Spinning of a Noll Simple Fluid

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Previous results for a class of flows dynamically possible in a Noll simple fluid are the starting point for a description of melt spinning or dry spinning in the limit of a rapidly extruded, small diameter polymer thread. Simultaneous energy and mass transfer, important in the real process, are not taken into account; also neglected are inertial effects, body forces, and surface tension.

In a typical process for the production of a synthetic fiber, either a molten polymer or a solution of polymer in a volatile solvent is continuously extruded through a small orifice (or spinnerette) into a chamber where, as the thread moves along, either the molten polymer cools (melt spinning) or the solvent is evaporated from the polymer solution into a surrounding gas phase (dry spinning). From this chamber the fiber runs through a wind-up device which forces it to move with a velocity greater than the velocity with which it left the spinnerette; this means that the thread deforms as it moves through the cooling or evaporation chamber.

From a design standpoint it would be of interest to predict in detail the simultaneous energy, mass, and momentum transfer to the fiber between the spinnerette and the take-up device, in order that the proper operating conditions for this operation could be arrived at with a minimum of preliminary experimental work. This problem is too difficult to solve at present. We realize that changes in the properties of the materials due to changes in temperature and composition may be more important than the fact that the materials are highly viscoelastic.† However, in the hope of learning more about the practical problem, we examine the limiting case of the spinning of a viscoelastic fluid where energy and mass transfer may be neglected. The rheological behavior of the material is assumed to be representable by Noll's theory of simple fluids (*1* to *4*).

Also, we outline some of the principal ideas which make up Noll's theory of simple fluids. Solutions based upon Noll's theory exist for only two classes of problems: the viscometric flows, which include flow through an infinitely long tube, and the unsteady relative extensions. With respect to this latter class, all that has been shown is that a velocity distribution of the form of Equation (4) is consistent with the equation of continuity under the restriction of Equation (6) and that together with the Cauchy stress equation of motion, this velocity distribution implies a stress distribution of the form of Equation (7). If one suspects that a particular flow belongs to this class of problems, one must show that Equations (4), (6), and (7) are consistent with the boundary conditions which describe the flow.

We also specify a set of boundary conditions [Equations (13) to (16)] which we feel describe a reasonable approximation to the flow which exists in a thread downstream of the swelling at the exit of a spinnerette. We find that these boundary conditions, together with two additional conditions suggested by symmetry [Equation (17)], can be satisfied by an unsteady relative extension described by Equations (18), (19), and (35).

Finally, we put together the principal results of our analysis. These are an expression for the axial stress in the thread in terms of the two functions which describe the behavior of a Noll simple fluid in an unsteady relative extension, and the dependence of thread diameter upon axial position and the velocity at a reference position. These results would allow one to obtain an expression for the stress applied to the thread by the wind-up device in terms of the final diameter of the thread, the properties of the fluid, and the velocity of the thread at a reference position.

† By viscoelastic we mean here that the fluid obeys neither Newton's law of viscosity nor Hooke's law of elasticity.

PREVIOUS RESULTS

This problem has been treated previously by Ziabicki and Kedzierska (*5*) and by Ziabicki (*6*, *7*). In their first paper (*5*), no attempt is made to obtain a dynamically consistent velocity distribution in the fiber. Calculations based upon the assumption of Trouton's law [see Equation (40)] are carried out for the case of constant viscosity, but inertial effects and gravitational effects are not neglected. Equation (40) is derived under the assumption that inertial effects and gravitational effects can be neglected. Since it is not obvious that this relation could be obtained without these assumptions, the meaning of their results is questionable.

Ziabicki (*6*) assumes in a second discussion that there is only one nonzero component of velocity in the thread, which means that diameter cannot be a function of distance along the fiber. He errs in treating surface effects as external body forces in the equation of motion rather than as boundary conditions to these equations.

In a third paper, Ziabicki (*7*) starts with an equation of motion apparently based on the assumption that the constitutive equation for stress is some generalization of Trouten's rule. There appears to be no justification for this.

THE NOLL SIMPLE FLUID AND PREVIOUS RESULTS

Let us look at the fluid in some arbitrary, fixed, rectangular, Cartesian coordinate system $x_i (i = 1, 2, 3)$ and describe the motion which took place in the material at all prior times $t + s$ $(-\infty < s \leq 0)$ by specifying as a function of time $t + s$ the coordinates X_i (in perhaps some other rectangular, Cartesian coordinate system) of the material which we find around the position $\mathbf{x}$ at time t:

$$X_i = \hat{X}_i (\mathbf{x}, t + s) \tag{1}$$

We term $\partial X_i / \partial x_j$ the relative deformation gradient (we do not use the summation convention) and

$$c_{ij} (t + s) = \sum_{m=1}^{3} \sum_{n=1}^{3} \delta_{mn} \frac{\partial X_m}{\partial x_i} \frac{\partial X_n}{\partial x_j} \tag{2}$$

the relative right Cauchy-Green tensor.

All previously proposed constitutive equations that have found any success at all have been founded on what Noll (*1*) has termed the ***principle of determinism,*** that is, the stress at the position **x** at time t is determined by the history of the motion of the material which is within an arbitrarily small neighborhood of **x** at t. Noll has defined as a simple material, one for which the stress t_{ij} at **x** and at time t is determined by the history of the relative deformation gradient $\partial X_i/\partial x_j$ for the material which is in an arbitrarily small neighborhood of **x** at t. An incompressible simple fluid has been defined by him to be one for which the stress t_{ij} at **x** and at time t is specified within an indeterminate pressure p by the history of the relative right Cauchy-Green tensor for the material which is within an arbitrarily small neighborhood **x** at t:

$$t_{ij} + p\,\delta_{ij} = \frac{\mu}{\tau} \overset{o}{\underset{\sigma=-\infty}{\mathcal{H}_{ij}}} [c_{km}(t + \tau\sigma)] \qquad (3)$$

Here we follow Truesdell's discussion of the dimensional invariance of the definition of a simple material (*8*). The quantity $\overset{o}{\underset{\sigma=-\infty}{\mathcal{H}_{ij}}}$ is a dimensionally invariant, tensor-valued functional, that is, an operator which maps tensor-valued functions into tensors; the constants μ and τ, defined by Truesdell (*8*), are discussed below.

Using only the definition of an incompressible simple fluid, Coleman and Noll (*2* to *4*) have been able to show that there are at least two classes of flows which are dynamically possible for every simple fluid. The first class, sometimes referred to as the viscometric flows, includes several geometries which are interesting to the experimentalist, such as flow through a tube. The behavior of a simple material in any one of these geometries is determined by three material functions: one of these expresses the relation between shear stress and shear rate; the other two give differences between the normal stress components as a function of shear rate. Equation (3) applies to an incompressible simple fluid which exhibits a linear viscosity μ, termed the natural viscosity, at sufficiently small shear rates and which shows some normal stress effects (*9*). The natural time τ is a positive constant which reflects the magnitude of the normal stress effect in the limit of small shear rates.

The second class (*4*), as recently generalized (*10*), might be termed the unsteady relative extensions and describes flows in which the dimensionless velocity distribution is of the form

$$v_i^* = [a_i^* x_i^* + V_i^*] e^{t^*} \qquad (4)$$

where

$$v_i^* = v_i/V, \quad x_i^* = x_i/R_o, \quad a_i^* = a_i R_o/V$$
$$\mathbf{V}_i^* = V_i/V \quad \text{and} \quad t^* = kt \qquad (5)$$

Here V, R_o, and k are characteristic constants with the dimensions velocity, length, and reciprocal time, respectively. All starred quantities are dimensionless. In order that the equation of continuity be satisfied

$$a_1 + a_2 + a_3 = 0 \qquad (6)$$

All nondiagonal elements of the corresponding stress distribution are identically zero, and the dimensionless diagonal elements are given by (this is the result of putting the discussion of reference *10* in a dimensionally invarient form as discussed above)

$$t_{ii}^* = \sum_{j=1}^{3} (N_1[(a_j^* x_j^*)^2/2 + a_j^* V_j^* x_j^*] e^{2t^*} + N_2[a_j^* x_j^{*2}/2 + V_j^* x_j^*] e^{t^*}) + N_3\,\phi^* + a_i^{**} H^* e^{t^*} + (a_i^{**})^2 L^* e^{2t^*} + n^*(t^*) \qquad (7)$$

where

$$t_{ii}^* = t_{ii}\,\tau/\mu, \quad a_i^{**} = a_i\,\tau, \quad \phi^* = \phi/(R_o g)$$
$$H^* = H^*(\overline{II}^*, \overline{III}^*, N_4), \quad L^* = L^*(\overline{II}^*, \overline{III}^*, N_4) \qquad (8)$$
$$\overline{II}^* = \sum_{j=1}^{3} [a_j^{**} e^{t^*}]^2, \quad \overline{III}^* = \sum_{j=1}^{3} [a_j^{**} e^{t^*}]^3 \qquad (9)$$
$$N_1 = \rho\,V^2\,\tau/\mu, \quad N_2 = R_o\,V\,\rho\,k\,\tau/\mu$$
$$N_3 = \rho\,g\,\tau\,R_o/\mu, \quad \text{and} \quad N_4 = k\tau \qquad (10)$$

The behavior of a simple fluid in these flows depends upon two dimensionally invariant material functions,† H^* and L^*, which are unrelated to the three which appear in the class of viscometric flows. We assume here that the external body force vector per unit mass **f** is representable in terms of a potential ϕ:

$$\mathbf{f} = -\nabla\phi \qquad (12)$$

The local acceleration of gravity is g.

It is important to note that in describing the class of unsteady relative extensions we say nothing about boundary conditions. If one believes that a certain flow belongs to this class, it is necessary to determine whether Equations (4), (6), and (7) satisfy the boundary conditions appropriate to the flow for a specific set of a_i^*, V_i^*, and $n^*(t^*)$. Our task is to do just this for the spinning of a thread of simple fluid.

APPLICATION TO SPINNING

We find it convenient here to work in cylindrical coordinates where the positive z axis points in the direction of flow and coincides with the axis of symmetry of the thread. Physical components of vectors and tensors are used in this section.

Neglecting all effects due to mass and energy transfer with the surroundings, we wish to describe the flow in a fluid thread between the exit of the spinnerette and the wind-up device in a spinning operation. A difficulty is encountered immediately in specifying a boundary condition at the exit of the tube; that the velocity distribution should not be that for infinitely long tubes is clear, since the length-to-diameter ratio for a spinnerette orifice is of the order of unity. In practice the thread diameter is observed to go through a maximum shortly after leaving the spinnerette (*11*); this suggests that as an approximation we assume that the axial component of velocity is uniform across the cross section at some $z = 0$ downstream of the cross section of maximum diameter:

$$z = 0: \quad v_z^* = 1 = \text{constant} \qquad (13)$$

If we neglect all surface effects (*12* to *14*) and if we neglect viscous effects in the surrounding phase (this is reasonable in melt spinning or dry spinning, where the thread is surrounded by a vapor between the spinnerette and the take-up device), the requirement of a balance of forces at the free surface yields

$$(t_{rr}|_{r=R} + P_o)\,n_r = 0 \qquad (14)$$
$$(t_{\theta\theta}|_{r=R} + P_o)\,n_\theta = 0 \qquad (15)$$

and

$$(t_{zz}|_{r=R} + P_o)\,n_z = 0 \qquad (16)$$

Here P_o stands for the ambient pressure in the cooling or evaporation chamber and **n** is the outwardly directed (into the vapor phase) unit vector normal to the free surface. Last, symmetry suggests that

† The relation of H^* and L^* to H and L introduced in reference *10* is

$$H^* = H/\mu, \quad L^* = L/(\mu\,\tau) \qquad (11)$$

and

$$r = 0: \quad v_r = 0$$

$$\text{everywhere:} \quad v_\theta = 0 \tag{17}$$

Our problem is to obtain a simultaneous solution of Cauchy's stress equation of motion, the equation of continuity, and the constitutive equation for a Noll simple fluid, Equation (3). We require that this solution satisfy the boundary conditions given in Equations (13) to (17). Let us see whether a particular case of Equations (4), (6), and (7), which satisfy the equation of continuity and Cauchy's stress equation of motion, represents a solution to this problem. To insure that the velocity distribution in Equation (4) satisfies the boundary condition, Equation (13), we take

$$V_3^* = 1 \tag{18}$$

Equations (6) and (17) imply that

$$V_1^* = V_2^* = 0, \quad a_1 = a_2 = -a/2, \quad a_3 = a \tag{19}$$

Finally, we must determine whether Equation (7), as amended by Equations (18) and (19), satisfies the remaining boundary conditions, Equations (14) to (16). If they do, the function $n^*(t^*)$ in Equation (7) will be specified. To examine these boundary conditions we need both the stress distribution in cylindrical coordinates and the shape of the fiber.

Equations (7), (18), and (19) yield in cylindrical coordinates (all nondiagonal components are identically zero) the dimensionless components

$$t_{rr}^* = t_{\theta\theta}^* = N_1 [a^{*2} r^{*2}/8 + a^{*2} z^{*2}/2 + a^* z^*] e^{2t^*} + N_2 [-a^* r^{*2}/4 + a^* z^{*2}/2 + z^*] e^{t^*} + N_3 \phi^* - a^{**} H^* e^{t^*}/2 + a^{**2} L^* e^{2t^*}/4 + n^*(t^*) \tag{20}$$

and

$$t_{zz}^* = N_1 [a^{*2} r^{*2}/8 + a^{*2} z^{*2}/2 + a^* z^*] e^{2t^*} + N_2 [-a^* r^{*2}/4 + a^* z^{*2}/2 + z^*] e^{t^*} + N_3 \phi^* + a^{**} H^* e^{t^*} + a^{**2} L^* e^{2t^*} + n^*(t^*) \tag{21}$$

where

$$r^* = r/R_o, \quad z^* = z/R_o \tag{22}$$

Here R_o is the radius of the thread at $z = 0$. For sufficiently small values of N_1, N_2, and N_3, the first three terms on the right of Equations (20) and (21) may be neglected with respect to the last three terms. Physically this means that inertial effects and the effect of the external body force vector may be neglected with respect to viscous effects, with the result that Equations (20) and (21) simplify to

$$t_{rr}^* = t_{\theta\theta}^* = -a^{**} H^* e^{t^*}/2 + a^{**2} L^* e^{2t^*}/4 + n^*(t^*) \tag{23}$$

and

$$t_{zz}^* = a^{**} H^* e^{t^*} + a^{**2} L^* e^{2t^*} + n^*(t^*) \tag{24}$$

The shape of the fiber may be determined from the streaklines (*13*, p. 81). At time t, the streakline through a point $\mathbf{x}_o$ is a curve going from $\mathbf{x}_o$ to $\mathbf{x}$, the position reached by the particle which was at $\mathbf{x}_o$ at time $t = 0$; this curve denotes the positions of all material particles which passed through the position $\mathbf{x}_o$ at some intermediate time β. The particle paths are solutions of

$$\frac{dx_i}{dt} = [a_i x_i + V_i] e^{kt}$$

with the boundary conditions

$$t = 0: \quad x_i = \xi_i$$

These solutions are

$$\frac{a_i x_i + V_i}{a_i \xi_i + V_i} = \exp\left[\frac{a_i}{k}(e^{kt} - 1)\right] \tag{25}$$

The particles which passed the point $\mathbf{x}_o$ at time β may be identified through

$$\frac{a_i x_{io} + V_i}{a_i \xi_i + V_i} = \exp\left[\frac{a_i}{k}(e^{k\beta} - 1)\right] \tag{26}$$

Elimination of the particle designation between Equations (25) and (26) gives the streakline

$$\frac{a_i x_i + V_i}{a_i x_{io} + V_i} = \exp\left[\frac{a_i}{k}(e^{kt} - e^{k\beta})\right] \tag{27}$$

In order to obtain the shape of the fiber, identify $\mathbf{x}_o$ with a point on the surface of the fiber at the cross section $x_3 = 0$. In view of Equations (18) and (19) we have from Equation (27)

$$x_1/x_{1o} = x_2/x_{2o} = [a\, x_3/V + 1]^{-\frac{1}{2}} \tag{28}$$

In terms of cylindrical coordinates, Equation (28) yields

$$r/r_o = [a\, z/V + 1]^{-\frac{1}{2}} \tag{29}$$

where

$$r_o = [(x_{1o})^2 + (x_{2o})^2]^{\frac{1}{2}} \tag{30}$$

From Equation (29) the physical components of the outwardly directed unit normal to the free surface are (*15*, p.197):

$$n_r = [1 + a^{*2} R^{*6}/4]^{-\frac{1}{2}} \tag{31}$$

$$n_\theta = 0 \tag{32}$$

and

$$n_z = \frac{a^* R^{*3}/2}{[1 + a^{*2} R^{*6}/4]^{\frac{1}{2}}} \tag{33}$$

where

$$R^* = R/R_o \tag{34}$$

Let us restrict ourselves to the limiting case where $a^* \to 0$. This is compatible with the previous assumption that N_1, N_2, and N_3 are so small that Equations (20) and (21) reduce to Equations (23) and (24). Physically this means that we are restricting ourselves to cases where a small diameter thread is extruded very rapidly (the diameter of the thread is nearly independent of position downstream of the cross section $z = 0$). Under these conditions, Equations (32) and (33) mean that Equations (15) and (16) are satisfied identically, and Equations (14), (23), and (31) imply that

$$\lim_{a^* \to 0} : \; n^*(t^*) = -p_o \tau/\mu + a^{**} H^* e^{t^*}/2 - a^{**2} L^* e^{2t^*}/4 \tag{35}$$

RESULTS

In an idealization of the practical problem one might wish to achieve a given thread diameter from a spinning operation, that is, the thread radius is specified at a particular axial position, say $z = z_1$:

$$z = z_1 \; : \; R = R_1 \tag{36}$$

A question which could be asked is: What axial stress must be exerted in the thread in order to achieve the desired product?

Equations (36) and (29) determine a for the operation

$$a = \frac{V}{z_1}\left[(R_o/R_1)^2 - 1\right] \qquad (37)$$

If we assume that the material functions H^* and L^* and the constants μ and τ have already been determined in other experiments on the material in question (*2 to 4, 8, 10*), Equations (24) and (35) yield the desired value of axial stress t_{zz} in terms of a:

$$t_{zz} = \frac{3\mu}{2\tau} a^{**} H^* e^{t^*} + \frac{3\mu}{4\tau} a^{**2} L^* e^{2t^*} - p_o \qquad (38)$$

It is interesting to note that Equation (38) has the form of a generalization of Trouton's law for viscous traction (*16*, p. 78). A special case of an incompressible Noll simple fluid is an incompressible Newtonian fluid for which

$$H^* = 2, \quad L^* = 0 \qquad (39)$$

For the steady state flow of a Newtonian fluid Equation (38) reduces to the usual form of Trouton's law:

$$t_{zz} + p_o = 3\,\mu\, a \qquad (40)$$

where a is the rate of extension. However, the derivation of Equation (38) should not be viewed as a justification for the use of Trouton's law in the usual sense, the continuous extension of a rod under a constant load, since the discussion of the boundary conditions for this situation is somewhat different.

Even in the situation where the material functions H^* and L^* are not known, we still have the form of the dependence of thread radius upon axial position and the velocity at the cross section $z = 0$. From Equation (29)

$$R/R_o = [a\,z/V + 1]^{-\frac{1}{2}} \qquad (41)$$

DISCUSSION

The data of Ziabicki and Kedzierska (*5*) indicate that it is probably reasonable to treat the limiting case as $a^* \to 0$ (from their Figure 13 and Table 5, for example, $a^* < 5 \times 10^{-3}$), though their data indicate that a thread of nearly uniform diameter is not achieved until more than ½ meter downstream of the spinnerette. This is not a contradiction, since a^* was not a constant in their experiments until a meter or more downstream of the spinnerette (see, for example, Figure 13), which we would identify with the locality of the cross section $z = 0$. This would seem to indicate that our results may be a reasonable description of the deformation taking place in the thread in a real spinning operation between a meter or more downstream of the spinnerette and the wind-up device.

The complicating factor, which must be kept in mind, is that in the real spinning process appreciable changes in properties result from the simultaneous energy and mass transfer between the thread and the surroundings. It probably is for this reason that a^* was not a constant until a meter or more downstream of the spinnerette. It may also be that inertial effects were not negligibly small; values of τ and μ for their fluids would be required to determine the magnitude of N_1 in their experiments.

The description of the spinning of a polymer fiber given here may be extended without difficulty to the drawing which takes place following extrusion of a flat film or of an axially symmetric, cylindrical film.

NOTATION

a = defined by Equation (19)
a_i = constant defined by Equations (4) and (5)
a_i^* = defined by Equation (5)
a_i^{**} = defined by Equation (8)
$c_{ij}(t+s)$ = relative right Cauchy-Green tensor defined by Equation (2)
$\mathbf{f}$ = external body force vector per unit mass
g = acceleration of gravity
H^* = one of the dimensionally invariant material functions in terms of which the behavior of a simple fluid is represented in an unsteady, relative extension. See Equations (7) and (8)
$\underset{\sigma=-\infty}{\overset{o}{\mathcal{H}_{ij}}}$ = dimensionally invariant tensor valued functional of the relative right Cauchy-Green tensor at a material point
k = constant defined by Equations (4) and (5)
L^* = one of the dimensionally invariant material functions in terms of which the behavior of a simple fluid is represented in an unsteady, relative extension. See Equations (7) and (8)
$n^*(t^*)$ = arbitrary function of dimensionless time t^* in Equation (7)
n_r, n_θ, n_z = physical components of the outwardly directed (into the gas phase) unit normal to the free surface
N_1, N_2, N_3, N_4 = dimensionless groups defined by Equation (10)
p = pressure
p_o = ambient pressure of the gas phase which surrounds the spun fiber
r = radial cylindrical coordinate
r^* = defined by Equation (22)
r_o = defined by Equation (30)
R = radius of the spun fiber, a function of z
t = time
t_{ij} = stress tensor
t_{ij}^* = defined by Equation (8)
$t_{rr}, t_{\theta\theta}, t_{zz}$ = physical components of the stress tensor in cylindrical coordinates
v_i = velocity vector
v_i^* = defined by Equation (5)
v_r, v_θ, v_z = physical components of the velocity vector in cylindrical coordinates
V_i = constant defined by Equations (4) and (5)
V_i^* = defined by Equation (5)
x_i = rectangular, Cartesian coordinate
x_i^* = defined by Equation (5)
X_i = coordinates (in perhaps some other rectangular, Cartesian coordinate system) at time $t + s$ ($-\infty < s \leq 0$) of the material which we find around the position $\mathbf{x}$ at time t
z = axial cylindrical coordinate
z^* = defined by Equation (22)

Greek Letters

δ_{ij} = Kronecker delta
μ = natural viscosity defined in reference *8* and discussed following Equation (3)
ρ = density
τ = natural time defined in reference *8* and discussed following Equation (3)
ϕ = potential in terms of which the external body force per unit mass f is represented $\mathbf{f} = -\nabla\phi$

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The P-V-X Behavior of the Liquid System Acetone-Carbon Disulfide at Elevated Pressures

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The change in volume on mixing for a system showing large positive deviations from ideality is examined at one temperature to pressures of 100,000 lb./sq.in. Original atmospheric pressure density data and compression measurements over the entire mole fraction range for this system, acetone–carbon disulfide, are reported at 0°C. These are correlated with the semiempirical Tait equation to yield change in volume on mixing as a function of mole fraction and pressure.

This volume change is found to decrease from the maximum of 1 cc./mole at atmospheric pressure to about 0.4 cc./mole at 100,000 lb./sq.in. The maximum also shifts during this pressure increase from 0.53 mole fraction acetone to 0.74.

Simultaneous determination of pressure, specific volume, temperature, and composition provides some of the most fundamental thermodynamic data. Relatively few measurements of this type on liquids have been reported in the literature.

Although some cursory investigations of the effect of pressure on the properties of liquids were conducted in the latter part of the 19th century, comprehensive studies of this type began with Bridgman in the early part of this century (*1*). It was the work of Bridgman which raised the limits of obtainable working pressures to over 1,000,000 lb./sq. in. However, his work was devoted exclusively to pure compounds (*2* to *6*). The effect of pressure on the physical properties of liquid mixtures has, as would be expected, received less attention. Aside from compressibilities at 1 atm., calculated from velocity of sound measurements (*7* to *9*), the works of Gibson (*10*), Eduljee (*11*), Reamer (*12*), and Cutler (*13*), concerning binary liquid compressions for a total of nine systems, stand alone. The prediction of the pressure effect on liquids has been almost completely limited to single component systems (*14* to *16*).

The purpose of this investigation was to obtain isothermal P-V-X data for the system acetone–carbon disulfide over the entire range of composition and for pressures up to 100,000 lb./sq. in. These data were then to be used in a study of the liquid-liquid phase behavior of this system.

THERMODYNAMIC RELATIONS

Isothermal P-V-X data over the entire range of composition and over a considerable pressure range result from experimental determinations of mixture densities at one atmosphere pressure and compressibility measurements from one atmosphere up to elevated pressures. Interpretation and application of such data are facilitated by the use of several thermodynamic relations summarized in the following paragraphs.

Densities at 1 Atm.

Experimental density data, originating under isothermal and isobaric conditions, may be correlated by first converting the data to change in volume on mixing:

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