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Don and his wife have recently moved into the Western Reserve community of Aurora, where the strong New England influence has rekindled fond memories of Boston. A variety of recreational and cultural interests and work around their new home successfully occupy most of his nontechnical time.

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The Role of *n*-Butane in Hydrate Formation

The role of *n*-butane in the formation of hydrates has been a matter of some uncertainty. The experimental measurements resulting from this work have shown conclusively that *n*-butane does enter the hydrate lattice when hydrates are formed in the presence of methane at pressures from about 1 000 to 10 000 kPa over a temperature range from 0° to about 13°C. At higher pressures and temperatures, *n*-butane ceases to enter the crystal and behaves like a nonhydrate former.

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SCOPE

The formation of hydrates from pure *n*-butane with water has never been confirmed, and the literature contains conflicting opinions on the role of *n*-butane in hydrate formation from mixtures. The object of the work undertaken in this study was to obtain new experimental

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data on the formation of hydrates from mixtures of methane and *n*-butane and from the results obtained to show conclusively whether or not *n*-butane molecules actually enter the hydrate crystal structure.

The significance of the work stems from the fact that modern methods of predicting hydrate formation such as that proposed by Parrish and Prausnitz (1972) require a set of parameters to characterize each molecule that participates in hydrate formation. For this reason, whenever *n*-butane is a component in a mixture, it is essential to know whether or not it should be included as a hydrate former. This matter assumes increasing importance whenever the possibility of hydrate formation in liquefied light petroleum product pipelines or in permafrost regions is considered.

The present investigation covered the experimental determination of initial hydrate formation along the hydrate-aqueous, liquid-vapor locus for one mixture of *n*-pentane and methane and four mixtures of *n*-butane and methane. The four-phase, hydrate-aqueous, liquid-hydrocarbon, liquid-vapor locus was obtained from 0.63° to 16.1°C at pressures from 1 020 to 12 770 kPa. Vapor phase compositions were determined along this locus at each of the twelve experimental conditions.

CONCLUSIONS AND SIGNIFICANCE

Theoretical considerations show that in the presence of methane, a nonhydrate former will increase the hydrating pressure for pure methane at any given temperature and that a structure II hydrate former will lower the hydrating pressure somewhat below that for pure methane at the same temperature.

As expected, the hydrate forming pressure for a mixture containing 1.36 mole % *n*-pentane in methane caused the hydrate forming pressure to increase about 3% above that for pure methane over a pressure range from 3 560 to 8 750 kPa. In the presence of concentrations of *n*-butane from 1.64 to 5.82 mole %, the hydrating pressure dropped significantly below that for pure methane. At a concentration of 5.82 mole % *n*-butane at a temperature of 4°C, the hydrating pressure in the mixture was only 58% of the value for pure methane. This phenomenon shows conclusively that within a temperature range from 0° to 13°C and at pressures from about 1 000 to 10 000 kPa, *n*-butane molecules do in fact enter the hydrate crystal lattice.

The observations made in this work combined with the earlier measurements of McLeod and Campbell (1961) show that at higher temperatures and at pressures beginning in the 10 000 to 13 800 kPa range, *n*-butane slowly reverts to behavior typical of a nonhydrate former. This is presumably related to the effect of pressure on the size of the cavities forming the crystal lattice.

The significance of this work is that it has shown conclusively that *n*-butane must be considered as a hydrate former when initial hydrate forming conditions are predicted in mixtures where *n*-butane is a component and where the hydrating pressures are below about 10 000 kPa. A transition zone exists between about 10 000 and 13 800 kPa, and above this *n*-butane behaves like a nonhydrate former.

The quadruple locus defining the hydrate, aqueous liquid-hydrocarbon, liquid-vapor equilibrium which was established in this work has been used together with the vapor pressure curve for pure *n*-butane to show that if hydrates in the pure *n*-butane-water system form at all they could only exist at temperatures considerably below 0°C.

Interest in problems related to the formation of hydrates in natural gas pipelines and related processing equipment dates back to the mid 1930's. Experimental work by Hammerschmidt (1934), Deaton and Frost (1940), and Katz and his co-workers (Wilcox et al., 1941; Carson and Katz, 1942; Unruh and Katz, 1949; Noaker and Katz, 1954) served to identify the conditions under which the light hydrocarbons such as methane, ethane, and propane and related gases such as carbon dioxide and hydrogen sulfide would form hydrates. Some of these studies included work on systems containing two or more hydrating substances such as methane with propane, carbon dioxide, or hydrogen sulfide. The work of Deaton and Frost included extensive measurements on mixtures of methane and ethane and methane and propane but only a few isolated measurements on mixtures containing isobutane or *n*-butane.

Since the object of the above work was primarily to learn about hydrate formation in natural gas systems where the concentration of butanes and heavier components were usually small, there was relatively little interest in studying mixtures contining the heavier components. Wilcox et al. (1941) report having seen evidence of hydrates with pure *n*-butane but were unable to repeat the observation. Carson and Katz (1942) noted that the presence of *n*-butane in methane tended to lower the pressure of hydrate formation but did not attempt to evaluate solid-vapor equilibrium ratios for this component. In a later study, MacLeod and Campbell (1961) observed that at high pressures methane-*n*-butane mixtures generally followed the curve for pure methane and in fact actually crossed it. They attributed this to deformation of the crystal lattice at the elevated pressures. They felt that *n*-butane had little effect on hydrate formation and may have acted as an inhibitor to some degree as pressure was increased.

In a comprehensive review of gas hydrates, Byk and Fomina (1968) report that Musaev (1966) believes *n*-butane does not participate in hydrate formation. Schneider and Farrar (1968) and Latini et al. (1967) tried systematically to nucleate *n*-butane hydrate under its own vapor pressure without success, even though a wide variety of forcing conditions and nucleating agents were tried. Harriot (1967) studied the growth of ice crystals in water by direct contact with *n*-butane. At one point he refers to hydrate crystals forming at 0.5°C, but there is no indication as to how he knew they were hydrate crystals rather than perhaps ice crystals forming in a small region locally cooled below 0°C by evaporating butane. No further investigation of the hydrate was carried out.

Rouher and Barduhn (1969) carried out extensive

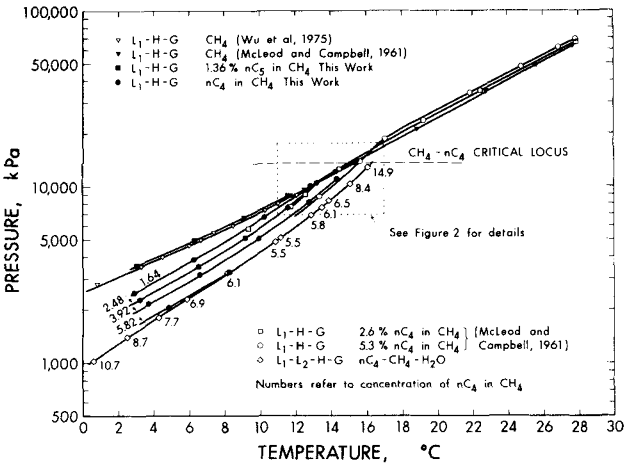

Fig. 1. Hydrate formation in mixtures of methane and *n*-butane and of methane and *n*-pentane.

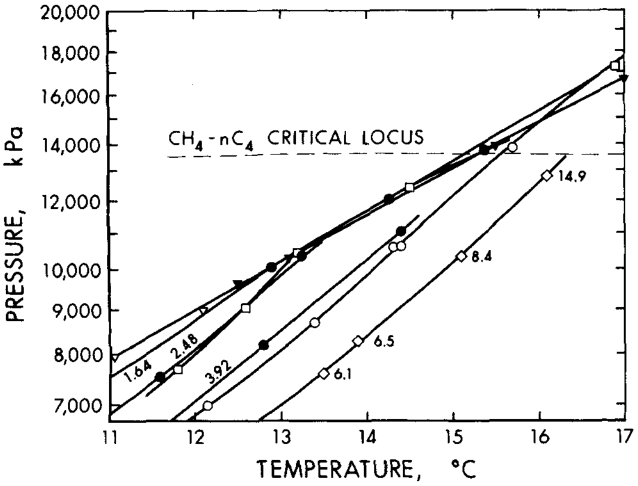

Fig. 2. Detail of three- and four-phase hydrate formation in mixtures of methane and *n*-butane.

tests on the formation of butane hydrates. They report one run equilibrated at 0.1°C with a mixture of *n*-butane and isobutane containing 11.5% *n*-butane in which hydrate crystals were formed. A drained sample of crystals was decomposed, and the resulting gas was found to contain 1 to 3% *n*-butane. However, they were not sure that this *n*-butane did not come from occluded gas. The final conclusion of their work was that it had been impossible to produce any hydrate from normal butane under its own vapor pressure in spite of a wide variety of forcing conditions and nucleating agents.

Parrish and Prausnitz (1972) in a recent theoretical treatment of hydrate dissociation pressures indicate that *n*-butane does not form either structure I or II hydrates because the molecule is too large to fit into the cavities.

It will be seen from the above discussion that somewhat conflicting evidence exists on the role of *n*-butane in hydrate formation. It seems clear that hydrates cannot form with pure *n*-butane at temperatures above 0°C; however, its role in the growth of hydrate crystals from mixtures containing other hydrating components is still open to speculation. Because of this, further experimental work with mixtures containing *n*-butane seemed to be warranted. Accordingly, a study of the three- and four-phase equilibrium for mixtures of methane and *n*-butane and methane and *n*-pentane was undertaken.

TABLE 1. EXPERIMENTAL L_1HG HYDRATE-FORMING CONDITIONS FOR A MIXTURE OF METHANE, *n*-PENTANE, AND WATER

Gas phase composition, mole % nC_5	Temperature, °C	Pressure, kPa
1.36	3.05	3 560
	6.35	4 950
	9.12	6 670
	11.60	8 750

TABLE 2. EXPERIMENTAL L_1HG HYDRATE-FORMING CONDITIONS FOR THE METHANE–η-BUTANE–WATER SYSTEM

Gas phase composition, mole % nC_4	Temperature, °C	Pressure, kPa
1.64	2.89	2 480
	6.29	3 820
	10.27	6 650
	12.90	10 080
	14.27	12 060
	15.37	13 720
2.48	3.20	2 300
	6.57	3 590
	9.20	5 130
	11.60	7 470
	13.25	10 400
3.91	3.76	2 150
	6.59	3 140
	9.97	5 090
	12.80	8 160
	14.40	11 050
5.82	4.84	2 050
	8.28	3 290

EXPERIMENTAL

As will be shown later, it follows from the solid-vapor equilibrium concept of Carson and Katz (1942) and from the statistical mechanical theory of hydrate formation developed by Van der Waals and Platteeuw (1959) that the presence of any appreciable amount of a hydrate II former with methane will lower the hydrating pressure at any temperature along the three-phase L_1HG locus; on the other hand, the presence of a nonhydrate former with methane will increase the hydrating pressure at the same temperature. This latter type of shifting of the three-phase equilibria by the addition of a nonhydrate former may also be viewed as an isobaric lowering of the hydrate formation temperature. This approach has been discussed in detail by Pieroen and Korvezee (1962).

Normal pentane, because of its molecular size, is known to be a nonhydrate former. From this it was reasoned that the hydrating pressure for a mixture of methane and *n*-pentane should be higher than for pure methane. Similarly, if *n*-butane actually did participate in hydrate II crystallization, the hydrating pressure for methane-*n*-butane mixtures should be less than for pure methane. Accordingly, a systematic series of experimental measurements were designed to investigate this hypothesis.

The equipment used to carry out the study was essentially the same as that used by previous workers (Jhaveri and Robinson, 1965; Robinson and Mehta, 1971). A detailed description of the equipment is given elsewhere (Wu et al., 1975). In brief, the sample under investigation was confined in a high pressure equilibrium cell made from type 316 stainless steel with Pyrex windows mounted both back and front. The capacity of the cell was about 80 ml., and the design working pressure was 3 500 lb./sq.in.* The temperature of the cell was controlled by circulating a coolant from an auxiliary temperature bath through a windowed jacket. The temperature of the jacket and the cell were measured by two Rosemount platinum resistance sensors. The pressure was adjusted by addition or removal of mercury, and it was measured with a 3 000 lb./sq.in.* calibrated Heise gauge. The analyses of the gas phase mixtures was made with a Hewlett-Packard Model 5750B thermal conductivity cell gas chromatograph. Equilibrium was established by mechanically rocking the cell and bath assembly back and forth about a horizontal position.

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* 1 lb./sq. in. = 6.894757 kPa

Matheson Incorporated ultra high grade methane of 99.97 mole % purity and research grade n-butane of 99.9 mole % purity were used for preparing the mixtures to study the three-phase L_1HG region and the four-phase L_1L_2HG locus. Fisher Scientific Company pesticide grade n-pentane, having a purity of better than 99.9 mole %, was used for measuring the three-phase L_1HG region of a mixture of methane and n-pentane.

After the cell had been charged with the desired mixture, hydrate formation was initiated by cooling the bath about 5° to 10°C below the estimated hydrate formation condition when agitation of the cell caused the hydrate to form. After this happened, the temperature was increased slowly until the hydrate began to melt. The temperature was kept a degree or so higher than the melting point to let almost all of the hydrate dissociate. The temperature was then lowered slightly to recrystallize the hydrate. The few crystals of hydrate that remained on the glass window served as seed crystals for new hydrate formation. The temperature was raised again very slowly until the hydrate on the window just began to melt. This was considered to be the equilibrium point. The amount of material present in the form of hydrate crystals at this point was exceedingly small because as far as possible the measurement was made when only one or two small crystals were present.

The temperature and pressure were then readjusted for the next datum point with the same mixture. A few unmelted hydrate crystals left over from the previous condition served as nucleation sites for the hydrate at the new condition, and thus the time needed to supercool, to wait for crystallization, and to reheat the bath to the desired temperature was shortened.

EXPERIMENTAL RESULTS

The first series of measurements were made on a methane-n-pentane-water mixture containing 1.36 mole % n-pentane in the gas phase on a dry basis. The results obtained for the L_1HG locus are given in Table 1 and shown in Figure 1.

The second series of measurements was made on four constant composition mixtures of methane, n-butane, and water containing from 1.64 to 5.82 mole % n-butane in the gas phase on a dry basis. The results obtained for this series are given in Table 2 and are also shown on Figure 1. An expanded section in the 7 000 to 17 000 kPa range is shown in Figure 2.

The final series of measurements was made on a mixture of n-butane in methane sufficiently rich in n-butane to maintain the hydrocarbon rich liquid phase throughout the entire range of pressure and temperatures along the four-phase quadruple locus L_1L_2HG from 0.63° to 16.1°C. After a short extrapolation of this locus to 16.3°C, it terminates with the appearance of the L_2G critical condition. The composition of the equilibrium vapor phase was determined at each four-phase point. During sampling, the pressure was maintained constant by addition of mercury. The four-phase equilibrium pressure, temperature, and vapor phase composition data are shown in Table 3, and the four-phase locus is plotted on Figure 1.

DISCUSSION

It will be noted from Figure 1 that the L_1HG locus for the methane–n-pentane mixture lies above and parallel to the L_1HG locus for pure methane. This is in agreement with the postulate that the hydrating pressure increases if a nonhydrate former such as n-pentane is added to methane.

At the lower temperatures and at pressures below about 8 275 to 10 000 kPa, the L_1HG curves for the methane-n-butane mixtures all lie significantly below the L_1HG curve for pure methane. This is in accordance with the requirement that the addition of a second component which participates in the hydrate II crystallization process will reduce the hydrating pressure below that for pure methane. This confirms the fact that in this temperature, pressure, and composition region n-butane does in fact enter the hydrate crystal.

One of the most interesting features of the behavior of this system, however, is the fact that as the hydrating temperatures increase and the pressures get into the 10 000 to 12 400 kPa range, the L_1HG loci begin to bend upward and eventually cross the curve for pure methane. This indicates that at the higher pressures something evidently happens to the crystal structure such that the n-butane molecules can no longer enter, and from then on n-butane behaves like any other nonhydrate former. The results in this region agree with the earlier work of McLeod and Campbell (1961). The temperature at which the mixture curves cross the pure methane curve decreases as the n-butane concentration in the gas phase decreases. The higher the concentration of n-butane in the gas phase, the more the hydrating pressure is increased over that for pure methane. This is in accordance with the postulates described earlier.

Table 3. Experimental Data for the L_1L_2HG Quadruple Locus for the Methane–n-Butane–Water System

Gas phase composition, mole % nC_4	Temperature, °C	Pressure, kPa
10.7	0.63	1 020
8.7	2.15	1 390
7.7	4.30	1 810
6.9	5.86	2 320
6.1	8.22	3 260
5.5	10.95	4 900
5.5	11.2	5 080
5.8	12.9	6 810
6.1	13.5	7 630
6.5	13.9	8 230
8.4	15.1	10 500
14.9	16.1	12 770

It is interesting to note from the data in Table 3 that the concentration of n-butane in the gas phase along the quadruple locus starts at 10.7 mole %, passes through a minimum at about 5.5%, and finally ends at the methane-n-butane critical locus where the concentration is 22.0%. This behavior is similar to that observed by Otto and Robinson (1960) in the methane-propylene system, by Verma et al. (1974) in the methane-propane system, and by Wu et al. (1975) in the methane-isobutane system.

THEORETICAL CONSIDERATIONS

Hydrate formation from gases in the presence of liquid water may be predicted by using the equilibrium ratio concept proposed by Carson and Katz (1942) or by the statistical mechanical theory of clathrate formation developed by Van der Waals and Platteeuw (1959).

Carson and Katz (1942) defined a solid-vapor equilibrium constant as the ratio between the concentration of any component in the vapor phase divided by the concentration of the same component in the hydrate phase, both on a water free basis. Based on this concept, the necessary and sufficient condition for hydrate formation is obtained when

$$\sum_{i=1}^{n} \frac{y_i}{K_i} = 1.0$$

The K_i values are always unity for pure component hydrate formation, and they decrease as pressure increases for any hydrate former. In a gas mixture consisting of a hydrate former and a nonhydrate former, the concentration of the hydrate former will be less than unity. Hence the value of K_i that will satisfy the relationship occurs at a higher pressure than it would for the pure component at the same temperature.

Van der Waals and Platteeuw (1959) derived the following general equation relating the thermodynamic properties of gas hydrates to their molecular parameters:

$$\Delta\mu_W^H = RT \sum_m \nu_m \ln\left(1 + \sum_j C_{mj}f_j\right) \qquad (1)$$

$$C_{mj} = \frac{1}{kT}\int_o^\infty \{\exp[-W(r)/kT]\}4\pi r^2 dr \qquad (2)$$

$$f_j = \psi_j y_j P \qquad (3)$$

where $\Delta\mu_W^H$ is the difference in the chemical potential between the filled gas hydrate lattice and the empty hydrate lattice, and f_j is the fugacity of component j. ν_m denotes the number of type m cavities per molecule of water, and $W(r)$ is the spherically symmetric cell potential in the cavity with r measured from the center. Equation (1) may be used when ice is present with hydrate. If liquid water is present, the chemical potential $\Delta\mu_W^L$ is

$$\Delta\mu_W^L = RT \sum_m \nu_m \ln\left(1 + \sum_j C_{mj}f_j\right) + RT\ln X_W \qquad (4)$$

where X_W is the mole fraction of water in the liquid phase.

If we consider Equation (4) at a given temperature for a binary mixture which contains a hydrate former (1) and a nonhydrate former (2), we obtain

$$(\Delta\mu_W^L)_{\text{mixture}} = RT \sum_m \nu_m \ln(1 + C_m 1 f_1) + RT\ln X_W \qquad (5)$$

whereas for a single hydrate former (1) only we obtain

$$(\Delta\mu_W^L)_1 = RT \sum_m \nu_m \ln(1 + C_m 1 f) + RT\ln X_W \qquad (6)$$

In equation (5), f_1 is the fugacity of the hydrate former in a gas mixture, whereas in Equation (6) f is the fugacity of the pure component. The hydrates formed from the mixture will be of the same structure as the hydrates from pure component (1). Consequently, $(\Delta\mu_W^L)_{\text{mixture}}$ will equal $(\Delta\mu_W^L)_1$ at any given T.

These fugacities may be replaced by pressures and fugacity coefficients; that is

$$f_1 = y_1 \psi_1 P_m \qquad (7)$$

and

$$f = \psi P \qquad (8)$$

Hence, from Equations (5) and (6)

$$\sum_m \nu_m \ln(1 + C_{m1}\psi_1 y_1 P_m) = \sum_m \nu_m \ln(1 + C_{m1}\psi P) \qquad (9)$$

Since y_1 is less than unity, P_m must be greater than P in order to satisfy the relationship. In other words, the L_1HG equilibrium curve for a mixture of a hydrate former and a nonhydrate former must lie above the L_1HG equilibrium curve of the pure hydrate former. This was confirmed by the experimental study of the methane-*n*-pentane-water system in this work.

A similar analysis to the above can be carried out for the case where component (2) also participates in the hydrate formation. Since $\Delta\mu_W^L$ for structure II hydrates is less than $\Delta\mu_W^L$ for structure I hydrates, (Parrish and Prausnitz, 1972), the addition of a component which changes the hydration from structure I to structure II will tend to decrease the hydration pressure to a value below that for pure component (1). This is what happens in the case of the methane-*n*-butane mixtures.

For materials which will form hydrates above 0°C, the maximum temperature at which the three-phase L_1HG equilibrium exists for a two-component system is the four-phase L_1L_2HG quadruple point for that system. This quadruple point usually lies very close to the vapor pressure curve for the hydrate former. Since the vapor pressure of *n*-butane at 0°C is only 103.4 kPa, it is clear from the data shown in Figure 1 that no hydrate would be found in the *n*-butane-water system above 0°C.

At 0°C the four-phase L_1L_2HG equilibrium will change to the IL_2HG equilibrium, and there will be a change in a slope to a lower value. Experimental evidence will be required in order to evaluate this quantitatively and to find where the IL_2HG locus for the methane-*n*-butane-water system intersects the IHG locus for the *n*-butane-water system if, in fact, such a locus does exist.

NOTATION

C_{mj} = Langmuir constant for component j in cavity m
f_j = fugacity of component j
G = vapor phase
H_I, H_{II} = hydrate of structures I and II
I = ice phase
k = Boltzmann's constant, 1.38×10^{-16} erg/K
K = solid vapor equilibrium ratios
L_1 = water rich liquid phase
L_2 = hydrocarbon rich liquid phase
P, P_m = total pressure
r = radial coordinate, A
R = gas constant
T = temperature K
$W(r)$ = spherically symmetric cell potential, ergs
X_W = mole fraction of liquid water
y_j = mole fraction of component j in vapor phase

Greek Letters

μ = chemical potential
$\Delta\mu_W^L$ = chemical potential difference of water between liquid phase and empty hydrate
$\Delta\mu_W^H$ = chemical potential difference of water between hydrate phase and empty hydrate
ν_m = number of cavities type m per water molecule in hydrate
ψ = fugacity coefficient

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The Fluid Mechanics and Heat Transfer of Injection Mold Filling of Thermoplastic Materials

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For injection flow of thermoplastic material in thin cavities, with some minor restrictions, both pressure and stream function obey Laplace equations. An analytical-numerical method, with a generalized viscous model used, is developed for determining the shape of a progressing flow front and for computing flow quantities and temperature distributions. Specifically, *flows in a rectangular cavity are solved and compared to experiments.*

SCOPE

The injection molding process is a very important fabricating method in producing plastic articles. Its technique, however, has been essentially an art, and the trial-and-error approach employed in production often cannot cope with variations in resin properties, complexity of molding geometries, and variations in process parameters. To seek optimum control of the molding variables, a model simulation of the process is highly desirable as it may enable the prediction of the filling behavior and mechanical properties of the finished products.

For convenience of analysis. the molding process can be divided into filling, packing, and cooling stages because of their respective characteristics, as outlined by Kamal et al. (1975). This paper deals with the fluid mechanics and heat transfer aspect of the filling stage of thermoplastic materials. Analyses of subsequent stages, which require the temperature and flow fields at the end of filling as given initial conditions, will be reported in separate papers.

Polymer melts are viscoelastic and compressible, and injection flows are three dimensional, unsteady, nonisothermal, and involve a free surface. An analysis involving every factor of the flow and the material is extremely difficult. In view of the fact that molded plastic parts are usually combinations of various thin sections, an analysis dealing with thin cavities is realistic and may lead to simplification of the problem. Such an approach has been employed in many typical numerical analyses, using finite difference techniques by Kamal and Kenig (1972), Wu et al. (1974), Lord and Williams (1975), and other characteristic studies by Richardson (1972) and White (1975) on injection mold filling. Some experimental studies by Menges and Wubken (1973), White and Dee (1974), and Schmidt (1974) used thin cavities.

In this paper, the implications of thin cavities is explored further. Based on thin cavity approximations, an energy equation and equations of stream function and pressure (two dimensional) are developed for solving flow quantities and temperature distributions in complex