\Delta H = 1\,000$ cal/mole) necessary in order to avoid computational complexities arising from the resulting explosive behavior for higher ΔH values. It is worth noting, however, that the theoretical curve (curve A), derived by the method of Frank-Kamenetskii by assuming a zeroth-order rate expression, predicts only a 5°K drop in T_0 in the depicted range of crystal thickness a and a linear dependence of T_{0c} on a, while the experimental curve (curve B) shows a 26.95°K drop in T_{0c} in the same range of a and a strongly nonlinear dependence of T_{0c} on a. On the other hand, curve C displays both a similar drop in T_{0c} (30°K) and a shape similar to the experimental curve. Consequently, the present theory can interpret the experimental observations in a more satisfactory manner, implying that the use of expressions that take into account the phenomena of nucleation and nuclear growth is necessary for a realistic description of the kinetics of transformation of solids.

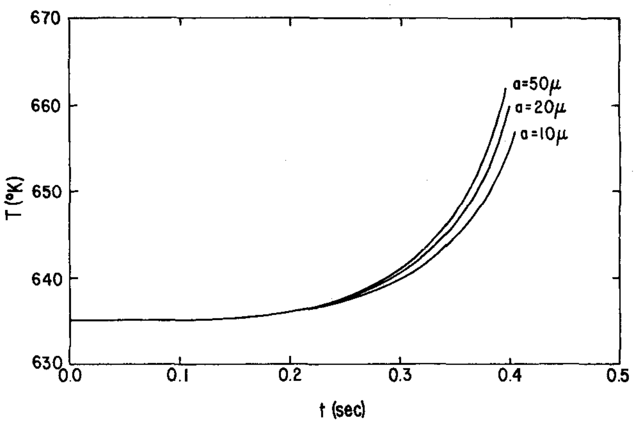

Fig. 5. The temperature T as a function of time t under the same conditions as in Figure 3 but with only radiative heat losses present. Reaction departs significantly from the regime of pronounced size effects. The values of the parameters are as in Figure 2.

The effect of crystal size (thickness) on the reaction kinetics is shown in Figures 2 and 3. In order to avoid the computational complexity characteristic of explosive behavior of the reaction under consideration, the value $\Delta H = 1\,000$ cal/mole was used. All computations indicated in Figures 2 and 3 were carried out for $T_a = T_o = 635$°K which corresponds to the critical value of T_o for $a = 10\mu$. The gradual increase in a corresponds to a gradual shift of the reaction behavior from the regime of pronounced size effects towards the adiabatic regime. In this sense the curve for $a = 100\mu$, representing the largest deviation from the regime of pronounced size effects in Figures 2 and 3, is characterized by higher temperatures (Figure 3) resulting in a smaller value of $t_{\max}$.

Figures 4 and 5 show the results of a series of computations similar to the ones shown in Figures 2 and 3 but taking into account heat losses due to radiation only. The resulting curves display only a weak size effect. Elimination of convectional heat losses, that is, carrying out the reaction in vacuum, shifts the reaction behavior away from the regime of pronounced size effects in a rather drastic manner. This observation is supported by the experimental results of Groocock (1958) on the thermal decomposition of batches of crystals of α lead azide for which he found no significant size effect. Comparison of Figures 2 and 3 with Figures 4 and 5 indicates that when both convective and radiative heat losses are present, the former are mostly responsible for the kinetic behavior of the system, while the latter play only a minor role.

Figures 6 and 7 show the results of a series of computations concerning the onset of explosion. All computations were carried out for $a = 10\mu$ and in the regime of pronounced size effects. The curve corresponding to $\Delta H = 10\,000$ cal/mole clearly displays explosive behavior, while the curve for $\Delta H = 5\,000$ cal/mole almost reaches similar behavior close to its upper end point. According to the characterization of such explosions by Ruckenstein and Vavanellos (1975), the observed explosion is of the first kind, that is, characterized by near infinite slopes in the V vs. t curve following a period of quiescent reaction, and, therefore, is controlled by nucleation phenomena. From additional computations of this type, it was found that the critical value of the dimensionless group α for which explosion occurs is $\alpha = 4$. Thus, the necessary condition for a reaction to reach explosion in the regime of pronounced size effects is $\alpha < 4$. However, it has to be noted that this criterion is an empirical one, valid under the particular conditions considered here rather than for every solid phase reaction, since the critical value of α may depend on the values of the whole set of parameters appear-

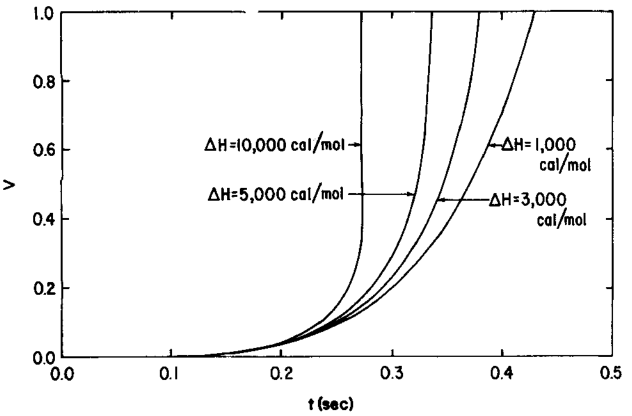

Fig. 6. The dimensionless volume V as a function of time t as reaction in the regime of pronounced size effects accompanied by convectional and radiative heat losses approaches explosion. The curve for $\Delta H = 10\,000$ cal/mole displays explosive behavior, while the curve for $\Delta H = 5\,000$ cal/mole lies very close to the limit. Except ΔH, the values of the parameters are as in Figure 2, and $a = 10\mu$.

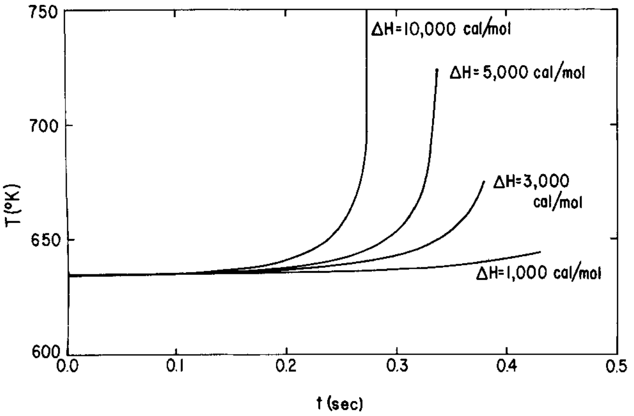

Fig. 7. The temperature T as a function of the time t as reaction in the regime of pronounced size effects accompanied by convectional and radiative heat losses approaches explosion. Except ΔH, the values of the parameters are as in Figure 2, and $a = 10\mu$.

ing in these computations. Thus, for the set of parameters considered here, and bearing in mind that the corresponding critical value of α for reaction in the adiabatic regime is $\alpha = 20$ (Ruckenstein and Vavanellos, 1975), an explosion criterion can be formulated as follows.

A solid phase reaction proceeding through nucleation and subsequent nucleus growth cannot reach explosion if $\alpha > 20$, will always reach explosion if $\alpha < 4$, and in the region $4 < \alpha < 20$ it may or may not reach explosion depending on whether it takes place closer to the adiabatic regime or to the regime of pronounced size effects.

Since the parameters c, T_o, and M appearing in the definition of α [Equation (7*a*)] can only vary within narrow limits, the only parameter that can account for large variations in α is ΔH. Because usually $\Delta H >> 5\,000$ cal/mole, it becomes obvious from the values of ΔH for which explosion occurs in Figure 6 that for most cases of practical interest the reaction, if nondecaying, will reach explosion.

CONCLUSIONS

The introduction of rate expressions accounting for the processes of nucleation and subsequent growth of the nuclei into the equations describing the kinetics of solid phase reactions adequately predicts and interprets the experimental observations. According to this theory, heat losses from the reacting solid by radiation and convection often have a marked effect on its reaction kinetics. In order for the reaction to be nondecaying, the initial temperature of the reactant must be higher than a critical value T_{oc}. The dependence of this critical value on crystal size indicates that crystal size plays a primary role in determining patterns of kinetic behavior. Variations in crystal size and initial temperature of the reactant cause variations in reaction behavior between two extremes, the regime of pronounced size effects and the adiabatic regime characterized by total absence of size effects. When both convective and radiative heat losses are present, the former are mainly responsible for determining the kinetic behavior of the system, while the latter play a lesser role. In the case of large ΔH values, explosion of the type characterized by steep slopes in the V vs. t curve, for which nucleation phenomena are the controlling factor, occurs.

NOTATION

a = crystal thickness
a_o = interatomic spacing
c = heat capacity
E = activation energy for nucleus formation
E^* = dimensionless activation energy for nucleus formation defined by Equation (9*b*)
h = heat transfer coefficient
I_c = integral of the heat loss term due to natural convection defined by Equation (11*b*)
I_R = integral of the heat loss term due to radiation defined by Equation (18*b*)
k = thermal conductivity of air
l = crystal length and width
L_c = heat loss term due to natural convection defined by Equation (11*a*)
L_R = heat loss term due to radiation defined by Equation (18*a*)
M = molecular weight of the new solid phase
N_o' = number of potential nuclei per unit volume of the old phase at time $t = 0$
R = gas constant
S = external surface of the reacting system
t = time
t_c = critical time defined by Equation (17)
$t_{\max}$ = time required for completion of the reaction
T = absolute temperature
T_a = ambient temperature
T_o = initial temperature of reactant
T_{oc} = critical initial temperature of reactant
V = volume of the new phase per unit volume of the old phase
V_o = initial guess of V for computational purposes
V_s = total volume of reacting system

Greek Letters

α = dimensionless group defined by Equation (7*a*)
β = dimensionless group defined by Equation (7*b*)
γ = dimensionless group defined by Equation (9*a*)
δ = dimensionless group defined by Equation (7*c*)
ΔG = change in chemical potential per mole of new phase accompanying the macroscopic transformation
ΔG^* = dimensionless form of ΔG defined by Equation (9*c*)
$\Delta G'$ = free energy of activation per mole for nucleus growth
$\Delta G'^*$ = dimensionless form of $\Delta G'$ defined by Equation (9*d*)
ΔH = heat of reaction per mole of the new phase
ϵ = emissivity
θ = dimensionless temperature defined by Equation (5*b*)
θ_a = dimensionless ambient temperature defined by Equation (7*d*)

θ_{ad} = dimensionless adiabatic temperature defined by Equation (12b)
$\theta_{\max}$ = maximum of θ reached at $\tau_{\max}$
θ_o = initial guess of θ needed for computational purposes
ν = frequency factor
ν_o = vibrational frequency at the interface of the new-old phase
ρ = density of the new phase
ρ' = density of the reacting mixture
σ = Stefan constant
τ = dimensionless time defined by Equation (5a)
$\tau_{\max}$ = dimensionless time needed for completion of the reaction

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Manuscript received October 2, 1975; revision received December 5 and accepted December 8, 1975.

A Multicomponent Film Model Incorporating a General Matrix Method of Solution to the Maxwell-Stefan Equations

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Convenient expressions for calculating multicomponent gas phase mass transfer coefficients and transfer rates are obtained by use of an exact matrix method of solution to the Maxwell-Stefan equations. The results are seen to be exact matrix analogues of classical binary relations and may also be applied as an approximation to describe liquid phase transport.

SCOPE

Many chemical engineering operations such as distillation, absorption, condensation, and evaporation involve steady state transfer of three or more species, and it is important in such cases to calculate the rates of transfer in either phase. Often in practice one has to rely on some theory of mass transfer which in almost all cases is based on a model involving molecular diffusion. Although binary molecular diffusion theory is well understood, the interesting transfer characteristics of multicomponent systems—systems for which $n \geqq 3$—have only relatively recently been recognized and studied (Toor, 1957, 1964; Stewart and Prober, 1964). Thus, in multicomponent systems it is possible to obtain various interaction phenomena such as osmotic diffusion (transfer of a component in the absence of a composition gradient for that species), diffusion barrier (no transfer of a component even though a composition gradient exists for it), and reverse diffusion (diffusion of a species against its composition gradient). The correct description of multicomponent transport phenomena is obtained by using a matrix of mass transfer coefficients with nondiagonal coefficients. This work is concerned with the development of a film model for multicomponent mass transfer for calculating the matrix of transfer coefficients and is based on an exact matrix method of solution to the Maxwell-Stefan equations. The method developed in this work does not make the assumption of constant matrix of diffusion coefficients as required in the linearized theory development of Toor (1964) and Stewart and Prober (1964).

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