A Study of Hydrates in the Methane-Propylene-Water System

FREDERICK D. OTTO and DONALD B. ROBINSON
University of Alberta, Edmonton, Alberta, Canada

Experimental data are presented to show the points of incipient hydrate formation in the methane-propylene-water system. The addition of 1.4% propylene to methane lowered the equilibrium pressure 400 lb./sq. in. at 50°F. The locus of the four-phase equilibrium consisting of hydrate, vapor, water-rich liquid, and hydrocarbon-rich liquid was determined. This was terminated by the appearance of a critical condition at 1,370 lb./sq. in. abs. and 69.3°F., where the vapor phase contained 34.8% propylene on a dry basis. Below this pressure the hydrate, vapor, water-rich liquid equilibrium does not exist for solutions containing more than about 25% propylene. Solid-vapor equilibrium ratios were estimated for propylene hydrates. The significant features of the phase diagrams for the system are discussed in some detail.

A number of gases, including the C_1 to C_4 paraffinic and olefinic hydrocarbons, when under pressure and in the presence of water will form hydrates. These substances are solid crystals having the appearance of snow or ice. The crystals may contain more than one hydrocarbon species, and experimental evidence indicates that about seven molecules of water exist for each molecule of hydrocarbon. The temperatures at which hydrates form for any mixture depend on the pressure and may extend considerably above 32°F. Generally hydrates may occur and consequently cause trouble in any equipment involved in the production, transmission, or processing of light hydrocarbons where water may be present at a favorable temperature and pressure.

Prevention of hydrate formation is ordinarily accomplished by dehydration. To determine when and to what extent the gas should be dehydrated it is necessary to know the conditions of temperature and pressure at which hydrate formation is possible for a given system. These conditions have been extensively studied for pure and mixed paraffin hydrocarbons and for some pure olefins. The fact that ethylene and propylene are common components in industrial petrochemical plants has warranted a further investigation of hydrate forming conditions for these compounds and for mixtures of gases containing them. This investigation concerned a study of hydrate forming conditions in the methane-propylene-water system.

PREVIOUS WORK

Hydrates in the methane-water system have been studied extensively by many investigators. Villard (*1*) observed hydrate formation in the hydrate—vapor—water-rich liquid region over a wide range in pressure and up to 70.7°F. Deaton and Frost (*2*) and Roberts (*3*) investigated the system in the range 33° to 55°F. and made a study of the ice hydrate-vapor region. Kabayashi and Katz (*4*) observed hydrates in the hydrate-vapor-water-rich liquid region up to 11,200 lb./sq. in. at 83.9°F.

Reamer, Selleck, and Sage (*5*) have reported equilibrium measurements for the propylene-water system in the hydrate–vapor–water-rich liquid region, the hydrate–water-rich liquid–hydrocarbon–rich liquid region and the vapor–water-rich liquid–hydrocarbon-rich liquid region at pressures up to about 300 lb./sq. in. and temperatures to about 75°F. The highest temperature where hydrates were observed was 35.2°F.

The significant difference between these two systems is that the methane system is typical of those for which the vapor-liquid critical temperature of the hydrate forming hydrocarbon is below the hydrate forming temperature, and the propylene system is typical of those for which the critical temperature is above the hydrate forming temperature. In the former case the hydrocarbon liquid region is terminated before hydrates exist, but in the latter case hydrates form in the presence of hydrocarbon-rich liquids. Consequently a quadruple point consisting of hydrate–vapor–water-rich liquid–hydrocarbon-rich liquid is possible in the propylene system but not in the methane system. These characteristics have a significant bearing on the hydrate forming conditions in systems containing both methane and propylene. The first object of this investigation was to establish the hydrate forming conditions in mixtures of methane, propylene, and water and to determine the composition of the vapor phase at each condition.

The work of Katz and co-workers (*6, 7*) has established the fact that hydrates formed in the presence of more than one hydrate forming compound are solid solutions, the composition of which depends on over-all composition and temperature and pressure. This feature led to the establishment of vapor-solid equilibrium ratios somewhat analogous to vapor-liquid equilibrium ratios. Values of these vapor-solid equilibrium ratios are available for the light normal paraffin hydrocarbons (*6*), carbon dioxide (*8*), and hydrogen sulfide (*9*). The second object of this investigation was to establish vapor-solid equilibrium ratios for propylene in mixed hydrates. In calculating these ratios it was assumed that they were primarily a function of temperature and pressure. It is recognized that this assumption is open to question.

APPARATUS AND EXPERIMENTAL PROCEDURES

The experimental equipment consisted of a variable volume, glass-windowed cell

---

Frederick D. Otto is presently at the University of Michigan. The data presented here forms part of his Master of Science thesis in Chemical Engineering at the University of Alberta.

having a capacity of about 120 cc. and capable of withstanding pressures up to 2,000 lb./sq. in. Mercury was used as the confining fluid. The cell was mounted on trunnions so that it could be rotated about an axis to establish equilibrium within the contents. Pressures were indicated by calibrated Heise Bourdon Tube gauges having 0 to 1,500 and 0 to 5,000 lb./sq. in. ranges. Temperatures were measured by a thermocouple inserted through the cell wall into the cell contents. This was found to be very important. It had been intended to use the temperature of the auxiliary circulating cooling bath as the temperature of the cell contents, but this technique had to be rejected when it was found that consistent results could not be obtained. A significant temperature lag existed between the outside and inside of the cell, and raising or lowering the bath temperature as slowly as 1°F. in 5 min. resulted in a lag of 2°F.

The method of supporting and mounting the cell within a temperature bath that permitted visual observation proved very satisfactory and is perhaps worthy of description. The cell was enclosed within a lucite tube closed at each end with lucite plates. Seals for outlets and inlets and for the end closure were made with O-rings. The steel trunnions were made from 1-in. steel rod coned at one end and drilled through axially to intersect a side outlet within the annular space between the cell and the lucite shell. The coned end was inserted into a seat in the side of the cell to act as a support and to permit rotation. The side outlet from the steel rod was connected to a rigid lucite tube extending to the top of the chamber at one side and to the bottom of the chamber on the other. The cooling fluid was circulated in one axis through the lucite tube at one end and out again from the other end through the axis back to the pump. The steel axes were held firmly and took the load of the entire assembly. The liquid seal between the lucite shell and the steel axes was made by O-rings. This arrangement was easily maintained and provided good control and visibility.

Mass spectroscope analyses indicated the methane used in the tests to be 99.8 mole % pure and the propylene to be 99.7 mole % pure.

In order to clearly establish the point of incipient hydrate formation a careful sequence of operation had to be followed. The cell was evacuated to remove residual gases and then filled with mercury. About 4 cc. of water were admitted at the top of the cell, and this was followed by admitting the desired quantities of hydrocarbon gases. The contents of the cell were then agitated to insure that mixing was complete and that vapor-liquid equilibrium existed at the pressure required for the hydrate formation. The cell contents were then cooled some 5° to 15°F. below the temperature at which hydrate formation was anticipated. Vigorous agitation of the cell then caused hydrates to form.

The desired hydrate equilibrium point is the pressure and corresponding temperature where hydrate just begins to form when a gas of known composition is in the presence of liquid water. In a two-component system in three phases hydrates exist at only one temperature for a given pressure. However in a three-component system in three phases, two degrees of freedom exist and the hydrate will melt over a range of temperatures. Thus the exact location of the desired point is somewhat difficult to determine for the three-component system.

A technique which was found satisfactory is as follows. The hydrate formed in the subcooled cell was brought to a point where it just began to melt by raising the temperature. Further very slow increases in temperature caused all but a few crystals of hydrate to melt. The temperature was then reduced a few tenths of a degree, and a few small crystals began to form on the inside face of the cell window. The temperature was slowly increased again, and the pressure and temperature were observed and recorded for the point where these new crystals melted. This melting point was very sharp and was reproducible. The procedure can be recommended for both binary and ternary systems.

Samples of the vapor phase were taken and analyzed for each equilibrium point determined. The sample was removed from the cell by adding mercury isobarically as gas was removed and collected at reduced pressure in evacuated glass bulbs. By taking the first point at a relatively high pressure a total of about five points could be

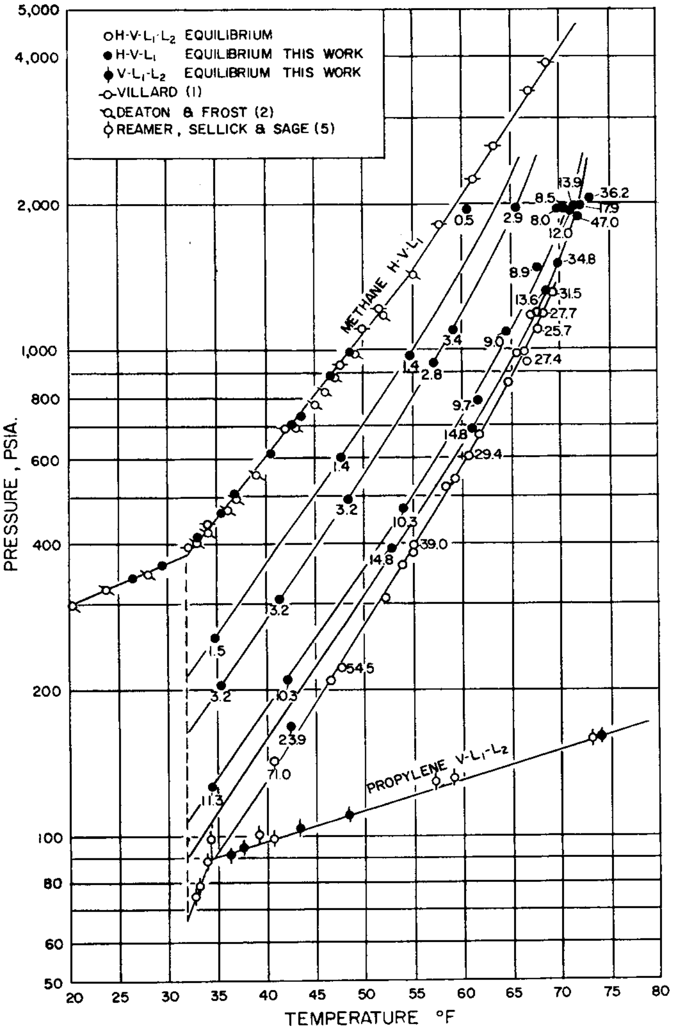

Fig. 1. Hydrate forming conditions in systems containing methane, propylene, and water.

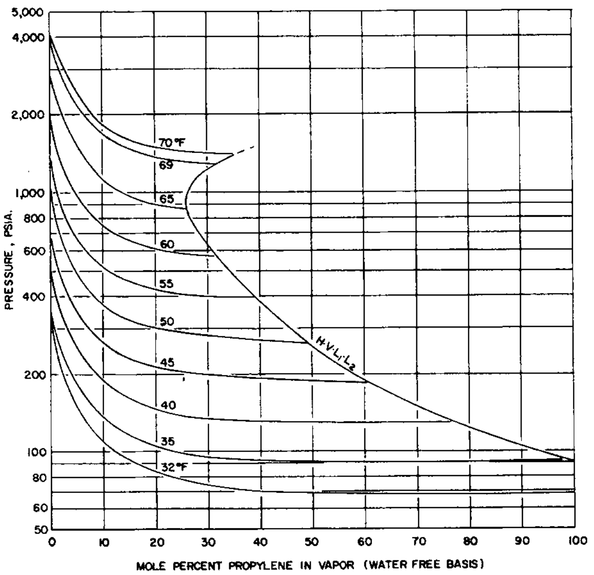

Fig. 2. Influence of composition on hydrate forming conditions.

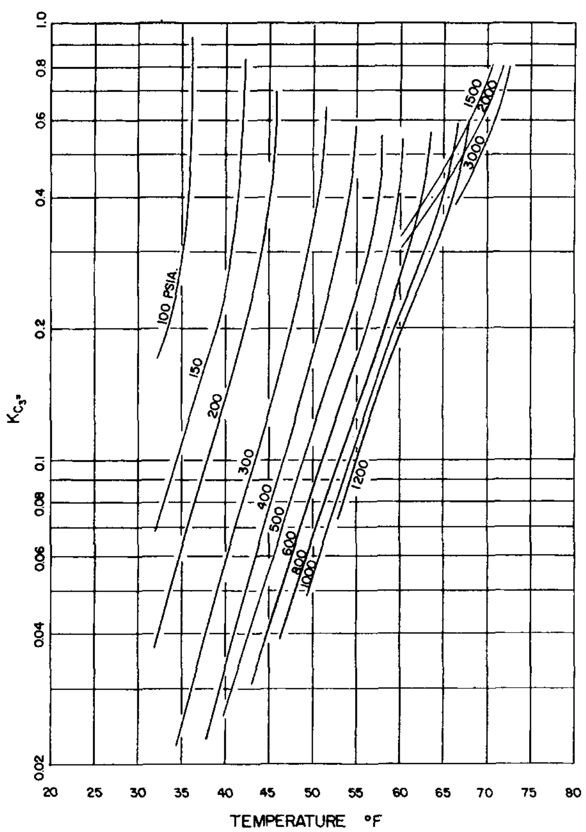

Fig. 3. Vapor-solid equilibrium ratios for propylene in hydrates.

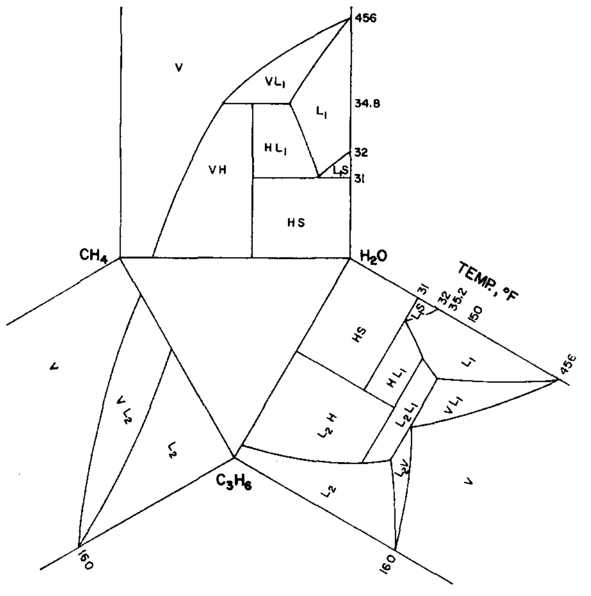

Fig. 4. Schematic phase diagram of the methane-propylene-water system at 450 lb./sq. in. abs.

obtained at successively reduced pressures for each original system.

HYDRATE CONDITIONS AND EQUILIBRIUM RATIOS

Several preliminary tests to determine the hydrate forming conditions for methane and water both in the hydrate–vapor–water-rich liquid and ice–hydrate–vapor regions were made in order to verify the experimental technique. The results agreed exceedingly well with those of Roberts (3), Kobayashi and Katz (4), and Villard (1).

The hydrate–vapor–water-rich liquid equilibrium for the propylene-water system exists over a very narrow temperature range from 32° to 34.5°F. Several unsuccessful attempts were made to produce hydrate in this region, but cooling to 32°F. and agitating for several hours failed to produce a hydrate. Several pressures and temperatures were determined for the hydrate–water-rich liquid–hydrocarbon-rich liquid equilibrium. The curve defined by these points agreed closely with the one obtained by Reamer, Selleck, and Sage (5).

The conditions of pressure and temperature at which mixtures of methane and propylene will just begin to form hydrates are plotted in Figure 1.* The results obtained for the pure components are also included in this figure. The effect of concentration is obtained by cross plotting the original data along isotherms as shown in Figure 2. For gaseous mixtures containing less than about 25 mole % propylene continuous hydrate–vapor–water-rich liquid curves exist and extend to pressures above 2,000 lb./sq. in. abs. Four curves have been drawn to indicate the initial hydrate forming conditions for methane-propylene mixtures between about 0.5 and 23.9 mole % propylene (water-free basis). The addition of very small amounts of propylene has a large effect on the hydrate–vapor–water-rich liquid equilibrium, for example the addition of 1.4% propylene to methane lowers the equilibrium pressure 400 lb. at 50°F.

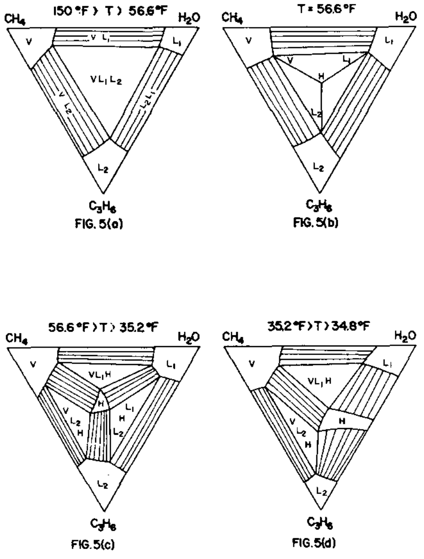

FIG. 5(a) FIG. 5(b) FIG. 5(c) FIG. 5(d)

Fig. 5. Typical constant temperature sections at 450 lb./sq. in. abs.

For mixtures containing more than about 25% propylene, the hydrate–vapor–water-rich liquid equilibria are terminated by the appearance of a new phase, the hydrocarbon-rich liquid. The addition of methane to the propylene-water system gives the mixture an additional degree of freedom such that the conditions for four-phase equilibrium hydrate–vapor–water-rich liquid–hydrocarbon-rich liquid define a line rather than a point. Experimental data were taken in order to define this quadruple locus.

Final and initial melting points were found to fall on the same curve, and the composition of the vapor was determined at each final melting point. As one progresses to higher pressures along the locus, the amount of hydrocarbon-rich liquid increases and the vapor becomes richer in methane. Just above 1,000 lb./sq. in. abs. the concentration of the methane reaches a maximum which was found to be 74.3%. At higher pressures the concentration of methane decreases in the vapor, and the amount of hydrocarbon-rich liquid decreases accordingly. The highest pressure where four phases would exist in equilibrium was found to be 1,370 lb./sq. in. abs. at 69.3°F., when the system was approximately 34.8 mole % propylene. At this point critical phenomena were encountered

---

* Tabular material has been deposited as document 6425 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or for 35-mm. microfilm.

and the hydrocarbon-rich liquid and vapor formed one phase, thus terminating the four phase equilibrium. At a pressure of 1,382 lb./sq. in. abs., that is above the region where a hydrocarbon-rich liquid existed, the system was colorless, but as the pressure or temperature were lowered the color changed to yellow and then brownish red. The color reached a maximum intensity at 49.3°F., when the pressure was 1,382 lb./sq. in. abs. This is probably close to the critical point for a 34.8% propylene 65.2% methane system.

Initial hydration points in the hydrate–vapor = hydrocarbon-rich liquid–water-rich liquid region were determined for mixtures containing 34.8, 36.2, and 47.0 mole % propylene at pressures above 1,370 lb./sq. in. abs. These three points lay on a smooth extrapolation of the quadruple locus.

From the experimental data for the methane-propylene-water system it was possible to calculate vapor-solid equilibrium ratios for the ethylene. This was done by use of the equation

$$Y_{c_1}/K_{c_1} + Y_{c_{3=}}/K_{c_{3=}} = 1$$

applicable at the point of incipient hydrate formation. The values for K_{c_1} were obtained from published curves at the appropriate temperature and pressure, and then the values of $K_{c_{3=}}$ were calculated at the same conditions. The calculated equilibrium ratios are presented at representative pressures as a function of temperature in Figure 3. The equilibrium ratios increase sharply at constant pressure as temperature increases. The isobars are terminated where four-phase equilibrium exists at each pressure. These curves are generally similar to equilibrium ratio curves for propane (*6*).

PHASE DIAGRAMS

It is common to represent the variation in concentration of three-component systems by means of isobaric, isothermal, triangular diagrams. Sufficient phase-composition data were not obtained to construct quantitative diagrams of this type; however a qualitative representation based on the information that is available is a distinct aid to an understanding of the phase relations peculiar to the system. An examination of these diagrams at selected temperatures for a fixed pressure illustrates the features which result in four-phase equilibrium and also those which result in its termination.

Figure 4 illustrates schematically the boundaries of the space diagram for the methane-propylene-water system at 450 lb./sq. in. abs. A quadruple point exists at 450 lb./sq. in. abs. and 56.6°F. Known temperatures for the three-phase and two-phase equilibria are indicated on the diagrams.

The quadruple point is an equilibrium between hydrate–vapor–water-rich liquid and hydrocarbon-rich liquid and must have associated with it the four three-phase equilibria vapor–water-rich liquid–hydrocarbon-rich liquid, hydrate–vapor–water-rich liquid, and hydrate–water-rich liquid–hydrocarbon-rich liquid. Since the three-phase equilibrium vapor–water-rich liquid–hydrocarbon-rich liquid is the only one occurring at a temperature above the quadruple point, the four-phase equilibrium will result in the appearance of one triangular region above and three triangular regions below the quadruple temperature. This is illustrated in the schematic constant-temperature sections in Figure 5.

Figure 5*a* is typical of sections at 450 lb./sq. in. abs. above 56.6°F. but below about 150°F. The vapor–water-rich liquid–hydrocarbon-rich liquid equilibrium is represented by a triangle having the phase compositions at its vertices. Associated with this three-phase region there must be three two-phase and three one-phase regions. The addition of a component to the vapor–water-rich liquid, vapor–hydrocarbon-rich liquid, or water-rich liquid–hydrocarbon-rich liquid equilibrium at the binary boundaries results in the generation of a two-phase, three-component locus which is terminated in each case by the appearance of a third phase. Thus the vapor–hydrocarbon-rich liquid line emanating from the methane-propylene boundary is terminated by intersection with the vapor–water-rich-liquid line and the appearance of the water-rich liquid phase. Two-phase regions are indicated by the schematic tie lines, whereas single-phase and three-phase regions are labelled.

Figure 5*b* shows a section at the quadruple temperature where the same features as at higher temperatures are still apparent but where the fourth phase or hydrate has just appeared. At slightly lower temperatures, as shown in Figure 5*c*, the hydrate phase exists over a range of compositions and hence occupies an area in the diagram. Similarly the three three-phase equilibria are each represented by an area. The hydrate–water-rich liquid–hydrocarbon-rich liquid equilibrium disappears at 35.2°F., and the hydrate–vapor–water-rich liquid equilibrium disappears at 34.8°F. Between these temperatures the cross section will appear as in Figure 5*d*, illustrating the hydrate–vapor–water-rich liquid and hydrate–vapor–hydrocarbon-rich liquid equilibria but noting that the hydrate–water-rich liquid–hydrocarbon-rich liquid equilibrium has been replaced by a hydrate region and the separate hydrate–water-rich liquid and hydrate–hydrocarbon-rich liquid equilibria.

CONCLUSIONS

1. The conditions of pressure and temperature at which hydrates just begin to form in the methane-propylene-water system have been defined up to 2,000 lb./sq. in. abs. for several mixtures ranging in composition from 0.5 to 23.9% propylene on a dry basis.
2. A four-phase locus is present in systems containing more than about 25% propylene but it is terminated at 1,370 lb./sq. in. abs. and 69.3°F. in a system containing approximately 34.8% propylene because the vapor and hydrocarbon rich liquid become identical.
3. Vapor-solid equilibrium ratios for propylene in hydrates have been obtained over the range of pressure and temperature studied. It should be emphasized that the calculated values are based on the assumption that the equilibrium ratios for methane are the same in olefinic hydrates as they are in paraffinic hydrates.

ACKNOWLEDGMENT

The financial assistance afforded by a Consolidated Mining and Smelting Company Fellowship and a National Research Council of Canada Grant are gratefully acknowledged.

NOTATION

H = hydrate
K_{c_1} = ratio of the mole fraction methane in the vapor phase to the mole fraction methane in the hydrate phase, both evaluated on a dry basis
K_{c_3} = ratio as above for propylene
L_1 = water-rich liquid
L_2 = hydrocarbon-rich liquid
V = vapor
S = ice

LITERATURE CITED

1. Villard, P., *Compt. Rend.*, **106**, 1602 (1888).
2. Deaton, W. M., and E. M. Frost, *Gas*, **16**, No. 6, 28 (1940).
3. Roberts, O. L., E. R. Brownscombe, and L. S. Howe, *Petrol. Eng.*, **12**, No. 6, 56 (1941).
4. Kobayashi, Riki, and D. L. Katz, *Trans. Am. Inst. Mech, Engrs.*, **186**, 66 (1949).
5. Reamer, H. H., F. T. Selleck, and B. H. Sage, *ibid.*, **195**, 197 (1952).
6. Carson, D. B., and D. L. Katz, *ibid.*, **146**, 150 (1942).
7. Wilcox, W. I., D. B. Carson, and D. L. Katz, *Ind. Eng. Chem.*, **33**, 662 (1941).
8. Unruh, C. H., and D. L. Katz, *Trans. Am. Inst. Mech. Engrs.*, **186**, 83 (1949).
9. Noaker, L. J., and D. L. Katz, *ibid.*, **201**, 237 (1954).

Manuscript received November 10, 1959; revision received March 14, 1960; paper accepted March 17, 1960.