the estimated upper limit of K. Due to uncertainty in estimating D_s, as well as to mathematical approximations that have been made, no more than semi-quantitative accuracy can be claimed for K. A more detailed study, not justified at present because of uncertainty regarding estimation of parameters, would require keeping more terms in the expansion, Eq. 11.

NOTATION

a $= 1 - K \sqrt{D_a/D_s}$
b $= 1 + K \sqrt{D_a/D_s}$
c = concentration of water
c^* = solubility of H_2O in the film
D = diffusion coefficient
δ = film thickness
H = Henry's law constant for solubility of water in the film
J = flux of evaporating water
K = distribution coefficient for water in air and in film
p^* = vapor pressure of water
Q_s = total evaporation from the film
Q_w = total evaporation from a pure water surface
R = gas constant
r = radius of ring
T = temperature
t = time
x = position coordinate

Subscripts

a = air region
i = initial condition
s = surfactant film region

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Manuscript received August 10, 1981, and accepted August 31, 1981.

Reaction Rate Oscillations during Fischer-Tropsch Synthesis on Fe-Precipitated Nu-1 Zeolite-Type Catalysts

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The phenomenon of reaction rate oscillations in catalytic systems has been the subject of intensive investigations in the last thirteen years. In 1968, Hugo (1968) observed for the first time thermochemical oscillations during the exothermic decomposition of N_2O on a CuO catalyst. Since then reaction rate oscillations have been observed in several other catalytic systems, such as H_2 oxidation over Pt foils and wires (Luss et al., 1980; Schmitz et al., 1979) and Pt and Pd supported catalysts (Boudart et al., 1976), CO oxidation over supported and unsupported Pt catalysts (Carberry et al., 1978; Schmitz and Shientuch, 1977), C_2H_4 oxidation over Pt films (Vayenas et al., 1980) and NH_3 oxidation over Pt wires (Schmidt et al., 1980). Several comprehensive review papers have now appeared (Schmitz and Sheintuch, 1977; Slinko and Slinko, 1978). The majority of the above studies were performed at or near atmospheric pressures and in most cases in a single pellet reactor.

Quite recently in our laboratory, reaction rate oscillations have been observed during Fischer-Tropsch synthesis reaction over 13% Fe-precipitated zeolite type catalysts at medium pressures (2.2×10^3 Kpa) in a multipellet Berty CSTR reactor. Some of our observations are summarized in the present publication.

The discovery of medium pore zeolites ZSM-5 by Mobil workers (Asgauer and Landolt, 1972) and Nu-1 type zeolite by ICI workers (Whittam and Spencer, 1978) have provided new routes in the indirect liquefaction of coal and its conversion to chemicals. Zeolites have from the point of view of catalysis, the very important property of solid acidity (Jacobs, 1977).

Due to their acidity Fe-precipitated ZSM-5 and Nu-1 type catalysts have been shown recently by one of the authors (Rao et al., 1980b) to produce during reaction with synthesis gas a lower percentage of olefins (C_2–C_4) in the gas phase than silicalite type catalysts [silicalite is a molecular-sieve type catalyst with structure very similar to that of ZSM-5 but with no acidity (Grose, 1977)] and a liquid phase with a higher percentage of aromatics and a lower percentage of olefins. During this study as well as in subsequent studies Rao and coworkers, on several separate occasions (in two runs with Fe-precipitated ZSM-5 type catalysts, in two runs with Co-ZSM-5 type catalysts and in one run with Fe-precipitated Nu-1 type catalysts), observed autonomous self-sustained reaction rate oscillations. A systematic study was therefore undertaken to verify the existence and self-generation of the oscillatory phenomena. Nu-1 zeolite type catalysts were selected for this study.

EXPERIMENTAL PROCEDURE

The Nu-1 type zeolite was prepared by methods described in the literature (Whittam, 1977). The preparation of the Fe-precipitated form of the catalyst is also described in detail elsewhere (Rao et al., 1980a). The catalyst was prepared into $3.2 \times 10^{-3} \times 3.2 \times 10^{-3}$ m cylindrical pellet form. 5×10^{-2} Kg of this catalyst was placed inside a Berty CSTR reactor. The catalyst volume was approximately 5.8×10^{-5} m^3 and the total reactor volume 5×10^{-4} m^3. The catalyst was reduced *in situ* at 2.2×10^3 kPa and 450°C in flowing H_2 for 24 h. It was then subsequently carbided at 7×10^2 kPa and 250°C for 24 h. A complete description of the experimental system is presented elsewhere (Rao, 1980b). The reactants are flowing through a carbon trap and were periodically analyzed at the exit of the trap for impurities with gas chromatography and flame photometric analytical techniques. The main impurity found was CO_2 (~0.1%). No detectable quanities of hydrocarbons were found (<0.1%). The sulphur impurity levels were found to be 20 ppb. CO_2 and hydrocarbons are, of course, primary products of the Fischer-Tropsch synthesis and can hardly be characterized as impurities. The gas phase products (C_1–C_4) were analyzed by gas chromatography and liquid product analysis was not attempted because of the large samples required.

EXPERIMENTAL RESULTS

Oscillatory behavior was observed for a bounded region of reactor wall temperatures (between 275 and 330°C). The oscillations were intrinsically nonisothermal, and fluctuations in the catalyst bed temperature were observed, sometimes as high as 200°C. As is also true with several prior studies of oscillatory phenomena, the nonisothermal nature of the observed oscillations poses severe limitations to a meaningful kinetic investigation of the phenomenon.

Several other experimental limitations were imposed on us which were inherent in our reactor system or else in our catalytic system. Reactor safety considerations imposed and upper reactor wall temperature of 400°C. The catalyst system is known to undergo "coking" for temperatures higher than 400°C. A maximum catalyst bed temperature of 450°C was imposed. The reactor had no provision for external preheating of the inlet reactant stream. Therefore, heating or cooling had to be provided either through the reactor wall or through an air coil inside the reactor. Two thermocouples were provided for gas phase temperature measurements, one very close to the inlet of the reactor and the other just above the catalyst bed. These two thermocouples showed the same temperature during steady state experiments. But once an oscillatory state was established an apparent difference of about 3°C in the temperature readings of the two thermocouples was also established. Both thermocouples were oscillating with an amplitude of 5–10°C and the same period as that of the catalyst bed, but the thermocouple above the catalyst bed was usually 5–10 min. out of phase. Although it was suggested to us that reactor plugging might be occurring, we do not believe that this is the case because once a steady state was again established the thermocouple readings again became identical. In view of this difficulty, oscillations are reported here as a function of reactor wall temperature, which remained constant during oscillations. This temperature was varied in fixed amounts by changing the amount of electric heating provided to the reactor. Normally, the Berty reactor is equipped with a temperature controller, and in order to rule out the possibility that controller instabilities might be triggering the oscillatory behavior, the controller was disconnected. This, however, resulted in 2–4°C irreproducibility in reactor wall temperature setting. The reactor is constructed from stainless steel. Although blank tests (without catalyst) indicated that no reaction occurs under the same experimental conditions, this does not necessarily preclude the existence of synergetic effects during oscillations. We are fairly confident, however, that this is not the case although it should be noted that in an industrial environment, where this type of catalyst is finding applications, anything but a stainless steel reactor is impractical.

Finally, the most severe limitations in our experimental study were imposed by the intrinsic nature of the oscillations themselves. Large periods were observed (1 to 2 h) and, because of the transient nature of the phenomenon, a time period of 12 to 24 h was required to uniquely establish the existence of a stable limit cycle. It is well known that carbon deposition is an integral part of the Fischer-Tropsch mechanism and coking is known to occur. Because of the high temperatures required for coke removal, which of course result in catalyst sintering and structural changes, there is no practical method for in situ catalyst regeneration. Thermodynamic limitations impose high pressures (our experiments were run at 2.2×10^3 kPa), and this, of course, severely limited our ability for in situ catalyst surface characterization. Our study, therefore, posed the optimization problem of generating the maximum amount of information with a minimum of catalyst surface deterioration. From our past experience an upper limit of continuous reactor operation of 350 hrs was set. At the end of our run our catalyst bed contained approximately 6% carbon deposits (compared to 2–3% under steady state operation) and no apparent plugging of the bed was evident. In view of these facts it is doubtful, in our opinion, that a more complete study of the phenomenon of oscillations could be attempted at usual Fischer-Tropsch synthesis conditions without a very painstaking design of a new reactor system.

Our experimental study was guided by our previous experience with runs with ZSM-5 and Nu-1 type catalysts, which were both shown to exhibit oscillatory behavior. In the first 50 h of operation, the reactor was operated under steady state conditions (flow rate 16.8×10^{-6} m^3/s). Attempts to trigger the oscillatory behavior by changing the reactor wall temperature for temperatures of up to 380°C proved unsuccessful (the same behavior had been observed on previous occasions, too). At the end of the 50 h of operation the inlet stream composition was changed from $CO/H_2 = 1/1$ to $CO/H_2 = 0.7/1$. During the next 50 h of operation, new attempts were made to generate oscillations but they also proved unsuccessful. At the end of 50 h of operation under the 0.7/1 mixture the inlet gas composition was again changed to 1/1 (at that time, T_w was 375°C). At this point an ignition phenomenon occurred. The catalyst bed temperature jumped momentarily to 500°C and then gradually a new steady state was estab-

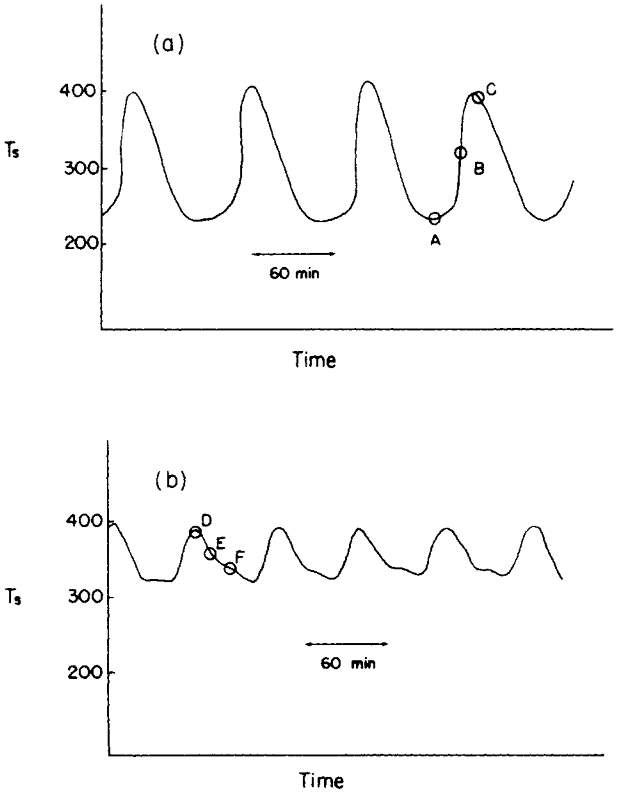

Figure 1. Temperature oscillations. Flow rate 16.8×10^{-6} m^3/s: (a) T_w = 293°C, (b) T_w = 319°C.

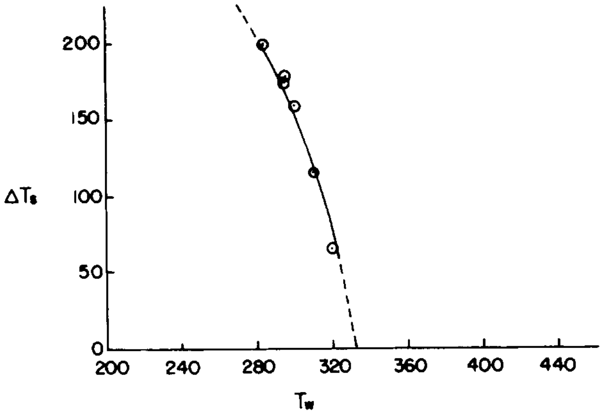

Figure 2. Period of oscillations vs. wall temperature. Flow rate 16.8 × 10^{-6} m^3/s.

lished for which T_b = 380, T_w = 375°C. This state was apparently different from previously established steady states in the first 50 hrs of operation for the same range of wall temperature because the temperature of the bed was slightly higher than the reactor wall temperature, while, in the previously generated states, the catalyst bed temperatures was generally 60–70°C less than the reactor wall temperature. This conclusion seemed also to be supported by product gas phase analysis. In the next 40 h of operation, the wall temperature was gradually decreased down to 333°C and several new steady states were established. Then the temperature was changed to 293°C. The catalyst bed temperature started increasing but, instead of achieving a new study state, oscillations were established. After 7 h of operation, during which eight peaks appeared (amongst them two double peaks), a fairly regular limit cycle was established which is shown in Fig. 1a. The amplitude of oscillations was approximately 170°C (between 240 and 410°C) and the period (although changing slightly in an irregular manner) 80 min. Ten regular peaks appeared until the wall temperature was deliberately decreased to 272°C. After 7 h, a single peak appeared; but then in the next 30 h, no new oscillations appeared. When the wall temperature was again increased from 272 to 283°C, a new steady state appeared for which the catalyst bed temperature was again about 60°C below the wall temperature. When the temperature was raised again to 300°C, no ignition phenomena occurred but an oscillation was once more established. Subsequently a total of six stable limit cycles (at least ten regular peaks per limit cycle) were observed between 275 and 330°C. The amplitude of oscillations seemed to decrease with increasing wall temperature (Figure 2) while the period, which ranged between 57 to 82 min. reached an asymptotic value. Our experimental observations seem to indicate a (IIIb) type of oscillatory behavior as classified by Uppal et al. (1973), although the strict applicability of their theoretical analysis to our reaction system is questionable.

Figure 1b shows the oscillatory behavior at T_w = 319°C. Figure 3 shows oscillatory behavior at a different flow rate (11.2 × 10^{-6} m^3/s). Decreasing flow rate seemed, in general, to decrease the amplitude of oscillations and increase the period. No attempt was made to establish a region of flow rates for which mass and heat transfer limitations would disappear. At the end of the run efforts were made to study the effect of total pressure on oscillations. These efforts proved unsuccessful because lowering the total pressure resulted in large oscillations which exceeded the upper limit of catalyst bed temperatures, 450°C. Because of supply limitations synthesis gas of only three compositions (2/1, 1/1 and 0.7/1) were available to us. No oscillations appeared when during steady state operation the inlet gas phase composition was changed from 1/1 mixture to either 2/1 or 0.7/1. However, when we attempted this change during a limit cycle large transients resulted exceeding the upper temperature limit of 450°C. Throughout the run the catalyst retained very favorable levels of conversion. However, due to experimental limitations, little can be said about its overall selectivity behavior.

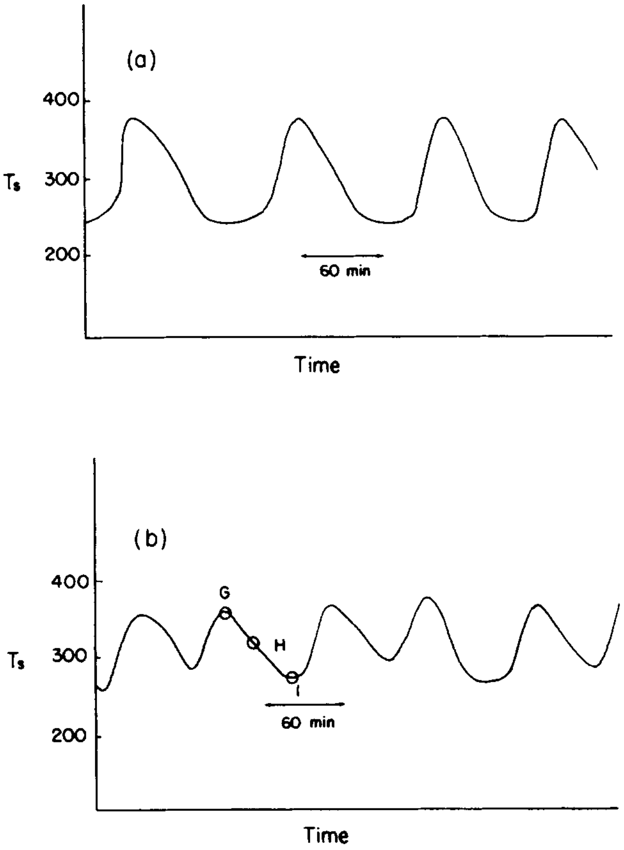

Figure 3. Temperature oscillations. Flow rate 11.2 × 10^{-6} m^3/s: (a) T_w = 300°C, (b) T_w = 310°C.

Table 1 shows the product gas phase compositions at points represented product gas phase concentration also oscillates, apparently 180° out of phase with the temperature oscillations. Note also that the CO_2 and hydrocarbon oscillations are apparently in phase. Quite recently a study has come to our attention (Krylov et al., 1973) which reports reaction rate oscillations during the oxidation of cyclohexane over NaY type zeolites. Krylov's experimental observations bear a striking similarity with ours. Oscillations were triggered by concentration perturbations. An ignition phenomenon preceded the onset of oscillations. Oscillations were established after the reactor temperature was decreased from the initial temperature of ignition. The reaction rate oscillations observed by Krylov were regular, single peak and the concentration oscillations were clearly out of phase with the temperature oscillations.

DISCUSSION

Fischer-Tropsch reactions have been the subject of intensive investigations for over half a century (Fischer and Tropsch, 1926; Ponec, 1978; Anderson, 1956; Vannice, 1976). Unfortunately, a well-accepted reaction mechanism has yet to be developed. Four basic reaction mechanisms have appeared so far in the literature: (a) CO dissociates and forms "carbides" which are then partially hydrogenated and the (CHx) groups polymerize into a hydrocarbon chain (Fischer and Tropsch, 1926; Craxford and Rideal, 1939); (b) CO is first partially hydrogenated into (H ∗ C ∗ OH) species, which polymerize by dehydrocondensation (Vannice, 1976); (c) CO insertion is the key reaction by which the Fischer-Tropsch

TABLE 1. PRODUCT GAS PHASE CONCENTRATION AT POINTS A, B, C, . . . OF FIGURES 1 AND 3

Composition vol. %	A	B	C	D	E	F	G	H	I
CO_2	6	3.4	3.3	3.6	9.6	17.1	14.4	14.6	15.5
CH_4	3.1	2.2	2.2	3.2	4.9	5	4.2	4.3	4.5
C_2H_4	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	0.2	0.2	0.2
C_2H_6	0.5	0.3	0.3	0.3	0.7	1.3	1.1	1.1	1.1
C_3H_6	0.3	0.2	0.2	0.2	0.4	0.7	0.7	0.7	0.7
C_3H_8	0.3	0.2	0.2	0.1	0.4	0.7	0.5	0.5	0.6

synthesis is initiated as well as propagated (Pichler et al., 1967); and (d) a combination of mechanisms 1 and 2 (Ponec, 1978).

A mechanistic scheme can be proposed (Bennett, 1978) which contains most of the important features of the above four mechanisms.

Initiation Reactions

(1) $CO_g \rightleftarrows CO_S$ (2) $CO_S \rightleftarrows C_S + O_S$ (3) $H_{2g} \rightleftarrows 2H_S$
(4) $O_{2g} \rightleftarrows 2O_S$ (5) $O_S + H_S \rightleftarrows (OH)_S$ (6) $(OH)_S + H_S \rightleftarrows H_2O$
(7) $CO_g + O_S \rightleftarrows CO_{2g}$ (8) $CO_S + O_S \rightleftarrows CO_{2g}$ (9) $H_{2g} + O_S \rightleftarrows H_2O$
(10) $C_S + xH_S \rightleftarrows (CH_x)_S$ (11) $CO_S + 2H_S \rightleftarrows HCOH_S$ (12) $C_S \rightleftarrows C_i$

C_i = inactive form of carbon

Propagation Reactions and Termination Reactions

Several fast propagation and termination reactions (Anderson, 1956; Vannice, 1976).

Several other experimental facts tend to make the mechanistic picture very complicated. The rate of Step (1) has been found to increase with H_2 surface coverage and decrease with CO coverage (Vannice, 1976). Furthermore, several forms of CO_S exist and is not well known which one participates in Steps (2), (8) and (11) (Ponec, 1978). Step (12) is very complicated. Several forms of inactive carbon have been identified such as amorphous carbon, graphite and several bulk carbides (Delgass and Raupp, 1979; Wise and McCarty, 1979), and what is considered to be an inactive form of carbon under some conditions might be active under other conditions. For example, H_2 has been found at high temperatures to restore catalytic activity (Wise and McCarty, 1979) and the bulk carbides have been found to be easily decomposed and participate in the reaction, especially when the surface carbide concentration is depleted (Delgass and Raupp, 1979). Both O and C have been observed to diffuse into the bulk of the catalyst (Samorjai and Sexton, 1979) and create a substrate favorable for the reaction. The role of CO_2 and H_2O is also more complicated than it is shown in Steps 1–12. Both CO_2 and H_2O can readsorb on the surface (particularly in the presence of H_2) and participate in several initiation and propagation steps, which are still not well understood (Nijs and Jacobs, 1980). Finally, the role of the zeolite is not clear. Possible effects would result from its shape selectivity properties, its acidity, and its ability to intercept and terminate propagation steps (Caesar et al., 1979).

Unfortunately, the dynamic phenomena reported here shed little light on the confused mechanistic picture. Although experience with other experimental systems (Luss et al., 1980) has shown that the oscillatory behavior is a result of catalytic surface processes rather than of the interaction between physical and chemical processes our observations, due mainly to experimental limitations, cannot support this argument (external mass and heat transfer limitations exist and are coupled with internal mass transfer limitations). Unfortunately, we have not been able to observe oscillations with the same catalytic systems during several runs in a micro-reactor system (1 cc of catalyst in a powder form). However, if, for a moment, we assume that purely kinetic reasons are behind the phenomenon of oscillations several combinations of Steps (1) to (12) can readily predict oscillatory behavior. Steps (1), (4), (7) and (8) (CO oxidation) have already been used to explain oscillation in the CO oxidation system (Schmitz and Sheintuch, 1977). Steps (3), (5), (6) and (9) have been used in a similar fashion to explain oscillations in the H_2 oxidation system (Luss and Pikios, 1977). Step (12) plays the same role that an oxidation-reduction scheme of a surface oxide plays in reactions over Pt. It acts as a reversible sink of an active intermediate and it has been shown to predict oscillatory behavior (Schmitz and Sheintuch, 1977). The role of an "unknown inhibitor" (Eigenberger, 1978) cannot be neglected. Step (2), for example, has been shown (Ponec, 1978) to require several surface sites and minute amounts of foreign substances (S, Cl, K, Cu) have a great effect on both conversion and selectivity. At higher temperatures several of the propagation reactions are endothermic. The role of the interplay between endothermic and exothermic processes (Schmidt et al., 1980) cannot, therefore, be overlooked.

Finally, the role of the zeolite remains unresolved. We have not observed any oscillations in several runs with usual Fischer-Tropsch catalysts, while we have observed oscillations on both ZSM-5 and Nu-1 and with both Co and Fe catalysts. Krylov's experiments seem to point also towards this direction. However, we have to admit that the evidence is still quite circumstantial and in any even Y-type zeolites (Jacobs, 1977) have a quite different structure from either ZSM-5 or Nu-1 type zeolites. Nevertheless, it has been shown (Caesar et al., 1979) that zeolites do modify the mechanism of Fischer-Tropsch reactions and the effect of the phenomenon of shape selectivity on catalytic dynamic behavior has yet to be investigated.

It is apparent from the above discussion that further investigation is needed of the dynamic behavior of Fischer-Tropsch synthesis reactions over both zeolite-supported and usual Fischer-Tropsch catalysts. The existence of the oscillatory behavior, particularly if it proved to be the result of intrinsic catalytic surface processes, can have far reaching consequences on both the industrial utilization of this reaction and the understanding of the reaction mechanism.

ACKNOWLEDGMENT

T.T.T. acknowledges the support of Oak Ridge Associated Universities Faculty Research Participation Program. The authors express their gratitude to Prof. J. D. Goddard for his many helpful comments and discussions during the preparation of this paper, and to Dr. B. D. Blaustein for his support and encouragement during the performance of this project.

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Manuscript received April 20, 1981; revision received August 5, and accepted August 24, 1981

Bubble Formation in a Vertically Vibrated System—Tate's Law Region

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Bubbles forming at small, single, circular orifices at constant, low flow rates obey "Tate's Law." When vertical oscillations are added to the system, low-viscosity fluids show modified behavior with oscillational plus gravitational acceleration influencing bubble release; high-viscosity fluids produce bubbles of the same size as predicted by Tate's law.

THEORY

Tate's law is derived by equating the surface tension force (assuming an angle of attachment of 90°) and the buoyant force and solving for the bubble volume.

$$V_t = \frac{2\pi R_0 \sigma}{\Delta\rho g} \tag{1}$$

Experiments show that Tate's law is a fair predictor (±20%) of bubble size for small orifices with vanishingly small gas flow and negligible chamber volume (Guyer and Peterhans, 1943; Datta et al., 1950; van Krevelen and Hoftijzer, 1950; Coppock and Meiklejohn, 1951; Benzing and Myers, 1955; Hughes et al., 1955; Soo, 1967; Blanchard and Syzdek, 1977; Park et al., 1977).

When the entire bubble-forming apparatus is placed on a vibratory table and placed in sinusoidal vertical motion, it experiences a sinusoidal acceleration, which can be expected to add to that of gravity. Thus, one would expect Tate's law to take the form

$$V_b = \frac{2\pi R_0 \sigma}{\Delta\rho(g + a\omega^2 \sin\omega t)} \tag{2}$$

Tate's law is static; it says that the bubble releases when the upward buoyant force exceeds the downward surface tension force. Equation 2 shows that the predicted volume for release is sinusoidally varying. This makes more sense if one considers that the downward surface force is constant while the upward, buoyant force is the product of a linearly increasing component (due to bubble growth) and a sinusoidally varying one. Thus, Eq. 2 indicates the bubble volume for which the peak of the sinusoidally varying upward force exceeds the constant downward surface tension force. If there were no resistance to fluid motion due to viscosity, the bubble would be expected to release at this instant; and its size would be given by Eq. 2 If there were considerable viscous resistance, then the bubble would be expected to release only when the upward force, averaged over the entire cycle, exceeded the downward force.

The logical way to express the effect of viscosity is in terms of some form of Reynolds number. The appropriate one for this system appears to be

$$\mathrm{Re} = \frac{D_b a \omega \rho}{\mu} \tag{3}$$

This choice of Reynolds number for vibrating bubble systems goes back at least as far as Jameson (1966).

Previous authors have shown that Eq. 1 is only a fair predictor of the observed bubble volumes; they have also discussed the causes of this variation. To eliminate this variability and focus on the effect of vibrations, all results in this note are presented in the form of the ratio of the observed bubble volume in the vibrated case (V_b) to the observed bubble volume for the same apparatus and conditions without vibrations (V_t). From the preceding theory for bubbles growing slowly, one would expect this ratio to be unity for small Reynolds numbers and to be $[C_o = (1/(1 + a\omega^2/g))]$ for large Reynolds numbers.

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