The Effect of the Hydrolysis Reaction Upon the Rate of Absorption of Chlorine into Water

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The rate of absorption of chlorine into water was studied in a short wetted-wall column. This absorption system is characterized by a liquid phase chemical reaction occurring simultaneously with the absorption process, and thus the absorption coefficient is greater than in the case of physical absorption.

The ratio of the absorption coefficient accompanied by the hydrolysis reaction to the physical absorption coefficient varied from 1.3 to 3, depending on the chlorine partial pressure and the liquid flow rate.

Penetration-theory solutions for absorption accompanied by the hydrolysis reaction were obtained by the use of an IBM-709 digital computer. Excellent agreement between the experimental and computed results was obtained on the assumption that the forward rate constant for the hydrolysis reaction was 13.7 sec.$^{-1}$ at 25°C. This value compared favorably with the published results of kinetic studies of the hydrolysis reaction.

The problem of predicting the effect of a simultaneous chemical reaction upon the rate of gas absorption has received considerable attention in the chemical engineering literature (*3, 5, 6, 8, 13, 15, 17*). The problem has been subjected to theoretical analysis by a number of investigators, and comparisons between experimental results and theoretical predictions have been published for quite a few systems. While theory and experiment have often shown qualitative agreement, quantitative agreement has been achieved for very few systems. Systems involving reversible chemical reactions have been studied very little, and no satisfactory agreement between theory and experiment has been achieved in these studies. Such a system is the chlorine-water system.

Because of its industrial importance as well as its theoretical interest the chlorine-water system has been the subject of several previous investigations. In 1937 Adams and Edmonds (*1*) presented and analyzed some packed tower absorption rate data which had been reported earlier by Gilmour, Lakhadt, and Welcyng in an unpublished report. Adams and Edmonds concluded that the liquid phase controlled the absorption rate, and they presented an empirical correlation for obtaining the absorption coefficient. Their analysis considered the effect of the chlorine hydrolysis reaction upon chlorine solubility in water, but the effect of this chemical reaction upon the absorption rate was not considered. In 1947 Vivian and Whitney (*17*) presented data on the rate of absorption of chlorine into water in a packed tower. By comparing their results with the oxygen desorption results of Sherwood and Holloway (*12*), Vivian and Whitney concluded that the rate of chlorine hydrolysis is an important factor in the absorption process. They proposed that the liquid phase absorption coefficient be based upon a driving force of unhydrolyzed chlorine concentration, and they demonstrated that the hydrolysis reaction causes this coefficient to exceed the coefficient that would be expected if no chemical reaction were accompanying the absorption process.

In 1950 Peaceman (*11*) studied the rate of desorption of chlorine from chlorine-water solutions. In order to control conditions closely a short wetted-wall column was used for the desorption experiments. He compared his results with approximate solutions to the film theory, but the experimental results did not agree with the film-theory predictions. Indeed the effect of liquid-phase chlorine concentration upon the absorption coefficient was quite different from that predicted by the theoretical equations.

This investigation was undertaken in order to obtain data on the rate of absorption of chlorine into water in a short wetted-wall column such as that used by Peaceman. Such a study was clearly indicated by the need to follow up the work of Vivian and Whitney with a study under the better-controlled conditions of the short wetted-wall column and also by the hope that these results would shed some light upon Peaceman's desorption results.

THEORY

The advantage of using models of the absorption process to facilitate the mathematical analysis of the effect of a liquid phase chemical reaction upon the rate of gas absorption has been discussed by a number of investigators (*3, 5, 6, 8, 13, 15*). In this study the penetration-theory model was chosen because it is a fairly accurate description of the absorption process in a short wetted-wall column (*6, 16*).

Chlorine hydrolysis may be represented by the equation

$$Cl_2 + H_2O \rightleftharpoons H^+ + Cl^- + HOCl \qquad (1)$$

and the equilibrium constant may be written as

$$K = \frac{(H^+)(Cl^-)(HOCl)}{(Cl_2)}$$

since the ionization of the hypochlorous acid is negligible. The rate of hydrolysis was assumed to follow the following kinetic equation:

$$r = k_F \left[(Cl_2) - \frac{(H^+)(Cl^-)(HOCl)}{K} \right] \qquad (2)$$

which is the kinetic expression used by Shilov and Solodushenkov (*14*) and by Lifshitz and Perlmutter-Hayman (*10*) in their studies of the rate of the hydrolysis reaction. With this assumption the penetration-theory partial-differential equations for the absorption of chlorine into pure water were solved by a finite-difference method on an IBM-709 computer. The method of solution was similar to that described by Brian, Hurley, and Hasseltine (*3*), and it will not be described here. The results are presented in Figure 1.

The variable ϕ in Figure 1 is a measure of the effect of the chlorine hydrolysis reaction upon the absorption rate, and the group $\sqrt{M}$ is a measure of how rapid the chemical reaction is relative to diffusion rates. The parameter η is an index of how irreversible the reaction appears to be, and this is determined by the concentration level as well as the chemical equilibrium constant. The curve for η equal to infinity corresponds to an ir-

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reversible first-order chemical reaction, and this curve is the analytical solution presented by Danckwerts (*5*) and by Sherwood and Pigford (*13*). The curves for finite values of η were computed numerically in this study. In computing these curves the ratio of the diffusivity of hydrochloric acid to the diffusivity of chlorine was taken to be 2.1. The ratio of the diffusivity of hypochlorous acid to the diffusivity of chlorine was taken to be 1.05. These ratios were derived from reported values of 3.1×10^{-5}, 1.55×10^{-5}, and 1.48×10^{-5} sq. cm./sec. for the diffusivities of hydrochloric acid (*9*), hypochlorous acid (*11*), and chlorine (*16*), respectively. In the theoretical development, gas-phase resistance was assumed to be negligible.

EXPERIMENTAL

The rate of absorption of chlorine gas from chlorine-nitrogen mixtures into distilled water in a short, wetted-wall column was measured at 25°C. and atmospheric pressure. The short, wetted-wall column was of the same design as that described by Vivian and Peaceman (*16*), and it was indeed the very same column as that used by Gilliland, Baddour, and Brian (*6*). The experimental procedure was essentially the same as that described in reference (*6*), except that the liquid fed to the column was distilled water. The liquid effluent from the column was analyzed by collecting a sample beneath the surface of an aqueous solution of sodium hydroxide and potassium iodide. After the addition of enough hydrochloric acid to make the solution slightly acidic, the liberated iodine was titrated with sodium thiosulfate to determine the total chlorine content of the original sample. This chemical analysis was compared, for a number of samples, with the chlorine concentration indicated by an electrical conductivity cell placed in the exit liquid line from the column. The two analytical methods agreed, and so the conductivity method was used for most of the runs, an occasional check being made by the iodimetric titration.

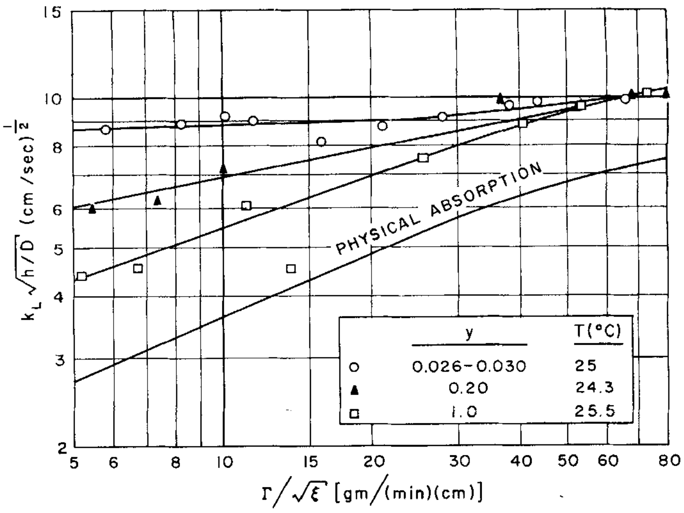

Fig. 2. Rate of absorption of chlorine into pure water.

In addition to the chlorine-water experiments some experiments were also performed in which the chlorine was absorbed into 0.2N hydrochloric acid. The hydrochloric acid suppresses the chlorine hydrolysis reaction, so that absorption into 0.2N hydrochloric acid is a physical absorption process. These runs were made as calibration runs in order to compare the results of this study with those of previous investigators using short wetted-wall columns. The details of the apparatus and procedure and the original data and results are reported in reference 7.

RESULTS AND DISCUSSION

Figure 2 presents some of the experimental results obtained in this investigation. The lowest curve is the physical absorption curve presented by Gilliland, Baddour, and Brian (*6*). The results of the present investigation for the absorption of chlorine into 0.2N hydrochloric acid agree well with this curve, but the experimental points were omitted from Figure 2 for clarity. The results are plotted as $k_L \sqrt{h/D}$ vs. $\Gamma/\sqrt{\xi}$ in order to correct the physical absorption results for minor variations in the column height and the liquid viscosity and diffusivity (*6*), but variations in these quantities were small; the important variables are liquid-phase absorption coefficient and liquid flow rate. The diffusivity of chlorine in water at 25°C. was taken as 1.48×10^{-5} sq. cm./sec., as reported by Vivian and Peaceman (*16*), and this value was corrected for temperature by the Stokes-Einstein equation

$$D \sim T/\mu$$

The three upper curves in Figure 2 present some of the results obtained for the absorption of chlorine into water. The variables are grouped as $k_L \sqrt{h/D}$ vs. $\Gamma/\sqrt{\xi}$ in order to facilitate their comparison with the physical absorption curve. The absorption coefficient k_L is defined as the gas absorption rate per unit interfacial area in the column divided by $(Cl_2)_i$, the concentration of molecular chlorine at the interface. This interfacial molecular chlorine concentration was obtained from the gas-phase chlorine partial pressure and the Henry's law constant, a small correction being applied for gas-phase resistance. The theoretical results of Boelter (*2*) were used to compute the gas phase resistance, but it should be emphasized that this correction never exceeded 5.5%. The Henry's law constant at 25°C. was taken as

$$H = 0.0623 \text{ (g. moles)/(liter) (atm.)}$$

as reported by Whitney and Vivian (*18*). This agrees with the value given by Yakovkin (*19*), but these investigators disagree on the temperature coefficient, and so their results were averaged as

$$\frac{d(\ln H)}{d(1/T)} = 3{,}180(°\text{K.})$$

in order to make small temperature corrections.

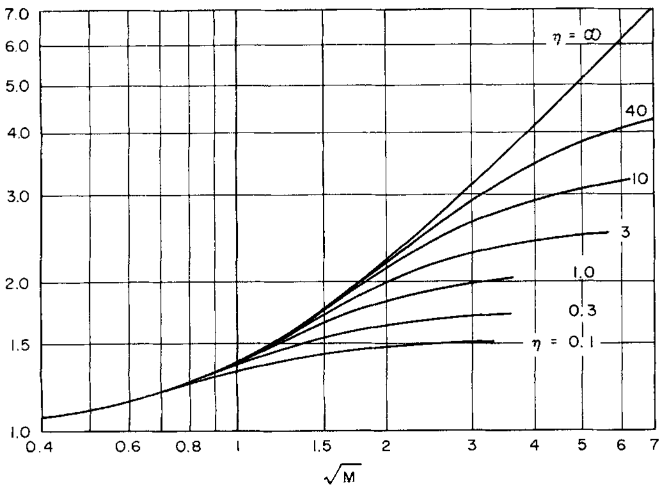

Fig. 1. Absorption of chlorine into pure water: penetration-theory solution.

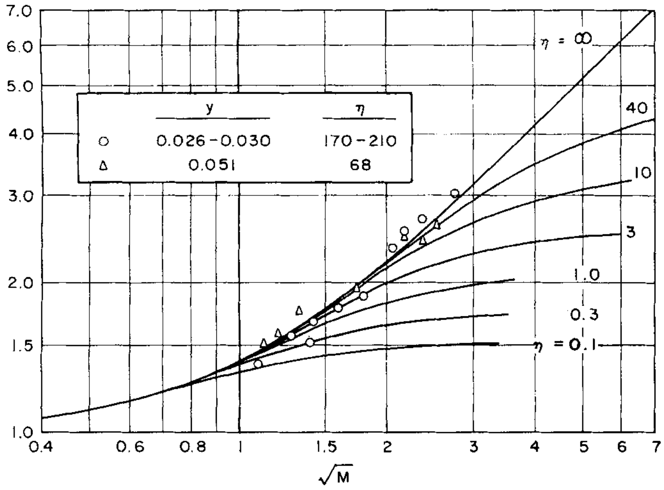

Fig. 3. Experimental results: comparison with theory.

The results in Figure 2 show that the chlorine hydrolysis reaction causes the absorption coefficient for absorption of chlorine into water to be higher than the correlation for physical absorption coefficients. Furthermore, in contrast to physical absorption results, there is a substantial effect of the chlorine gas-phase mole fraction on the absorption coefficient for chlorine absorption into water. The effect of liquid flow rate upon the absorption coefficient is less than that for physical absorption, and the effect decreases with decreasing chlorine partial pressure.

Comparison with Theory

In Figures 3 through 5 all of the results for chlorine absorption into water are presented in a form suggested by the theoretical predictions in Figure 1. The ordinate in these graphs is ϕ, the enhancement factor due to the chlorine hydrolysis reaction. For any experimental point ϕ is computed by dividing $k_L \sqrt{h/D}$ by the value of $k_L{}^* \sqrt{h/D}$ read from the physical absorption curve at the same value of $\Gamma/\sqrt{\xi}$ (see Figure 2). The abscissa in Figures 3 through 5 is $\sqrt{M}$; this quantity is computed from the reaction rate constant, the column height, and the value of $k_L{}^* \sqrt{h/D}$ corresponding to the value of $\Gamma/\sqrt{\xi}$. The value of k_F was taken to be 13.7 sec.$^{-1}$ at 25°C., as will be discussed later. The effect of temperature on k_F was assumed to be

$$\frac{d \ln (k_F)}{d\,(1/T)} = -4{,}900\ (^\circ\text{K.})$$

but a large error in this assumption would have little effect upon the computed values of $\sqrt{M}$ because temperature variations from 25°C. were small. Thus the variation in the abscissa largely represents liquid flow rate variation; the variation in k_F due to temperature variations is of minor importance.

Figures 3 through 5 present the results for different chlorine gas-phase mole fractions, corresponding to different values of η. In computing the values of η reported on the graphs the equilibrium constant was taken from the recent results of Connick and Yuan-tsan Chia (*4*), in which the value of K is shown to vary with the hydrochloric acid concentration because of variations in the activity coefficient for hydrochloric acid. The value of K used to compute η was taken at the hydrochloric acid concentration that would be in equilibrium with the interfacial concentration of molecular chlorine. While the true average K value might well be different from this, this procedure is justified by the relatively small variation in K with hydrochloric acid concentration and the insensitivity of the theoretical curves in Figure 1 to small variations in η.

The experimental results in Figure 3 are for the lowest values of the chlorine partial pressure studied, corresponding to values of η between 68 and 210. For comparison the penetration-theory curves from Figure 1 are shown with the experimental points. For values of ϕ less than 3 the theoretical curves predict that the reaction is essentially irreversible for values of η equal to 68 and higher, and the value of k_F selected in computing $\sqrt{M}$ resulted in excellent agreement between the experimental results and the theoretical curve for $\eta = \infty$. The agreement of the slopes of the theoretical and experimental curves is not affected by the choice of k_F. Consequently it may be concluded that the chemical reaction is first order and essentially irreversible. The absolute agreement between the experimental and theoretical curves suggests that the value of k_F is 13.7 sec.$^{-1}$ at 25°C.

In Figures 4 and 5 the experimental results for higher chlorine partial pressures are compared with the penetration-theory predictions from Figure 1. The values of $\sqrt{M}$ were computed with the same value of k_F which produced the agreement in Figure 3. The results in Figures 4 and 5 show very good agreement with the penetration-theory curves for the corresponding values of η, demonstrating that the theoretical model is quite capable of predicting the effects of liquid flow rate and chlorine partial pressure on the rate of absorption of chlorine into water.

The effect of the reversibility of the hydrolysis reaction at high chlorine partial pressures can be seen by comparing Figures 3 and 5. At the lowest liquid flow rate, corresponding to a value of 3 for $\sqrt{M}$, ϕ varies from 3 at very low partial pressures to about 1.55 at a partial pressure of 1 atm. This decrease in ϕ, manifesting the effect of the reversibility of the reaction, is predicted quantitatively by the penetration theory results.

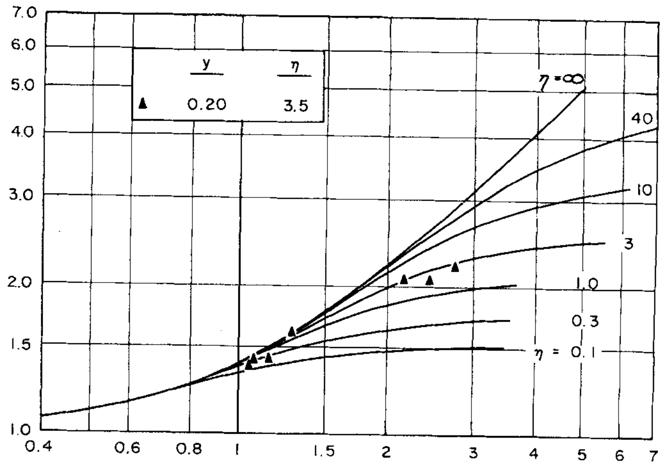

Fig. 4. Experimental results: comparison with theory.

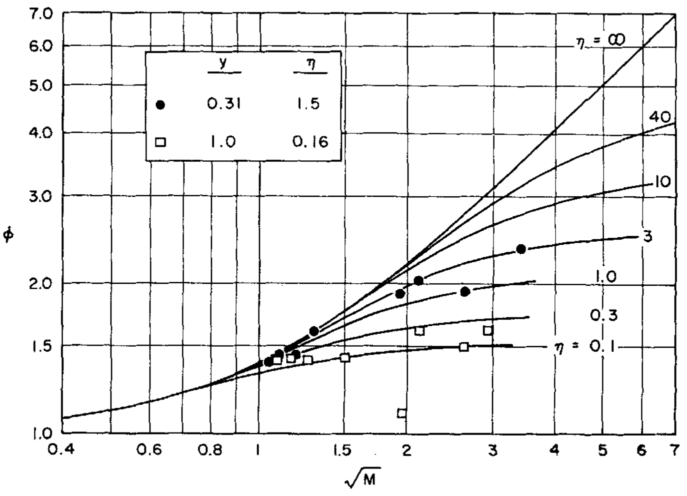

Fig. 5. Experimental results: comparison with theory.

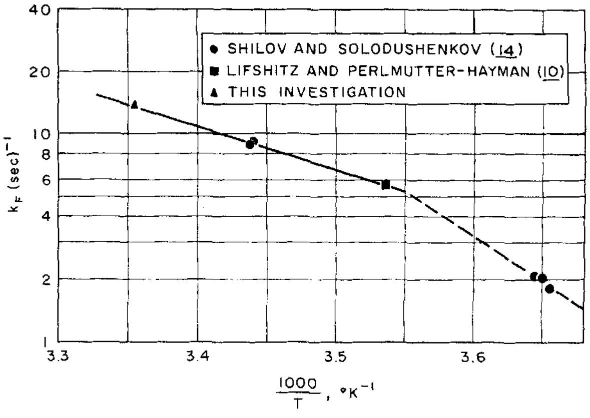

Fig. 6. Hydrolysis reaction rate constant.

Reaction Rate Constant

The rate of chlorine hydrolysis has been measured by Shilov and Solodushenkov (*14*) and more recently by Lifshitz and Perlmutter-Hayman (*10*). These investigators concluded that the kinetics were described by Equation (2). The values of k_F which they reported are shown in Figure 6, along with the value of 13.7 sec.$^{-1}$ at 25°C. inferred from the results of this study. A straight-line relationship in the Arrhenius plot is satisfied by the results at the higher temperatures, but the results near 0°C. depart from this straight line. Such a departure is not unexpected in view of the formation of chlorine hydrate at this low temperature (*10*).

In Figure 6 it is readily apparent that the value of k_F selected to match the absorption rate results with the theoretical curve in Figure 3 is in excellent agreement with the values of k_F determined in the kinetic experiments of Shilov and Solodushenkov (*14*) and of Lifshitz and Perlmutter-Hayman (*10*). This agreement is additional confirmation of the models chosen for the fluid mechanics and for the chemical kinetics in the penetration-theory analysis and suggests the use of devices such as the short wetted-wall column for kinetic studies of relatively fast chemical reactions.

Reverse Reaction Mechanism

It is not surprising that the results for low values of chlorine partial pressure agree with the theoretical curves. It would be expected that the chemical reaction would be essentially pseudo first order and irreversible under these conditions. It is more surprising that the effect of increasing the partial pressure should check quantitatively with the theoretical predictions, because the theoretical analysis was based upon the assumption that the reverse reaction is third order. It is true that the reaction rate data of Shilov and Solodushenkov and of Lifshitz and Perlmutter-Hayman support Equation (2), and equilibrium was approached fairly closely in their experiments. However their data were for the forward reaction, and the reverse reaction rate was of secondary importance in their experiments, as it was in these experiments. Even if Equation (2) is an adequate reaction rate expression, it is doubtful that the reverse reaction mechanism is a trimolecular combination as shown in Equation (1).

Gilliland, Baddour, and Brian (*6*) pointed out that reaction mechanisms which involve transient intermediate species can have markedly different effects upon the gas absorption rate than could be produced by a reaction conforming to the over-all stoichiometric equation, no matter what kinetic equation is assumed for the latter. This occurs when the rate of consumption of the intermediate species is low relative to its formation rate and to diffusion rates, so that it can diffuse an appreciable distance before it is consumed. When this happens, simultaneous mass transfer and chemical reaction experiments are likely to encounter effects not present in reaction rate experiments involving no diffusion.

It was believed at first that a complex mechanism for the reverse chemical reaction was responsible for the disagreement between Peaceman's chlorine desorption results and his theoretical predictions, but the agreement between theory and experimental results shown in Figures 3 through 5 supports the use of a theoretical model based upon Equations (1) and (2). However it is still true that the rate of chlorine absorption is less sensitive to the reverse reaction mechanism than is the rate of desorption. These considerations certainly suggest that further work should be done to extend these absorption data, particularly to other temperatures, and to probe the discrepancy between absorption and desorption for the chlorine-water system. Investigations of this nature are presently under way in this laboratory.

CONCLUSION

The chlorine hydrolysis reaction causes the chlorine absorption coefficient to be greater for absorption into water than for absorption into 0.2N hydrochloric acid, which is essentially physical absorption. The magnitude of this increase varied from approximately 30 to 200% in these experiments.

For the lowest chlorine partial pressures studied the hydrolysis reaction is essentially irreversible and pseudo first order. The absorption rate results agree well with penetration-theory predictions and confirm the reaction rate constant values reported by Shilov and Solodushenkov (*14*) and by Lifshitz and Perlmutter-Hayman (*10*).

For the highest chlorine partial pressures studied the reversibility of the chemical reaction is appreciable, causing a reduction in ϕ from 3 to 1.6 at the lowest liquid flow rates. This effect is predicted quantitatively by the penetration theory solution.

The agreement between these experimental results and the theoretical predictions is good. Since the theoretical analysis contained the assumption of a third-order reverse chemical reaction rate, this agreement was somewhat unexpected. Further work on chlorine desorption, which should be more sensitive to the kinetics and mechanism of the reverse reaction, is suggested.

ACKNOWLEDGMENT

The machine computations of the penetration-theory solution were performed at the Massachusetts Institute of Technology Computation Center. The authors are grateful to the Center for the use of its facilities.

NOTATION

(Cl_2) = molar concentration of molecular chlorine in the liquid phase. Analogous definitions for molar concentrations of other species

D = liquid-phase diffusivity of molecular chlorine, sq. cm./sec.

H = Henry's law constant for molecular chlorine, (g.moles)/(liter) (atm.)

h = height of the short wetted-wall column, cm.

K = equilibrium constant for chlorine hydrolysis, (g.moles/liter)^2

k_F = reaction rate constant, (sec.)$^{-1}$

k_L = liquid-phase absorption coefficient in the presence of the simultaneous chemical reaction, cm./sec.

k_L^* = liquid-phase absorption coefficient that would exist if no chemical reaction accompanied the absorption process, cm./sec.

M = $k_F D/(k_L^*)^2$

r = rate of chlorine hydrolysis, g.moles/(sec.) (liter)

T = temperature, °K. or °C.

y = mole fraction of chlorine in the gas phase

Γ = mass flow rate of liquid per unit perimeter of the column, g./(min.) (cm.)

η = $K/(Cl_2)^2_i$

ξ = liquid-phase density-viscosity product divided by this same product for water at 25°C.

ϕ = k_L/k_L^*

Subscripts

i = gas-liquid interface

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Experimental Determination of Critical Temperatures and Pressures of Mixtures: the Methane-Ethane-*n*-Butane System

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An experimental unit has been designed and constructed for the study of critical phenomena in multicomponent systems. This unit has been built to utilize a new visual PVT cell capable of operating at temperatures up to 300°F. and pressures to 10,000 lb./sq. in. abs. This cell is of the liquid piston type with mercury as the pressurizing fluid and affords unobstructed visual observation of its contents. The dependability of the unit has been tested on two mixtures of ethane and *n*-butane. Phase equilibria data were obtained, which in turn were used to establish the critical temperature and pressure.

Critical temperatures and pressures have been determined for six different compositions of the methane-ethane-*n*-butane system. These mixtures consisted of two series, each of three compositions differing only in methane content. The data obtained from them, in conjunction with previously reported critical values for the binaries of this system, have been utilized to generate the complete critical locus for the ternary system. The results for the six mixtures of this study have been compared with critical values predicted by methods available in the literature.

The present state of the field concerned with critical constants of hydrocarbon systems for the most part can be divided into two main classifications. A good deal of work is reported for binary systems (*6*), and for the other extreme considerable information is presented for complex mixtures (*8*). Although all of this information is basic and has been used extensively for correlation of critical properties, a gap exists between these two extremes. Experimental data on three- and four-component systems available in the literature are limited (*2*, *4*, *5*, *16*).

The majority of the critical data presented for these systems is a by-product of vapor-liquid equilibrium studies and frequently is not presented in a useful manner. At this time it appears appropriate to undertake a systematic study of these properties as particularly applied to a specific system. A background of this type on several systems is highly desirable in order to bridge the gap presently existing

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