# The Phase Behavior of Two Mixtures of Methane, *n*-Pentane, and Silica

**H. H. REAMER, J. H. LOWER, and B. H. SAGE**

**California Institute of Technology, Pasadena, California**

During the past three decades a substantial number of investigations of the pressure-volume-temperature relations of hydrocarbons have been made. This work has for the most part been carried out at equilibrium. Equations of state have been used to describe the volumetric and phase behavior of pure hydrocarbons and their mixtures (*10*), and ingenious means have been developed to predict the equilibrium behavior of hydrocarbons based upon a modicum of experimental information concerning the system (*7*).

Interest in the molecular transport of hydrocarbons in the liquid and gas phases has persisted since the early work of Lacey (*2, 4, 5, 11*). In addition there has been some experimental activity upon the behavior of hydrocarbon systems under strain (*6, 9, 15*). Recently a reconnaissance study (*12*) was carried out which indicated a marked difference in the behavior of hydrocarbon systems under strain when in contact with relatively small areas of silica per unit weight of hydrocarbon, and their behavior in the absence of silica. It is possible that adsorption at the hydrocarbon-silica interface might influence such behavior under strain. The objective of the current study was to determine the order of magnitude of the effects of the hydrocarbon-silica interfacial surfaces on the phase behavior of a binary hydrocarbon mixture.

Three types of equilibrium are involved. First there is the ordinary type of physical equilibrium between the gas and the liquid hydrocarbon phases which may be materially hastened by mechanical agitation. Under such circumstances the transport of material from one part of the gas or liquid phase to another is associated with the transport of momentum as the result of the agitation and with the molecular transport as the result of existing concentration gradients.

A second type of equilibrium is that of temperature homogeneity within the heterogeneous system. Such homogeneity may be hastened by mechanical agitation which, as a result of the gross relative motion of the fluid and of the solid phases, causes a transport of internal energy from one portion of the system to another. This process is aided by molecular thermal transport.

A third type of equilibrium, associated with the adsorbed material at the hydrocarbon-silica interface, is not influenced greatly by mechanical agitation of the macroscopic type considered here. The dimensions of the adsorbed layer are sufficiently small that molecular transport in the ordinary sense is not of great importance. However such molecular transport within the liquid phase may be of controlling importance in establishing the macroscopic phase behavior of the system as physical equilibrium is approached at the hydrocarbon-silica interface.

## METHODS AND APPARATUS

A spherical, isochoric vessel of stainless steel (*12, 14*) was used. The vessel was provided with a slack diaphragm (*14*) for the measurement of pressure and was immersed in an agitated silicone bath for the maintenance of temperature. The bath was provided with rather active agitation in order that macroscopic temperatures might be changed without large local variations from point to point in the bath. Pressures were measured with a balance (*13*) which was calibrated against the vapor pressure of carbon dioxide at the ice point (*3*). The pressures within the equilibrium chamber were determined within 0.2 lb./sq.in. throughout the range of conditions covered by this investigation. The presence of silica somewhat degraded the accuracy with which pressure measurements could be made with a slack diaphragm. This was caused by the accumulation of silica at the edges of the diaphragm, a condition which tended to prevent freedom of motion. Temperatures of the bath were determined by means of strain-free, platinum, resistance thermometers (*8*) with a precision of 0.001°F. The temperature of the bath was known relative to the international platinum scale (*1*) with an uncertainty of not more than 0.05°F. Mechanical agitation within the isochoric vessel was accomplished by means of intermittent oscillation of the spherical vessel, within which two 0.75-in. steel balls were located. Temperature and the associated pressure equilibrium could be obtained with the liquid, hydrocarbon-silica system in a period of not more than 0.5 hr.

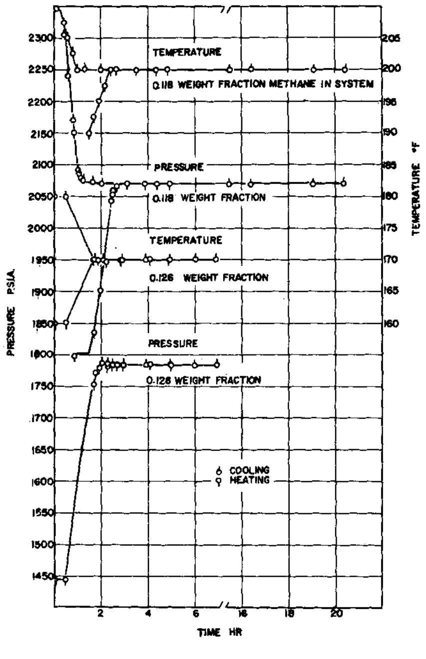

Fig. 1. Approach to eqiulibrium from a lower and a higher temperature in the liquid phase.

The sample of silica was introduced and the vessel evacuated to a pressure less than 1.0 μ at a temperature of 250°F. for a period of over 24 hr. before the *n*-pentane was introduced. Methane was then added to bring the composition of the system to the desired value. The total quantity of samples introduced was such that the equilibrium bubble-point pressure of one mixture, hereafter referred to as *Mixture A*, was 1,428 lb./sq.in.abs. at a temperature of 176.3°F., and that of the other mixture, referred to as *Mixture B*, was 1,479 lb./sq.in.abs. at 159.6°F. The pertinent information concerning the volume of the isochoric vessel and the two mixtures investigated is set forth in Table 1. The changes in state for these mixtures were accomplished by changing the temperature of the system.

The pressure within the spherical vessel followed changes in temperature closely, and isobaric conditions were reached not more than 15 min. after the attainment of isothermal conditions. Such equilibrium is the macroscopic equilibrium involving homogeneity of temperature and composition in the fluid parts of the system and does not necessarily involve equilibrium at the solid-liquid interface. Agitation during which the steel balls did not fall through the heterogeneous mixture did not appreciably influence the approach to or departure from equilibrium at the interface, except for the slight rise in temperature of the contents of the isochoric vessel. For the most part the approach to equilibrium at the inter-

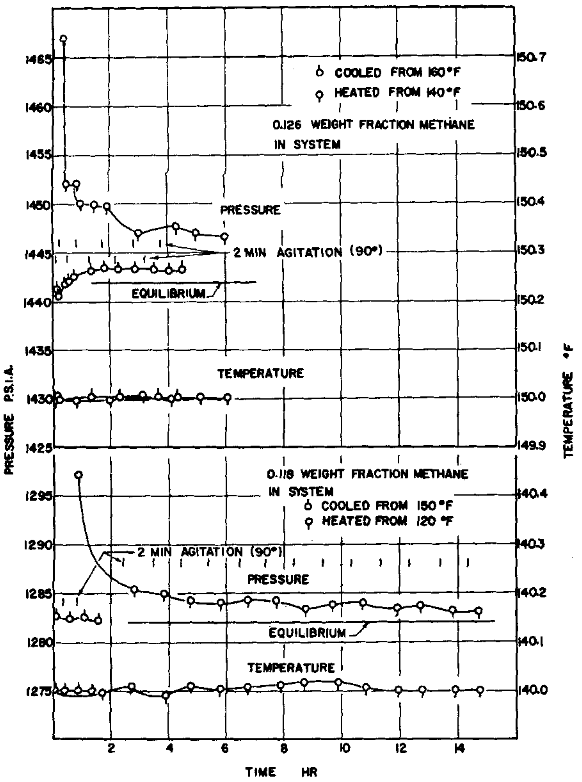

Fig. 2. Approach to equilibrium from a lower and a higher temperature when a liquid and a gas phase are present.

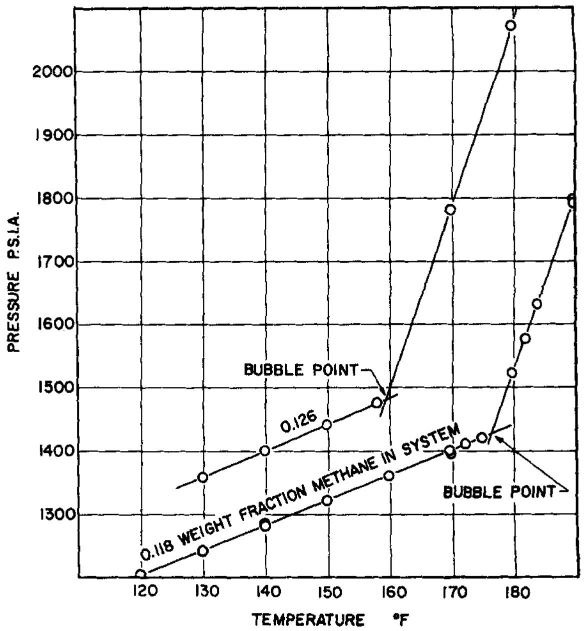

Fig. 3. Pressure-temperature diagram at equilibrium.

face occurred somewhat more rapidly at the higher temperatures than at the lower temperatures.

## MATERIALS

Photomicrographs of the silica employed are available (*12*). The material is angular and the surfaces relatively flat. The average particle size is approximately 300 mesh. The surface area, as determined from adsorption of argon, was 3,515 sq. ft./lb.

After passage through a condenser at the temperature of solid carbon dioxide and acetone and a purification tube containing calcium chloride, activated charcoal, Ascarite, and anhydrous calcium sulfate, the methane employed contained less than 0.001 mole fraction of material other than methane.

The *n*-pentane was obtained as pure grade and was reported to contain not more than 0.010 mole fraction of material other than *n*-pentane. After deaeration the *n*-pentane was stored in stainless steel weighing bombs (*13*) and was transferred to the isochoric vessel (*12, 14*) by conventional high-vacuum techniques.

## EXPERIMENTAL RESULTS

Equilibrium behavior was established by approach in two directions, that is by an increase in temperature and by a decrease in temperature to reach the same state. Results of these two approaches to the same state in the liquid hydrocarbon-silica system are shown in Figure 1. In the case of Mixture A, containing 0.118 weight fraction methane, the approach was to a temperature of 200°F., whereas in the case of Mixture B, which contained 0.126 weight fraction methane, the approach was to a temperature of 170°F. It is apparent that the pressure after an isothermal period of 1 hr. was the same whether equilibrium was approached by an increase or by a decrease in temperature.

The corresponding behavior at temperatures where a liquid and a gas hydrocarbon phase existed is shown in Figure 2. The situation under these conditions is somewhat different. When Mixture A was cooled to 140°F., equilibrium was obtained in less than 1 hr. However when it was heated from 120° to 140°F., equilibrium was not obtained in 14 hr. Nearly 40 hr. were required to bring the system to equilibrium upon an increase in temperature under conditions where a gas phase was present. In the case of Mixture B a similar situation was encountered, except that the deviation from equilibrium upon cooling from 160°F. was approximately 1 lb./sq. in. after 4 hr., as compared with a deviation of approximately 0.5 lb./sq. in. for Mixture A after 1 hr. When Mixture B was heated from 140°F., marked deviation from equilibrium still existed after 6 hr. It should be emphasized that agitation involving a 90-deg. oscillation of the sphere oc-

TABLE 1. SOME PROPERTIES OF MIXTURES INVESTIGATED

| | Mixture A | Mixture B |
|---|---|---|
| Composition of system, weight fraction methane | 0.1182 | 0.1263 |
| Volume of cell, cu. ft. | 0.008597 | 0.008597 |
| Weight of silica, lb. | 0.5468 | 0.5468 |
| Volume of silica, cu. ft. | 0.003338 | 0.003338 |
| Surface area of silica, sq. ft./lb. | 3,515 | 3,515 |
| Weight of *n*-pentane, lb. | 0.1365 | 0.1365 |
| Conditioning temperature, °F. | 190 | 180 |
| Bubble-point temperature, °F. | 176.3 | 159.6 |
| Bubble-point pressure, lb./sq. in. abs. | 1,428 | 1,479 |

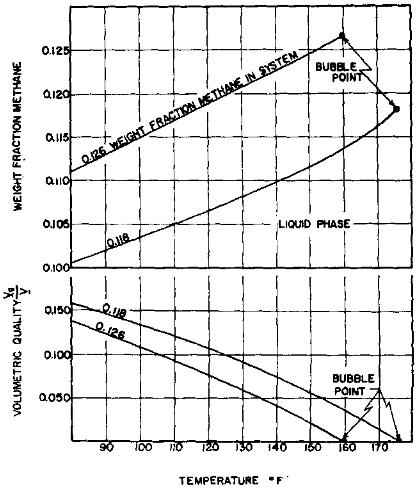

Fig. 4. Composition of liquid phase and volumetric quality of mixtures A and B at equilibrium.

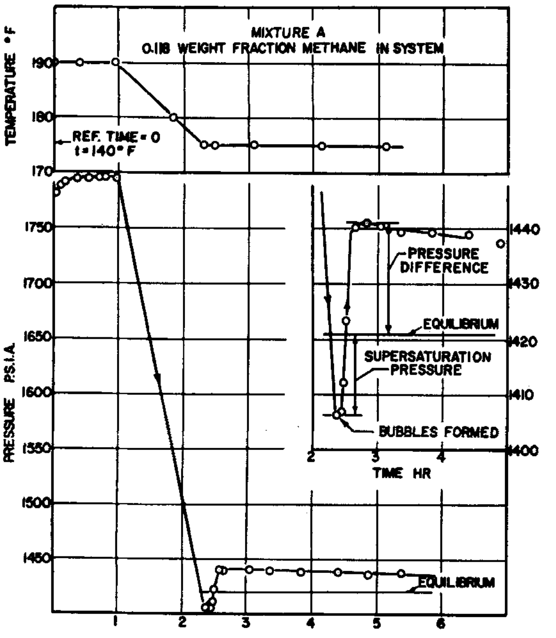

Fig. 5. Pressure-time relationship at 175°F.

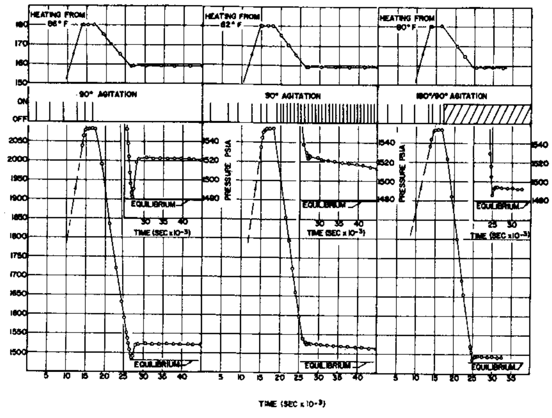

Fig. 7. Effect of agitation upon approach to equilibrium.

curred intermittently for an interval of 2 min. throughout the period shown in Figure 2. These intervals have been indicated by vertical lines on the figure.

The pressure-temperature relationships at equilibrium for the two mixtures of methane, *n*-pentane, and silica are shown in Figure 3. The experimental points of pressure represent values obtained by approach to the temperature indicated from a higher and a lower value. As the temperature is decreased at equilibrium, the volume of the gas phase coexisting with the volume of the liquid phase progressively increases. The composition of the liquid phase and volumetric quality of Mixtures A and B at equilibrium have been indicated as a function of temperature in Figure 4.

For a substantial part of the experimental work to be described the behavior of Mixture A at 175.0°F. was employed as a reference. This temperature was slightly below the bubble point of 176.3°F. For Mixture B a reference temperature of 159.0°F. was used, which again was slightly below the bubble-point temperature of 159.6°F.

In studying the nonequilibrium behavior near bubble point an arbitrary conditioning period of 1 hr. at 190°F. was employed for Mixture A, followed by a decrease in temperature to 175.0°F. Mixture B was conditioned for 1 hr. at 180°F., and then the temperature was reduced to 159.0°F. These time-temperature histories were considered standard conditioning periods with no implication that this period permitted an approach to equilibrium at the liquid hydrocarbon-silica interface at temperatures of 190° and 180°F.

The behavior in the vicinity of bubble point under nonequilibrium conditions is illustrated in Figures 5 and 6. Figure 5 shows the pressure-time relationship for Mixture A at 175°F. after equilibrium was obtained in the gas-liquid, hydrocarbon-silica system at 140°F., followed by a conditioning period of 1 hr. at 190°F. and then cooling to 175°F. Figure 6 portrays similar information for Mixture B at 159°F. after equilibrium was reached at 150°F., followed by conditioning at 180°F. for 1 hr. and then decreasing the temperature to 159°F. The equilibrium pressure values are represented by solid horizontal lines. It is apparent that the pressure drops rapidly below the equilibrium value, approaches nearly a steady value, then rises again upon bubble formation to a maximum which is above equilibrium bubble point, and then gradually falls toward the equilibrium value.

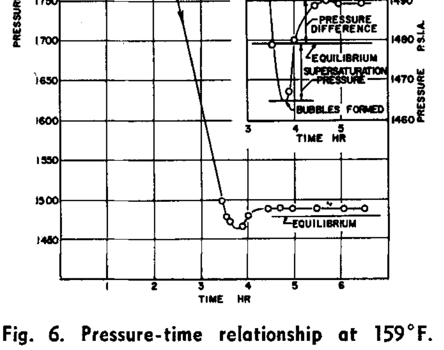

Fig. 6. Pressure-time relationship at 159°F.

The maximum increase above the equilibrium value that is encountered as a result of a specified prior history of the system has been designated as the *pressure difference* and is shown in the insert on each of the figures. This pressure difference was approximately 20 and 10 lb./sq. in. for Mixtures A and B, respectively. The time required for the attainment of the maximum pressure difference and the supersaturation pressure varied in a random fashion, as would be expected for a system understrain (9). A period of some 40 hr. was required to bring the gas-liquid, hydrocarbon-silica system to equilibrium. The behavior depicted in Figures 5 and 6 possibly indicates that the composition of the liquid phase is an important influence in determining the extent of selective adsorption of methane or *n*-pentane.

The approach to equilibrium with normal 90-deg. agitation and without agitation is shown in Figure 7. All the information on this figure was obtained after the attainment of equilibrium near room temperature over a period of some 66 hr. The isochoric vessel was then heated to 180°F. with Mixture B, then cooled to 159°F. in a period of about 2 hr., and again held constant at the latter temperature. The marked difference in behavior near bubble point for the mixture with and without agitation is clearly evident. Agitation also hastens the approach to equilibrium after bubble point has been reached. Furthermore there is much less tendency for supersaturation with agitation than without it. The gross change in pressure with time in the condensed liquid region is of nearly the same order with and without agitation.

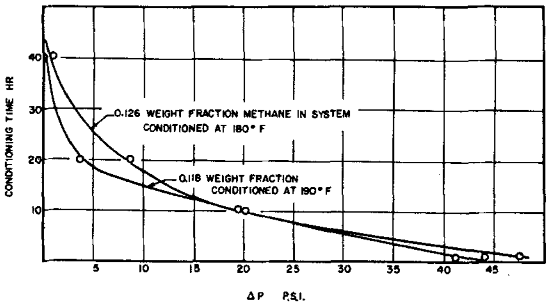

Fig. 8. Effect of conditioning time upon pressure difference at equilibrium temperature.

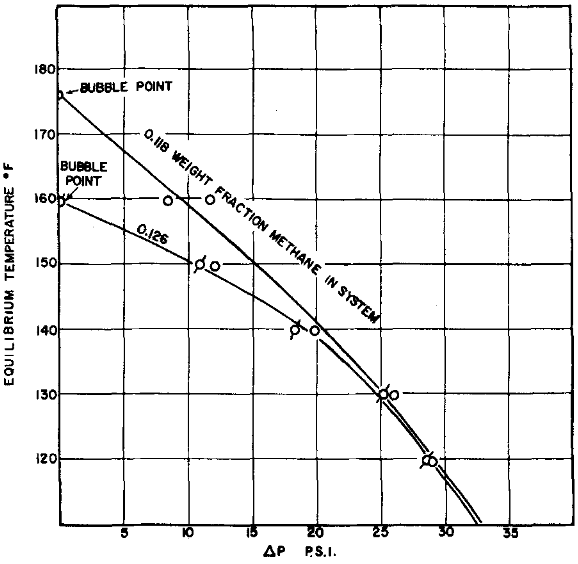

Fig. 9. Effect of equilibrium temperature upon pressure difference.

Intense agitation, with the associated reduction in particle size of the silica, was obtained by oscillating the pressure vessel through 180-deg. followed by 90-deg oscillation. Under such circumstances the two steel balls fell freely through the hydrocarbon-silica mixture and impacted the steel pressure vessel audibly, with the associated gross crushing of silica particles. Under these conditions of agitation significant abrasion of the silica surfaces was obtained and the pressure excess decreased by nearly a factor of 2 in a period of 1,000 sec. Less intense agitation was obtained by oscillating the pressure vessel through 90-deg. In this case the steel balls maintained contact with the pressure vessel except at one point of change in section where audible impact was detectable by appropriate acoustic amplification. The degree of abrasion of the silica was small, and negligible gross crushing of the silica particles was encountered. No significant change in the pressure excess with agitation for periods up to 10,000 sec. was noted.

The time of conditioning influenced the approach to equilibrium. The samples were maintained at 80°F. for a period of some 66 hr. with occasional agitation. Mixture A was then heated to 190°F. and maintained at this temperature with agitation for different periods, varying from 1 to 40 hr. The same procedure was followed in the case of Mixture B except that the conditioning temperature was 180°F. The results for both mixtures are shown graphically in Figure 8. It is apparent that there is a regular decrease in the pressure difference measured at 175° and 159°F., with an increase in residence time at 190° and 180°F., respectively.

It was established that the effect of temperature and pressure at fixed composition of liquid upon the adsorption equilibrium was small. The system was conditioned at various temperatures above the bubble-point temperature for extended periods. The temperature of Mixture A was raised to 190°F. for 1 hr. and then returned to 175°F. In the case of Mixture B the temperature after conditioning was raised to 180°F. for 1 hr. and then returned to 159°F.

At 80°F. the liquid phase of Mixture A contained 0.100 weight fraction methane, whereas throughout the homogeneous liquid region encountered at temperatures above 176°F., the liquid phase contained 0.118 weight fraction methane. In the case of Mixture B the liquid phase at 80°F. contained 0.111 weight fraction methane. Throughout the homogeneous liquid region encountered at temperatures above 159°F. the liquid phase of Mixture B contained 0.126 weight fraction methane. The data shown in Figure 8 could indicate that an extended period is required for the attainment of equilibrium at the interface.

Another trend investigated was the effect of the temperature at which equilibrium between the hydrocarbon liquid, gas, and silica was attained before subjecting the samples to the standard conditioning cycle. The results are shown in Figure 9, and as would be expected a marked decrease in the pressure difference occurred with an increase in the original equilibrium temperature. It appears that the pressure difference decreases to a value near zero at a temperature equal to the equilibrium bubble-point temperature of the mixture.

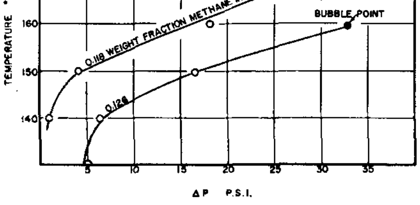

Fig. 10. Effect of temperature upon pressure difference after equilibrium at 100°F.

The magnitude of the pressure difference for temperatures other than 175°F. for Mixture A and 159°F. for Mixture B, after equilibrium was obtained at 100°F., was investigated. The experimental data shown in Figure 10 indicate nearly a linear variation in the pressure difference in the temperature interval between 175° and 150°F. in the case of Mixture A, and 159° and 140°F. in the case of Mixture B. The details of behavior with equilibrium at temperatures below 140°F. could not be effectively investigated because of uncertainties in the short conditioning times. The pressure difference for Mixture A determined at 175°F. after equilibrium at 100°F. was 36 lb./sq. in. For Mixture B the pressure difference at 159°F. after equilibrium at 100°F. was 33 lb./sq. in. These values are in good agreement with the information set forth in Figure 9.

There are many ways in which this phenomenon can be explained, but it appears that it is associated with the approach to equilibrium at the interface between the hydrocarbon and the silica. It does not appear that there is adequate experimental information to justify speculation as to the microscopic nature of the cause of such behavior. The results do indicate that, under the conditions encountered in these experiments, the presence of silica does influence the approach to equilibrium of hydrocarbon phases.

## ACKNOWLEDGMENT

This work is a contribution from Research Project 37 of the American Petroleum Institute at the California Institute of Technology. The methane was obtained through the courtesy of Texaco, Inc.

## LITERATURE CITED

1. Am. Inst. Physics, "Temperature, Its Measurement and Control in Science and Industry," Reinhold, New York (1951).
2. Bertram, E. A., and W. N. Lacey, *Ind. Eng. Chem.*, **28**, 316 (1936).
3. Bridgeman, O. C., *J. Am. Chem. Soc.*, **49**, 1174 (1927).
4. Hill, E. S., and W. N. Lacey, *Ind. Eng. Chem.*, **26**, 1324 (1934).
5. *Ibid.*, p. 1327.
6. Hunt, E. B., Jr., and V. J. Berry, Jr., *A.I.Ch.E. Journal*, **2**, 560 (1956).
7. Kay, W. B., *Ind. Eng. Chem.*, **28**, 1014 (1936).
8. Meyers, C. H., *Bur. Standards J. Research*, **9**, 807 (1932).
9. Nichols, W. B., L. T. Carmichael, and B. H. Sage, *Ind. Eng. Chem.*, **49**, 1165 (1957).
10. Opfell, J. B., C. J. Pings, and B. H. Sage, "Equations of State for Hydrocarbons," American Petroleum Institute, New York (1959).
11. Pomeroy, R. D., W. N. Lacey, N. F. Scudder, and F. P. Stapp, *Ind. Eng. Chem.*, **25**, 1014 (1933).
12. Reamer, H. H., and B. H. Sage, *J. Chem. Eng. Data*, **5**, 38 (1960).
13. Sage, B. H., and W. N. Lacey, *Trans. Am. Inst. Mining Met. Engrs.*, **136**, 136 (1940).
14. Schlinger, W. G., and B. H. Sage, *Ind. Eng. Chem.*, **42**, 2158 (1950).
15. Silvey, F. C., H. H. Reamer, and B. H. Sage, *Ind. Eng. Chem., Chem. Eng. Data Series*, **3**, 181 (1958).

*Manuscript received November 8, 1961; revision received March 19, 1962; paper accepted April 5, 1962.*

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# Transient and Steady State Size Distributions in Continuous Mixed Suspension Crystallizers

**A. D. RANDOLPH and M. A. LARSON**

**Iowa State University of Science and Technology, Ames, Iowa**

Miller and Saeman (*4*) experimentally demonstrated that at a given production rate superior ammonium nitrate crystals could be produced in an Oslo type of crystallizer when one worked with a mixed rather than a classified crystal suspension. This difference in crystal quality was due to the differences in crystal growth rate which occurred in the two types of crystal suspensions. In a classified crystal suspension there is a gradient of supersaturation from bottom to top, with the highly supersaturated solution entering the bottom and a solution relieved of most of its supersaturation leaving the top. Most inorganic crystals have an upper limit of supersaturation which produces too high a growth rate and results in poorly formed, weak, and friable crystals, as well as crystals with a considerable amount of occluded crystallizing solution. In the case of a mixed suspension the average growth rate is much less than the maximum growth rate at the bottom of a classified crystal suspension. It was this high initial value in the latter case that was reported to cause the difference in crystal quality between the two systems.

In actual practice many industrial crystallizers are operated at higher than design throughput and result in a crystal suspension approaching perfect mixing. Saeman (*7*) has derived relationships for the size distribution, expressed as cumulative weight of crystals vs. size, for a single-tank continuous mixed suspension crystallizer operating at steady state and for the separate cases of mixed and classified product removal. It was observed that the size distribution from a large commercial crystallizing unit was a reasonable approximation of the theoretically predicted distribution. A major point that was brought out in this work was the extreme influence of nucleation rate on resultant size distribution. Methods of controlling size distribution by dissolving excess nuclei were discussed.

Newman and Bennett (*5*) also emphasize the importance of nucleation rate in determining the size of crystals. Net nucleation rate is the sum of nuclei formed at the boiling surface, homogeneously in solution, from attrition of the crystal bed, and by seeding. These authors conclude that the former two sources of nuclei can be reduced by proper crystallizer design. It was also stated that the nucleation rate present in any industrial equipment tends to limit the average product crystal size to a range characteristic of that particular crystal system.

Robinson and Roberts (*6*) made a mathematical study of the size distribution which leaves the $k$'th stage of $k$ agitator-crystallizers operated in series with nucleation in only the first stage. They compared their equation for the case of a single tank with the size distribution from a commercial unit producing ammonium sulphate. The results from the theory agreed quite well with data from this unit. This work also emphasized the role of nucleation in determining crystal size distribution. Logically all sources of crystal nuclei except deliberate seeding and crystal attrition should be some function of the supersaturation in solution. These authors presented a possible kinetic nucleation equation for the ammonium sulphate system of the form

$$dN^\circ/dt = k_1\,(s - s_o)^{k_2} \qquad (1)$$

The value of $k_2$ was given as $\geqq 4$, but no data were given to support this equation.

The purpose of the present work was to derive a general size distribution equation which describes the transient behavior of particles in an arbitrary suspension. It was shown that long term transients in product size distribution from a continuous crystallizer can occur in spite of steady state heat and material inputs which can be enforced on the system. This equation

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A. D. Randolph is with the American Potash Company, Trona, California.