A Population Balance Approach to the Modeling of Solid Phase Reactions

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A population balance approach is used to model solid phase reactions in terms of nuclei of the product phase dispersed in the reactant matrix. A conversion-time relationship is obtained by the solution of a set of moment equations derived from the population balance. Some previously known solutions for both homogeneous and heterogeneous nucleation are developed by this approach to demonstrate the relative ease of solution when compared with previously used integral techniques. A model for nucleus impingement at low conversions is formulated and applied to published data on the oxidation of cuprous iodide to illustrate the practical use of this technique. The classical Avrami model (Avrami, 1939, 1940, 1941) is modified to include the initial volume of a nucleus, and it is shown that insensitivities in the original model are removed by this improvement. The need for direct measurements of nucleation and growth rates is emphasized.

SCOPE

A population balance approach to the analysis of solid phase reactions is used to develop a conversion-time relationship by means of the solution of a set of simultaneous differential equations. Prior approaches to this problem were based on techniques that called for numerical solutions of integral equations (Ruckenstein and Vavanellos, 1975) or lengthy power series procedures (Von Göler and Sachs, 1932).

The procedure developed here is generally easier than those of the corresponding integral equations and has the added advantage that the size dependent interaction of nuclei can be readily incorporated through the use of birth and death rate functions. A procedure for the calculation of these functions is presented which is valid for the early stages of the reaction.

The classical model of Avrami (1939, 1940, 1941) has limited applicability in interpreting experimental results, since a fit to conversion-time data is rather insensitive to the choice of the parameters (Young, 1966). Because of this, researchers have used an empirical relation of Erofeev (1961), but such a treatment detracts from a mechanistic interpretation of the conversion process. The present work removes the insensitivity in the model of Avrami by the addition of a pertinent new parameter which concerns the initial volume of a nucleus.

The fit of the modified Avrami model to a specific set of experimental data is compared with that of a model presented in this paper to emphasize the importance of direct measurements of nucleation and growth rates in the determination of a correct impingement model.

CONCLUSIONS AND SIGNIFICANCE

The modeling of phase-transformation kinetics is approached through a balance over the number density of nuclei, which incorporates birth and death functions that arise from nucleus impingement. This approach for obtaining the conversion-time relationship results in a set of first-order differential equations. The technique offers an advantage over the previously used methods because of the relative ease of solution of these equations. It can also be used to calculate the nucleus size density for correlation with experimental data.

For comparison purposes, the well-known Avrami model is modified to include a term for the initial volume of a growth nucleus in order to increase the sensitivity of the least-squares fit to the choice of parameter values. The two models are equally satisfactory in fitting a specific set of experimental data in the low to moderate conversion range, showing that conversion-time data alone are insufficient to distinguish between the two models for nucleus impingement. Direct measurements of nucleation and growth rates are needed to identify the more accurate model.

The simplified theory presented does not predict the sigmoidal shape of the conversion-time curve since it does not account for the higher-order impingement among nuclei at high conversion. The constraining effect of the outer surface of a reacting particle is also an important consideration not addressed in this work, but which may have significant effect during the later stages of the transformation process.

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0001-1541-79-2126-0298-$01.05.

It is generally agreed (Avrami, 1941; Young, 1966; Erofeev, 1961; Russel, 1970) that solid phase chemical reactions proceed by the initiation of discrete nucleus forming sites, followed by formation of nuclei (submicroscopic particles) of the solid product phase. Further chemical reaction is localized at the reactant-nucleus interface, causing the nuclei to grow in size as the reaction proceeds. Theoretical justification for this mechanism has been provided for some specific reactions by Bulgakov and Boldyrev (1973), who demonstrated that the reactant is less stable at the reactant-product interface for the reactions considered.

Most studies of such chemical systems have focused on reactions of the type

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

but it is recognized (Young, 1966) that the results are also applicable to decompositions where

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

The formation and growth of nuclei are also considered to be essential (Pavlyuchenko and Rubinchik, 1951) in certain solid-fluid reactions of the type

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

among which are a number of industrially important processes including the oxidation of cuprous iodide and the reduction of cupric oxide (Neuburg, 1970; Bond and Clark, 1960). The former is used in a process for copper recovery from dilute solutions of cupric sulfate, and the latter is the main step in the reduction of copper ore.

Models for solid phase reactions with heterogeneous nucleation (Avrami, 1939, 1940; Erofeev, 1961; Ruckenstein and Vavanellos, 1975) as well as for those with homogeneous nucleation (Von Göler and Sachs, 1932) have hitherto used integral techniques. In the present study, a population balance approach to the modeling of solid phase reactions is presented. This treatment derives from the work of Hulburt and Katz (1964) who have provided a convenient framework for the analysis of particulate systems through the definition of a multivariate number density. The state of any given particle is represented by a vector in a state space, and the multivariate number density is the number of particles per unit volume of this state space. Hulburt and Katz (1964) have derived the basic conservation equation for the number density, in the state space over which it is defined, and this has come to be known as the population balance equation. This equation is analogous to the classical Liouville equation of statistical mechanics (Gibbs, 1902) which expresses the conservation of probability in the phase space of a mechanical system and has found important application (Hulburt and Akiyama, 1969) in the modeling of agglomeration and dispersion processes. In other work, Argyriou et al. (1971) have applied the population balance equation to describe bubble growth in fluidized beds, while Guin et al. (1971) and Schechter and Gidley (1969) have used it to analyze changes in pore size distributions during chemical reactions in porous media.

It is shown that the use of the population balance approach in deriving conversion-time relationships in problems of solid phase reactions results in a set of first-order ordinary differential equations that are numerically easier to solve than the corresponding integral equations obtained through the conventional approaches of Avrami (1939, 1940), Ruckenstein and Vavanellos (1975), and Von Göler and Sachs (1932). The treatment has the advantage that it possesses the potential to allow for size dependent impingement of growth nuclei, thus circumventing the averaging process used by Avrami in postulating the extended volume concept. A specific example of binary interaction of nuclei is considered, and the solution is applied to the data of Neuburg (1970) on the oxidation of cuprous iodide. Good fit is obtained for the early stages of the reaction, and, as anticipated, the rate constants follow an Arrhenius temperature dependence. The lack of fit in the later stages is attributed to the nonadherence to the binary agglomeration hypothesis.

THE POPULATION BALANCE APPROACH

Following the development of Hulburt and Katz (1964), a number density is defined such that $\psi(V, t)dV$ is the number of nuclei per unit volume, at time t, having size in the interval dV. Application of the population balance equation of Hulburt and Katz (1964) yields

$$\frac{\partial \psi}{\partial t} + \frac{\partial}{\partial V}\left[\psi \frac{dV}{dt}\right] + D(V,t) - B(V,t) - \delta(V - V_b)\, R(t) = 0 \quad (1)$$

where $\delta(V - V_b)$ is the Dirac delta function having a nonzero value only for $V = V_b$, and the functions $D(V, t)$ and $B(V, t)$ allow for the disappearance and production, respectively, of nuclei as they grow into each other. The function $D(V, t)$ is defined such that $D(V, t)dV$ is the instantaneous rate at which nuclei in the size interval lose their identity (die) as they impinge on other nuclei. In a similar fashion, $B(V, t)$ refers to nuclei that are formed (born) as a result of impingement of growth nuclei.

The process of impingement of growth nuclei is as yet not clearly understood, and the nature of the functions $D(V, t)$ and $B(V, t)$ is one of the major uncertainties of the transformation process. As growing nuclei impinge upon each other, they form clusters which have external as well as internal surface area. Since the growth of the outer surface of the clusters would be constrained by the external surface of the particle, a maximum in the rate is to be expected. After the external growth is restricted, a cluster growth proceeds. Reaction at the receding internal surface of the clusters would predominate, producing the commonly observed sigmoidal shape in the conversion-time relationship (Young, 1966).

A rigorous analysis of the impingement of growth nuclei would require the inclusion of some measure of the radial distribution of nuclei within the reacting particle. Such a treatment can, however, be simplified by assuming a random distribution of nuclei, as was done by Avrami (1940). His analysis was, however, approximate since it assumed an average, size independent, impingement of nuclei. There has been some difficulty in correlating the model with experimental data. Nakamori et al. (1974) found satisfactory fit to data on the decomposition of silver oxide only above $\alpha = 0.25$ in some experiments and above $\alpha = 0.05$ in others. Similarly, Jacobs and Ng (1972) found it necessary, in the range below $\alpha = 0.03$, to use empirical correlations to fit their data on the thermal decomposition of ammonium perchlorate.

In the analysis that follows, the volume of a nucleus is taken as a measure of its size in the population balance, but it should be noted that this choice is one of convenience and depends upon the assumption that the total volume of the product phase remains constant as the impingement process proceeds. The same argument emerged in the work of Argyriou et al. (1971) who used bubble volume as a measure of size in their analysis of bubble growth by coalescence in fluidized beds. In other studies, Schecter and Gidley (1969) and Guin et al.

(1971) assumed that total surface area is conserved in collisions between pores and thus chose pore surface area as representative of pore size. On the other hand, Hashimoto and Sylveston (1973) used pore radius to develop a size distribution.

Given suitable nucleation and growth rates, and birth and death rate functions, Equation (1) can, in principle, be solved for known boundary and initial conditions to yield the number density $\psi(V, t)$. The conversion $\alpha(t)$ can then be obtained from the first moment

$$\mu_1(t) = \int_0^\infty V\psi(V,t)\, dV = \alpha(t) \tag{2}$$

In most cases, however, a closed form analytical solution to the population balance equation is not possible, and numerical techniques must be used to obtain $\psi(V,t)$. In order to avoid this difficulty, Hulburt and Katz (1964) suggested a procedure by which the population balance may be reduced to a system of first-order differential equations in the time dependent moments of the number density $\psi(V,t)$. Following their development, the n^{th} moment of $\psi(V, t)$ is defined as

$$\mu_n(t) = \int_0^\infty V^n\, \psi(V,t)\, dV \tag{3}$$

Multiplying Equation (1) by V^n and integrating from 0 to ∞, we get

$$\frac{d\mu_n}{dt} = n \left\langle V^{n-1}\, \psi \frac{dV}{dt}\right\rangle - \langle V^n D\rangle + \langle V^n B\rangle + V_b{}^n R(t), \quad n \geq 0 \tag{4}$$

where, for any function $X(V, t)$, the symbol

$$\langle V^m X\rangle = \int_0^\infty V^m\, X(V,t)\, dV \tag{5}$$

The initial conditions for Equation (4) may be written as

$$\mu_n(t) = \mu_{n0} \quad \text{at} \quad t = 0, \quad n \geq 0 \tag{6}$$

With appropriate expressions for nucleation and growth rates and birth and death rates substituted, Equation (4) represents a system of first-order differential equations in the time dependent moments, with initial conditions specified by Equation (6). The solution of this system of equations will yield the conversion through Equation (2).

DeHoff (1972) introduced the use of a number density viewpoint in his growth path analysis of the kinetics of phase transformations. His approach used an integral analysis, however, and did not yield a population balance equation. Further, DeHoff made no provision for impingement of nuclei. Yost (1975) extended DeHoff's analysis to show that the number density satisfies an equation analogous to the continuity equation in fluid mechanics, but still did not account for the impingement of nuclei.

As developed to this point, the population balance equation is applicable to nuclei growth or decay from any source and has no explicit expression for chemical reaction per se. To incorporate such an expression, it may be assumed (Young, 1966) that the volume of a nucleus is proportional to the cube of a single linear dimension:

$$V = \sigma X^3 \tag{7}$$

and

$$\frac{dV}{dt} = 3\,\sigma X^2 \frac{dX}{dt} \tag{8}$$

Tompkins (1976) has noted that diffusion contributions to nucleus growth rate are several orders of magnitude smaller than those of immobile reactants. Under such circumstances, the growth rate (dX/dt) will be constant, and therefore

$$\frac{dV}{dt} = 3\,k\sigma^{1/3}V^{2/3} \tag{9}$$

and for a nucleus growing from zero volume at time τ

$$V = \sigma k^3\,(t - \tau)^3 \tag{10}$$

Substitution of Equation (9) into Equation (4) yields

$$\frac{d\mu_n}{dt} = 3n\sigma^{1/3}\,k\mu_{n-1/3} - \langle V^n D\rangle + \langle V^n B\rangle + V_b{}^n R(t), \quad n \geq 0 \tag{11}$$

The above equation and the initial conditions in Equation (6) can be readily applied to any system with known functions $D(V,t)$, $B(V,t)$, and $R(t)$ to obtain the conversion-time relationship.

In contrast to the above technique, the past approach in solid phase reactions has been to use Equation (10) and define the conversion in terms of the volume fraction of the reactant transformed to give

$$\alpha(t) = \sigma k^3 \int_0^t R(\tau)\,(t-\tau)^3\, d\tau \tag{12}$$

In addition to considering that nuclei grow from zero volume, this result assumes no impingement of nuclei. For the special case of heterogeneous nucleation, Equation (12) has been modified by Avrami (1939, 1940, 1941) to allow for this latter effect. In the following sections we consider some specific situations in solid phase reactions and illustrate the application of the present approach. Additionally, a model for nucleus interaction is developed and compared with the model of Avrami.

HOMOGENEOUS NUCLEATION

Following the assumptions of Von Göler and Sachs (1932), consider nucleation to start from centers of zero volume ($V_b = 0$) at a rate proportional to the untransformed volume

$$R(t) = k_1\,[1 - \alpha(t)] \tag{13}$$

and, further, take the birth and death rates to be negligible ($D = B = 0$). Substitution of these assumptions into Equation (11) results in

$$\frac{d\mu_0}{dt} = k_1\,(1 - \mu_1) \tag{14}$$

and

$$\frac{d\mu_n}{dt} = 3n\sigma^{1/3}\,k\mu_{n-1/3}, \quad n > 0 \tag{15}$$

For $n = 1/3, 2/3, 1$, Equation (15) yields

$$\frac{d\mu_{1/3}}{dt} = k\sigma^{1/3}\mu_0 \tag{16}$$

$$\frac{d\mu_{2/3}}{dt} = 2k\sigma^{1/3}\mu_{1/3} \tag{17}$$

$$\frac{d\mu_1}{dt} = 3k\sigma^{1/3}\mu_{2/3} \tag{18}$$

Combining Equations (14) and (16) to (18), we get

$$\frac{d^4\mu_1}{dt^4} + 6\sigma k^3 k_1 \mu_1 = 6\sigma k^3 k_1 \tag{19}$$

The initial condition

$$\mu_n(0) = 0, \quad n \geqq 0 \tag{20}$$

combines with Equations (14) and (16) to (18) to provide

$$\mu_1 = \frac{d\mu_1}{dt} = \frac{d^2\mu_1}{dt^2} = \frac{d^3\mu_1}{dt^3} = 0, \quad \text{at} \quad t = 0 \tag{21}$$

Solution of Equation (19) with the initial conditions (21) yields

$$\alpha(t) = 1 - \cosh(at)\cos(at) \tag{22}$$

where $a = (3\sigma k^3 k_1/2)^{1/4}$.

To emphasize the advantages of this population balance approach, it is useful to compare the alternative technique developed by Von Göler and Sachs (1932). By substituting Equation (13) into Equation (12), these authors obtained

$$\alpha(t) = \sigma k^3 k_1 \int_0^t (t - \tau)^3 [1 - \alpha(\tau)]\, d\tau \tag{23}$$

To solve this equation, Von Göler and Sachs substituted a power series for $\alpha(t)$ and developed recursion formulas for the coefficients. This yielded a series solution

$$\alpha(t) = \frac{6\sigma k^3 k_1 t^4}{4!} - \frac{(6\sigma k^3 k_1 t^4)^2}{8!} \cdots - \frac{(-6\sigma k^3 k_1 t^4)^n}{(4n!)} \tag{24}$$

which converges to Equation (22).

The population balance approach has the advantage of producing differential equations in place of the more cumbersome integral relationship. In situations where an analytical solution does not exist, the moment equations must be solved by numerical methods, but this case is still more convenient than the integral equation alternative.

HETEROGENEOUS NUCLEATION

Heterogeneous nucleation proceeds through the initiation of reaction at discrete sites called germ nuclei. Adopting the assumption of Avrami (1939, 1940, 1941) that in a unit volume of the old phase the rate of nucleation is directly proportional to the instantaneous number of germ nuclei, we get

$$N = N_o\, e^{-k_b t} \tag{25}$$

and

$$\frac{dN}{dt} = -\, k_b\, N_o\, e^{-k_b t} \tag{26}$$

Since the ratio of the volume of the old phase to total volume is $[1 - \alpha(t)]$, the above result leads to the rate of nucleation:

$$R(t) = -[1 - \alpha(t)] \frac{dN}{dt} = k_b N_o [1 - \alpha(t)]\, e^{-k_b t} \tag{27}$$

The factor $[1 - \alpha(t)]$ may be considered as accounting for the ingestion of germ nuclei into growth nuclei. Further assuming, as did Avrami, that nuclei grow from zero volume ($V_b = 0$), and substituting the above result into Equation (11), with $D = B = 0$, we get

$$\frac{d\mu_0}{dt} = N_o k_b e^{-k_b t}(1 - \mu_1) \tag{28}$$

with Equations (16) to (18) and (20) unchanged.

Combining Equation (28) with these others, we get

$$\frac{d^4\mu_1}{dt^4} + 6\sigma k^3 N_o k_b\, e^{-k_b t} \mu_1 = 6\sigma k^3 N_o k_b\, e^{-k_b t} \tag{29}$$

to replace Equation (19), but the initial conditions remain as in Equation (21). Equation (29) does not possess any simple analytical solution and must be solved numerically. Avrami (1940) derived the integral equation for this problem by substituting Equation (27) into Equation (12) and obtained

$$\alpha(t) = \sigma k^3 N_o k_b \int_0^t e^{-k_b \tau} (t - \tau)^3 [1 - \alpha(\tau)]\, d\tau \tag{30}$$

This Volterra integral equation of the second kind (Tricomi, 1970) can only be solved numerically or by approximations. The solution was accomplished by Ruckenstein and Vavanellos (1975) using a method of successive approximations, a technique more cumbersome and less familiar than the numerical methods that can be employed on differential moment equations, and probably less exact.

A MODEL FOR NUCLEUS INTERACTION

Studies of phase transformations have hitherto either neglected interaction among the nuclei during the growth process (DeHoff, 1972) or have used an averaging method due to Avrami (1940). The former clearly has limited applicability, while the latter results in a formula that is difficult to reconcile with experimental data (Nakamori et al., 1974). Avrami's method involves the definition of an extended volume

$$\alpha_{\text{ext}} = \sigma k^3 N_o k_b \int_0^t e^{-k_b \tau} (t - \tau)^3\, d\tau \tag{31}$$

which may be construed as the total volume of all nuclei, including overlapping regions and including, as well, those nuclei which would have been formed had germ nuclei not been ingested. To account for the impingement of growth nuclei as well as the ingestion of germ nuclei, Avrami assumed that

$$d\alpha = (1 - \alpha)\, d\alpha_{\text{ext}} \tag{32}$$

Substitution into Equation (31) gives

$$-\ln(1 - \alpha) = \sigma k^3 N_o k_b \int_0^t e^{-k_b \tau} (t - \tau)^3\, d\tau \tag{33}$$

which integrates to

$$-\ln(1 - \alpha) = \frac{6\sigma k^3 N_o}{k_b^3} \left[e^{-k_b t} - 1 + (k_b t) - \frac{(k_b t)^2}{2!} + \frac{(k_b t)^3}{3!} \right] \tag{34}$$

An alternative approach which eliminates the averaging assumption of Avrami [Equation (32)] and treats impingement as a size dependent process may be developed by considering only binary impingement, and that the collision of two nuclei of shape factor σ results in the formation of a single nucleus of shape factor σ and a volume equal to the combined volume of the two parent nuclei. These assumptions, however, may not be expected to hold at high conversions, where tertiary and higher-order collision are significant. Even more important may be the formation of clusters of nuclei with entrapped grains of reactant within them, for which the assumption that the shape factor is preserved when nuclei overlap may be invalid. Despite these shortcomings, the theory may be expected to yield a better approximation at low conversions than the extended volume concept, and with this in view, the collision functions $D(V, t)$ and $B(V, t)$ are introduced. The development follows arguments analogous to those used by Schechter and Gidley (1969) in their analysis of the collision of pores.

The rate of disappearance of nuclei in a volume interval dV may be calculated from the number of collisions between nuclei of volume V and all other nuclei. Consider a small time interval during which a nucleus of volume V increases in volume by an amount $(dV/dt)dt$. The total volume increase for nuclei of this size will be the product of this change by the number of such nuclei present, $\psi(V, t)\ (dV/dt)\ dVdt$. Since the number of nuclei of volume V_1 is $\psi(V_1, t)dV_1$, the product $[\psi(V_1, t)dV_1]\ [\psi(V, t)(dV/dt)dV\ dt]$ represents the number of collisions between nuclei of volume V and those of volume V_1, due to growth of nuclei of size V. Similarly, the number of collisions between nuclei of these sizes due to growth of nuclei of size V_1 is given by $[\psi(V, t)dV]\ [\psi(V_1, t)\ (dV_1/dt)dV_1\ dt]$. The total number of collisions between nuclei of size V and all other nuclei, in a unit volume, is then given by

$$D(t, V)dV\,dt = \int_0^\infty \psi(V, t)\psi(V_1, t) \left[\left(\frac{dV}{dt}\right) + \left(\frac{dV_1}{dt}\right)\right] dV_1 dV\,dt \qquad (35)$$

provided that each collision eliminates one nucleus and all collisions are independent. Assuming the growth law given by Equation (9)

$$D(t, V) = 3k\sigma^{1/3} \int_0^\infty (V^{2/3} + V_1^{2/3})\ \psi(V, t)\psi(V_1, t)dV_1 \qquad (36)$$

Thus, referring to Equation (11), we obtain

$$<V^nD> = 3k\sigma^{1/3} \int_0^\infty \int_0^\infty V^n\ (V^{2/3} + V_1^{2/3})\ \psi(V, t)\ \psi(V_1, t)\ dV_1\,dV \qquad (37)$$

In terms of the moments, Equation (37) becomes

$$<V^nD> = 3k\sigma^{1/3}\ [\mu_0\mu_{n+2/3} + \mu_n\mu_{2/3}],\quad n \geqq 0 \qquad (38)$$

The production (birth) function can also be calculated from the number of collisions between all possible combinations of nuclei, such that the resultant nucleus has volume V. To derive this, consider the collisions of nuclei of volume V_1 with those of volume $(V - V_1)$. Following the arguments presented above, we obtain

$$B(t, V) = 3k\sigma^{1/3} \int_0^V V_1^{2/3}\,\psi(V - V_1, t)\ \psi(V_1, t)dV_1 \qquad (39)$$

Taking the n^{th} moment of $B(t, V)$, we have

$$<V^nB> = 3k\sigma^{1/3} \int_0^\infty \int_0^V V^nV_1^{2/3}\,\psi(V - V_1, t)\ \psi(V_1, t)dV_1dV \qquad (40)$$

which simplifies to

$$<V^nB> = 3k\sigma^{1/3} \sum_{\tau=0}^{n} \binom{n}{\tau} \mu_\tau\mu_{n-\tau+2/3},\quad n \geqq 0 \qquad (41)$$

Substitution of the above results and the growth law given by Equation (9) into Equation (11) gives

$$\frac{d\mu_n}{dt} = 3k\sigma^{1/3}\Big[n\mu_{n-1/3} - \mu_0\mu_{n+2/3} - \mu_n\mu_{2/3} + \sum_{\tau=0}^{n} \binom{n}{\tau} \mu_\tau\mu_{n-\tau+2/3}\Big] + V_b^n\,R(t),\quad n \geqq 0 \qquad (42)$$

Combining this result with Equation (27), the Avrami model for nucleation and ingestion of germ nuclei, we get

$$\frac{d\mu_n}{dt} = 3k\sigma^{1/3}\Big[n\mu_{n-1/3} - \mu_0\mu_{n+2/3} - \mu_n\mu_{2/3} + \sum_{\tau=0}^{n} \binom{n}{\tau} \mu_\tau\mu_{n-\tau+2/3}\Big] + N_oV_b^nk_b\,e^{-k_bt}\,(1 - \mu_1),\quad n \geqq 0 \qquad (43)$$

Writing the moment equations for $n = 0, 1, 2$, we obtain

$$\frac{d\mu_0}{dt} = N_ok_b\ (1 - \mu_1)\ e^{-k_bt} - 3k\sigma^{1/3}\,\mu_0\mu_{2/3} \qquad (44)$$

$$\frac{d\mu_1}{dt} = N_oV_bk_b\ (1 - \mu_1)\ e^{-k_bt} + 3k\sigma^{1/3}\mu_{2/3} \qquad (45)$$

$$\frac{d\mu_2}{dt} = N_oV_b^2k_b\ (1 - \mu_1)\ e^{-k_bt} + 6k\sigma^{1/3}\mu_{5/3}\ (1 + \mu_1) \qquad (46)$$

If we assume no nuclei of the product phase at $t = 0$, the initial conditions are

$$\mu_0 = \mu_1 = \mu_2 = 0 \quad \text{at} \quad t = 0 \qquad (47)$$

Inspection of Equations (44) to (46) reveals that the moment equations do not form a closed set owing to the presence of the $\mu_{n+2/3}$ term. As a consequence, a numerical approximation must be used to close these equations. For this purpose, it is convenient to adopt a technique suggested by Hulburt and Katz (1964) by which the number density function is expanded in a Laguerre series of the form

$$\psi(V, t) = \frac{\lambda}{a}\,p^{(\lambda)}\left(\frac{\lambda V}{a}\right) \sum_{i=0}^{\infty} \phi_i\,L_i^{(\lambda)}\left(\frac{\lambda V}{a}\right) \qquad (48)$$

where

$$p^{(\lambda)}(\chi) = \frac{1}{(\lambda - 1)!}\,\chi^{\lambda-1}\,e^{-\chi} \qquad (49)$$

is the normalized gamma probability density function, and

$$L_i^{(\lambda)}(\chi) = \sum_{j=0}^{i} (-1)^j \frac{i!\ (i + \lambda - 1)!}{j!(i - j)!(i + \lambda - 1 - j)!}\,\chi^{i-j},\quad i = 0, 1, 2, \ldots \qquad (50)$$

are the associated Laguerre polynomials. The coefficients λ, a, and ϕ_i in the above series are time dependent. As an approximation, the series may be truncated after the third term to give the distribution

$$\psi(V, t) = \frac{\lambda\,\phi_0}{a(\lambda - 1)!}\left(\frac{\lambda V}{a}\right)^{\lambda-1} e^{-\lambda V/a} \qquad (51)$$

where ϕ_1 and ϕ_2 have been arbitrarily set equal to zero since the first three terms contain five coefficients. The n^{th} moment of this distribution is

$$\mu_n = \int_0^\infty \frac{\lambda\,\phi_0}{a(\lambda - 1)!}\left(\frac{\lambda V}{a}\right)^{\lambda-1} V^n\,e^{-\lambda V/a}\,dV = \frac{\phi_0\Gamma(n + \lambda)}{\Gamma\,(\lambda)}\left(\frac{a}{\lambda}\right)^n,\quad n \geqq 0 \qquad (52)$$

Setting $n = 0$, 1, and 2, respectively, we get

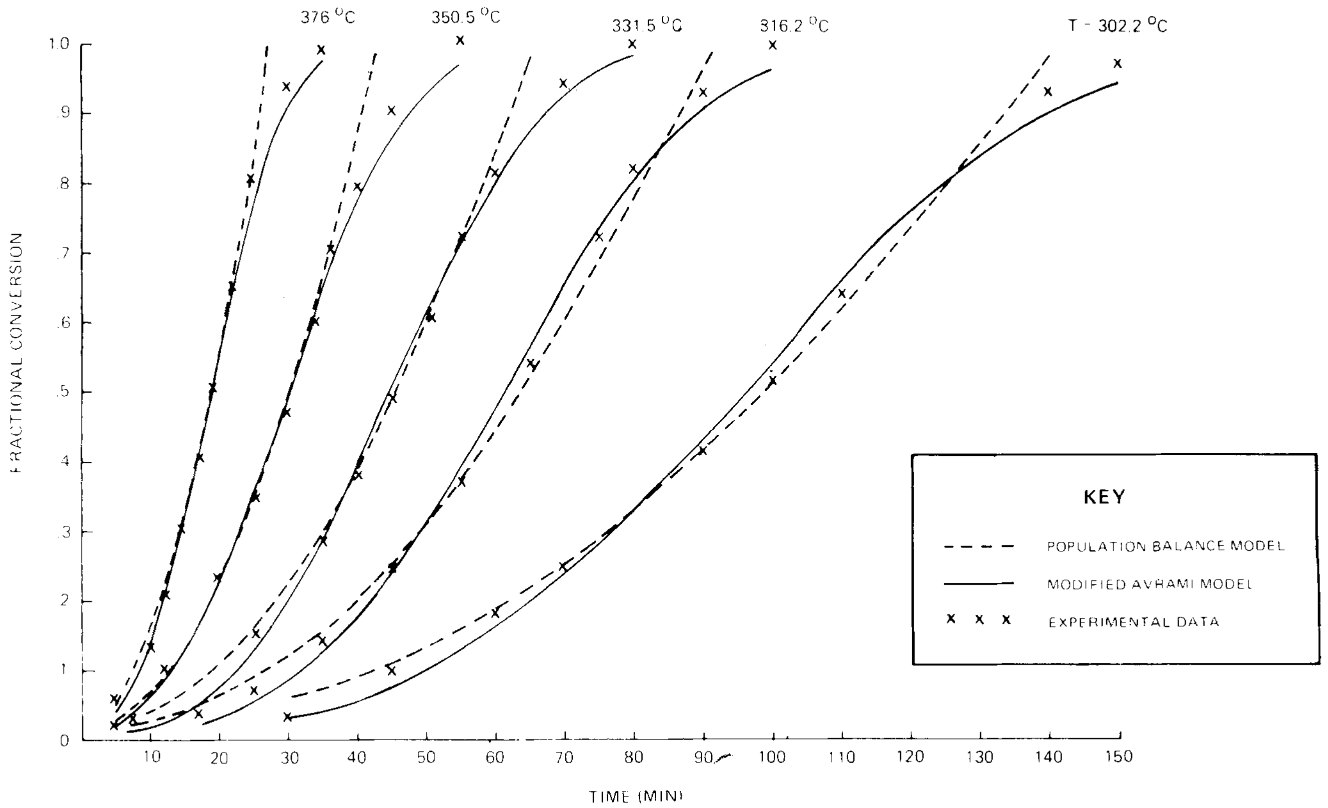

Fig. 1. Conversion vs. time for Cu_2I_2 oxidation at various temperatures.

$$\phi_0 = \mu_0 \tag{53}$$

$$a = \frac{\mu_1}{\mu_0} \tag{54}$$

$$\lambda = \frac{a^2}{\left[\dfrac{\mu_2}{\mu_0} - a^2\right]} \tag{55}$$

Since ϕ_0, a, and λ are now functions of μ_0, μ_1, and μ_2 through Equations (53) to (55), $\mu_{2/3}$ and $\mu_{5/3}$ may now be obtained from Equation (52) by setting $n = 2/3$ or $5/3$. Equations (44) to (46) and (52) to (55) form a closed set of nonlinear first-order differential equations that can be solved for the initial conditions Equation (47) by standard Runge-Kutta or comparable techniques.

It was noted by Hulbert and Akiyama (1969) that a larger number of terms of the Laguerre series may be required to approximate $\psi(V, t)$ for distributions that are not unimodal. In such a case, it may be advantageous to use the method of weighted residuals with problem specific polynomials, as illustrated by Singh and Ramkrishna (1977).

APPLICATION TO EXPERIMENTAL DATA

To demonstrate the utility of the population balance and moments approach, it is instructive to apply the technique to analyze a set of experimental results. To this end it is convenient to transform Equations (44) to (47) into the dimensionless set

$$\frac{d\mu_0^*}{dt} = \frac{A}{\gamma}\,(1 - \mu_1^*)\,e^{-t/\gamma} - C\mu_0^*\,\mu_{2/3}^* \tag{56}$$

$$\frac{d\mu_1^*}{dt} = \frac{A}{\gamma}\,(1 - \mu_1^*)\,e^{-t/\gamma} + C\,\mu_{2/3}^* \tag{57}$$

$$\frac{d\mu_2^*}{dt} = \frac{A}{\gamma}\,(1 - \mu_1^*)\,e^{-t/\gamma} + 2\,C\,\mu_{5/3}^*\,(1 + \mu_1^*) \tag{58}$$

with initial conditions

$$\mu_0^* = \mu_1^* = \mu_2^* = 0 \quad \text{at} \quad t = 0 \tag{59}$$

These equations were solved numerically using a Runge-Kutta technique, and the three parameters A, C, γ were estimated for the oxidation of cuprous iodide particles using the data of Neuburg (1970). In fitting the data, only the range of conversion below $\alpha = 0.6$ was utilized, since the model is not expected to hold at high conversions. Also, data for the highest temperature were not used because of the decreased resolution associated with the determination of conversion when only very steep graphical representations are available. The parameters were estimated by fitting the conversion-time relationship $\mu_1^*(t)$ to Neuburg's results in the range below $\alpha = 0.6$ by a nonlinear least-squares method. These results are presented in Table 1, and the model predictions are shown as the dashed curves (model A) in Figure 1. The agreement over all five temperatures gives a root-mean-square deviation of 0.0134 (fractional conversion) for all the data in the range $\alpha \leq 0.6$, but it is apparent that the model fits the experimental data even when extended well beyond this limit. The model does not, however, predict the sigmoidal shape of the conversion-time curves. This was to be anticipated in view of the neglect of tertiary and higher-order interactions and of cluster formation during the impingement process.

For comparison, the conversion-time relationship resulting from Avrami's model [Equation (34)] was also fitted to the data of Neuburg, but the sum of the squares of the deviations of calculated conversions from the experimental quantities is quite insensitive to the parameter values. This difficulty in fitting Avrami's model to experimental data has previously been noted (Young, 1966)

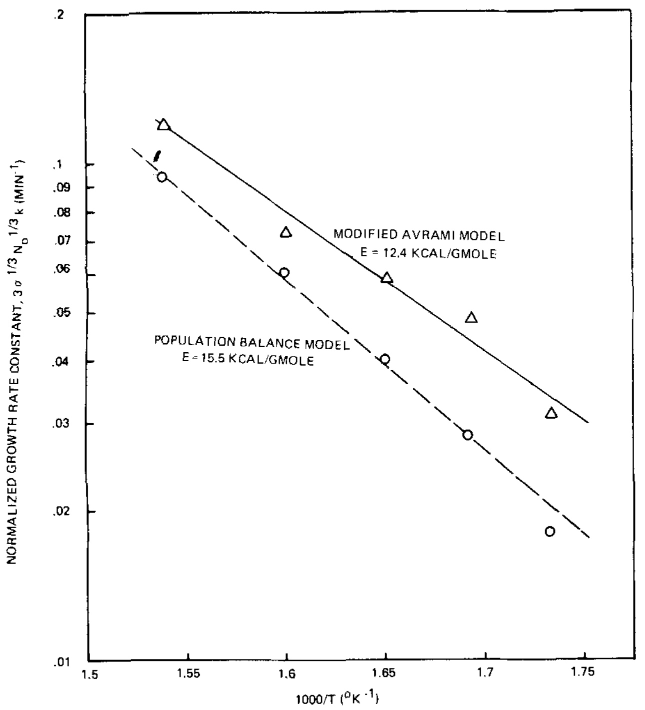

Fig. 2. Arrhenius plot for nucleus growth comparing two models.

and has prompted researchers to use an empirical equation due to Erofeev (1961). This was the equation used by Neuburg (1970) in modeling his experimental data on the oxidation of cuprous iodide. In attempting to overcome this difficulty in the present investigation, the Avrami model was modified to include a nonzero initial volume of a growth nucleus. For this situation, Equation (10) is transformed to

$$V = [V_b^{1/3} + k\sigma^{1/3}(t-\tau)]^3 \tag{60}$$

Using the Avrami approach for nucleation and ingestion [Equation (27)] and the extended volume concept [Equation (32)], one obtains

$$-\ln(1-\alpha) = \frac{2}{9}AC^3\gamma^3\left[\left(1-\frac{3}{C\gamma}\right)\left[e^{-t/\gamma}-1 + \left(\frac{t}{\gamma}\right) - \frac{1}{2}\left(\frac{t}{\gamma}\right)^2\right] + \frac{1}{6}\left(\frac{t}{\gamma}\right)^3\right] + AC\gamma\left(e^{-t/\gamma}-1+\frac{t}{\gamma}\right) + A\,(1-e^{-t/\gamma}) \tag{61}$$

The parameters A, C, and γ in Equation (61) have the same meaning as in Equations (56) to (58) and were evaluated for Neuburg's data using a nonlinear least-square approach. These results are also listed in Table 1. During the evaluation of these parameters, it was noticed that the insensitivity observed in using the original Avrami model was no longer present. The fit of the above equation to the data is shown as the solid lines (model B) in Figure 1. The root-mean-square deviation for this fit is 0.019, comparing well with that obtained using the new impingement model presented in this study.

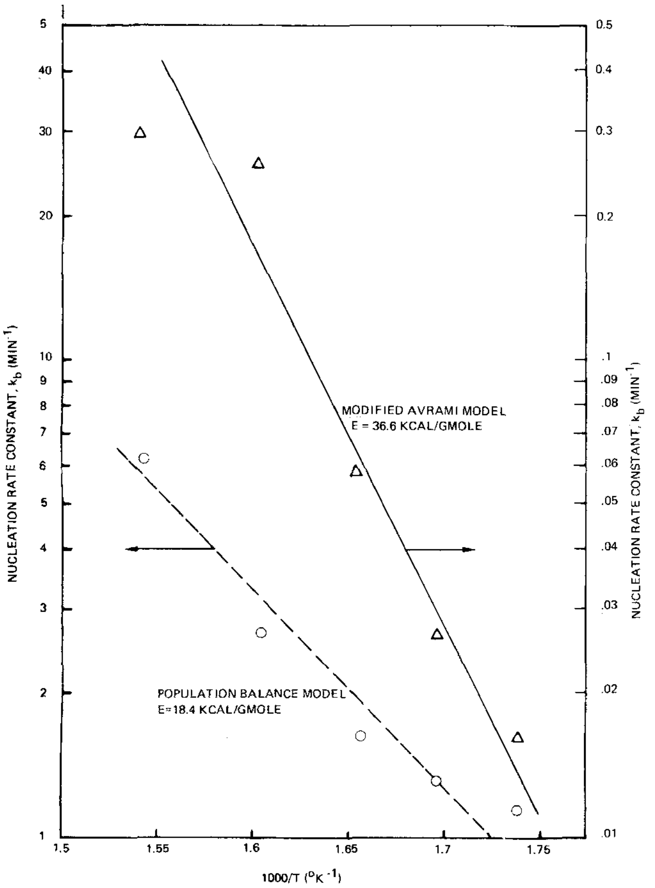

Fig. 3. Arrhenius plot for nucleus formation comparing two models.

Significant differences were obtained, however, in the calculated values of the activation energies. The temperature dependences of the normalized nucleus growth rate constant are shown in Figure 2 in terms of the group $CA^{1/3} = 3\sigma^{1/3}N_0^{1/3}k$ for each model. Regardless of model, the rate constant follows an Arrhenius temperature dependence, but the calculated activation energies for nucleus growth differ by about 25% (12.4 vs. 15.5 Kcal/gmole). A much greater difference is observed in the activation energy of nucleation as shown in Figure 3, where the value of 36.6 Kcal/gmole for the modified Avrami model is about twice that obtained using the new model presented in Equations (56) to (59). This rate constant for nucleus formation k_b is obtained as the reciprocal of the parameter γ; it may be noted that the data show a considerably greater degree of scatter than for the growth constant.

DISCUSSION

In interpreting his experimental data on the oxidation of cuprous iodide, Neuburg (1970) used an empirical model of Erofeev (1961):

$$\frac{d\alpha}{dt} = k'\alpha^a(1-\alpha)^b \tag{62}$$

This model has several weaknesses. First, it calls for a zero rate at $\alpha = 0$, which is inconsistent with the general finding that solid phase reactions can be initiated in the absence of the product. Furthermore, it requires differentiation of conversion-time data, an inherently inaccurate procedure. In addition, the model does not distinguish between the activation energies of nucleation and growth, thereby avoiding the fundamental mechanisms of the conversion process. The only apparent advantage of the model is that it removes the insensitivity problems often encountered in fitting the two-parameter Avrami model. This improvement is achieved by the addition of a third empirical parameter in the Erofeev equation, but at the sacrifice of the interpretation of the basic phenomena of nucleation and growth.

The success in fitting either the population balance model or the modified Avrami model to experimental

TABLE 1. PARAMETERS ESTIMATED BY LEAST SQUARES FIT

$T(^{\circ}C)$	$A=N_0V_b \times 10^{-3}$		$C=3\sigma^{1/3}k/V_b^{1/3}$		$\gamma=1/k_b$	
	POPULATION BALANCE MODEL	MODIFIED AVRAMI MODEL	POPULATION BALANCE MODEL	MODIFIED AVRAMI MODEL	POPULATION BALANCE MODEL	MODIFIED AVRAMI MODEL
302.2	7.50	8.70	0.10	0.16	0.88	61.15
316.2	8.00	9.00	0.15	0.25	0.75	37.58
331.5	8.05	9.27	0.21	0.29	0.60	17.00
350.5	8.43	9.57	0.31	0.36	0.37	3.89
376.0	9.80	11.26	0.46	0.55	0.16	3.35

data suggests that the difficulty in fitting the Avrami model [Equation (34)] is probably due to its neglect of the volume of nuclei upon formation. While the two successful models each have three parameters as does the Erofeev equation, they have the advantage that all the parameters have mechanistic interpretations. A further indicator of the importance of the initial volume of a nucleus may be found in the observation of Neuburg (1970), to the effect that the conversion-time relation correlated his data if it was assumed that $\alpha = 0.004$ at $t = 0$. This suggests that if the effect of the time dependent nucleation process were to be treated as an initial condition, a total fractional volume $\alpha = 0.004$ would be considered as instantly nucleated at $t = 0$. This quantity is of the same order of magnitude as $N_0 V_b$, the estimated total initial volume of nuclei (see Table 1). The introduction of the initial volume of a growth nucleus has, therefore, yielded values of $N_0 V_b$ that are physically meaningful and reflect the mechanistic nature of the nucleation process. In contrast, the constants of the Erofeev equation are empirical parameters with little direct mechanistic interpretation.

Another comparison of the respective models may be based on the relative magnitudes of the computed activation energies. The activation energy for nucleation calculated from the modified Avrami model is much larger (by 24.2 Kcal/gmole) than the corresponding activation energy for nucleus growth. Following Young (1966), this large difference suggests the possibility of multistep nucleation, a finding inconsistent with Avrami's assumption of a single step nucleation. The latter assumption is also a basis of the population balance model, for which the data results for low conversions ($\alpha \leqq 0.6$) are entirely consistent.

The essential difference between the population balance model presented in Equations (56) to (59) and the modified Avrami model is in the inherent representation of the impingement process. The conversion-time data are alone insufficient to determine which of the two models is the better representation of the impingement process. Rather, this analysis demonstrates that contrasting interpretations of the same data can arise from the use of different models for the process. Direct measurements of nucleation and growth rate, such as those made by Wischin (1939) and Garner and Southon (1935), provide a firmer basis for the determination of activation energies than is feasible from this wholly kinetic analysis. The comparison of such direct measurements with those obtained by model fitting may make it possible to identify the correct model of the impingement process.

ACKNOWLEDGMENT

This research was funded by the U.S. Department of Energy, Division of Basic Engineering Sciences (formerly ERDA, Division of Physical Research), under Contract No. EY-76-S-02-2747.

NOTATION

a = coefficient in Laguerre expansion, Equation (48)
A = $N_0 V_b$
$B(V, t)$ = nucleus production function
C = $3\sigma^{1/3} k/V_b^{1/3}$
$D(V, t)$ = nucleus disappearance function
k = nucleus growth rate constant
k_1 = rate constant for homogeneous nucleation
k' = reaction rate constant
k_b = rate constant for heterogeneous nucleation
N = number of germ nuclei per unit volume of old phase, at time t
N_0 = number of germ nuclei per unit volume of old phase, at time $t = 0$
$R(t)$ = nucleation rate
t = time
T = reaction temperature
X = linear dimension of nucleus
V = volume of a growth nucleus
V_b = volume of a growth nucleus upon formation

Greek Letters

α = volume of new phase per unit volume of old phase
α_{ext} = extended volume
γ = $1/k_b$
μ_n = n^{th} moment of the nucleus size density distribution
μ_{n0} = initial value of n^{th} moment
μ_n^* = $\mu_n/V_b^{(n-1)}$
$\psi(V, t)$ = nucleus size distribution
σ = shape factor of nucleus
τ = time of formation of nucleus
ϕ = coefficient in Laguerre expansion, Equation (48)
λ = coefficient in Laguerre expansion, Equation (48)

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Manuscript received April 7, 1978; revision received Aug. 18, and accepted September 6, 1978.

Catalytic Removal of Sulfur, Nitrogen, and Oxygen from Heavy Gas Oil

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Removal of sulfur, nitrogen, and oxygen from heavy gas oils is affected by the chemical composition of supported molybdate catalysts. Cobalt and nickel, when added to these catalysts, have a promoting effect on these reactions. However, the relative rates always follow the same trend; that is, the hydrodesulfurization is the fastest, followed by hydrodenitrogenation and hydrodeoxygenation.

SCOPE

Sulfur, nitrogen, and oxygen are present in various compounds in petroleum fractions. During catalytic hydrotreatments, the elements are removed simultaneously as hydrogen sulfide, ammonia, and water. Sulfur must be removed from products to avoid corrosion and to meet environmental requirements. Some nitrogen containing compounds may have a harmful effect on the properties of the products. Nitrogen bases are also effective poisons of the catalyst surface. Certain oxygen containing compounds are acidic, and their presence, especially in commercial petroleum products, is unwelcome.

To accomplish a high degree of refining, an active catalyst must be used. Supported molybdate catalysts, promoted by either cobalt or nickel, are the most frequently used. The hydrogen sulfide, ammonia, and water produced modify the catalyst surface. While hydrogen sulfide is responsible for sulfiding, ammonia, and to some extent also water, poisons the surface. The extent of these effects depends on the amount of the elments in feedstocks and on the relative rates of their removals. The rates might be dependent on relative stabilities of S, N, and O containing compounds present in the feed. The reactions occur on the catalyst surface, and as such they are not well understood. In the present study, these effects were compared under conditions similar to those encountered in industrial operations.

CONCLUSIONS AND SIGNIFICANCE

Relative rates of S, N, and O removal from a heavy gas oil are in qualitative agreement with the C-S, C-N, and C-O bond strengths; thus, the rate of hydrodesulfurization (HDS) is highest, followed by hydrodenitrogenation (HDN) and hydrodeoxygenation (HDO). The comparison is based on heterocyclic compounds; that is, the O containing species which may be products of reactions between air and the feed are not included. These observations are supported by a number of mechanistic surface phenomena and other thermochemical considerations.

The presence of carbonaceous deposits on the catalyst surface had little effect on these trends. N and O accumulate in the deposits because N and O containing heterocyclic compounds resist the catalytic reactions. De-

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