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Bubble Nucleation in Viscous Material Due to Gas Formation by a Chemical Reaction: Application to Coal Pyrolysis

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Most coals swell when heated, and their plastic properties change. These phenomena are explained qualitatively and semiquantitatively using a theory which combines classical nucleation theory and chemical kinetics.

Classical bubble nucleation theory is modified to include cases where gases are formed in a liquid as a result of a chemical reaction. Part of the gas that is formed in the liquid escapes through the surface. However, the concentration of gas that remains in the solution increases until a critical concentration is reached. When the critical concentration of gas in the solution is reached, bubbles will begin to nucleate.

The value of the rate of nucleation has a critical upper limit which is determined by the thermodynamic properties of the solution. However, the kinetics of the heat, momentum, or mass transfer may reduce the thermodynamic rate.

The criteria to decide which transport mode limits the kinetics of the nucleation were derived and applied to melting coal. In coal, the rate of bubble nucleation appears to be limited by the rate of momentum transfer in the melt.

The size of the melting coal particle determines the ratio of surface area to volume and thus affects the kinetics of the accumulation of gaseous reaction product in the melt. Thus, smaller rates of bubble nucleation will be observed in smaller coal particles (very viscous melts).

Kinetic equations are derived and used to estimate the time that is required for bubbles to appear inside a coal particle. A general method is proposed to calculate the time-temperature contour at which nucleation will occur. The effect of the particle size on the time of nucleation is calculated. The results of the calculations yield values which compare very well with experimental results on coal.

SCOPE

The rate of bubble nucleation in coal due to the formation of gaseous reaction products plays a critical role in the pyrolysis process. The bubbles transport volatiles from the interior of the coal particle and serve as microreactors for secondary chemical reactions. Thus, the bubble nucleation process determines to a large extent the products and yields of pyrolysis reactions.

The theory of bubble nucleation in pure boiling liquid

was developed by Volmer and Weber (1926), Farkas (1927) Becker and Doring (1951), Zeldovich (1943), and Frenkel (1943). Modifications of the theory to include the effect of the rate of heat transfer and the viscosity of the liquid were done by Kagan (1960). Blander et al. (1971) studied bubble nucleation in liquid mixtures. The theories of homogeneous and heterogeneous nucleation were reviewed by Blander and Katz (1975) and by Cole (1974).

The author is not aware of any experimental studies of bubble nucleation due to a chemical reaction in viscous

media. Bubble nucleation in a coal melt is a particular case of such processes.

In the present work, criteria for the onset of bubble nucleation in reactive material are developed and applied to coal melts. At the initial stages of coal decomposition, the gases which are formed dissolve in the melt. When their concentration reaches a critical value, bubble nucleation commences. The criteria show that the viscosity will control the rate of bubble nucleation in the melt. Based

CONCLUSIONS AND SIGNIFICANCE

A theory has been developed for bubble nucleation in reactive viscous medium and applied to coal melts. Relations were derived between the gas concentration in the coal and the rate of nucleation.

A maximum possible rate of nucleation is determined by the thermodynamic properties of the system. However, smaller rates may be realized owing to the resistance of the solution to heat, mass, or momentum transfer.

In a coal melt, the viscosity controls the rate of nucleation according to the criteria which were developed. Gas, presumably methane, is formed by the chemical decomposition of the coal. When its concentration in the melt reaches the critical value N^* , bubbles will nucleate. The critical concentration can be calculated from the equation

$$N^* = 1.9504 \times 10^{-29} \left(\frac{\eta}{\sigma} \right) \left(\frac{T}{\sigma} \right)^{1/2} \times \exp \left[\frac{1.1825 \cdot 10^5 \sigma^3}{T K_H^2 N^{*2}} \right]$$

Whether this concentration will be realized or not depends on the properties of the coal and on the operation conditions of the pyrolyzer. Homogeneous nucleation will

on this conclusion, the critical gas concentration that should be reached so that bubble nucleation will commence is calculated.

An approximate relation between the coal properties and the critical gas concentration is derived. The combination of the equations for the initial rate of gas formation in coal melt with the critical concentration allows the calculation of conditions in the temperature-time domain at which bubble nucleation will occur.

occur when

$$\beta^2 = \frac{D\pi^2}{a^2 k_1} < 1$$

When this criterion is not met, the diffusion of gases out through the particle surface should be taken into account. A combination of the rate of gas formation with the criteria for bubble nucleation allows estimation of the point in the temperature-time domain at which nucleation will occur.

The critical concentration for nucleation of methane at 420°C, in coal with typical properties like bituminous coal, was estimated to be about 0.064 mole/l.

As anticipated, drastic changes occur in the properties of coal melt when bubbles nucleate in it. Such changes are indeed observed in the viscosity, density, thermal and electrical conductivity, etc., and the change is followed by an enhanced rate of volatilization of the coal. The abrupt change in the properties of the melt depends on the time-temperature history of the coal, and its location in the time-temperature domain was found to be in a qualitative agreement with the theoretical predictions.

When the products of a chemical reaction in nonviscous liquids are sparsely soluble gases, they first saturate the solution. The concentration of gas continues to increase as the reaction progresses, and when it reaches the saturation concentration, the excess will escape out of the liquid. However, when the reaction occurs in a very viscous material, different phenomena are observed. Melting coal (see definition below) is a special case of such a system. The following presentation refers specifically to coal;* however, extension to other viscous systems is straightforward.

Loisson et al. (1963) reviewed the literature on the plastic properties of coal. The following brief description of the behavior of coal upon heating was extracted from their review.

When coal is gradually heated, it first contracts and then swells to a much larger volume than the original. The temperature at which the coal begins to swell is called the initial swelling temperature. The temperature at which the swelled coal reaches its maximum volume is called the final swelling temperature. In the temperature range between the initial and final swelling temperatures, the solid coal behaves like a very viscous liquid or melt. In the following discussions, the state of the coal in this range of temperatures is referred to as coal melt. Shortly after the coal begins to swell, gas bubbles begin to evolve

from it (Van Krevelen and Schuyer, 1957, p. 290; Ergun et al., 1959; Woods et al., 1967). The source of the bubbles are gaseous products of the hydrocarbon decomposition reactions (Van Krevelen and Schuyer, 1957; Von Fredersdorff and Elliott, 1963; Anthony and Howard 1976). Although voluminous data are available on the plastic properties of coal melts, very little is known about the fundamental processes which control the initiation of a bubble in the melt.

An attempt to investigate the fundamental processes which occur in melting coal is presented below. First, a brief summary of the classical theory of bubble nucleation is presented. The theory is then extended to the case where the nucleating gas is formed by a chemical reaction. The theory shows that when a critical gas concentration is reached in a point in the solution, a gas bubble will nucleate. A formula is derived which permits one to calculate the critical gas concentration. The kinetics of the coal decomposition reaction and the diffusion of gases through the viscous melt determine the concentration of the solution of gas in the viscous melt. The gas that diffuses to the melt surface is released; thus, larger gas concentration will be present in the interior of the melt. An attempt is made to estimate the time required for the concentration of dissolved gas to reach the critical concentration. Several types of surfaces are analyzed, and their effect on the nucleation is studied. In order to test the theory, the values of various properties of coal are required.

Empirical data on the properties of coal are first critically

* It should be noted that only the general trends of the behavior of most of the coals are described. The behavior of many others shows only part of the features described or deviates from it in other manners.

evaluated and then used to test the theoretical predictions. The agreement between the theory and the experimental observations is very good, although the proposed model is rather simple.

MECHANISM OF BUBBLE NUCLEATION IN A REACTIVE HOMOGENEOUS MEDIUM

The formation of a bubble in reactive medium is closely tied with the boiling of a pure liquid. Therefore, bubble formation in boiling liquid will be considered first.

Classical nucleation theory distinguishes between homogeneous nucleation (HMN) and heterogeneous nucleation (HTN). The difference between a homogeneous and a heterogeneous system is due to the presence of surfaces in heterogeneous material. A surface is the location where an abrupt change in the properties of the material occurs. Since every system has a finite size, every system is inherently heterogeneous. However, many processes occur in homogeneous subsystems. A homogeneous system is such a finite medium which the surfaces have little or no effect on the process which occur in it. In other words, the phenomena which are considered and the conditions in which they occur determine whether the system should be modeled as homogeneous or heterogeneous. A criterion which can be used to decide when to use a homogeneous or heterogeneous nucleation mechanism for coal melt is discussed later. First, HMN is detailed, and then the effect of surfaces on the nucleation is briefly described.

Bubble Nucleation During Boiling of a Homogeneous Liquid

The theory of phase transitions and bubble formation in homogeneous media has been developed by Volmer and Weber (1926), Farkas (1927), Becker and Doring (1935), Zeldovich (1943) and Frenkel (1943). Extension of the theory to bubble formation in viscous media or under the constraints of the rate of heat transfer was proposed by Kagan (1960). Blander et al. (1971) developed the theory for bubble formation in a mixture where diffusion controls. Two excellent reviews of the theory of homogeneous and heterogeneous nucleation have been recently published by Blander and Katz (1975) and by Cole (1974).

The previous theories may be combined and extended as follows:

1. The rate of bubble nucleation has an upper limit J which is controlled by the thermodynamic properties of the liquid. An approximate expression for J is

$$J = N \left(\frac{3\sigma}{\pi m} \right)^{1/2} \exp \left[- \frac{16\pi\sigma^3}{3kT[P_V - P_L]^2} \right] \quad (1)$$

2. The bubble nucleus or embryo is formed when a sufficiently large agglomerate of ordered molecules is formed instantaneously. A critical size r_c of an embryo exists that if reached, the embryo will continue to grow to a bubble:

$$P_V = P_L + \frac{2\sigma}{r_c} \quad (2)$$

3. The rate of nucleation cannot exceed the thermodynamic limit J ; however, rates smaller than J will be realized if the transport kinetics is slow. The inhibition of the rate of nucleation due to the transport kinetics can be accounted for using the transport resistance terms δ_m , δ_t , and δ_η as defined. If the rate of heat transfer in the liquid is slow and cannot supply the heat of evaporation q , then J_t , the thermally controlled rate of nucleation will be observed. An approximate expression for J_t is

$$J_t = \frac{J}{1 + \delta_t} \approx N \frac{\lambda}{\sigma} \left(\frac{3\sigma T}{2k} \right)^{1/2} \left(\frac{kT}{q} \right)^2$$

$$\left(1 - \frac{P_L}{P_V} \right) \exp \left[- \frac{16\pi\sigma^3}{3kT[P_V - P_L]^2} \right] \quad (3)$$

$$\delta_t = \left(\frac{q}{kT} \right)^2 \frac{\sigma}{\lambda} \left(\frac{2k}{\pi m T} \right)^{1/2} \frac{P_V}{P_V - P_L} \quad (4)$$

If the rate of momentum transfer in the liquid is slow, and the Newtonian viscosity is η , then the viscosity controlled rate of nucleation J_η is

$$J_\eta = \frac{J}{1 + \delta_\eta} \approx N \frac{\sigma}{\eta} \left(\frac{\sigma}{kT} \right)^{1/2} \left(1 - \frac{P_L}{P_V} \right) \exp \left(- \frac{16\pi\sigma^3}{3kT[P_V - P_L]^2} \right) \quad (5)$$

$$\delta_\eta = \frac{\eta}{\sigma} \left(\frac{3kT}{\pi m} \right)^{1/2} \frac{P_V}{P_V - P_L} \quad (6)$$

If the rate of mass transfer is too slow, then it will control the rate of nucleation. Mass transfer occurs by diffusion of molecules to the embryo. Therefore, when diffusion controls, the rate of nucleation J_m will be

$$J_m = \frac{J}{1 + \delta_m} \approx ND(C_V - C_L) \left(\frac{kT}{\sigma} \right)^{1/2} \exp \left[- \frac{16\pi\sigma^3}{3kT(P_V - P_L)^2} \right] \quad (7)$$

$$\delta_m = \frac{2\sigma}{D(2\pi mkT)^{1/2}(C_V - C_L)} \quad (8)$$

C_V and C_L are the concentration of the volatile component around the nuclei in the gas and in the liquid, respectively. D is the diffusivity of the volatile component of the mixture or the self-diffusion coefficient of the pure liquid. The latter formula was developed for dilute ideal solutions.

Note that the transport resistances are in series. Therefore, in each given situation, the smallest J_i will control the overall rate of nucleation.*

Although Kagan (1960) developed Equation (3) for a pure liquid, the formula can be derived for a dilute solution of a volatile component in a nonvolatile solvent. In such a case, q will denote the heat of solution of the gas in the liquid. The value of σ and λ of the solvent should be used with m of the gas. N in this case will be molecular density of the gas in the solution. The same rules should be used with formula (7). Several additional transport related resistances may be suggested; however, they will not be analyzed here.

In order to find which resistance controls, the ratio of the rates of bubble nucleation α_{ij} are compared. Define

$$\alpha_{m\eta} = \frac{J_m}{J_\eta} = \frac{\eta D}{\sigma^2} kT \frac{C_V - C_L}{1 - \frac{P_V}{P_L}} \quad (9)$$

and

$$\alpha_{t\eta} = \frac{J_t}{J_\eta} = \frac{\eta \lambda T}{\sigma^2} \sqrt{\frac{3}{2}} \left(\frac{kT}{q} \right)^2 \quad (10)$$

When the solution of a slightly soluble ideal gas is considered, then

$$\frac{P_V}{P_L} \ll 1 \quad (11)$$

and

* The inertial forces are negligible in the case of very viscous melt. Different relations should be used when they are important (Kagan, 1960).

$$C_V - C_L \approx C_V = \frac{P_V}{RT} N_o \quad (12)$$

Substitution of (11) and (12) in (9) yields

$$\alpha_{m\eta} \equiv \frac{\eta D}{\sigma^2} P_V \quad (13)$$

If the gas concentration in the solution N is small, Henry's law will be obeyed:

$$P_V = K_H N \quad (14)$$

Henry's constant, K_H , is in general a function of the temperature and of the pressure. Substitution of (14) in (13) yields

$$\alpha_{m\eta} \equiv \frac{\eta D}{\sigma^2} K_H N \quad (15)$$

Let

$$\alpha_{ij} = \frac{J_i}{J_j} \quad (16)$$

To identify j , the mode of transport which controls, find i such that

$$\begin{aligned} \alpha_{ij} &> 1 \\ \text{all } i &\neq j \end{aligned} \quad (17)$$

Note that a larger viscosity may reduce the rate of nucleation, while a larger diffusivity or thermal conductivity may increase the rate of nucleation.

Heterogeneous Nucleation

Blander and Katz (1975) and Cole (1974) reviewed the various aspects of heterogeneous nucleation. The consensus is that the basic principles which apply to homogeneous nucleation can be extended to heterogeneous nucleation, with the following modifications.

1. To account for nucleation around smooth and plane wetted surfaces, the value of σ , the surface tension, should be corrected to include the properties of the surface.

2. Around rough surfaces, the surface curvature determines the critical nucleation radius and may therefore significantly accelerate the rate of nucleation.

3. Gas bubbles that are trapped in cavities in surfaces may act as continuous nuclei and thus enhance the phase transition from liquid to gas.

In the case of a coal melt, two types of surfaces should be distinguished: permeable surfaces from which gas can escape, and impermeable surfaces which do not let gas pass through.

A mineral particle which is embedded in the coal melt may serve as an impermeable surface for gas. The properties of the surface and the shape and size of the coal particles (melt) will affect the rate of nucleation by a heterogeneous mechanism. Several special cases are discussed later.

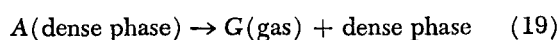
GAS NUCLEATION DUE TO REACTION IN A DENSE VISCOUS MEDIUM

Criteria to Differentiate between Homogeneous and Heterogeneous Nucleation

Consider a homogeneous section in which a chemical reaction occurs which produces a gaseous product. Since a coal melt is very viscous and essentially does not flow, only the diffusion transport is significant. Thus

$$\frac{\partial G}{\partial t} = \nabla \cdot D \nabla G + r \quad (18)$$

where r is the volumetric rate constant of the reaction



The gas concentration increases until it nucleates as a bubble or until such a concentration gradient is created that gas transported by diffusion to the surface removes the excess gas. The evolution of gas from coal at the initial stages of the reaction follows more or less a first-order kinetics (Campbell and Stephens, 1976). Therefore, it will be assumed that the reaction is first order in A and that A is homogeneously distributed; therefore

$$- \frac{dA}{dt} = k_1 A \quad (20)$$

$$A = A_o e^{-k_1 t} \quad (21)$$

A_o will depend, in the case of coal, on the volatility of the particular sample. For the sake of simplicity, it is assumed that the concentration gradient of the gas is important in one direction only,* and that the length of the homogeneous section in that direction is a . Then, Equation (18) becomes

$$\frac{\partial G}{\partial t} = D \frac{\partial^2 G}{\partial x^2} + k_1 A_o e^{-k_1 t} \quad (22)$$

In dimensionless form, Equation (22) becomes

$$C_\theta = \beta^2 C_{zz} + e^{-\theta} \quad (23)$$

where

$$\theta = k_1 t \quad (24)$$

$$z = \frac{x}{a} \pi \quad (25)$$

$$\beta^2 = \frac{D \pi^2}{k_1 a^2} \quad (26)$$

$$C = \frac{G}{A_o} \quad (27)$$

Two extreme cases may be differentiated according to the value of the module β^2 (similar to Thiele modulus):

$$\beta^2 = \frac{D \pi^2}{k_1 a^2} \quad (28)$$

1. If $\beta^2 \ll 1$, the system can be considered homogeneous, and the effect of a concentration gradient will be negligible.

2. If $\beta^2 > 1$, the surface effects and concentration gradients should be taken into account.* The nucleation of a gas bubble in each case is considered in the following sections. Note that β^2 assumes different values at different temperatures because both D and k_1 depend on the temperature. Typically

$$D \propto T^2 \quad (29)$$

and

$$k_1 \propto e^{-\frac{E_a}{RT}} \quad (30)$$

Therefore

$$\beta^2 \propto \frac{T^2}{a^2} e^{\frac{E_a}{RT}} \quad (31)$$

and

$$\frac{\partial \beta^2}{\partial T} < 0 \quad \text{for all } T < \frac{E_a}{2R} \quad (32)$$

Since $4 < E_a < 80$ kcal/mole for most reactions, an increase in T will make the homogeneous mechanism more favorable for most practical temperature regions.

* Extension to other geometries is a matter of mathematical exercise only.

* When $\beta^2 \gg 1$, the solubility of the gas in the coal at the gas partial pressure in the system will determine its concentration.

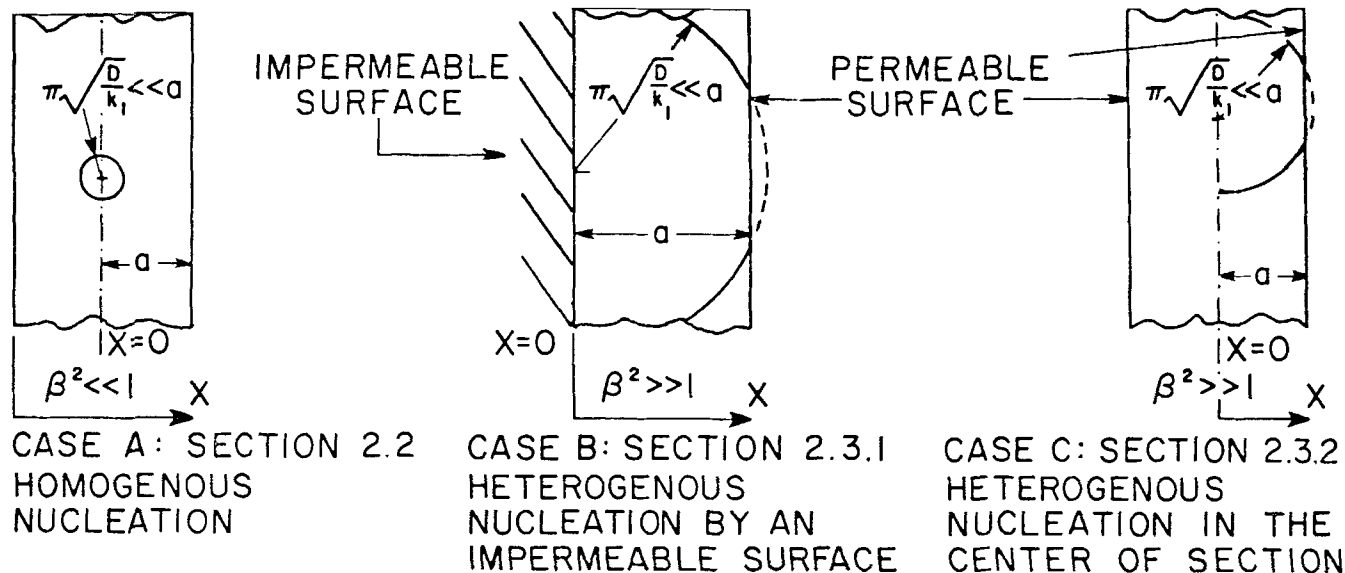


Fig. 1. Nucleation of a pore in coal. (a) Homogeneous nucleation—the surface does not influence the nuclei. (b) Heterogeneous nucleation by an impermeable surface. (c) Heterogeneous nucleation in a homogeneous section where gas can diffuse out from both sides.

Three particular cases are discussed in detail later. When $\beta^2 \ll 1$, the surface does not influence the nucleation, and HMN will occur. When $\beta^2 > 1$, HTN will occur. If an impermeable surface prevents the gas from diffusing out, nucleation will occur by the impermeable surface. But if $\beta^2 \ll 1$ and gas can diffuse out from both sides of the homogeneous section, then the gas concentration will have a maximum at the center of the section. In the latter case, gas will not diffuse through the center line of the section, and thus the center will act as an impermeable surface. Figure 1 shows the three cases.

Gas Nucleation by a Homogeneous Mechanism (NHM)

When $\beta^2 \ll 1$, Equation (23) becomes

$$C_\theta = e^{-\theta} \quad (33)$$

If the initial gas concentration was 0, then

$$C = 1 - e^{-\theta} \quad (34)$$

or

$$\frac{G}{A_0} = 1 - e^{-k_1 t} \quad (35)$$

G , the gas concentration in the solution, can be easily converted to N , the molecular density of the gas in the solution. Substitution in Equations (3), (5), or (7) will yield the rate of gas nucleation in the media in the various transport controlled nucleation modes. In the case of coal melt, it is found that momentum transport is the controlling mode. An example of the calculations of the period of time required for nucleation to occur in coal at 420°C is given later.

Gas Nucleation by a Heterogeneous Mechanism (NHT)

The major difference between NHM and NHT is that in heterogeneous mechanism the special location of the nuclei should be considered as well as the particular choice of boundary conditions. Three types of boundary conditions may be important from the physical point of view:

1. Impermeable heterogeneous surface, by which heterogeneous nucleation may occur. The concentration gradient by the impermeable surface ($z = 0$) will be 0 for all the values of θ ; thus

$$\frac{\partial C}{\partial z}(0, \theta) = 0 \quad (36)$$

where the location of the surface is chosen as $z = 0$. (Figure 1, case b).

2. Negligible gas phase resistance to mass transfer. The concentration of the gaseous product is zero by the surface of the melt:

$$C(\pi, \theta) = 0 \quad (37)$$

3. Finite resistance to mass transfer (linearized). The concentration of the gaseous product by the surface $C(\pi, \theta)$ is finite:

$$-\frac{D\pi}{a} \frac{\partial C}{\partial z}(\pi, \theta) = k_m C(\pi, \theta) \quad (38)$$

The initial condition which will be applied is

$$C(z, 0) = 0 \quad (39)$$

Two cases will be analyzed:

1. Heterogeneous nucleation by an impermeable smooth plane surface. Negligible resistance of the gas phase mass transfer is assumed (Figure 1, b).

2. Heterogeneous nucleation in the center of a homogeneous section when the gas phase resistance on both sides of the section is negligible (Figure 1, c).

Heterogeneous Nucleation by an Impermeable Smooth Surface. The boundary conditions

$$C_z(0, \theta) = 0 \quad (\text{impermeable surface}) \quad (40)$$

$$C(\pi, \theta) = 0 \quad (\text{negligible gas phase resistance}) \quad (41)$$

$$C(z, 0) = 0 \quad (42)$$

Solution of Equation (22) with boundary conditions (40), (41), and (42) is done by finite Fourier transform, with the kernel

$$\cos \frac{2n-1}{2} z$$

The result is

$$C = \sum_{n=0}^{\infty} \frac{2}{\pi} \frac{(-1)^{n+1}}{\lambda_n} e^{-\beta^2 \lambda_n^2 \theta} [1 - e^{-\theta}] \cos \lambda_n z \quad (43)$$

where

$$\lambda_n = \frac{2n-1}{2} \quad (44)$$

At the surface, $z = 0$; therefore

$$C = \frac{G}{A_0} = \sum_{n=0}^{\infty} \frac{4}{\pi} \frac{(-1)^{n+1}}{(2n-1)} e^{\frac{-\beta^2 (2n-1)^2}{4} \theta} (1 - e^{-\theta}) \quad (45)$$

Again, G can be converted to the molecular density of the gas, and with the aid of Equations (3), (5), or (7),

TABLE 1. TYPICAL PROPERTIES OF COAL MELT AT 420°C

Variable	Value	Units	Source
Viscosity, η	3×10^6	poise	Van Krevelen and Schuyer (1957), p. 301
Density, ρ	1.31	g/cm ³	Tschamler and deRuiter (1963), p. 106
Thermal conductivity, λ	5.1×10^{-4}	cal/s · cm °C	Badzioch et al. (1964)
Diffusion coefficient of CH ₄ , D	$>10^{-8}$	cm ² /s	See discussion
Surface tension, σ	30	dyn/cm	Estimated
Henry's constant for CH ₄ , K_h	4 800	kilobar/mole l	Estimated
First-order reaction rate constant, k_1	7.92×10^{-8}	s ⁻¹	Campbell and Stephens (1976)

according to the prevailing controlling mechanism, θ^* can be found at which N will reach the critical concentration required for nucleation. Note that in this case σ should be modified according to the properties of the impermeable surface. The modification of σ due to a surface is described by Blander and Katz (1975) and will not be discussed here. However, it is not expected that the effect will be large. Of much more serious concern is the crystallinity of the surface. Most of the heterogeneous materials, which can be expected in coal, are crystalline and contain cavities of a size comparable to the critical bubble dimension. Such cavities may promote nucleation at a substantially earlier time than those that can be predicted by Equation (45). An example of calculation of the nucleation time by heterogeneous mechanisms is discussed later.

Further examination of Equation (45) suggests that when diffusion of gas out is possible, nucleation may be eliminated altogether, for example, if $\beta^2\theta \gg 1$ or if the volatility of the coal is small.

Heterogeneous Nucleation in a Homogeneous Section. If gas can diffuse out of the surface on both sides of the z axis, the gas concentration will reach a maximum at its center (Figure 1, *c*). Boundary conditions (40), (41), and (42) apply again, except that z is defined in this case with respect to a different a . In this case, a is the distance from the center of z to the surface. The solution of the problem is again (43), and the concentration of the gas in the center will be given by (45). However, β^2 is defined now based on a different value of a .

APPLICATION OF THE THEORY TO BUBBLE NUCLEATION IN COAL MELT

Very little data are available in the literature on the elementary properties of coal, and what could be found were derived on different coals. The data which were estimated or located are critically reviewed. Typical values of the elementary properties of coal melt at 420°C are presented in Table 1.

Luckily, some useful information can often be deduced just by specifying the order of magnitude of a variable. The author does not claim that the data are more accurate than to an order of magnitude. Some numbers are presented, however, with two or three digits, mainly because the sensitivity of the algorithms requires it.

The values of the properties of coal melt at 420°C are discussed first and then are used to prove that the melt viscosity controls the rate of pore nucleation in coal. The critical concentration of methane that should be reached so that a nuclei will form is estimated. The time that will elapse before a nuclei will be formed is calculated for homogeneous and heterogeneous nucleation.

Numerical Values of the Physical Constants

The physical properties of coal were reviewed by Tschamler and de Ruiter (1963) and by Van Krevelen and Schuyer (1957). Some data are taken from these sources without specific reference.

Viscosity and the Onset of Decomposition. The viscosity of coal melt depends on the temperature-time-pres-

sure history of the coal (Van Krevelen and Schuyer, 1957). Several attempts have been made to correlate it, the most successful by Fitzgerald (1956) and by Bronowski et al. (1953). The most striking phenomenon is that coal melts and homogenizes first, before decomposition begins (Waters, 1962). Up to the decomposition point, where the coal begins to lose weight, it behaves as a Newtonian fluid, and the process is more or less reversible with respect to the temperature (Macrae and Murthi, 1962). The same authors note an extreme sensitivity of the fluidity to the temperature around the softening temperature and attributed the phenomenon to the increased porosity of the melt due to foaming (in other words, bubble nucleation).

The data of Waters (1962) and of Van Krevelen et al. (1956) show that the temperature at which the rate of decomposition reaches its maximum is slightly higher but almost coincides with the temperature at which the fluidity reaches its maximum.

The previous discussion suggests that the temperature at which pore nucleation occurs is slightly smaller than the temperature of minimum viscosity; once the nuclei are formed, a step reduction in the viscosity occurs. The temperature at which coal begins to lose weight ranges from 370° to 430°C. So, a temperature of 420°C will be used in the estimates. The minimum viscosity of coal melts is in the range of 2 to 7×10^6 poise. Lewellen (1975) used in his study of growth of bubbles a value of the order of 3×10^6 poise. This value will be used here.

Coal Density. The density of coal and its relation to coal structure has been discussed by Van Krevelen and Chermin (1954). The most important variables that influence the density are the rank, the elementary composition, the petrographic composition, and the temperature. Tschamler and de Ruiter (1963), p. 106, discussed in length the effect of each variable on the density. For the purpose of this discussion, it will be assumed that the density is 1.31 g/cm³ at 420°C. This value is consistent with the data of Franklin (1949) who demonstrated that density of bright coal is essentially constant until 450°C.

Coal Thermal Conductivity, Diffusivity, Surface Tension and Heat of Solution. The thermal conductivity of numerous coals was measured as a function of the temperature by Badzioch et al. (1964). Their data show that the thermal conductivity does not vary much with the temperature up to about 450°C. The average value for many coals is about 5.1×10^{-4} cal/cm · s °C.

Two modes of gas diffusion in coal should be differentiated: diffusion through pores which exist in the coal structure, and diffusion through the coal melt. For the purpose of the analysis of pore nucleation, the diffusivity through the melt should be used. The author is not aware of any study of gas diffusivity through coal melts. However, the diffusivities of methane and helium in coal disks were measured by Karl et al. (1970). Nandi and Walker (1970) used the unsteady state technique to measure the diffusion parameter $\sqrt{D/r_o^2}$ of methane (r_o is the diffusion path length). From the description of the experimen-

tal procedures, it seems that in both studies the diffusion through the pores in the solid was measured. The most important findings were:

1. D is unisotropic and may vary by a factor of four in different directions.

2. The diffusion is activated and follows Arrhenius type of temperature dependence in both directions of the disk. Karl et al. (1970) found the value $E_D = 13.6$ kcal/mole for the diffusion activation energy for methane. Nandi and Walker (1970) quote activation energies in the range of 3.9 to 5.4 kcal/mole. However, in their work on various coals they measured activation energies in the range of 3.5 to 7.6 kcal/mole. Larger E_D was observed when the volatility was larger.

3. The diffusivity of methane at 72°C calculated based on Karl's data is about 1.3×10^{-10} and 2.1×10^{-10} cm²/s for flow across and along the coal disk, respectively (Pittsburgh Seam). For St. Nicolas coal (anthracite) at 72°C, Nandi and Walker estimate the diffusivity as 2.8×10^{-15} cm²/s for 42 to 65 mesh particles and 8×10^{-16} cm²/s for 100 to 150 mesh particles. Extrapolation of the data of Karl et al. to 420°C gives values of D of the order of 10^{-5} - 10^{-6} cm²/s. Nandi's and Waters' data lead to substantially smaller numbers. However, Thimons and Kissel (1973), who measured the diffusivity of methane at ambient temperature, report numbers of the order of 10^{-5} - 10^{-6} cm²/s, which is substantially larger than the number quoted by others.

Although it is not clear which value of diffusivity should be used for the melt, it will be shown that if the diffusivity is larger than 10^{-8} cm²/s, mass transport will not control the rate of nucleation.

The author is not aware of any published experimental work on the surface tension of coal melts. Therefore, correlations of hydrocarbon surface tension with its density and chemical composition and with its molar refraction were used to estimate it (Meissner, 1949). The surface tension of the coal model molecule, presented by Aczel et al. (1976), is 15 to 30 dyne/cm, depending on the exact value assumed for the density.

Schuyer and Van Krevelen (1954) proposed a method to calculate the molar refraction of coal based on its elementary composition. A combination of this method with Meissner's (1949) method leads to numbers in the range of 20 to 35 dyne/cm. Numbers in this range are similar to the values of the surface tension of liquid hydrocarbons around room temperature. The surface tension of liquids does not change much with the temperature; however, in the case of coal pyrolysis, the range of temperature is large. Tschamler and de Ruiter (1963), p. 57, quote Chandra et al. (1956) who observed a drastic change in the reflectance of coal with the increase in the temperature. A drastic change in the reflectance may indicate a step function in the surface tension. Lewellen (1975) in his study of coal melt used the value of 55 dyne/cm. In this study $\sigma = 30$ dyne/cm is used.

The author is not aware of any measurement of the heat of solution of methane or hydrogen in coal melt. However, such a solution is expected to be dilute and very close to ideal. Heat of solutions in the range of 0.5 to 2 kcal/mole can be expected. If the ideal solution concept is carried on further, it can be shown that the vapor pressure of ideal solution of methane in a high molecular weight hydrocarbon can be approximated by

$$P_V = K_H N$$

For P_V in atmospheres and N in gram moles per liters, the value of K_H around 420°C is estimated as 4 800 atm/mole/l.

Numerical Values of Kinetic Constants

Two questions are addressed: what is the gas that causes the bubble nucleation, and what is the rate of the reaction which produces it. The chemical composition of the gases which evolve from coal during carbonization were studied by several investigators. Most recently, Campbell and Stephens (1976) examined the rate of evolution of gases from coal using Juntgen's method (Juntgen, 1964). Several other studies were published on this matter, notably the work of Fitzgerald and Van Krevelen (1959). The most important gases which were reported were hydrogen, methane, carbon dioxide, ethane, propane, and ethylene. If it is assumed that the gas that begins to evolve first is the one which nucleates the bubble, then, based on the data of Campbell and Stephens (1976), one would assume that carbon dioxide is the gas which nucleates. Evolution of carbon dioxide becomes measurable at temperatures as low as 200°C. Methane, carbon monoxide and hydrogen evolution become measurable slightly below 400°C. The latter observation is inconsistent with the data of Fitzgerald and Van Krevelen (1959) who recorded very small evolution of carbon dioxide.

It seems that the evolution of carbon dioxide is more important in the case of low-rank coals, while the evolution of hydrogen and methane are more important for coals with higher ranks. The analysis of gas samples which evolved from melting coals from West Virginia and Alabama (Melton and Giardini, 1976) shows that methane and hydrogen are invariably the dominant components. Therefore, it was assumed that methane and/or hydrogen are the gases which nucleate the pores. The kinetic data of Campbell and Stephens (1976) were used to obtain a first-order approximation.

The Arrhenius parameters of the first-order rate constant for the evolution of methane are $k_o = 1.6 \times 10^6$ min⁻¹, $E_a = 31$ kcal/mole, $1.2 \cdot 10^8$ min⁻¹, and $E_a = 22.3$ kcal/mole for hydrogen. Note that the rate of evolution of gases is not identical with the volumetric rate of gas formation in the coal melt (mole per cubic centimeters coal). In fact, intraparticle mass transfer become important for gas evolution when the coal particle size is larger than 0.6 mm (for small heating rates).

The Viscosity and Momentum Transfer are the Controlling Mechanism for Pore Nucleation in Coal

The criteria which allow the determination of the controlling mechanisms are given in Equations (10) and (15). Application to coal gives

$$\begin{aligned} \alpha_{t\eta} &= \frac{\eta \lambda T}{\sigma^2} \sqrt{\frac{3}{2}} \left(\frac{kT}{q} \right)^2 \\ &= \frac{3 \cdot 10^6 \times 5.1 \times 10^{-4} \cdot 4.18 \times 10^7 \cdot 693}{30^2} \\ &\quad \left(\frac{1.99 \times 693}{2 \times 10^3} \right)^2 \sqrt{\frac{3}{2}} \\ \alpha_{t\eta} &= 2.9 \times 10^{10} \gg 1 \end{aligned}$$

If it is assumed that the viscosity is the controlling mechanism, then pore nucleation will commence when $N^* \cong 10^{-2}$ - 10^{-4} mole/l (see below). At this range of concentrations

$$\begin{aligned} \alpha_{m\eta} &= \frac{\eta D}{\sigma^2} K_H N^* \\ &= \frac{3 \cdot 10^6 \cdot 10^{-3} (4 800 \cdot 10^{-4}) \cdot (1.013 \cdot 10^6)}{30^2} \end{aligned}$$

$$\alpha_{m\mu} = 1.6 \cdot 10^6 \gg 1$$

Since $\alpha_{m\eta}$ and $\alpha_{t\eta}$ are much larger than 1, according to the criteria of Equations (16) and (17), the viscosity is controlling the rate of pore nucleation in coal.

The critical concentration of dissolved gas that should be reached in the coal melt so that homogeneous nucleation will begin can be calculated assuming that the onset of nucleations is when $J^* = 1$ bubble/cm³ (Cole, 1974). Note that because of the structure of Equation (5), the exact value which is chosen for J^* will have very small effect on N^* , the critical concentration at the onset of nucleation. Therefore, although the choice of J^* , the critical rate of nucleation, may be argued, the effect of the particular choice of J^* on the value of N^* is small. From (5) and (14)

$$N^* = J^* \frac{\eta}{\sigma} \left(\frac{kT}{\sigma} \right)^{1/2} \exp \left(\frac{16\pi\sigma^3}{3kT K_H^2 N^{*2}} \right) \quad (46)$$

It was assumed again that $P_L/P_V \ll 1$. When common units are used for the coal properties, then

$$N^* = 1.9504 \times 10^{-29} \frac{\eta}{\sigma} \left(\frac{T}{\sigma} \right)^{1/2} \exp \left(\frac{1.1825 \times 10^5 \sigma^3}{T K_H^2 N^{*2}} \right) \quad (47)$$

where N^* is in mole per liter of dissolved gas, T in degrees Kelvin, σ in dyne per centimeter, η -poise, and K_H in atmosphere per liter. An approximate value for N^* , assuming that the viscosity limited mechanism is obtained by a trial-and-error solution of (48), is

$$N^* = 1.9504 \times 10^{-29} \frac{3 \times 10^6}{30} \left(\frac{693}{30} \right)^{1/2} \exp \left(\frac{1.1825 \times 10^5 \times 30^3}{693 \cdot 4800^2 N^{*2}} \right), \quad T = 693^\circ \text{K}$$

$$N^* = 9.374 \times 10^{-24} \exp \left(\frac{0.2}{(N^*)^2} \right) \quad (48)$$

$$N^* \cong 0.06307 \text{ mole/l} \approx V^* = 1.08 \text{ std cm}^3/\text{g coal}$$

(Four digits are written because of the extreme sensitivity of the formulation to the value of N^* and not because it has physical significance.)

Example 1: Calculation of the critical methane concentration and nucleation time in homogeneous material. At 420°C, the rate constant for methane evolution is about $k_1 = 2.85 \times 10^{-4} \text{ min}^{-1}$. If it is assumed that the total standard volume of methane that can evolve from a gram of coal v^* is 70 cm³/gm coal, then $C^* = V^*/V^\infty = 1.08/70$. The critical time t^* for the formation of the critical concentration C^* in isothermal decomposition is given by

$$t^* = -\frac{1}{k_{\text{CH}_4}} \ln \left(1 - \frac{v^*}{v^\infty} \right) \quad (49)$$

t^* is an order of magnitude estimate of the period of time that will elapse until nucleation will take place in isothermal decomposition of coal around 420°C in homogeneous medium, when the viscosity controls the rate of nucleation. The value that is obtained for t^* is 54 min.

Example 2: Calculation of the critical methane concentration in heterogeneous nucleation. From Equation (45) it can be seen that the maximum concentration of gas will be in the center of the section, and its value will be

$$\begin{aligned} \max \cdot C &= \sum_0^\infty \frac{4}{\pi} \frac{(-1)^{n+1}}{(2n-1)} e^{-\frac{\beta^2(2n-1)^2}{4}\theta} (1 - e^{-\theta}) \\ &= \frac{4}{\pi} (1 - e^{-\theta}) \sum_0^\infty \frac{(-1)^{n+1}}{2n-1} e^{-\frac{\beta^2(2n-1)^2}{4}\theta} \end{aligned}$$

The series converges very rapidly, and if the terms higher than the second are neglected, we get

$$\max C = \frac{8}{\pi} (1 - e^{-\theta}) e^{-\frac{\beta^2\theta}{4}}$$

The maximum concentration C^* will be reached after θ^* time:

$$\begin{aligned} \theta^* &= \ln \left(1 + \frac{4}{\beta^2} \right) \\ C^* &= \frac{8}{\pi \left(1 + \frac{\beta^2}{4} \right)} \left(1 + \frac{4}{\beta^2} \right)^{\frac{\beta^2}{4}} \end{aligned}$$

The critical value of C^* at 420°C has been estimated to be $1.08/70 = 1.543 \cdot 10^{-2}$. The corresponding value for $\beta^2/4$ is 60 and of θ^* is $1.6529 \cdot 10^{-2}$. The value of t^* , the real time of nucleation, is obtained using the value $k_1 = 2.85 \cdot 10^{-4} \text{ min}^{-1} \cdot t^* = 58 \text{ min}$. Such a value is very close to the corresponding number which is obtained when a homogeneous mechanism is assumed. The corresponding critical dimension is obtained from

$$\begin{aligned} \frac{\beta^2}{4} &= 60 = \frac{\pi^2 D}{4k_1 a^2} \\ a &= \frac{\pi}{\sqrt{240}} \sqrt{\frac{D}{k_1}} = 0.20279 \sqrt{\frac{D}{k_1}} \end{aligned}$$

If it is assumed again that D is of the order of $10^{-4} \text{ cm}^2/\text{s}$ and $k_1 = 2.85 \cdot 10^{-4} \text{ min}^{-1} = 4.75 \cdot 10^{-6} \text{ s}^{-1}$, then

$$a = 0.20279 \sqrt{\frac{10^{-4}}{4.75 \cdot 10^{-6}}} = 0.93046 \text{ cm}$$

If we consider the large uncertainty about the value of D , this value is in excellent agreement with the experimental values. If D is indeed of the order of $10^{-6} \text{ cm}^2/\text{s}$, as some of the data suggest, then the corresponding a is 0.093 cm. Data are available (for example, Mackowsky and Wolff, 1966) which show that the frequency of appearance of pores in coal particles smaller than 0.02 cm is three to seven times smaller than the frequency of pores in particles 0.1 to 0.3.

Calculations similar to the example can easily be carried out for other temperatures and for nonisothermal process. The result will yield the coal particle size in which nucleation will occur.

RELEVANCE TO EXPERIMENTAL OBSERVATIONS

Two types of observations should be distinguished: microscopic observations on coal samples, and bulk measurements of the physical and plastic constants of the sample. When gas bubbles nucleate in the coal sample, the pore nucleus should be accounted for by microscopic observations, and a drastic change in the bulk properties of the sample should be observed. Since the critical time t^* at which the critical gas concentration N^* is reached depends very sharply on the temperature, the change in the properties of the sample should occur at

a rather narrow range of the time temperatures domain. Indeed, sharp changes in the properties of coals are observed in the temperature range of 390° to 460°C for all coals when the time scale for these observations is 1 to 200 min.

Microscopic Observations

The length scale for bubble nuclei is of the order of $0.01\ \mu$ which is obviously too small to be observed by microscopy. However, the developed bubbles can be examined by microscopy once they reach size of the order of $1\ \mu$. The results of such observations may, however, be distorted because of the bubble transport mechanism in the coal particles. Post nucleation bubble transport phenomena in coal melts were discussed by Lewellen (1975).

Mackowsky and Wolff (1966) and Hays et al. (1976) examined the microscopy of the coking process. The main observations follow similar lines for most of the coals that they examined; Hays et al. (1976) summarized their observations as follows:

1. Pore nucleation is observed in large particles (larger than 0.2 mm when the heating rate was 3°K/min).

2. Swelling leads to fusion and filling of the interparticulate volume.

3. Post fusion pore growth occurs and is probably accompanied by additional nucleation.

The theory has been developed for isothermal processes; however, it is qualitatively applicable to nonisothermal states, the main difference due to the increase with the temperature of the rate of the chemical reaction. The results of the microscopic studies can be interpreted as follows:

1. Gas diffusion from small particles can be fast enough so that the critical gas concentration, N^* , is never reached. The particle decomposition follows the model described previously or its nonisothermal analogue.

2. At a given set of conditions, a critical particle size exists, that the rate of gas diffusion from it is not large enough and the critical concentration required for nucleation will be reached. A previously described model or its nonisothermal analogues can be applied for this case to obtain the critical particle size.

3. When fusion occurs, the space dimension a becomes large. As a result, β^2 decreases and nucleation by homogeneous mechanism becomes more favorable. When fusion occurs at a higher temperature, the homogeneous nucleation is even more favorable [Equation (31)].

4. The strong correlation between the pore formation process and the viscosity of the coal (plasticity and dilatation) further supports the prediction that the nucleation is viscosity controlled. A very sharp decrease in the viscosity occurs when the first gas bubbles evolve.

Segments can be identified in microscopic samples of coke, in which pores with surprisingly uniform size are present (for example, Adair et al., 1972). The size of such uniform pores is of the order of $1\ \mu$. Uniform pores can grow only from equal sized nuclei in an isotropic homogeneous medium. Therefore, one must conclude that at least a limited number of pores nucleate in coal by a homogeneous mechanism. Note that adsorption data on coal and on cokes indicate that pores of fairly uniform size, around $0.003\ \mu$, do exist in coal (for example, Gan et al., 1972). However, adsorption data can be obtained only on connected pores. Swelling of coal, on the other hand, must occur around closed unconnected pores only, such as created by gas nucleation.

Changes of the Bulk Properties

Drastic changes in the bulk properties are expected and are observed when gas bubbles nucleate in it. The prop-

erties most often referred to are the viscosity, the dilatation, the electrical conductivity, the density, and the refractance. Tschamler and de Ruiter (1963) reviewed most of the data on these properties. An account of the mechanical properties was published by Brown and Horns (1963) and of the plastic properties by Loison et al. (1963). Recently, studies of specific volume were published by Toda (1973).

The data of Van Krevelen et al. (1956), Waters (1962), and others show that a large increase in the rate of volatilization follows the decrease in the viscosity of the melt. Since volatilization occurs due to bubble transport of gases to the surface of the melt, and because the reduction in the viscosity occurs due to bubbles nucleation, the two phenomena correlate according to the theory.

Dilatation curves, which were derived at different rates of heating (for example, Van Krevelen et al., 1956), show that when a smaller rate of heating is used, the commencement of swelling occurs at a higher temperature and the total swelling that is observed is smaller. When a small rate of heating is used, more gas escapes from the surface and the critical concentration is reached after longer periods of time, in agreement with the theory.

NOTATION

a	= characteristic dimensions for diffusion
A	= concentration of organic material that can decompose into volatile products
A_o	= initial value of A
C	= dimensionless concentration
C_L	= concentration of gas in the liquid around a nuclei
C_V	= concentration of gas in the vapor around a nuclei
D	= diffusivity
E_a	= activation energy
E_D	= activation energy for diffusion
G	= concentration of gas in an arbitrary point in the solution
G^*	= value of G when J^* is reached
i	= index
j	= index
J	= rate of bubble nucleation
J_j, J_i	= value of J sub m, t , or y
J_m	= mass transfer limited rate of nucleation
J_t	= heat transfer limited rate of nucleation
J_n	= momentum-transfer limited rate of nucleation
J^*	= value of J when spontaneous homogeneous nucleation occurs
k	= Boltzman constant
k_{CH_4}	= rate constant for the formation of methane
K_H	= Henry's gas solubility constant
k_m	= mass transfer coefficient for particular surface
k_o	= Arrhenius preexponential constant for k_1
k_1	= rate constant for the decomposition reaction
m	= mass of a molecule
n	= index
N	= molar concentration of gas in the solution
N_o	= Avogadro number
N^*	= value of N when J^* is reached
P_L	= pressure of the gas in the solution
P_V	= pressure of the gas above the solution in equilibrium
q	= heat of vaporization or heat of solution
r	= rate of gas formation/unit volume
R	= ideal gas constant
r_c	= critical radius of nuclei
r_o	= mean free path for diffusion
t	= time
t^*	= time at which spontaneous homogeneous nuclea-

tion begins
 T = absolute temperature
 V^* = STP equivalent of G^*
 X = space length in the direction of maximum concentration gradient
 Z = dimensionless space coordinate in the direction of maximum concentration gradient

Greek Letters

α_{ij} = ratio of the J_i to the J_j
 α_{mn} = ratio of J_m to J_n
 $\alpha_{t\eta}$ = ratio of J_t to J_η
 β^2 = system constant = $D\pi^2/(k_1a^2)$
 ∇ = gradient operator
 δ_m = mass transfer resistance to bubble nucleation (equation 8)
 δ_t = heat transfer resistance to bubble nucleation (equation 4)
 δ_η = momentum transfer resistance to bubble nucleation (equation 6)
 θ = dimensionless time θ^* — the value of θ when J^* is achieved
 λ = thermal conductivity of solvent
 λ_n = eigenvalues of the solution
 σ = surface tension

Subscripts

θ, z = differentiation with respect to θ and z

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