Chemical Transport in Nonconvective Systems

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Many practical chemical vapor transport systems are gaseous diffusion limited. For a single-reaction system under moderate supersaturations, the diffusive transport rate is readily expressed in a form which enables the effect of surface kinetic limitations to be included. Attempts to observe surface limitations in a closed-tube experiment are described together with experiments which confirm the diffusion theory. The treatment of multireaction systems is briefly discussed.

This paper is concerned primarily with one-dimensional, diffusion-controlled vapor transport in which one reaction is dominant, with some attention, however, being given to multireaction systems. The system under consideration is illustrated in Figure 1. The solute (for example, a metal) dissolves at temperature T'' in the vapor phase under the influence of a vapor solvent (for example, a halogen) and is transported by diffusion to the seed at temperature T'. Solute is deposited on the seed while solvent diffuses back to the source. In place of the source, one may postulate a boundary on which the composition of the gaseous mixture is known.

In such a system, common sense would seem to suggest that transport should occur from regions where there is a high density of solute atoms (combined or uncombined) to regions where this density is smaller. One's first approach therefore is to attempt to relate the growth rate of the seed to the total concentration gradient of the solute in the vapor phase. That this cannot be done is due to two effects.† The first is what, following Schaefer (*1*), may be called *streaming*. The second is due to the fact that it is not always a valid approximation to treat the gases in contact with the seed as if they were in equilibrium with it. In fact, gaseous transport rates cannot be calculated without allowing for streaming, while the consideration of the overall transport rate should include the effect of possible surface limitations. These two points will be illustrated with reference to a specific example, namely, the silicon–chlorine system in which transport of silicon occurs by means of the reaction

$$\mathrm{Si(s.)} + \mathrm{SiCl_4(g.)} = 2\,\mathrm{SiCl_2(g.)} \qquad (1)$$

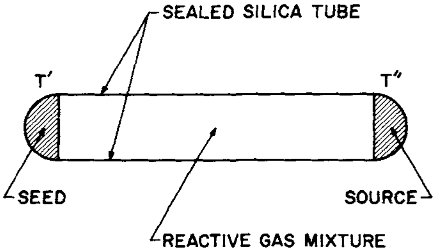

Fig. 1. Schematic view of closed-tube, vapor-growth system.

STREAMING

Since each molecule present in the gas phase contains one silicon atom, and since the pressure in the system is constant, there is clearly no appreciable concentration gradient of silicon in the system. Indeed, the concentration of silicon will be slightly higher near the seed because of the temperature gradient and the operation of the gas laws. Nevertheless, diffusive transport occurs by means of reaction (1) down the temperature gradient (from hot to cold). This is explained by noting a significant feature of (1), namely, that the number of gaseous species are not conserved in the reaction. For every molecule of silicon tetrachloride that disappears at the source, two molecules of silicon dichloride are created, while for each two silicon dichloride molecules which disappear at the seed, only one silicon tetrachloride molecule is released. There is, therefore, a *net drift* or *streaming* of the gas between source and seed which is responsible for the transport of silicon. Such streaming will occur for any reaction in which deposition or dissolution of solid causes a change in the total number of molecules in the gas phase. The amount of this streaming, however, is determined by the requirement that there be no net flux of chlorine† in the system, that is, that each silicon tetrachloride molecule moving toward the source be balanced by two silicon dichloride molecules moving away from the source in accord with reaction (1). There is, of course, a very small gradient in the total pressure associated with this flow which, however, will be neglected.

Since the transport of silicon by reaction (1) is entirely due to streaming, one might wonder how Schaefer (*1*) was able to calculate a reasonable value for the silicon transport rate even though he explicitly neglected streaming. The reason lies in the close relationship between the diffusive flux of silicon dichloride and silicon tetrachloride relative to the gas stream, and the streaming flux, as shown below.

Let the total flux of gas molecules due to streaming be J_T moles/(sq. cm.) (sec.), y_2 and y_4 the mole fractions of silicon dichloride and silicon tetrachloride, respectively, and J_2 and J_4 the respective total fluxes. From Fick's law, one obtains

$$J_2 = J_T y_2 - DN\,dy_2/dz \qquad (2)$$
$$J_4 = J_T y_4 - DN\,dy_4/dz$$

The first term on the right-hand side of each equation is the flux due to streaming and the second is the flux due

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† It is shown later that a potential for vapor transport is provided more nearly by the solute-solvent density ratio, not by the solute density alone.

† Here is meant, of course, chlorine as a *component* of the system and not a *species*, that is, total chlorine, not free chlorine.

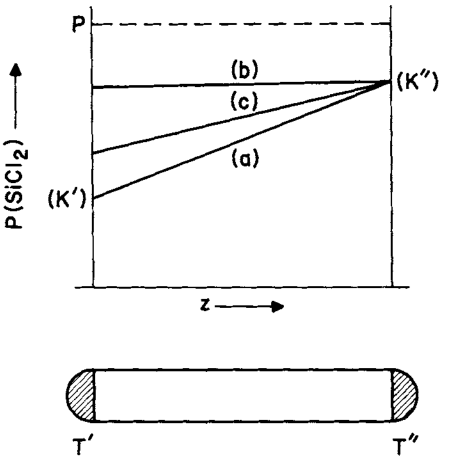

Fig. 2. Composition vs. distance in closed-tube system where transport occurs by the reaction Si + SiCl$_4$ = 2SiCl$_2$, and equilibrium exists at the source. (a) Transport entirely diffusion-limited. (b) Transport entirely surface-limited. (c) Transport both diffusion- and surface-limited.

to diffusion relative to the gas stream. The total fluxes of silicon and chlorine are then obtained by addition as

$$J_{Si} = J_T(y_2 + y_4) - DN(dy_2/dz + dy_4/dz) \qquad (3)$$

$$J_{Cl} = J_T(2y_2 + 4y_4) - DN(2dy_2/dz + 4dy_4/dz) \qquad (4)$$

One sees (9) that the relation

$$J_i = J_T y_i - DN\, dy_i/dz \qquad (5)$$

applies equally well to the *species* silicon dichloride and silicon tetrachloride and to the *components* chlorine and silicon. As shown in Appendix *A*, this is generally true in any multispecies system if all the binary diffusion coefficients are considered to be equal (9).

For the system under consideration, $y_{Si} = y_2 + y_4 = 1$ and $dy_2/dz + dy_4/dz = 0$. Hence, from the above

$$J_{Si} = J_T \qquad (6)$$

$$J_{Cl} = J_T(4 - 2y_2) + 2\,DN\, dy_2/dz \qquad (7)$$

The diffusive contribution to the silicon flux is zero and the entire transport is due to streaming. However, this streaming is essentially diffusion controlled via the requirement that J_{Cl} be zero, there being no sources or sinks in the system for the chemical component chlorine. Hence, putting $J_{Cl} = 0$ one obtains

$$J_{Si} = J_T = \frac{-DN}{2 - y_2}\frac{dy_2}{dz} \qquad (8)$$

SURFACE LIMITATIONS

Another factor of major concern in vapor transport is the composition of the gas in contact with a growing or etching crystal surface. If equilibrium at the crystal surface can be assumed, the transport process will be entirely diffusion limited. However, for a single-reaction transport process, it is possible to include in the theory the supersaturation over the growing surface and the undersaturation at the etching surface. The nature of the problem may be illustrated by reference to Figure 2. In order to simplify the discussion, equilibrium will be assumed to exist at the source, that is, the composition of the gaseous mixture will be taken as known at the source plane. The undersaturation which exists at the source may readily be included when required.

In Figure 2 are plotted three possible spatial distributions of p_2, the partial pressure of silicon dichloride. The total pressure P is taken as constant, while p_4, the partial pressure of silicon tetrachloride, is simply $P - p_2$. At any point one may define a quantity $Q = p_2^2/p_4$. It is assumed for simplicity that the gas is in equilibrium with the source, so that at the source $Q = K(T'')$, where $K(T'')$ is the equilibrium constant of reaction (1) at temperature T''. At the seed, allowance is made for the fact that, in practice, the crystal will not grow unless $Q > K(T')$, that is, there must be a finite supersaturation over the surface. This supersaturation is defined in general as the Gibbs free energy change associated with dissolving a mole of solute into the vapor phase at constant T, P, and composition, divided by RT (see Appendix *C*).

$$\sigma = \Delta G/RT = \ln Q/K \simeq (Q - K)/K \qquad (9)$$

For curve *a* the assumption is made that $Q - K'$ is negligible compared with $K'' - K'$, so that the transport may be regarded as purely diffusion limited. The gas composition is shown to vary approximately linearly with distance, although in the presence of streaming, dp_2/dz cannot be both nonzero and constant, so that some curvature is actually present (see Appendix *B*). For curve *b*, on the other hand, the assumption is made that the seed is in some way poisoned so that growth is extremely slow. In this case the growth is surface limited, the required diffusive flux involves negligibly small pressure gradients, and therefore, $Q = K''$ at the seed. Curve *c* represents a situation where both surface and gaseous diffusion limitations apply and $K' < Q < K''$. In case *a*, where the supersaturation over the seed is negligible, the rate of growth is $J_{\max}$, the maximum value permitted by gaseous diffusion limitations. In case *b*, where the rate of growth is negligible, the supersaturation over the seed is the maximum possible, namely, ln (K''/K'). In case *c*, the fact that $J < J_{\max}$ is clear from the fact that the partial pressure gradient is less than in case a, while the fact that $\sigma < \sigma_{\max}$ is clear from the fact that p_2 is less than in case b and hence ln (Q/K') at the seed is less than ln (K''/K').

These considerations are best illustrated in Figure 3 in which J is plotted against σ. Two curves are drawn. One is the crystal growth curve which shows how a crystal surface of given orientation, cleanliness, etc., will respond to a given departure from equilibrium with the gas phase, at a given temperature and total pressure. The other is the diffusion curve which shows how the diffusive flux drops as the supersaturation over the seed rises. The actual growth rate in a particular experiment is given by the intersection of these two curves. It is worth noting that if both the crystal characteristic and the diffusion characteris-

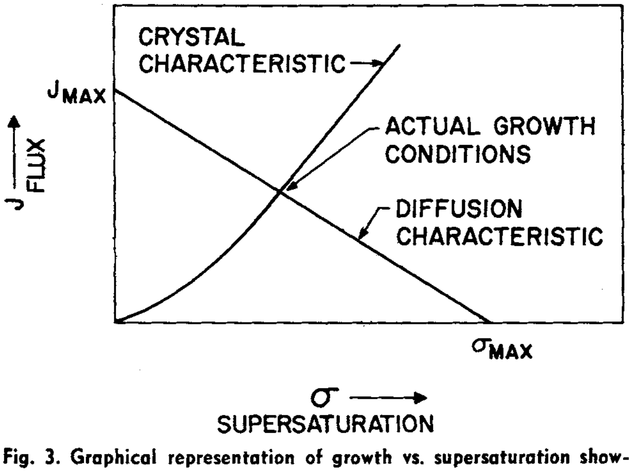

Fig. 3. Graphical representation of growth vs. supersaturation showing how the growth conditions depend on both the crystal characteristic and the diffusion characteristic.

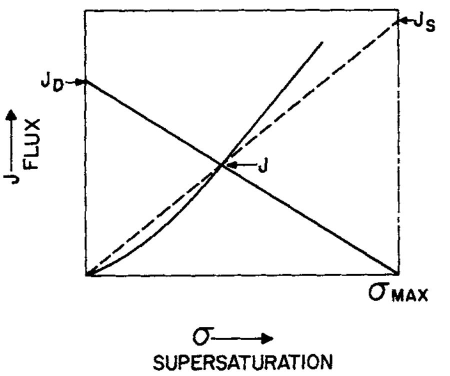

Fig. 4. Graphical illustration of the relationship $J^{-1} = J_D^{-1} + J_S^{-1}$, together with the definition of J_S when the crystal characteristic is nonlinear.

tic are linear, then, by similar triangles

$$J^{-1} = J_D^{-1} + J_S^{-1} \qquad (10)$$

where J_D is the value $J_{\max}$ when the system is diffusion limited and J_S is the surface-limited rate which would be obtained if the seed were exposed to a supersaturation equal to $\sigma_{\max}$. This point is illustrated in Figure 4.

In this paper it is shown that the diffusion-limited curve has the form $J = J_{\max}\,(1 - \sigma/\sigma_{\max})$ and an expression is derived for $J_{\max}$ in terms of the binary diffusion coefficients, average partial pressures, total pressure, temperature, and the standard enthalpy of the transport reaction.

THEORY

The starting point for a discussion of diffusive limitations in vapor transport is the general relation for multicomponent diffusion (*2*, *3*):

$$\frac{dp_s}{dz} = \sum_r \frac{J_r p_s - J_s p_r}{N D_{rs}} \qquad (11)$$

where thermal diffusion has been neglected (*6*). Equation (11) gives the gradient in the partial pressure of a particular species *s* in terms of the fluxes and partial pressures of all species. J_r, J_s represent the flux of species *r* and *s* in moles/(sq. cm.) (sec.) and p_r, p_s represent the partial pressures of species *r* and *s* at any point. D_{rs} is the binary diffusion coefficient for a mixture of gaseous species *r* and *s* evaluated at the *total pressure* which is actually present in the system. The quantities ND_{rs} are evaluated at the mean temperature of the system and are taken as constants for the system (*6*), dependent only on the nature of the two species *r* and *s*. An alternative form of Equation (11) which is physically more meaningful may be written as

$$\frac{dp_s}{dz} = \sum_r \frac{p_r p_s}{P} \frac{(v_r - v_s)}{D_{rs}} \qquad (12)$$

where v_r is the average velocity of molecules of type *r*. Each term represents an interaction between the species *s* and one of the species *r* proportional to their relative velocities and to the product of their partial pressures.

A general analysis of a multicomponent system can be quite complex (*2*). If there are *n* species present, then there will be $(n - 1)$ independent equations of the form of Equation (11) to be combined with some constraint on the *J*'s, such as, for example, $\sum_s J_s = 0$. There are, however, two simplifying assumptions which can be made, either of which greatly facilitate the analysis.

A first possible assumption is that all the D_{rs} values be equal (*9*). This converts Equations (11) into a system of independent equations in the p_s:

$$ND \frac{dp_s}{dz} = J_T p_s - J_s P \qquad (13)$$

This is particularly convenient in analyzing *multireaction* systems, since it can readily be shown that Equation (13) applies not only to molecular *species* but also to *components*. It follows directly from this (*9*) that a potential for diffusive flow is provided by the solute–solvent ratio (for example the silicon–chlorine ratio in the case of the silicon–chlorine or the silicon-hydrogen-chlorine system) (see Appendix *A*). That is, in multicomponent systems, flow is *not* in the direction of decreasing solute density but in the direction of decreasing solute–solvent ratio. Since in such a system many reactions may proceed in parallel, no simple formalism exists for including the effects of supersaturation at the seed or undersaturation at the source. For this reason, the multireaction system will not be discussed further in this paper and the assumption of equal D_{rs} values will not be made. The treatment of a single-reaction system to be given below can, however, be generalized to multireaction systems, as discussed by Mandel (*5*), who also considered surface kinetic limitations in more detail.

A second simplifying assumption is to consider a single-reaction system where transport is caused by the single reaction

$$M(s) = \epsilon_1 A_1 + \epsilon_2 A_2 + \ldots . \epsilon_r A_r + \ldots . \qquad (14)$$

The reaction coefficients ϵ_r are negative for reactants and positive for reaction products. They may be taken as zero for species which are present, thereby providing a barrier to diffusion, but do not take part in the reaction. All fluxes J_r may then be written in terms of J_M, the flux of $M (J_r = J_M \epsilon_r)$; hence,[†] from Equation (11):

$$dp_s/dz = J_M \sum_r (\epsilon_r p_s - \epsilon_s p_r)/N D_{rs} \qquad (15)$$

In general, dp_s/dz is an unknown function of *z*. However, one may, at least conceptually, integrate (15) between z' and z'' to obtain $\Delta p_s/\Delta z$ in terms of the spatial mean pressures $\bar{p}_r$, namely

$$\Delta p_s/\Delta z = J_M \sum_r (\epsilon_r \bar{p}_s - \epsilon_s \bar{p}_r)/N D_{rs} \qquad (16)$$

Hence, each Δp_s is given in terms of J_M and the known values of ϵ_r, D_{rs}, Δz and the approximately known value of $\bar{p}_r$.

If the assumption were made that all the D_{rs} be the same for a single-reaction system, then (15) could be integrated directly as shown in Appendix *B*. However, it is instructive to retain the separate D_{rs} values in this treatment at the price of not being able to integrate Equation (15). While the resulting treatment can be applied rigorously only to systems where the partial pressure of a given species never departs by a large fraction from its mean value, the treatment may nevertheless be applied to a large number of practical systems.

In addition to enabling all the J_s values to be written in terms of J_M, the existence of reaction (14) also imposes

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[†] It should be noted at this point that the following treatment may be applied to *any* surface-catalyzed reaction and is not limited to deposition or etch processes. For a catalytic process that does not involve using up or depositing solid material, one writes the J_r terms, not in terms J_M, but in terms of *one* of the species, for example, *A* in which case (*4*) $J_r = J_a(\epsilon_r/\epsilon_a)$.

boundary conditions on the gas composition (see Appendix *C*), namely

$$\sum_s \epsilon_s \ln p_s' = \ln K' + \sigma'$$

$$\sum_s \epsilon_s \ln p_s'' = \ln K'' + \sigma'' \qquad (17)$$

where K' is the equilibrium constant of (14) at the seed temperature T', K'' is the equilibrium constant at temperature T'', σ' is the supersaturation over the seed associated with the growth, and σ'' is the supersaturation (negative) over the source associated with the etch process.

Hence $$\sum_s \epsilon_s \Delta \ln p_s = \Delta \ln K - \sigma \qquad (18)$$

where $\sigma = \sigma' - \sigma''$. It is very convenient to write (18) in an alternative form by using the logarithmic mean defined by

$$p^* = (p'' - p')/(\ln p'' - \ln p') \qquad (19)$$

One then obtains

$$\Delta \ln K - \sigma = \sum_s \epsilon_s \Delta p_s / p_s^* \qquad (20)$$

Having rewritten (18) in this form, one may now divide through by Δz and substitute for $\Delta p_s/\Delta z$ from (16) to obtain the relationship

$$\frac{\Delta \ln K - \sigma}{\Delta z} = J_M \sum_s \frac{\epsilon_s}{p_s^*} \sum_r \frac{\epsilon_r \bar{p}_s - \epsilon_s \bar{p}_r}{ND_{rs}} \qquad (21)$$

This may be expanded into a series in which each *pair* of species is taken once irrespective of order:

$$\frac{\Delta \ln K - \sigma}{J_M \Delta z} = \frac{1}{2} \sum_r \sum_s \left(\frac{\epsilon_r}{p_r^*} - \frac{\epsilon_s}{p_s^*} \right) (\epsilon_s \bar{p}_r - \epsilon_r \bar{p}_s)(ND_{rs})^{-1} \qquad (22)$$

Equation (22) illustrates well one important point, namely, that for any species which takes part in the reaction ($\epsilon_s \neq 0$), a very small value of p_s^* will result in very slow transport. This is to be expected, since reaction (14) cannot proceed readily if any one of the species taking part in the reaction is in short supply.

In general, the logarithmic mean, given by

$$\frac{1}{p^*} = \frac{\int_{p'}^{p''} dp/p}{\int_{p'}^{p''} dp} \qquad (23)$$

does not have the same value as the spatial mean

$$\bar{p} = \frac{\int_{x'}^{x''} p dz}{\int_{x'}^{x''} dz} \qquad (24)$$

except when the pressures have the form $p = Ae^{bz}$. However, for small values of $\Delta \ln K$, the difference between p^* and $\bar{p}$ will be small and one can write $p^* \approx \bar{p} \approx p$. Hence, one may write (*6*) an expression for the growth in the following form:

$$J = \frac{\Delta \ln K - \sigma}{\psi \Delta z} \qquad (25)$$

where $J = -J_M$ is the growth rate of the seed and

$$\psi = \frac{1}{2} \sum_r \sum_s (\epsilon_s p_r - \epsilon_r p_s)^2 / (p_r p_s ND_{rs}) \qquad (26)$$

From the van't Hoff equation, $\Delta \ln K$ may be written in terms of ΔH, the standard enthalpy of reaction (14), the average temperature T and the temperature difference $T'' - T' = \Delta T$, namely, $\Delta \ln K = (\Delta H/RT^2)\Delta T$. One sees that Equation (25) is indeed of the form $J = J_{\max} (1 - \sigma/\sigma_{\max})$ illustrated in Figure 3, where $J_{\max} = \Delta \ln K/\psi \Delta z$ and $\sigma_{\max} = \Delta \ln K$.

Equation (25) represents a limitation on vapor transport analogous to the effect of the load line on the flow of current through an electrical device. The analogy may be pursued by defining a crystal growth impedance Z equal to $\sigma/J(\sigma)$. This is, of course, purely a surface property dependent on the temperature, pressure, composition of the gas phase at the surface, and the state of the surface itself. It does not depend on gaseous diffusion coefficients or the composition of the gas phase anywhere except at the surface. One may then write Equation (25) in the alternative form:

$$J = \frac{\Delta \ln K}{\psi \Delta z + Z} \qquad (27)$$

One sees that the quantity $\psi \Delta z$ appears as a vapor transport impedance in series with Z. This is analogous to the relation $I = V/(Z_s + Z_D)$ for the current through a device of impedance Z_D when a voltage V is applied through a series resistor Z_s.

An appreciation of the physical meaning of ψ, the vapor impedance per unit spacing, is more readily obtained by writing out in full the value of ψ for a specific reaction. Consider, for example, the reaction

$$M(s) = -aA + bB + cC \qquad (28)$$

One then obtains

$$\psi = \frac{(ap_B + bp_A)^2}{p_A p_B ND_{AB}} + \frac{(bp_C - cp_B)^2}{p_B p_C ND_{BC}} + \frac{(cp_A + ap_C)^2}{p_C p_A ND_{CA}} \qquad (29)$$

If the reaction is stoichiometrically balanced so that $p_A/a = p_B/b = p_C/c$, then the middle term vanishes and the first and third term take on their minimum values. Hence

$$\psi_{\min} = 4ab/ND_{AB} + 4ac/ND_{AC} \qquad (30)$$

where $\psi_{\min}$ corresponds to the maximum possible growth rate by virtue of Equation (25).

The effect of adding an inert gas Y is readily apparent (*6*). Three more terms will be added to the expression for ψ, representing the interaction between the pairs of species AY, BY, and CY but with $\epsilon_Y = 0$. Hence ψ is increased by

$$\Delta\psi = (a^2 p_Y/p_A)/ND_{AY} + (b^2 p_Y/p_B)/ND_{BY} + (c^2 p_Y/p_C)/ND_{CY} \qquad (31)$$

The increase in the diffusive impedance $\psi \Delta z$ is therefore directly proportional to p_Y, the partial pressure of the added inert gas.

DISCUSSION

After it had been shown that a crystal growing from the vapor phase by means of a single reaction obeys the equation

$$J = \Delta \ln K/(\psi \Delta z + Z) \qquad (27)$$

the remaining question of greatest interest was the value of $Z(\sigma)$ or, expressed slightly differently, the form of $J(\sigma)$, the crystal characteristic. As has been shown, the value of ψ is readily calculated from the average partial pressures,

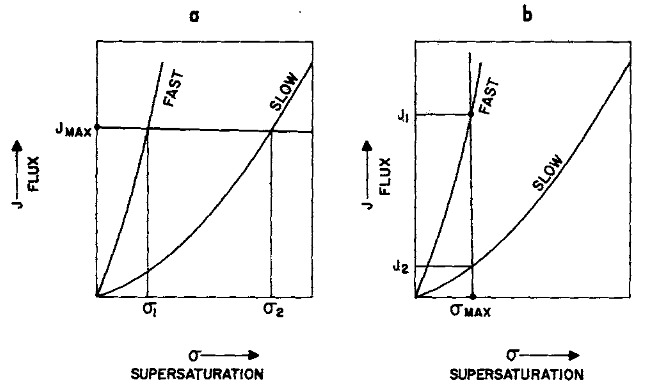

Fig. 5. Illustration of two approaches to measure the crystal characteristic.

the reaction coefficients, and the binary diffusion coefficients. The average pressures which exist in the system can be calculated from the experimentally imposed vapor solvent density and the temperature, provided that the equilibrium constant of the transport reaction is known as a function of temperature. The value of $\Delta \ln K$ is obtained from the standard enthalpy of the reaction and the experimentally imposed temperatures. On the other hand, as was discussed in detail by Mandel (5), the nature of the crystal characteristic is not readily analyzed theoretically. The experimental determination of the crystal characteristic is also a matter of considerable difficulty, as will be described.

There are basically two approaches to measuring J as a function of σ. The first is to operate with a high vapor impedance such that $\psi\,\Delta z >> Z$. This is readily obtained in practice by making Δz large, 20 cm. for example. In this case one has a diffusion-limited growth rate equal to $\Delta \ln K/\psi\,\Delta z$ as shown in Figure 2*a* and the crystal characteristic must be determined by measuring σ, the supersaturation at the surface. The second approach is to operate with a low vapor impedance so that $\psi\,\Delta z << Z$. This may be achieved in practice by operating with ψ near to its minimum value $\psi_{\min}$, corresponding to the reactants being present in nearly stoichiometric proportions, and by making Δz small. In this case the growth is surface limited as in Figure 2*b* and is given by $J = \Delta \ln K/Z$. The value of σ is imposed experimentally, being equal to $\Delta \ln K$, and $J(\sigma)$ is measured. The main problem in this case is the measurement of $\Delta \ln K$ which requires an accurate measurement of the source-seed temperature difference.

The two different approaches are illustrated graphically in Figures 5*a* and 5*b*. Suppose one wishes to measure the growth characteristic of two different crystal surfaces, one fast growing and the other slow growing. Such a difference between growth rates of two surfaces of the same material growing by means of the same reaction could arise because of difference in crystallographic orientation, or simply because of the cleanliness of the surface, the growth of which may be more or less catalyzed by impurities. In Figure 5*a*, $\psi\,\Delta z$ is considered large so that the vapor transport load line is almost horizontal. The different behaviors of the two surfaces are then apparent in that the supersaturation that builds up in order to drive the growth of the slow surface is higher than that for the fast surface. It is worth noting that in such a geometry, the maximum possible supersaturation $\sigma_{\max}$ is very large indeed, well in excess of the value needed for spontaneous nucleation of new crystals, and necessarily much greater than the supersaturation actually present at the crystal surface. In Figure 5*b*, on the other hand, $\psi\,\Delta z$ is so small that the vapor transport load line is almost vertical and $\sigma \approx \sigma_{\max}$. In this case the different behavior of the two surfaces is reflected in a difference in observed growth rates. Although $\sigma_{\max}$ will be rather small, the diffusion-limited growth rate $J_D = \Delta \ln K/\psi\,\Delta z$ is very large because of the small value of $\psi\,\Delta z$, it being essential to the method that $J << J_D$. These considerations may also be discussed in terms of the equation

$$\frac{1}{J} = \frac{1}{J_D} + \frac{1}{J_S} \qquad (32)$$

illustrated in Figure 4, provided that the meaning of J_S is remembered. J_S may only be regarded as the crystal growth rate at a supersaturation of $\sigma_{\max}$ if the crystal characteristic is linear up to $(\sigma_{\max}, J_S)$. Otherwise, J_S is given by $\sigma_{\max}/Z$ as illustrated graphically in Figure 4.

EXPERIMENTS

The possibility of using the first approach (Figure 5*a*) to measure $J(\sigma)$ was seriously considered. In order to measure σ at a growing surface one must obtain: the composition of the gas at the growing surface and hence $\Sigma\, \epsilon_i \ln p_i$, the temperature T', and the equilibrium constant as a function of temperature $K(T)$. The supersaturation is then obtained by difference as (see Appendix *C*)

$$\sigma = \sum_i \epsilon_i \ln p_i - \ln K(T') \qquad (33)$$

Exploratory work was undertaken to determine the feasibility in the germanium–iodine system of optical absorption measurements to measure the partial pressures at the surface. The conclusion was that nothing like the required precision could be obtained, since the variation of the individual absorption spectra with temperature could not be measured. The approach illustrated in Figure 5*a* was therefore abandoned as impractical.

Two series of experiments will be described, both on the germanium–iodine system by using the transport reaction

$$\mathrm{Ge(s.)} = -\,\mathrm{GeI_4} + 2\,\mathrm{GeI_2} \qquad (34)$$

The first, with the use of the principle of Figure 5*b*, established conditions for surface-limited, orientation-dependent growth. Absolute measurements of the $J(\sigma)$ were not obtained, however. The second series of experiments utilized randomly nucleated growth with $\Delta z = 20$ cm. The observed growth rates agreed well with theoretical predictions, and constitute a simple test of the diffusion theory given previously here. In the experiments described below the iodine was added as germanium iodide and as iodine, respectively. The form in which the vapor solvent is added in such experiments is not theoretically significant, since equilibrium is soon established. In practice, the amount of iodine present during transport is negligible.

Measurement of Growth Rate at Constant Supersaturation

In these experiments a very small value of Δz was employed as shown in Figure 6, which shows a sealed silica tube containing the reactive gas mixture. The tube was placed in a firebrick insulated horizontal tube furnace arranged so that the top of the tube was not as well insulated than the bottom, so that a temperature difference was established between upper and lower wafers. The lower crystal or source was a slab of {110} oriented single-crys-

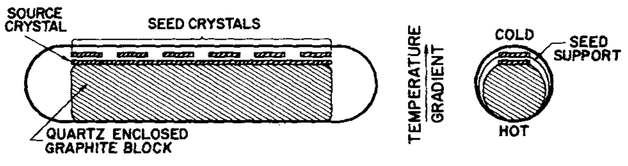

Fig. 6. Apparatus for observing orientation-dependent growth rates.

tal germanium which rested on a silica-enclosed graphite block. Several differently oriented germanium slabs, shorter in length than the source, were placed on a support cut from a piece of silica tubing. The source-seed spacing was approximately 2 mm.

It was found that the growth rates of the seeds, measured by weighing, varied appreciably with orientation (7). For growth at temperatures near 400°C. the growth rates for the orientations {111}, {112}, and {110} were in the ratio 1:3:7, respectively, {110} surfaces growing seven times faster than {111}. Crystals with {100} orientation were somewhat variable in behavior, sometimes resembling {111} and sometimes {112} in growth rate. Growth at 550°C. showed much less marked differences, {112} being similar to {111} and {100}, with {110} growing about 50% faster. Growth runs made at 450° and 500°C. showed intermediate behavior. A single *etching* run at 460°C. with the source and seed crystals interchanged showed similar behavior. The etch rates of {111}, {100}, {112}, and {110} were in the ratio 1:1:2:3, showing a variation in the J vs. σ characteristic with orientation for etching as well as growth.

The decrease in the orientation dependence of growth rate at higher temperatures could be associated with two possible causes. The first is based on the fact that the observed growth rates were considerably higher at higher temperatures, being about 0.2 μ/hr. for {110} crystals at 400°C., 1.0 μ/hr. at 450°C., 2 μ/hr. at 470°C., 20 μ/hr. at 500°C., and 80 μ/hr. at 550°C. These increases were probably due in part to higher values of ΔT at higher temperatures and partly due to an actual decrease in crystal impedance with temperature. Insofar as the latter explanation holds true, one would expect diffusion limitations to become more important as crystal growth impedance decreases so that orientation dependence in the growth rates would not be as clearly observed. The second possible cause of this effect is a genuine decrease in the effect of orientation on crystal growth impedance at higher growth temperatures. Such a decrease would be expected, since an examination of the surface morphology showed a much greater tendency for faceting to occur at the higher temperatures. *Faceting* means the tendency of the crystal to bound itself with low growth rate surfaces. For a system where faceting is complete, the only effect of orientation is to change the effective surface area. (For example, a complete development of {111} facets would give wafers oriented in the <100> direction an increased surface area due to the formation of pyramids.)

The orientation dependence of the growth rates clearly indicates that the growth (and etch) process was surface limited. Unfortunately, these results could not be put on a quantitative footing, since no way could be devised to measure ΔT, the difference between source and seed temperature. Platinum, platinum-rhodium thermocouples reacted with the germanium iodides to form platinum germanides, while attempts to protect them with coatings of low melting point glasses were not successful. The above experiments were valuable, however, in demonstrating the existence of a practical vapor transport system in which surface effects were dominant.

Measurement of Diffusion-Limited Transport

Having failed to obtain absolute information on growth rate vs. supersaturation, we next carried out experiments with a geometry similar to that shown in Figure 1 in order to verify the predictions of diffusion theory. Since in these experiments the values of $\psi \Delta z$ are approximately 100 times higher than in the preceding, diffusion-limited growth would be expected. For reaction (34) the value of ψ, from (26), is given by

$$\psi = (p_2/p_4 + 4p_4/p_2 + 4)/ND_{24} \qquad (35)$$

where, in this expression, p_2 and p_4 are the partial pressures of GeI_2 and GeI_4 respectively and D_{24} is the binary diffusion coefficient for the mixture of GeI_2 and GeI_4. Examination of (35) shows that ψ has a minimum value when $p_2 = 2p_4$ when $\psi = 8/ND_{24}$ and one may write

$$J_D{}^{\max} = \frac{\Delta H}{RT^2} \frac{\Delta T}{\Delta z} \frac{ND_{24}}{8} \qquad (36)$$

All runs were made at $T'' = 427$°C. and $T' = 395$°C., that is, with $\Delta T = 32$°C. The main independent variable was the quantity of added iodine expressed as a partial pressure of iodine at 298°K. Hence we have a given p_{I_2} given by

$$p_{I_2} = p_2 + 2p_4 \qquad (37)$$

where p_2 and p_4 denote partial pressures of GeI_2 and GeI_4, respectively. A theoretical curve of J vs. p_{I_2} was generated by a parametric approach. Values of a ratio $\phi = p_2/p_4$ were first assumed and were combined with the relation $p_2/p_4 = K$ derived from reaction (34), the value of K being known from equilibrium studies (*10*). Hence $p_2 = K\phi^{-1}$ and $p_4 = K\phi^{-2}$ were calculated and so p_{I_2}, ψ, and J_D were obtained. Examination of the preceding equations readily leads to the conclusion that the maximum value of J_D occurs at $p_{I_2} = K$; that at low values of p_{I_2} where $p_2 >> p_4$, $J \propto p_{I_2}$; and that at high values of p_{I_2} where $p_4 >> p_2$, $J \propto p_{I_2}{}^{1/2}$.

Seed crystals were not employed in the actual experiments, since $\Delta \ln K$ was high enough for spontaneous nucleation to take place. If a flat seed is placed across the tube in the geometry of Figure 1, difficulties often arise due to nucleation of new seeds on the necessarily colder wall on the low temperature side of the seed. In these experiments a large number of small seeds nucleated on the cold end of the tube, thereby avoiding this problem.

The experimentally observed vapor transport rates are shown in Figure 7 as a function of p_{I_2}. The theoretical curve was moved *vertically* to obtain the best fit to the experimental results. This, in effect, constituted an experimental determination of ND_{24}. The resulting value of D_{24} (3.4×10^{-2} sq. cm./sec.) agreed well with values calculated from semiempirical formulas (8) (3.9×10^{-2} and 4.9×10^{-2}/sec.). The two experimental points obtained at the highest values of p_{I_2} are high relative to the theoretical curve. This is due to the condensation of GeI_2 within the sample tube at high values of added iodine content, so that a degree of freedom was removed and addition of further iodine to the system no longer influenced the composition of the gas phase.

It is seen that the diffusion theory is quantitatively verified by these experiments since the form of the log J vs. log p_{I_2} curve is correctly predicted, the value of p_{I_2} for $J_{\max}$ agrees with measured values of the equilibrium

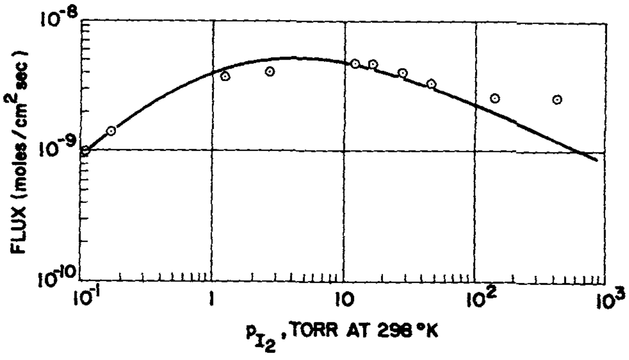

Fig. 7. Vapor transport rate vs. iodine content illustrating an experimental confirmation of the diffusion theory for the germanium-iodine system.

constant, and the magnitude of J_D gives a reasonable value of the binary diffusion coefficient for the system.

The good agreement of the experimental results with the predictions of diffusion theory precludes the possibility that convection might play a major role in mass transport. If the condensation of GeI_2 did not occur, thereby preventing the effective iodine pressure from exceeding about 50 torr, natural convection might be expected to enhance the transport at higher pressures. Approximate calculations by Keyes (*16*), which allowed for the enhancement of the variation of density with temperature due to the chemical reaction, suggest that convection should become appreciable in the pressure range 0.1 to 1 atm. where a length of 1 cm. is inserted into the Grashof number (*20*).

Transport rates considerably in excess of diffusion theory were, in fact, observed in the zinc sulfide–iodine system at high values of p_{I_2}. The convective nature of this enhancement was established by the insertion of porous plugs into the reaction tubes (*17*) which substantially reduced the transport rates. On the other hand, experiments in zinc sulfide–hydrogen chloride system gave transport rates in excellent agreement with diffusive transport theory (*18*) and porous plugs had no effect on the transport rates (*19*).

It is of interest to note that similar experiments with the germanium–bromine system (*8*) did not verify the diffusion theory. In these experiments growth rates were from 3 to 80 times lower than the calculated J_D values and also were very nonreproducible. This was taken as an indication that in the germanium–bromine system, surface-growth limitations are much more severe, that is, the crystal growth is highly susceptible to poisoning.

Experiments have also been carried out in the germanium–gallium–iodine system in which transport rates consistent with diffusion limitations were observed (*12*). In this case, the partial pressures of the germanium-bearing species were very small, leading to such a high value of ψ that the system was diffusion limited even though it had the close-spaced geometry of Figure 6.

CONCLUSIONS

The gaseous diffusive limitations on vapor transport in nonconvective single-process systems are well understood. If all binary diffusion constants are taken as equal, explicit solutions are readily obtained for the partial pressure distributions and for the growth rate, provided surface limitations are neglected. The treatment given in this paper preserves the different binary diffusion coefficients and also enables the effect of the finite supersaturation required for growth to be included. The theory is, however, only exact for systems where the variations of composition in the gas phase are small. The effect of the gaseous diffusion barrier is that an impedance $\psi\,\Delta z$ may be added to the crystal growth impedance Z defined by $Z = \sigma/J(\sigma)$ where Δz is the thickness of the diffusion barrier.

This theoretical treatment is written in terms of a vapor transport reaction in which the reaction rate at the surface may be measured as the rate of deposition or etching of solid M. However, it is clear that the treatment is equally valid for any surface-catalyzed reaction. The problem of separating out the effects of diffusion and catalytic activity at the surface would be identical to the problem as discussed above, amounting to a consideration of the relative magnitudes of the quantities $\psi\,\Delta z$ and $\sigma/R(\sigma)$ where R is some measure of the rate of reaction at the surface.

The determination of the form of $J(\sigma)$ represents a formidable task both theoretically and experimentally. For further discussion of the theoretical problem, the reader is referred to the work of Mandel (*5*).

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NOTATION

A_r = chemical formula of species r
D = diffusion coefficient, sq. cm./sec.
J = transport rate of various gaseous species or components, moles/(sq. cm.) (sec.)
J_M = transport rate of M through the gas phase, moles/(sq. cm.) (sec.)
$J = -J_M$ = rate of growth of seed, (moles/(sq. cm.) (sec.)
J_T = total molar flux due to streaming, moles/(sq. cm.) (sec.)
K = equilibrium constant
M = solid undergoing transport (solute)
N = total molar density in gas phase, moles/cc.
p_r^* = logarithmic mean pressure of species r as defined by Equation (23)
$\bar{p}_r$ = spatial mean pressure of species r as defined by Equation (24)
p = partial pressure of substance indicated by suffix
P = total pressure
Q = reaction ratio (see Appendix C)
r,s = indices denoting species r and s, respectively
T = temperature
v_r = mean velocity of molecules of species r
y = mole fraction
z = spatial coordinate
Z = surface impedance, (sq. cm.) (sec.)/mole
ϵ_r = reaction coefficient of species r
σ = supersaturation over solid surface not in equilibrium with the vapor (see Appendix C)
ψ = vapor impedance per unit thickness of vapor, (cm.) (sec.)/mole

Superscript

$''$, $'$ = conditions at source and seed, respectively

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APPENDIX *A*: MULTIREACTION SYSTEMS WITH $D_{rs} = D$

It has been shown that the assumption, that all binary coefficients D_{rs} may be replaced by a common value D, has the effect of separating the set of linear equations (11) into the set of *independent* linear equations (13), which may be rewritten as

$$J_s = J_T\, y_s - ND\, dy_s/dz \qquad (A1)$$

$$\text{where } y_s = p_s/P$$

Since a mole of species s contains a certain number of gram atoms α_{cs} of component c, we have

$$y_c = \sum_s \alpha_{cs}\, y_s \text{ and } J_c = \sum_s \alpha_{cs}\, J_s$$

and hence by summation (9)

$$J_c = J_T\, y_c - ND\, dy_c/dz \qquad (A2)$$

where

$$y_c = \frac{\text{number of gram atoms of component } c \text{ per unit volume}}{\text{total molar density}}$$

For *solvent* components (for example, chlorine, bromine, iodine, hydrogen, and oxygen) one may write $J_c = 0$, since there are no sources or sinks for solvent in the system. Hence

$$J_T/ND = (d/dz) \ln y\,(\text{solvent}) \qquad (A3)$$

The desired net flux of solute is then given by substituting (*A*3) into (*A*2):

$$J_{\text{solute}}/ND = y\,(\text{solute})\,(d/dz) \ln y\,(\text{solvent}) - (d/dz)\, y\,(\text{solute})$$

Hence

$$J_{\text{solute}} = -ND\, y\,(\text{solvent}) \frac{d}{dz} \left(\frac{y\,(\text{solute})}{y\,(\text{solvent})} \right) \qquad (A4)$$

From the above it is apparent that flow will always occur in the direction of decreasing solute–solvent ratio with a magnitude proportional to the gradient of this ratio. As pointed out previously, the local solute density is *not* a potential for flow unless streaming is absent, that is, $J_T = 0$. In this case, from (*A*3), the quantity (d/dz) y (solvent) is zero and (*A*4) may be written as

$$J_{\text{solute}} = -ND(d/dz)\, y\,(\text{solute}) \qquad (A5)$$

Generally, however, streaming is not absent and Equation (*A*5) is then incorrect as is obvious in the example given in the section on streaming. y (solute) can, of course, be regarded as a potential for the flow of solute *relative to the gas stream.*

It is worth noting that the solute–solvent ratio is also a potential for deposition of solute in flow, or open tube systems (*11*). In an open tube system, the flux of any component is given by

$$J = n\, Av \qquad (A6)$$

where n is the local density of the component in moles/cc., v is the local gas flow velocity in cm./sec., and A is the local cross section of the containing tube. In such a flow system one is interested in variations in J (solute), subject to the condition that J (solvent) is constant for all solvent species. Since it follows from (*A*6) that one may write

$$J\,(\text{solute}) = J\,(\text{solvent}) \frac{y\,(\text{solute})}{y\,(\text{solvent})} \qquad (A7)$$

then it follows that a change in the solute-solvent ratio implies a proportionate change in J (solute). The foregoing analysis assumes that any growth or etch regions are sufficiently far apart that regions can be found in between where (*A*6) is obeyed, that is, that material transfer between active regions by diffusion is negligible.

APPENDIX *B*: SINGLE-REACTION SYSTEM WITH $D_{rs} = D$

If all D_{rs} values are equal to D, then Equation (15) becomes

$$dp_s/dz = (p_s\, \delta - \epsilon_s P)\, J_M/ND \qquad (B1)$$

where $\delta = \sum_r \epsilon_r$ and P is the total pressure. This equation may be integrated directly (*4*).

For a stoichiometrically balanced reaction for which $\delta = 0$, streaming is absent, dp_s/dz in constant, and J_M is given by

$$\epsilon_s\, J_M = -(D/RT)\, \Delta p_s/\Delta z \qquad (B2)$$

For an unbalanced reaction for which $\delta \neq 0$, (*B*1) may be integrated to give

$$p_s = \epsilon_s\, P/\delta + Ae^{\beta z} \qquad (B3)$$

where A is a constant of integration and $\beta = J\delta ND$. It has been shown by Hougen and Watson (*4*) that an expression for J_M may be written

$$J_M = \frac{ND}{(p_s\delta - \epsilon_s P)^*} \frac{\Delta p_s}{\Delta z} \qquad (B4)$$

where the asterisk denotes the logarithmic mean of the quantity in brackets, defined by the relation $\Delta \ln f = \Delta f/f^*$.

It is seen that because of streaming, the partial pressure gradients are not in general constant between source and seed but have an exponential form.

APPENDIX *C*: DEFINITION OF SUPERSATURATION

In considering the growth of crystals or liquid droplets from their own vapor, a quantity called the supersaturation ratio is usually defined, namely

$$\alpha = p/p_o \qquad (C1)$$

where p is the partial pressure of the condensed material in the gas phase and p_o is the saturation vapor pressure. For ideal gases, α is simply the activity of the material in the gas phase relative to that in the condensed phase. It has the property that $\alpha = 1$ when the vapor is in equilibrium with a plane surface of the condensed phase, condensation requiring $\alpha > 1$ and evaporation $\alpha < 1$. The *supersaturation* σ has been defined both as $\sigma = \alpha - 1$ for crystal growth (*13*) and as $\sigma = \ln \alpha$ for droplet condensation (*14*). The latter definition has the advantage that it relates the supersaturation directly to the difference in chemical potential between the phases by means of the relation

$$\Delta G = \mu_v - \mu_s = RT \ln p/p_o \qquad (C2)$$

and hence

$$\sigma = \Delta G/RT \qquad (C3)$$

where ΔG is the Gibbs free energy change in transferring one mole of material from the solid to the gas phase at pressure p and temperature T.

The same definition of supersaturation may readily be applied to chemical vapor transport as follows. Consider the heterogeneous equilibrium

$$M(s) = \sum_r \epsilon_r\, A_r \qquad (C4)$$

The free energy change on transferring one mole of M to the vapor at partial pressures $p_1, p_2, \ldots p_r \ldots$ is simply (*15*)

$$\Delta G = \Delta G^o + RT \sum_r \epsilon_r \ln p_r \qquad (C5)$$

where the gases are treated as ideal and ΔG^o is the standard free energy change associated with the reaction at the temperature considered. Let us define the reaction ratio Q by the relation

$$\ln Q = \sum_r \epsilon_r \ln p_r \qquad (C6)$$

One then obtains from (*C*5) the relation

$$\frac{\Delta G}{RT} = \ln \frac{Q}{K} \qquad (C7)$$

where K is the value of Q at equilibrium, that is, when ΔG

$= 0$. We see that Q/K is the analog of the supersaturation ratio, while $\ln Q/K$ is the supersaturation defined according to ($C3$) from which one obtains Equation (17):

$$\ln Q = \ln K + \sigma \tag{17}$$

The form of the dependence of J, the crystal growth rate, on supersaturation is the province of crystal growth theory, as discussed by Mandel (*5*). Thermodynamically, we have only that $J = 0$ when $\sigma = 0$ and that the sign of J must be equal to that of σ.

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Physical and Chemical Absorption in Two-Phase Annular and Dispersed Horizontal Flow

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Overall mass transfer coefficients for physical desorption and chemical absorption of carbon dioxide in annular and dispersed two-phase flow in a 1-in. horizontal pipe have been measured. These coefficients have been correlated with gas and liquid flow rates and with the normality of the sodium hydroxide solutions used.

A new method of analysis was used to separate overall coefficients into individual gas and liquid film coefficients. Penetration theory equations were used to calculate the effective interfacial surface area and the penetration contact time. Changes in these variables have been explained in terms of the changes in flow pattern.

Annular and dispersed two-phase flow appear to offer an excellent vehicle for mass transfer. Both the liquid and the gas phases are in turbulent flow and the surface area of the dispersed liquid phase is very high. Research in concurrent gas-liquid flow has been directed primarily toward understanding and correlating pressure drop, holdup, and entrainment. A comparatively limited number of mass transfer studies have been reported (*1* to *3*, *18*).

TWO-PHASE FLOW THEORY

This work is a study of liquid phase controlled mass transfer in annular and dispersed two-phase flow in a horizontal 1-in. pipe. In annular flow some of the liquid is entrained but a majority of it is turbulently pushed along the wall. In dispersed flow a majority of the liquid is entrained as droplets. An increase in either the gas or liquid flow rate can bring about the transition from annular to dispersed flow.

Both pressure drop and holdup in two-phase flow have been correlated with the pressure drop of each phase flowing alone (*14*). In the range of variables involved in this work, the holdup is related to the mass flow rates and the specific volume of the gas by

$$R_L = \phi' \frac{(L)^{2/3}}{(G)^{2/3}(\bar{V})^{1/3}} \tag{1}$$

The amount of entrained liquid has been correlated with the volume flow rate of the liquid and gas and the critical Weber number (*10*).

$$E = \phi'' \frac{Q_L Q_G}{N_{We}} \tag{2}$$

Gas flow rates of 150 to 300 lb./hr. and liquid flow rates of 500 to 2,500 lb./hr. were used in this work. The change in flow pattern produced by the change in either flow rate can be expected to result in a change in the turbulence in both phases and a change in the interfacial surface area, the penetration contact time, the liquid film coefficient, and the gas film coefficient.