$$HP = 0.0015607\, F\, T \ln(P_{out}/P_{in})$$

and

$$OP = 63\, HP$$

where:

HP = brake horsepower
F = feed flow rate, lb moles/hr.
T = feed temperature, °R
P_{out} = discharge pressure, lb./sq.in.abs.
P_{in} = suction pressure, lb/sq.in.abs.
OP = annual operating cost, \$/yr.

This subroutine was used not only to compute pumping costs for intermediate process streams but also for the feed stream to the initial separator in the sequence. Thompson and King did not attach a pumping cost to the process feed stream.

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A Deborah Number for Diffusion in Polymer-Solvent Systems

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A Deborah number is introduced as a means of characterizing diffusional transport in amorphous polymer-solvent systems. Two types of temperature-penetrant concentration diagrams are constructed, and the various regions on these figures are identified by their Deborah number values. The utility of the diffusion Deborah number is demonstrated by using this dimensionless group to anticipate conditions under which thickness anomalies can be expected in sorption experiments for the atactic polystyrene-pentane system.

SCOPE

Investigations of diffusion phenomena in amorphous polymer-solvent systems have shown that it is possible to observe widely differing behavior by traversing a large enough range of temperature, concentration, and polymer molecular weight. It is convenient to depict the different types of diffusional transport of penetrants in high polymers by utilizing a temperature-penetrant concentration diagram. The various regions on such a diagram are distinguished by the ratio of two characteristic times, a characteristic relaxation time for the polymer-solvent system and a characteristic diffusion time. Since the situation is analogous to that encountered in the flow behavior of viscoelastic fluids, it is reasonable to expect that a diffusion Deborah number can be defined which corresponds to the Deborah number used to characterize flow of polymeric materials. In this paper we propose a Deborah number which can be used to characterize diffusional transport in amorphous polymer-solvent systems and consider the calculation and utilization of this dimensionless group.

CONCLUSIONS AND SIGNIFICANCE

From examination of the various stable and metastable states of polymers which are invariably observed in amorphous configurations, justification is given for treating such polymers as viscoelastic fluids at all temperatures. A diffusion Deborah number can then be defined in terms of the characteristic length of the diffusion path and the shear modulus and self-diffusion coefficients of the polymer-solvent mixture. Reasonable estimates of the Deborah number can be obtained over wide ranges of conditions, even though the slow orientation of molecules of polymeric materials below T_g causes difficulties in conducting meaningful experiments in this temperature range. Two types of temperature-concentration diagrams depicting polymer-penetrant diffusion can be constructed, and the various regions on these figures are identified by their Deborah number values. The utility of the diffusion Deborah number is demonstrated by using this dimensionless group to anticipate conditions under which thickness anomalies can be expected in sorption experiments for the atactic polystyrene-pentane system.

Investigations of diffusion phenomena in amorphous polymer-solvent systems have shown that it is possible to observe widely differing behavior by traversing a large enough range of temperature, concentration, and polymer molecular weight. Alfrey (1965) and Hopfenberg and Frisch (1969) depicted the different types of diffusional transport of penetrants in high polymers by utilizing a temperature-penetrant concentration diagram. It was later noted (Duda and Vrentas, 1970) that the various regions on this diagram could be distinguished by the ratio of two characteristic times, a characteristic relaxation time for the

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polymer-solvent system and a characteristic diffusion time. The situation is analogous to that encountered in the study of the flow behavior of viscoelastic materials, where the nature of the deformation is said to depend on a ratio of characteristic times called the Deborah number (Metzner et al., 1966). It is reasonable to expect that a similar dimensionless group would be of use in the study of deformations induced by concentration gradients, and, in this paper, we propose a Deborah number which can be used to characterize diffusional transport in amorphous polymer-solvent systems.

To examine the behavior of polymeric materials over wide ranges of conditions, we must first consider the various stable and metastable states of polymers which are invariably observed in amorphous configurations. We do this to support the contention that it is both reasonable and convenient to treat such polymers as viscoelastic fluids at all temperatures. A definition for a diffusion Deborah number is introduced, and the calculation of the parameters in this dimensionless group is discussed. The various regions of the temperature-penetrant concentration diagram are then identified by their Deborah number values. Finally, the utility of the concept of a diffusion Deborah number is demonstrated by using this dimensionless group to anticipate conditions under which thickness anomalies can be expected in sorption experiments. This is done for the atactic polystyrene-pentane system by determining the variation of the Deborah number with temperature and the thickness of the polymer film.

STABLE AND METASTABLE STATES OF POLYMERIC SYSTEMS

The various stable and metastable states of the class of polymers which crystallize with difficulty are depicted in Figure 1. The time t^* can be regarded as a conventional experimental time ranging from minutes to, say, 10 hr., and T_m is the melting point of the polymer which has been represented as a single sharp temperature. Since we are considering polymers which do not crystallize easily, the time required for crystallization is represented as being greater than t^* for the complete temperature range of interest. The time needed to achieve an equilibrium liquid structure and the time required for crystallization should be viewed as characteristic times for these rate processes at a given temperature.

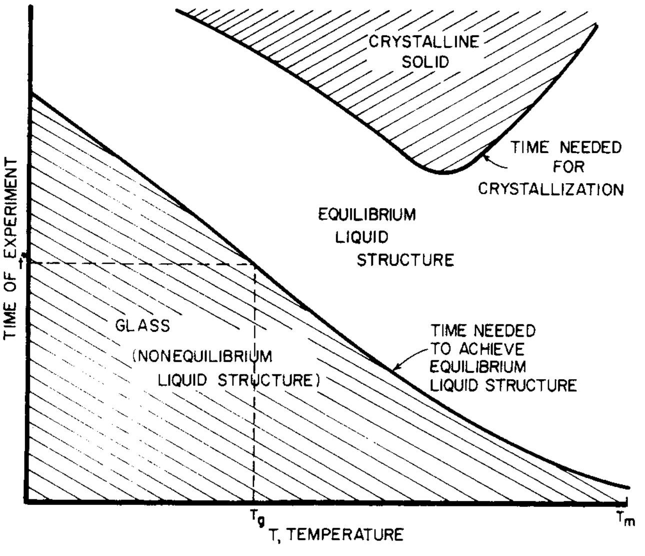

Fig. 1. Representation of states of polymeric systems.

A polymer can exist as a crystalline solid, as a liquid whose structure is in thermodynamic equilibrium with its surroundings, and as a nonequilibrium liquid configuration which is called a glass. In the glassy state, certain degrees of freedom characteristic of liquids are effectively frozen in since the relaxation times for these degrees of freedom are long compared to the time of the experiment. Above the melting point of the polymer, the equilibrium liquid state is the stable configuration, whereas below T_m, it is reasonable to expect that an ordered or crystalline structure will be formed. However, in certain instances, crystallization is suppressed, and the crystalline solid is not observed below T_m. Many polymers have a certain structural irregularity, and the formation of a stable crystalline lattice is prevented. For such polymers, the part of the diagram in Figure 1 representing an ordered or crystalline structure effectively does not exist. In addition, some polymers which appear to possess the necessary requirements of structural regularity have never been observed in a crystalline form because of kinetic factors. The crystallization rate for bulk polymers depends on the height of the energy barrier for the formation of a nucleus of critical size and on the magnitude of the energy barrier for the jump rate of a polymer molecule from a position in the liquid phase to a position in the crystal phase (Kauzmann, 1948). The first barrier decreases markedly as the temperature is lowered below T_m, whereas the second increases because the movement of polymer molecules becomes more difficult. Hence, there exists a maximum value of the crystallization rate and a minimum time required for crystallization, as is depicted in Figure 1. For some polymers, the time needed to overcome the energy barriers to spontaneous crystallization is presumably longer than any reasonable time interval during which the system is observed after the surroundings have been changed. If, in addition, the time needed to form the stable crystalline solid is, for all temperatures, much longer than the time needed to form the equilibrium liquid, it is reasonable to confer upon the equilibrium liquid state the status of an effectively stable configuration. Hence, for certain polymers, the equilibrium liquid structure is the effectively stable state below T_m, and the glassy state of liquids is metastable with respect to this structure because of energy barriers impeding changes in the configurations of molecules. The glass transition temperature T_g can then be regarded as the temperature below which it is not possible to obtain, in an experimental time t^*, a liquid with internal degrees of freedom which are in equilibrium with their surroundings.

The temperature dependence of any property of the equilibrium liquid below T_g is obviously difficult to determine, since a considerable amount of time is needed for the liquid to move from one equilibrium structure to another. Hence, equilibrium properties below T_g are usually inferred from the properties of the equilibrium liquid above T_g by appropriate extrapolation. It has been observed that linear extrapolation of curves of liquid thermodynamic properties through T_g can lead to unreasonable results. For example, such an extrapolation of a liquid entropy—temperature curve predicts that the entropy of the liquid becomes less than that of the crystalline solid (Kauzmann, 1948). One resolution of this dilemma is to postulate that the slope of the entropy curve of the supercooled liquid decreases steadily with decreasing temperature. This appears to us to be a reasonable conjecture as to the behavior of the equilibrium liquid structure below T_g. However, Kauzmann (1948) and Gibbs and DiMarzio (1958) have proposed alternative explanations for the inconsistency which results when the position of the equilibrium liquid curve below the glass temperature

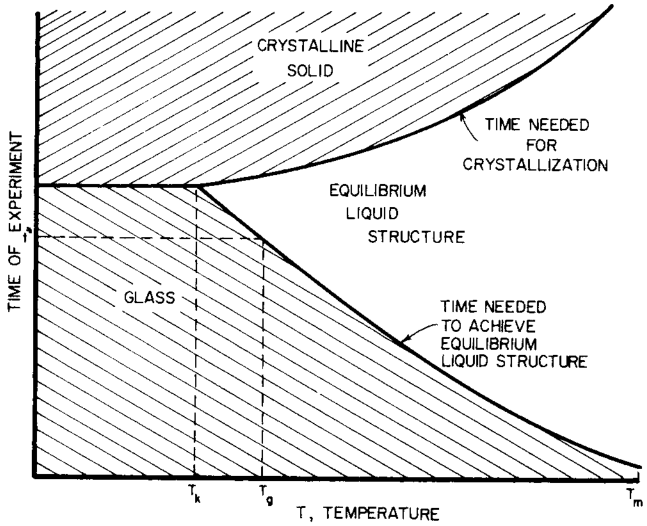

Fig. 2. Representation of states of polymeric systems as proposed by Kauzmann (1948).

is deduced from a linear extrapolation procedure.

Kauzmann's resolution of this possible paradox is the invocation of prior crystallization. He argues that as the temperature is lowered, the time needed for crystallization approaches the time required for the liquid to change its structure after some change in its surroundings. Hence, the curves describing these two processes would intersect at some temperature T_k, below which a liquid will crystallize before it has a chance to conform to a change in its surroundings. The behavior that Kauzmann envisages is depicted in Figure 2.

Existence of a temperature T_k would not permit us to consider the equilibrium structure to be an effectively stable configuration at all temperatures for polymers which can crystallize but do not because of the unfavorable kinetics of the crystallization process. We take issue with the conjecture of Kauzmann for the following reasons. In the first place, we see no indication that nature prefers a linear extrapolation over large temperature intervals and, hence, it is not clear that there is a paradox below T_g which must be resolved. Furthermore, Kauzmann states that the energy barrier to crystallization will decrease as the temperature is lowered (See Figure 2), where in fact it decreases only just below T_m and increases with further decrease in temperature. Thus, it seems that the conjecture of Kauzmann is both questionable and unnecessary.

Gibbs and DiMarzio concern themselves with the nature of the equilibrium liquid structure below T_g and postulate the existence of a thermodynamic second-order transition point T_2, which is the temperature at which the system achieves a ground state of amorphous packing with zero configurational entropy. Verification of the existence of T_2 is virtually impossible. However, the existence of T_2 is of no concern in the present study, since the phenomenon associated with this temperature involves the precise behavior of the equilibrium structure below T_g, and this is not at issue here.

THE LIQUID STATE OF AMORPHOUS POLYMERS

From the above discussion, we see that if we take a broad view of amorphous polymers, they can reasonably be classified as viscoelastic fluids for all temperatures of interest. Ferry (1970) considers amorphous polymers below their glass transition to be viscoelastic solids because they do not exhibit viscous flow and because they closely approach an equilibrium deformation under a constant stress. However, it is reasonable to expect that such polymers will flow and behave like fluids if one is willing to wait a sufficiently long period of time. The classification of Ferry is thus one of convenience since, over conventional time intervals, the fluidlike properties of these materials are not evident. Hence, for most deformations it is useful to consider amorphous polymers at sufficiently low temperatures to be viscoelastic solids with one undeformed configuration (as contrasted to the unlimited number of undeformed configurations that a viscoelastic fluid may have) and with a nonzero equilibrium modulus. However, a wider view of such materials eschews such a classification, and, indeed, utilization of a Deborah number as a means of distinguishing between various types of diffusional or flow behavior is a viable concept only if amorphous polymers can always be treated as viscoelastic fluids.

In such a picture, elastic response is the short-time behavior of viscoelastic fluids, and viscous response constitutes the long-time behavior of such materials. Clearly, the decreased resistance to flow of these materials with increased temperature is due to the effect of temperature on the relaxation modulus and, hence, on the spectrum of relaxation times. On a molecular level, we see that amorphous polymers can be classified as viscoelastic fluids because the individual long chain molecules are held together by secondary bonding forces (van der Waals forces), and, hence, over long time intervals they have unlimited mobility with respect to each other. The secondary bonding forces are significantly stronger in crystalline polymeric structures, and the tendency for appreciable molecular movement is considerably reduced; therefore, it is consistent to deny the existence of fluidlike properties for such materials.

As noted above, the sluggish reorientation of polymer molecules below T_g makes it virtually impossible to experimentally determine the properties of the equilibrium liquid structure below this temperature, and it becomes necessary to utilize judicious extrapolations from measurements carried out on the equilibrated liquid structure at higher temperatures and to apply theoretical models for liquid behavior (such as the free-volume model of liquids). Furthermore, it is not easy to perform a meaningful analysis of an experiment or of a transport process for polymers below T_g. This problem arises because of the nonuniqueness of the glassy state of the supercooled liquid. The exact nature of the nonequilibrated liquid structure depends on the manner in which the sample is deformed and cooled as it is taken below T_g. In principle, this configuration will slowly change to that of the equilibrated liquid, but, in practice, the structure will effectively be unchanged in the time interval between cooling and the next time the polymer is subjected to a change in external conditions. Further deformation will thus be significantly influenced by the thermal and mechanical history of the polymer. In effect, the memory of the polymeric fluid fades very slowly at low temperatures, and events which occurred in the distant past are still important in the determination of the present deformation. The experiments of McLoughlin and Tobolsky (1951) clearly illustrate this type of behavior.

Clearly then, diffusion experiments on glassy polymer samples are difficult to interpret, and diffusional transport in such systems is not readily predictable. Indeed, most measurements of diffusion coefficients and relaxation moduli below T_g reflect, to some degree, the existing structure of the nonequilibrated liquid or, more precisely perhaps, the thermal and mechanical history which has been effectively frozen into the sample. We consider below the problem of calculating diffusion Deborah numbers for polymer samples below T_g.

THE DIFFUSION DEBORAH NUMBER

We now define a Deborah number for diffusion in the absence of externally induced flow so that all deformations are the direct result of concentration gradients, and effects of surface tractions and body forces are entirely negligible. To illustrate the concept of this dimensionless number, we examine the unsteady, one-dimensional diffusion of a penetrant from an effectively pure gas phase into a polymer film of initial thickness L and initial solvent concentration ρ_{10}. At $t = 0$, the pressure in the gas phase is changed suddenly to a pressure which gives a solvent concentration ρ_{1E} when equilibrium has been reestablished between the phases. Such one-dimensional transport of solvents in polymer films occurs frequently, an example being sorption experiments conducted to provide data needed for a better understanding of diffusional behavior in polymer-solvent systems.

For this particular physical situation, it is instructive to distinguish between two cases. For instances where $\rho_{1E} - \rho_{10}$ is sufficiently small, we can describe the diffusional transport with a single set of material properties which can be considered to be representative of the temperature, polymer molecular weight, average pressure, and average concentration $(\rho_{1E} + \rho_{10})/2$ of the diffusion process. A single value of the Deborah number can be calculated, and this number characterizes the nature of the diffusional transport at the conditions of interest. On the other hand, for situations where $\rho_{1E} - \rho_{10}$ is large, the diffusion process can not be described by a single value of the Deborah number because of the strong concentration dependence of some of the properties of polymer-solvent systems. However, Deborah numbers can be calculated from the properties of the initial and final states of the system, and it is both the magnitudes and the differences of these dimensionless numbers which depict the nature of the transport in the binary mixture. Differential and integral sorption experiments (Odani et al., 1961) are examples of instances where small and large concentration changes are realized in polymer films.

A Deborah number for the flow behavior of viscoelastic fluids has been defined as (Astarita and Marrucci, 1974)

$$(DEB)_F = \frac{\lambda_m}{\Theta_F} \qquad (1)$$

The quantity Θ_F is a measure of the time needed to effect a significant change in the kinematic conditions of a material particle. For steady flows, it represents the time a particle spends in nonviscometric portions of a flow field; for unsteady flows it indicates the time needed to proceed from one steady state to another, and for periodic flows it is related to the period of the oscillation. We can define an analogous dimensionless group for diffusive processes as

$$(DEB)_D = \frac{\lambda_m}{\Theta_D} \qquad (2)$$

A characteristic diffusion time for unsteady, one-dimensional mass transfer in polymeric films can be defined in the usual way as

$$\Theta_D = \frac{L^2}{D^*} \qquad (3)$$

It remains to define λ_m and D^* and to discuss methods for calculation of these quantities. The material properties λ_m and D^* and, hence, the diffusion Deborah number $(DEB)_D$ are calculated at a given temperature, pressure, and concentration for a mixture of a solvent and a polymer of a given molecular weight. To eliminate any ambiguities, the properties of an equilibrium liquid structure are used in carrying out this calculation.

Of the many possible definitions for λ_m, it seems natural to take λ_m to be a mean relaxation time for the polymer-solvent system at the conditions of interest:

$$\lambda_m = \frac{\int_0^\infty s\, G(s)\, ds}{\int_0^\infty G(s)\, ds} \qquad (4)$$

Here, $G(s)$ is the shear relaxation modulus which appears in the theory of infinitesimal linear viscoelasticity, and the denominator in Equation (4) is simply the viscosity at zero shear rate:

$$\mu_0 = \int_0^\infty G(s)\, ds \qquad (5)$$

The shear modulus can, in principle, be obtained from transient or periodic experiments on the polymer-solvent system. The mean relaxation time can then be calculated by direct application of Equation (4) or, alternatively, by utilization of the following series expansion, valid for sufficiently small p, for the Laplace transform of $G(s)$:

$$\overline{G}(p) = \mu_0 [1 - p\, \lambda_m + \ldots] \qquad (6)$$

The classical theory of diffusion is valid for a mixture of purely viscous fluids, and, for such systems, a mutual diffusion coefficient is introduced to facilitate the analysis of diffusional transport. However, diffusion of matter in viscoelastic systems is significantly more complex and can not be characterized in an unambiguous manner by an equivalent material property. Hence, in the definition of D^* it is convenient to utilize self-diffusion coefficients, since these quantities can always be defined for polymer-solvent systems. Viscoelastic effects are not in evidence because the polymer-solvent mixture is uniform, and only labeled and unlabeled molecules appear to be undergoing movement. Consequently, unique values of the self-diffusion coefficients D_1 and D_2 exist for each temperature, pressure, concentration, and polymer molecular weight, and we thus define D^* as

$$D^* = x_2 D_1 + x_1 D_2 \qquad (7)$$

This form is suggested by the relationship between mutual and self-diffusion coefficients for solutions which, in the notation of Bearman (1961), are regular. Experimentally, the labeling of a material can be achieved by the use of isotopic species (Moore and Ferry, 1962) or by distinguishing the direction of the nuclear spins, as in a spin-echo nmr experiment (Boss et al., 1967). The self-diffusion coefficient is simply an indication of the rate at which a concentration gradient of the labeled species is dissipated in an otherwise uniform solution. Finally, in instances where a mutual diffusion coefficient D can be defined unambiguously, it can easily be shown that

$$\lim_{x_1 \to 0} D^* = D_1 = D \qquad (8)$$

$$\lim_{x_2 \to 0} D^* = D_2 = D \qquad (9)$$

We conclude this section by suggesting methods for the determination of D_1, D_2, and $G(t)$. Above T_g, the entire G vs. t curve can be constructed by combining transient or periodic experiments with judicious utilization of the time-temperature superposition principle (Ferry, 1970).

Indeed, if the method of reduced variables is assumed valid, it follows that

$$(\lambda_m)_{T=T} = a_T\,(\lambda_m)_{T=T_o} \tag{10}$$

where a_T is the shift factor and T_o is the reference temperature for which $a_T = 1$. The shift factors can be determined experimentally, and Equation (10) gives the mean relaxation time at all temperatures where $G(t)$ data are available. Below T_g, it is effectively impossible to perform a meaningful experiment because of the prohibitively long time needed to prepare a sample which initially has an equilibrium liquid structure. However, a reasonable approximation to the temperature dependence of the shift factor can be deduced from extrapolation of data for a_T taken above T_g and from judicious utilization of whatever data exist below T_g for nonequilibrium liquid structures. Combination of such an approximate a_T vs. temperature curve with Equation (10) gives the temperature dependence of λ_m at a given polymer concentration, pressure, and polymer molecular weight.

Difficulties also exist in the determination of D_1 and D_2. Once again, there is the virtual impossibility of producing an equilibrium liquid sample at temperatures below T_g. Furthermore, it is difficult to measure small values of D_1 and D_2 with present experimental capabilities. Nevertheless, it is possible to utilize whatever D_1 and D_2 data exist above T_g in conjunction with extrapolated volumetric data for the equilibrium liquid and to predict D_1 and D_2 over wide ranges of temperature, concentration, and polymer molecular weight by applying a free-volume theory of liquid transport. Details of the utilization of such an approach in the determination of the concentration and temperature dependence of polymer-solvent diffusion coefficients will be presented in a future communication. It suffices to say that reasonable approximations to D^* and λ_m can be obtained over wide ranges of conditions. Such approximations are quite acceptable, since the goal is not an accurate analysis of the transport but rather the calculation of a dimensionless group whose value serves to indicate the character of the diffusion.

TEMPERATURE—PENETRANT CONCENTRATION DIAGRAMS

The various types of penetrant transfer in high polymers can conveniently be depicted in a temperature-penetrant concentration diagram. In such diagrams, the proposed regions of diffusional transport are delineated in terms of two variables the investigator can control: the temperature and the penetrant concentration. It proves useful to construct such figures by drawing lines of constant Deborah number by calculating this dimensionless group as a function of temperature and composition for a given pressure, polymer molecular weight, and sample thickness. A graphical representation of what is presumably a typical temperature-concentration diagram for an amorphous polymer-solvent system is presented in Figure 3. Three proposed regions of diffusional transport, separated by lines of constant $(DEB)_D$, are included in this figure as well as a curve representing the effective glass transition temperature T_g of the polymer-penetrant system as measured by experiments of conventional duration. A diffusion Deborah number, based on the properties of the equilibrium liquid structure, can be identified for each temperature and penetrant composition on diagrams such as Figure 3, and this dimensionless group can be quite useful in determining the character of the mass transport in the polymer-solvent mixture.

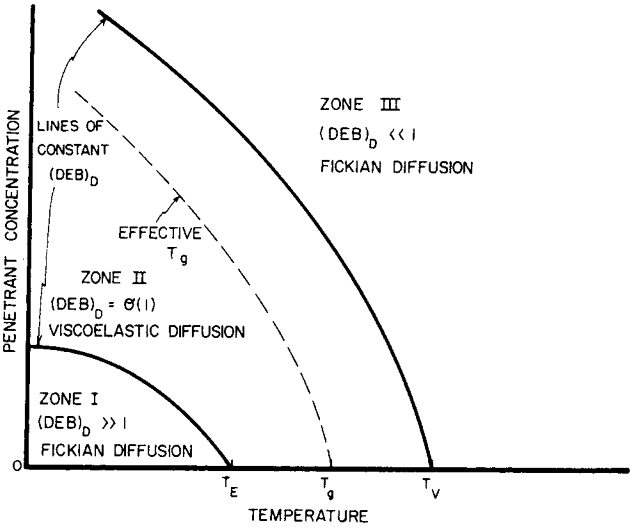

Fig. 3. General temperature-penetrant concentration diagram.

For $(DEB)_D >> 1$ (say 10), a diffusing molecule is moving in a medium which approximately has the characteristics of an elastic material, and, hence, there is effectively no time variation of the polymeric structure during the diffusion process. Even though the system is clearly not a purely viscous fluid mixture, this type of diffusion is often analyzed by using the classical diffusion equation with a diffusion coefficient which is independent of concentration. Hence, zone I is sometimes described as a Fickian diffusion region below T_g, since the equations of the classical theory apply. For $(DEB)_D << 1$ (say 0.1), a molecule is diffusing in what is essentially a purely viscous binary mixture, and conformational changes in the polymer structure appear to take place instantaneously. This is diffusion in the classical sense, and zone III diffusion involves application of the usual diffusion equation with a mutual diffusion coefficient which can be strongly dependent on concentration. For $(DEB)_D = 0(1)$ (say from 0.1 to 10), we have diffusing molecules moving in a viscoelastic binary mixture. As the penetrant diffuses into the polymer, rearrangement of the polymer chains does not all take place immediately, and the instantaneous configuration differs, in general, from the equilibrium structure of the polymer molecules at the concentration of interest. Diffusional behavior in zone II is sometimes called *anomalous transport* because the influence of relaxation on the diffusive process leads to non-Fickian effects in permeation and sorption experiments. No general theory has as yet been formulated to describe diffusional transport under conditions where viscoelastic effects are important. We note that the line of constant Deborah number separating zones II and III is drawn above the glass transition temperature of the mixture, since careful experiments (Odani, 1967) have shown that viscoelastic diffusional behavior can persist above the effective glass temperature.

If small concentration changes occur in the sample during the diffusion process, the value of $(DEB)_D$ calculated from the temperature and average concentration of the polymer-solvent mixture immediately suggests to the investigator whether to expect elastic, viscous, or viscoelastic behavior. Furthermore, the character of the diffusion changes significantly as the temperature and concentration ranges of zone II are traversed. Such behavior is evident from the investigation of Odani, Havashi, and Tamura (1961) who conducted isothermal differential sorption experiments by varying the average penetrant concentration from nearly zero to the composition at which the polymer-penetrant system undergoes glass transition at the temperature of the experiment. No quantitative analysis of the changing nature of the diffusion in zone II is as yet available.

If diffusion in a polymer film involves large concentration changes, we must be concerned not only with the magnitudes of the Deborah numbers calculated at the initial and final conditions, but also with the change that takes place. If the initial and final values of $(DEB)_D$ are both much greater than 1 or both much less than 1, we have elastic or viscous behavior, respectively, throughout the sample during the entire course of the diffusion process. Considerably more complex phenomena are observed, however, if, for example, the initial value of $(DEB)_D$ is large and the final value is small. For diffusive transport under such conditions, part of the sample, at a given time, can behave like an elastic material and part like a purely viscous substance. It is large changes of $(DEB)_D$ of this type which give rise to phenomena such as case II transport, solvent crazing, and swelling fracture (Duda and Vrentas, 1970). Case II transport is apparently a consequence of the fact that diffusion in the part of the sample which behaves approximately like a viscous liquid is much faster than the polymer relaxation process at the boundary between the viscous and elastic regions of the sample. Similarly, the large difference in the mobility and response of the viscous and elastic regions leads to solvent crazing and possibly to fracture of the sample. The point that should be emphasized is that these phenomena are not associated with particular regions of the temperature-penetrant concentration diagram but rather with the change in $(DEB)_D$ that occurs during the diffusion process. Better understanding of such phenomena can be gained by conducting an extensive series of integral sorption experiments (Odani et al., 1961; Alfrey et al., 1966; Hopfenberg et al., 1969).

The temperature-penetrant concentration diagram discussed above is generally useful since it permits the investigator to determine appropriate Deborah numbers for a wide variety of diffusive processes, and it is the values that this dimensionless group take which provide important input as to the nature of the transport expected in the system. Unfortunately, important effects such as case II transport and solvent crazing can not be included in general diagrams such as Figure 3, since these phenomena are not associated with a particular temperature-concentration point on these figures. Since it is of interest to know when to expect such phenomena, it is useful to construct diagrams which include this type of diffusional behavior, even though such diagrams are necessarily more specific in nature. Diagrams of this type have been proposed by Alfrey (1965) and by Hopfenberg and Frisch (1969). Since the precise nature of the diagrams these investigators proposed is, in our opinion, not made sufficiently clear in their publications, we have constructed our version of such a diagram which is presented in Figure 4. This figure describes the diffusional phenomena which are observed when a pure polymer is exposed to various solvent concentrations or activities. The initial value of $(DEB)_D$ is thus that of the polymer at the temperature of interest, whereas the final value can be varied by exposing the system to different penetrant activities. The diagram is constructed by associating various phenomena with the final value of $(DEB)_D$ for the system as calculated from the temperature and final concentration.

At temperatures above $T = T_V$, the effectively pure polymer behaves like a viscous fluid in diffusive transport, and, hence, mass transfer at all penetrant concentrations follows the classical theory of diffusion with a diffusion coefficient which is strongly dependent on concentration.

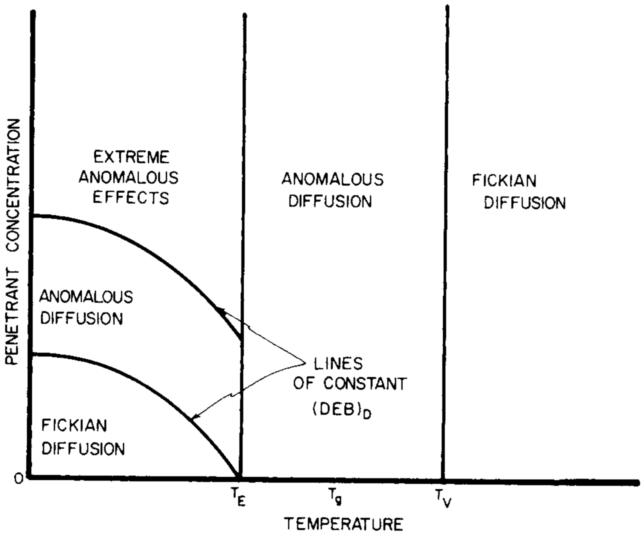

Fig. 4. Special form of temperature-penetrant concentration diagram.

For $T_E < T < T_V$, the calculated value of $(DEB)_D$ for the pure polymer is typically between 0.1 and 10 so that the system behaves like a binary viscoelastic mixture in diffusion processes. Hence, some aspects of anomalous mass transport will be in evidence for all final values of $(DEB)_D$. For temperatures below $T = T_E$, a mixture of polymer and a trace of penetrant behaves elastically in a diffusion process, and a spectrum of transport behavior can be observed depending on the ultimate penetrant concentration in the sample. For small amounts of penetrant, the final value of $(DEB)_D$ is large, and zone I or Fickian diffusion is observed. As the ultimate Deborah number is progressively decreased at each temperature by utilizing higher penetrant activities, anomalous diffusion and extreme anomalous effects, such as case II transport, solvent crazing, and fracture, are observed. The precise nature of the extreme behavior will be somewhat dependent on the geometry of the system as well as on the Deborah number. The regions which are encountered as the concentration is increased at temperatures below $T = T_E$ are separated by lines of constant Deborah number.

Finally, it should now be clear why it is necessary to consider amorphous polymers to be liquids at all temperatures if the concept of a Deborah number is to be utilized. For a liquid with a relaxation function $G(t)$ with the property

$$\lim_{t\to\infty}[t^2G(t)] = 0 \qquad (11)$$

it follows that $0 < \lambda_m < \infty$, and a complete range of Deborah numbers is clearly possible. On the other hand, for a viscoelastic solid, we have

$$G(t) = G_\infty + G^*(t) \qquad (12)$$

$$\lim_{t\to\infty}[G(t)] = G_\infty \qquad (13)$$

$$\lim_{t\to\infty}[t^2G^*(t)] = 0 \qquad (14)$$

and λ_m is necessarily unbounded. Hence, a viscoelastic solid has an infinite Deborah number, if the definition of this study is used. For such materials, the concept of a diffusion Deborah number is clearly meaningless, and, indeed, once we state that an uncross-linked, amorphous material is a viscoelastic solid, we are restricting ourselves to examining a narrow range of behavior for this substance.

UTILIZATION OF THE DEBORAH NUMBER CONCEPT

As an example of the utility of the Deborah number concept, we consider thickness anomalies which have been observed during sorption experiments conducted by using various amorphous polymer-organic penetrant systems (Odani et al., 1961; Odani, 1967). If diffusional transport during a sorption experiment follows the classical equations, the following behavior is observed:

1. In the initial stages of sorption, a plot of M vs. $t^{1/2}$ is linear.
2. Above the linear portion, the M vs. $t^{1/2}$ plot is always concave with respect to the $t^{1/2}$ axis.
3. Sorption data obtained for films of different thickness must reduce to a single curve when M/M_∞ is plotted against $t^{1/2}/L$.

Odani (1967) conducted extensive integral sorption experiments using the methyl ethyl ketone-atactic polystyrene system with polymer samples of different thicknesses. The initial penetrant concentration in the system was equal to or greater than the composition at which the polymer-solvent mixture undergoes glass transition at the temperature of the experiment. The sorption experiments showed that the sorption appeared to be Fickian in nature because the shape of individual sorption curves fulfilled the first two criteria listed above. However, reduced absorption and desorption curves (M/M_∞ vs. $t^{1/2}/L$) for films of different thicknesses did not yield a single curve as is required by the equations of the classical theory. This is a subtle form of non-Fickian behavior, since the thickness effect is rarely tested experimentally because sorption experiments can be quite time consuming. This film thickness effect is viscoelastic in nature, being due to the slow change of the polymer structure accompanying diffusion of the penetrant. Erroneous values of diffusion coefficients will obviously be deduced from sorption experiments where there is evidence of a thickness anomaly unless the data treatment is modified appropriately. Estimates of the mutual diffusion coefficient can be obtained by extrapolating the experimental results to $L \rightarrow \infty$ where $(DEB)_D \rightarrow 0$ and, hence, where classical diffusion behavior can be expected.

Since this type of anomalous diffusion is difficult to detect, it is of some interest to use the concept of a diffusion Deborah number to predict conditions for which it is possible to carry out meaningful experiments. We thus consider diffusion of n-pentane in atactic polystyrene in the limit of zero solvent concentration. For this system, we determine the thickness of the polymer film that must be used at a given temperature so that the value of $(DEB)_D$ is small enough to ensure that the sorption experiment will exhibit classical behavior. This particular binary mixture is chosen because sufficient data exist to carry out an analysis.

Lines of constant $(DEB)_D$ are plotted on a sample thickness-temperature diagram in Figure 5. This figure depicts diffusional behavior in the limit of zero weight fraction of n-pentane for a polymer with a weight average molecular weight of 2×10^5. The diagram presented in Figure 5 was constructed by using the diffusivity data of Duda and Vrentas (1968) above T_g, the diffusivity data of Holley, Hopfenberg, and Stannett (1970) below T_g, and the viscoelastic modulus and shift factor data of Fujita and Ninomiya (1957). The regions of elastic, viscoelastic, and viscous behavior for differential sorption experiments are depicted in this diagram, and, hence, a good estimate of what size samples must be utilized for meaningful experiments can be deduced from this figure. Such information is particularly useful below 110°C because of the strong temperature dependence of material properties in this temperature range. In the above discussion, it is implied that the thickness of the polymer sample is identical to the length L of the diffusion path. Of course, L will be one half of the actual film thickness if the penetrant is in contact with two sides of the sample.

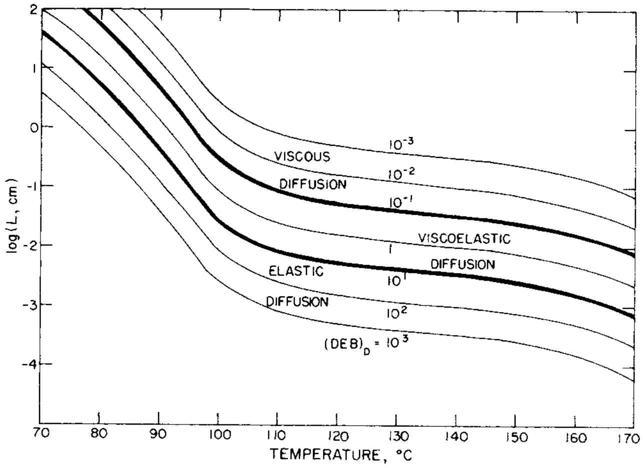

Fig. 5. Variation of Deborah number with temperature and film thickness for n-penetane-atactic polystyrene system.

Quantitative versions of Figures 3 and 4 would clearly be quite useful in planning experiments and in anticipating the type of transport behavior that can be expected at various temperatures and concentrations in polymer-solvent systems. Some effort is presently being expended in the construction of such diagrams.

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NOTATION

a_T = shift factor
D = binary mutual diffusion coefficient
D_I = self-diffusion coefficient of component I
D^* = diffusion coefficient for process defined by Equation (7)
$(DEB)_D$ = diffusion Deborah number defined by Equation (2)
$(DEB)_F$ = Deborah number for viscoelastic flow defined by Equation (1)
$G(t)$ = shear relaxation modulus
G_∞ = value of G at infinite time for viscoelastic solid
$G^*(t)$ = shear modulus defined by Equation (12)
$\overline{G}(p)$ = Laplace transform of $G(t)$
L = length of diffusion path
M = amount of solvent absorption or desorption per gram of polymer
M_∞ = value of M at sorption equilibrium
p = Laplace transform variable
t = time
t^* = time of conventional experiment
T_E = temperature below which pure polymer acts like an elastic solid
T_g = glass transition temperature
T_k = temperature below which it is not possible to observe an equilibrium liquid structure
T_m = melting point of polymer
T_V = temperature above which pure polymer acts like a viscous fluid
T_0 = reference temperature for shift factor
T_2 = temperature at which a system achieves zero configurational entropy

x_I = mole fraction of component I

Greek Letters

Θ_D = characteristic diffusion time
Θ_F = characteristic time of flow process
λ_m = characteristic or natural time of fluid
μ_0 = viscosity at zero shear rate
ρ_{1E} = final or equilibrium mass density of solvent in sample
ρ_{10} = initial mass density of solvent in sample

LITERATURE CITED

Alfrey, T., "Glassy Polymer Diffusion," *Chem. Eng. News,* **43,** No. 41, 64 (1965).

———., E. F. Gurnee, and W. G. Lloyd, "Diffusion in Glassy Polymers," *J. Polymer Sci.,* **C12,** 249 (1966).

Astarita, G., and G. Marrucci, *Principles of Non-Newtonian Fluid Mechanics,* McGraw-Hill, London (1974).

Bearman, R. J., "On the Molecular Basis of Some Current Theories of Diffusion," *J. Phys. Chem.,* **65,** 1961 (1961).

Boss, B. D., E. O. Stejskal, and J. D. Ferry, "Self-Diffusion in High Molecular Weight Polyisobutylene-Benzene Mixtures Determined by the Pulsed-Gradient, Spin-Echo Method," *ibid.,* **71,** 1501 (1967).

Duda, J. L., and J. S. Vrentas, "Diffusion in Atactic Polystyrene Above the Glass Transition Point," *J. Polymer Sci.,* **A-2,** No. 6, 675 (1968).

———————., "Physical Properties of Styrene Polymers-Diffusion," *Encyclopedia of Polymer Science and Technology,* Vol. 13, pp. 326-342, Wiley, New York (1970).

Ferry, J. D., *Viscoelastic Properties of Polymers,* 2 edit., Wiley, New York (1970).

Fujita, H., and K. Ninomiya, "Dependence of Mechanical Relaxation Spectra of Linear Amorphous Polymers on the Distribution of Molecular Weights," *J. Polymer Sci.,* **24,** 233 (1957).

Gibbs, J. H., and E. A. DiMarzio, "Nature of the Glass Transition and the Glassy State," *J. Chem. Phys.,* **28,** 373 (1958).

Holley, R. H., H. B. Hopfenberg, and V. Stannett, "Anomalous Transport of Hydrocarbons in Polystyrene," *Polymer Eng. Sci.,* **10,** 376 (1970).

Hopfenberg, H. B., and H. L. Frisch, "Transport of Organic Micromolecules in Amorphous Polymers," *J. Polymer Sci.,* **B7,** 405 (1969).

Hopfenberg, H. B., R. H. Holley, and V. Stannett, "The Effect of Penetrant Activity and Temperature on the Anomalous Diffusion of Hydrocarbons and Solvent Crazing in Polystyrene, Part I: Biaxially Oriented Polystyrene," *Polymer Eng. Sci.,* **9,** 242 (1969).

Kauzmann, W., "The Nature of the Glassy State and the Behavior of Liquids at Low Temperatures," *Chem. Rev.,* **43,** 219 (1948).

McLoughlin, J. R., and A. V. Tobolsky, "Effect of Rate of Cooling on Stress Relaxation of Polymethyl Methacrylate," *J. Polymer Sci.,* **7,** 658 (1951).

Metzner, A. B., J. L. White, and M. M. Denn, "Behavior of Viscoelastic Materials in Short-Time Processes," *Chem. Eng. Progr.,* **62,** No. 12, 81 (1966).

Moore, R. S., and J. D. Ferry, "Diffusion of Radioactively Tagged Cetane in Polyisobutylene-Cetane Mixtures and in Three Methacrylate Polymers," *J. Phys. Chem.,* **66,** 2699 (1962).

Odani, H., "Diffusion in Glassy Polymers. IV. Diffusion of Methyl Ethyl Ketone in Atactic Polystyrene Above the Critical Concentration," *J. Polymer Sci.,* **A-2,** No. 5, 1189 (1967).

Odani, H., J. Hayashi, and M. Tamura, "Diffusion in Glassy Polymers. II. Effects of Polymer-Penetrant Interaction; Diffusion of Ethyl Methyl Ketone in Atactic Polystyrene," *Bull. Chem. Soc. Japan,* **34,** 817 (1961).

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Dissipation Effects in Hydrodynamic Stability of Viscoelastic Fluids

In this paper an analysis is made of the hydrodynamic stability of a Boussinesq viscoelastic fluid undergoing plane Couette flow with a superposed temperature gradient. Of special interest is the effect of including the dissipation term in the energy equation. This term is shown to destabilize the fluid for most values of disturbance wave number and material parameters and to cause overstability for all values of the Brinkman number. At a critical Weissenberg number of 1, a rheological instability is developed which is essentially independent of the Reynolds, Prandtl, and Brinkman numbers.

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SCOPE

One of the most common and important processing operations in the polymer industry is fiber spinning. This operation is depicted schematically in Figure 1 and consists of many sequential flows, each of which is important in the production of an end product of satisfactory material properties. For the purposes of the research described, the process will be divided heuristically into four regimes:

1. The die entry. Here the polymer melt is forced (by an extruder or other pressure source) from the reservoir into a capillary of very small diameter (relative to reservoir dimensions). The entry flow is very complicated and combines aspects of a complicated shear flow with an accelerated elongational flow.

2. The capillary. Here an approximation to simple shear flow is developed. Viscous dissipation induced temperature effects may be important.

3. Die exit. The complex phenomenon of die swell is encountered in this region.

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