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Michael W. Clark and C. Judson King

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EVAPORATION RATES OF VOLATILE LIQUIDS
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PART II: LIQUID MIXTURES

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ABSTRACT

An approach has been developed for predicting rates of interphase mass transfer under conditions of high flux and high concentration level. A rectangular channel device has been used to measure rates of evaporation of four solutes -- carbon disulfide, n-pentane, cyclopentane and ethyl ether -- from n-tridecane into flowing nitrogen. The evaporation rate of carbon disulfide agreed with the prediction of the interphase theory up to a CS₂ mole fraction of 0.30 in the bulk liquid. For the other three systems a concentration gradient-induced, surface tension-driven cellular convection served to increase liquid phase coefficients substantially. A correlation was obtained for the effect of this cellular motion on the liquid-phase mass transfer coefficient.

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INTRODUCTION

In Part I of this series, which deals with the evaporation of a pure liquid into an adjacent gaseous stream, the analysis of the mass transfer performance of the system was simplified by the lack of mass transfer resistance in the liquid phase. The interfacial concentration of the evaporating species in the gas phase could be obtained directly from the vapor pressure-temperature relationship for the liquid in question. The calculation of mass transfer rates for the evaporation of liquid mixtures is considerably more complex, since the mass transfer resistance can lie in both the gas and the liquid phases. The interfacial gas-phase concentration of a species evaporating from a liquid mixture into an inert gas is not only a function of interfacial temperature, but is also dependent on the ratio of the mass transfer coefficients in the two phases. From a mathematical viewpoint we see that, since the mass transfer resistance is divided between two phases, the problem requires the simultaneous solution of two partial differential equations -- the convective transport equations for both phases. If the complicating factors of high flux and high concentration level are also important, the mathematical problem becomes still more difficult.

The purpose of this portion of the present work was to investigate high-flux, high-concentration-level mass transfer under conditions where the transfer resistance is divided between two phases. A simplified mathematical approach to the situation

was developed, and its predictions were compared with experimental measurements. During the course of the experimental work, cellular convection was observed in the evaporating liquid phase. Because of the large effect which these convection cells had upon the liquid-phase mass transfer coefficients, a detailed study of this effect was also conducted.

The experimental equipment utilized in this study was the same rectangular duct described in Part I. A number of experiments were carried out which involved the evaporation of a volatile component from a nonvolatile solvent (n-tridecane) into a flowing nitrogen stream. The mass transfer conditions and flux level of the experimental system could easily be varied by changing either the nature of the transferred species, the concentration of the transferred species in the liquid or the temperature of the system. Since the equipment had already demonstrated predictable behavior with respect to the stream flow variables,^{6,7,8} the bulk velocities of both streams were fixed for all the experimental runs. The inlet nitrogen flow rate was held at $166 \text{ cm}^3/\text{sec}$, while the feed liquid flow was 0.400 gal/min . The interfacial temperature was controlled to within 0.2°C of a constant value for each solute system.

INTERPHASE MASS TRANSFER

The first major contributions toward the solution of the general two-phase resistance, mass transfer problem were made by Lewis¹⁵ and Whitman.³¹ The "two-film" approach used by these authors resulted in a simple addition of the individual phase resistances to yield the over-all mass transfer resistance. In

recent years this "addition of resistances" principle has been invoked for many other models besides the simple film approach for which it was originally developed.

King¹¹ has shown that there are a number of criteria which should be satisfied by the physical situation in order for the additivity of independently measured individual phase resistances to be valid. In practice, it has been found that the effects of these criteria tend to cancel out one another in equipment providing only a single exposure of the contacting phases, particularly when the additivity principle is applied to the average rather than the local mass transfer coefficients. In complex contacting equipment, such as packed and plate columns, the departure from additivity can be much more severe.

Byers and King^{7,8} have shown that for the cocurrent laminar flow contacting device used in this study the additivity of resistances principle is accurate to better than 2%, provided that the Graetz number ($D_{AB}L/U_{avg} b^2$) is less than 0.50 for the situation in question. It should be noted, however, that this conclusion was for the special case of low flux and low concentration level. From the few other exact solutions of the interphase mass transfer problem, it can be generally stated that the principle of the addition of independently measured resistances tends to be valid if the individual coefficients have similar functionalities with respect to exposure time, or length of contact between phases. The theoretical work discussed in Part I demonstrated that the existence of high flux and high concentration level corrections do not affect the x-direction functionality of

the individual phase mass transfer coefficients; therefore the application of the additivity principle to the rectangular duct apparatus under conditions of high flux and high concentration level should lead to a satisfactory prediction of the over-all behavior of the system.

In order to carry out the addition of resistances under high flux and high concentration level conditions, it is first necessary to define several quantities. A convenient and accurate assumption for most liquid-phase mass transfer calculations is that of constant partial molal volume. This assumption leads to a mass transfer coefficient for the liquid phase which is based on volume fraction driving forces:

$$k'_{\phi,loc} = \frac{N_{A0} - \phi_{A0}(N_{A0} + (\tilde{V}_B/\tilde{V}_A)N_{B0})}{\phi_{A0} - \phi_{A\infty}} \quad (1)$$

$\phi_{A\infty}$ refers to the inlet liquid concentration.

For the limiting case of low flux mass transfer we may then write:

$$k_{\phi,loc} = \lim_{(N_{A0} + (\tilde{V}_B/\tilde{V}_A)N_{B0}) \rightarrow 0} [k'_{\phi,loc}] \quad (2)$$

In a similar manner, we can also develop a set of dimensionless high-flux parameters for the liquid phase, analogous to those used in Part I for the gas phase but based upon volume fraction rather than mole fraction:

$$R_{AB,L} = \frac{\phi_{A0} - \phi_{A\infty}}{N_{A0}} \quad (3)$$

$$\frac{N_{A0} + (\tilde{V}_B/\tilde{V}_A)N_{B0}}{N_{A0}} - \phi_{A0}$$

$$\theta_{AB,L} = k'_{\phi} / k_{\phi} \quad (4)$$

In addition to the local mass transfer coefficients, it is also convenient to define average mass transfer coefficients which are based upon average values of the interfacial flux and the various concentration variables, for example:

$$k'_{\phi, \text{avg}} = \frac{N_{A0(\text{avg})} - \phi_{A0(\text{avg})} \left(N_{A0(\text{avg})} + (V_B/V_A) N_{B0(\text{avg})} \right)}{\phi_{A0(\text{avg})} - \phi_{A\infty}} \quad (5)$$

where the interfacial flux and concentration variables are averaged over the entire mass transfer exposure.

If we now divide Equation 5 into its gas-phase equivalent, while realizing that $-N_{A0,G}$ must be equal to $N_{A0,L}$, we obtain:

$$\frac{k'_{x, \text{avg}}}{k'_{\phi, \text{avg}}} = - \frac{(\phi_{A0} - \phi_{A\infty})(1 - x_{A0})}{(x_{A0} - x_{A\infty})(1 - \phi_{A0})} = \frac{k_{x, \text{avg}}^{\theta_{AB,G}}}{k_{\phi, \text{avg}}^{\theta_{AB,L}}} \quad (6)$$

In order to simplify the remaining calculations the following assumptions will now be made.

1. The perfect gas laws are applicable to the gas phase; i.e., the gas-phase mole fraction can be found from the equation

$$p_A = x_A P \quad (7)$$

2. The liquid phase is a binary mixture, with the components having a constant partial molal volume,

$$C_{AL} = \phi_A / \tilde{V}_A \quad (8)$$

3. Species A is the only substance undergoing mass transfer between the two phases. The liquid solvent is nonvolatile and the second gas-phase component is noncondensable ($N_{B0} = 0$).

Equations 7 and 8 can be combined with a linearized equilibrium expression, $p_A = HC_{A,L} + \text{constant}$, to yield a relation between the liquid-phase volume fraction and the equilibrium value of the gas-phase mole fraction:

$$x_{A0} = (H / p\tilde{V}_A) \phi_{A0} + (\text{constant}) \quad (9)$$

The solution of Equations 6 and 9 determines the two unknown interfacial concentrations, x_{A0} and ϕ_{A0} . Unfortunately Equation 6 is implicit in the unknown interfacial concentrations, because the high-flux correction factors, $\theta_{AB,G}$ and $\theta_{AB,L}$, are both dependent upon the value of the interfacial concentration in the phase in question. Thus a trial-and-error procedure was necessary in order to achieve a final solution of Equations 6 and 9. A brief sketch of the solution technique is given by the following steps.

1. Use the low-flux, low-concentration-level solutions for each phase separately to obtain trial values of x_{A0} and ϕ_{A0} from Equations 6 and 9, ignoring the θ_{AB} , $1-x_{A0}$ and $1-\phi_{A0}$ factors.
2. Using these values for x_{A0} and ϕ_{A0} , obtain a value of $R_{AB,L}$ from Equation 3 and a value of $R_{AB,G}$ from the analogous gas-phase expression. These values of R_{AB} can be used, along with the penetration or Leveque curve (Figure 3, Part I), to obtain values for $\theta_{AB,L}$ and $\theta_{AB,G}$.
3. Using these initial values for the flux-level correction factors in Equation 6, we can solve Equations 6 and 9 for new values of x_{A0} and ϕ_{A0} . These values of the interfacial concentration can then be substituted into step 2, and the

calculation repeated until the value of x_{A0} does not change from one iteration to the next. The assumption of a linear equilibrium relationship is not really necessary. A nonlinear relationship could be used, but it makes the trial-and-error solution more complex.

4. Using the final value of ϕ_{A0} , the average individual liquid phase mass transfer coefficient can be calculated from Equation 5. Alternatively, a gas-phase coefficient can be computed. The resulting average mass flux is then converted into a fraction saturation, and the results can be compared with experimental data. Fraction saturation (F_g) is defined as the ratio of the cup-mixing gas phase solute mole fraction to the mole fraction which would be in equilibrium with the bulk liquid composition at the interfacial temperature.

PHYSICAL PROPERTIES

Four different binary liquid systems were used during the course of the experiments. In each case the nonvolatile solvent was n-tridecane. The volatile species were n-pentane, cyclopentane, ethyl ether and carbon disulfide. For each of these systems it was necessary to accumulate several physical properties for use in the equations to predict F_g from theory. Values of these physical properties are summarized in Table 1.

Vapor-liquid equilibrium data were measured experimentally for each system as a function of concentration level by measuring the bulk exit gas composition for a number of runs made at very low gas flow rates. These data are reported in detail elsewhere,⁹

and were used as the basis for computed F_s . It was found that all systems agreed reasonably well with Raoult's law; the most extreme deviations occurred for ethyl ether, which exhibited an activity coefficient of about 1.25 at high dilution in n-tridecane.

Surface tensions were taken from standard references;^{1,28} that for n-tridecane was calculated to be 26.1 and 25.2 dynes/cm at 20 and 30°C, respectively. Surface tensions of liquid mixtures were computed as

$$\gamma_{\text{mix}} = \sum_j x_j \gamma_j \quad (10)$$

Koefoed and Villadsen¹³ report surface tensions for heptane-hexadecane mixtures as a function of composition. From their data it can be concluded that values of $(\partial\gamma/\partial x_A)$ computed from Equation 10 will be within 5 to 15% of the true value for the various experimental situations encountered in this study.

Densities were determined with a 10-ml pycnometer. The density of n-tridecane was found to be 0.756 and 0.749 g/ml at 20 and 30°C, respectively. Densities for all liquid mixtures showed that there was essentially no volume change upon mixing, thus validating the assumption of constant \tilde{V}_A and \tilde{V}_B .

Gas-phase diffusivities were computed by the methods reported in Part I of this series.

Liquid viscosities were measured as a function of composition with a capillary flow viscometer, kept isothermal in a constant-temperature bath. The results were fitted to a polynomial of the form

$$\mu(\text{cp}) = A + B (xL_A) + C (xL_A)^2 \quad (11)$$

Values of the constants are given in Table 1.

Liquid-phase diffusivities were obtained as a function of concentration by taking the group D_{AB}^{μ} to be linear in mole fraction. Bidlack and Anderson⁵ have shown that the systems hexane-dodecane, heptane-hexadecane and hexane-carbon tetrachloride obey this assumption closely. The diffusivities at infinite dilution were computed by the method of King et al.,¹² which matches the Bidlack and Anderson data well.

Since the liquid-phase diffusivities were strong functions of composition, the computer calculation for k_{ϕ} was modified to provide for a computation of a value of diffusivity at the concentration corresponding to each point in the Crank-Nicholson matrix. These diffusivities were used in the computation of the next set of concentrations in the iterative procedure.

The solution of the convective diffusion equation for each phase was carried out using physical properties evaluated at the known value of T_0 . This procedure constituted a major simplification since it eliminated any need to solve the mass and heat transfer problems simultaneously. The assumption was a reasonable one in view of the relative sensitivity of gas-phase properties to temperature and the fact that the penetration of the temperature profile into the liquid was much deeper than that of the concentration profile.

EXPERIMENTAL RESULTS

Figure 1 shows the results for the evaporation of carbon disulfide from n-tridecane into nitrogen, plotted as F_g vs. bulk liquid mole fraction of solute. The lower solid line represents

the results of the trial-and-error addition of resistances calculation of the interphase mass transfer rate for this system. The upper solid line gives the results for the system if the liquid-phase resistance is hypothetically taken to be negligible compared to the gas-phase resistance. As can be seen, the resistance to mass transfer is nearly evenly divided between phases. The experimental data agree fairly well with the theoretical curve, up to a liquid-phase mole fraction of 0.300. Figures 2, 3 and 4 give a comparison of experimental results with theory on a similar basis for three other solutes evaporating from n-tridecane. As can be seen, the argument for these systems is quite poor, with the ethyl ether system showing the most marked deviation from the predicted behavior. Full experimental data are reported elsewhere.⁹

The behavior of the n-pentane, cyclopentane and ethyl ether systems was traced to a form of cellular convection which was operative in the liquid phase. Under close visual examination of the liquid in the surface region, small streamers could be seen, which were moving in a vertical direction as they were swept along by the fluid motion.

A confirmation that the anomalous mass transfer behavior was caused by a liquid-phase phenomenon is given in Figure 5, which represents an experimentally obtained concentration profile for the n-pentane system. As can be seen, the experimental profile is at an intermediate position between the predicted profile and the profile for $k_{\phi} = \infty$, which again indicates that the liquid-phase mass transfer coefficient is much higher than its

predicted value, while the gas phase is behaving in the manner predicted. Using the experimental values of x_{A0} and F_g we can calculate a value of $k_\phi(\text{exp}) / k_\phi(\text{theory})$ of 1.4, whereas a calculation of $k_x(\text{exp}) / k_x(\text{theory})$ from the same data was found to be 0.921. Thus the gas-phase coefficient was within 8% of its predicted value, whereas the liquid coefficient was off by 40%.

Another manifestation of this cellular interfacial motion was a randomly fluctuating output signal from the thermocouple temperature probes (both inlet and outlet) when they were in the liquid phase. The fluctuation was most pronounced in the region 0.025 to 1.00 inches below the liquid surface, and probably resulted from the intermittent downward mixing of the cooler interfacial liquid.

After it had been shown that the increased liquid-phase mass transfer coefficient was caused by cellular convection, it was next necessary to ascertain which of four possible mechanisms was producing the flow instability. These four mechanisms can be summarized as:

1. Surface tension driven, induced by temperature gradients.
2. Surface tension driven, induced by concentration gradients.
3. Density driven, induced by temperature gradients.
4. Density driven, induced by concentration gradients.

In order to make this decision, it was necessary to examine the previous work which has been carried out in the area of interfacial cellular convection.

Cellular Convection

A large portion of the work on cellular convection has been devoted to the prediction of the onset of the flow instability. The actual driving forces which produce the fluid motion have been shown to be related to the spatial variation of two fluid properties, density and surface tension. This variation can be brought about whenever the fluid is undergoing either heat or mass transfer. A number of investigators have considered the density-driven, temperature-induced problem using linear perturbation theory and a simple situation of a fluid between two semi-infinite flat plates. The initial solution carried out by Lord Rayleigh²⁶ assumed that both the upper and lower surfaces were at constant temperatures, and that the liquid could circulate freely at the surface with no slip. Subsequent solutions by Pellew and Southwell,²³ Low¹⁶ and Sparrow et al.²⁷ have extended the solution to a number of other boundary conditions. A listing of the various solutions and the assumptions inherent in each can be found in the summary by Berg, Acrivos and Boudart.³ The primary value of all these solutions is their ability to predict the conditions required for the onset of cellular convection. Although the exact stability criteria of the system are dependent upon the wavelength of the initial disturbance, the theory is also able to predict a region that is stable to any disturbance provided that a single dimensionless variable, R , is less than a given critical value.

$$R = g \beta_T \frac{\partial T}{\partial y} h^4 / \alpha \nu \quad (12)$$

This dimensionless group, which is called the Rayleigh number, has different critical values ranging from 657 to 1710, depending upon the applicable boundary conditions.

In 1958, Pearson²² succeeded in obtaining a similar solution for the surface tension-driven phenomenon. The results of Pearson's analysis can be expressed in a manner similar to those of the density-driven problem, where the region of stability is defined by one dimensionless variable, the Thompson number,

$$Th = - \left(\frac{\partial \gamma}{\partial T} \right) \left(\frac{\partial T}{\partial y} \right) h^2 / \alpha \mu \quad (13)$$

The critical values for the Thompson number were found to be 80 for the isothermal case and 48 for the constant flux case.

Since Pearson's theoretical work was published in 1958, several experimenters have attempted to verify his theoretical predictions. The experimental results have thus far exhibited a large amount of scatter; however, convection has not been encountered at a Thompson number which was below the theoretically predicted value. Recent data published by Berg *et al.*⁴ give experimentally observed values of critical Thompson number which are one to two orders of magnitude higher than the theoretically predicted ones.

An assumption which is inherent in the analyses which have been made of both the density- and surface tension-driven flows is that of a linear temperature gradient between the upper and lower surfaces. This is often a good assumption for a temperature profile, but for the analogous problems that are caused by concentration gradients it frequently becomes quite poor. This

is primarily because of the exceedingly low values of liquid-phase diffusivity, which lead to small penetration depths and therefore nonlinear, undeveloped profiles in many situations. Another difference between the temperature-dependent and the concentration-dependent problems is in the properties entering into the Thompson and Rayleigh numbers; these are given in their concentration-dependent form below.

$$\text{Th} = \left(\frac{\partial \gamma}{\partial C_A} \right) \left(\frac{\partial C_A}{\partial y} \right) h^2 / D_{AB} \mu \quad (14)$$

$$\text{R} = \text{g} \left(\frac{\partial \rho}{\partial C_A} \right) \left(\frac{\partial C_A}{\partial y} \right) h^4 / D_{AB} \nu \quad (15)$$

Nonlinear Theory

The key to a successful theoretical prediction of the flow patterns and hence the mass transfer coefficients for finite cellular convection lies in the nonlinear terms in the equations of motion. Thus far the basis of the nonlinear work attempted has been an incomplete form of the equations of motion obtained by neglecting the temperature dependence of all physical properties except density. This method of attack is known as the Boussinesq approximation. Only the density-driven problem has been considered using the nonlinear approach.

Cellular convection was first treated in this manner by Pillow²⁵, who considered the problem of two-dimensional flow between two flat plates at different temperatures. After making several simplifying assumptions, he was able to predict a 5/4 power dependence of heat transfer rate upon the temperature driving force, a number that has been frequently confirmed

experimentally for natural convection from a heated horizontal plate.¹⁰ This is equivalent to the well-known experimental relationship for natural convection, which gives²⁴

$$h = (\text{const.})(\text{Gr}^{\frac{1}{4}}).$$

Several other solutions have been obtained by various techniques. Malkus and Veronis¹⁷ used a perturbation technique which retained the first three terms in an expansion of the variables. Kuo¹⁴ obtained the 5/4 power dependence, or equivalently the 1/4 power dependence of the Nusselt number upon the Rayleigh number by expanding the dependent variables in orthogonal series.

The nonlinear mathematical approach has a high potential, since a complete solution would yield the entire flow pattern for the problem under consideration. Unfortunately the high degree of mathematical complexity required for such a solution makes the task appear quite formidable, at best. To date there does not appear to have been any attempt to use the nonlinear approach to analyze the surface tension-driven problem of cellular convection.

There has been relatively little experimental work carried out in the general area of surface tension-driven, cellular convection and its effect upon mass transfer. Of the papers which have been published, a number have been concerned with the photographic observance of the phenomenon. A number of investigators^{19,20,21,29,etc.} have reported increases in liquid-liquid and gas-liquid mass transfer coefficients which they attributed to instabilities of this sort. Bakker, Buytenen and Beek² used

an order-of-magnitude physical argument to estimate the increase in mass transfer rate due to interfacial instabilities. These authors found a two- to threefold increase in mass transfer coefficients which agreed fairly well with their calculational approach. Maroudas and Sawistowski¹⁸ have obtained quantitative mass transfer data for liquid-liquid systems undergoing surface tension-driven cellular convection. They calculated fractional rates of surface renewal from their experimental data for use in the Danckwerts surface renewal approach. The fractional rate of surface renewal cannot be predicted a priori, but must instead be correlated against experimental data.

Evaluation of Experimental Results

In view of the work which has been carried out thus far, there does not appear to be any satisfactory method for predicting the quantitative effect of surface tension-driven cellular convection upon mass transfer coefficients.

Since each of the four mechanisms cited previously can be associated with an appropriate form of the Thompson or Rayleigh group, an estimate of the value of these groups operative during the present experiments should give an indication of which mechanism was most important. A qualitative analysis of the situation shows that any of the above mechanisms could have been responsible for the observed cellular convection in three of the four cases, since all of the driving forces were in the direction leading toward an unstable situation. In order to assign a numerical value to the Thompson and Rayleigh groups, a number of assumptions were necessary, because of the large

differences between the flow situation at hand and the theoretical problems for which critical Thompson and Rayleigh numbers have been devised.

The concentration and temperature profiles used for obtaining values of h , $\frac{\partial C_A}{\partial y}$, and $\frac{\partial T}{\partial y}$ were calculated following the simple penetration approach for the liquid phase, and ignoring the presence of the cells. Thus

$$\frac{\partial C_A}{\partial y} = \left(\frac{\partial C_A}{\partial y} \right)_0 = - \Delta C_A \sqrt{\frac{U_{int}}{\pi D_{AB} x}} \quad (16)$$

Similarly,

$$\frac{\partial T}{\partial y} = \left(\frac{\partial T}{\partial y} \right)_0 = - \Delta T \sqrt{\frac{U_{int}}{\pi \alpha x}} \quad (17)$$

h was found from the equations

$$h = \sqrt{D_{AB} x / U_{int}} \quad (18)$$

$$h = \sqrt{\alpha x / U_{int}} \quad (19)$$

for the concentration-dependent and temperature-dependent situations, respectively. These equations provide an indication of the depth to which the concentration profile has penetrated, in the absence of convection cells.

All of the other physical properties in the Rayleigh and Thompson groups were assumed to be constant at the values associated with the interfacial conditions. For convenience, the interfacial temperature was taken as the measured value but the value of interfacial concentration was taken as that obtained by using the interphase solution in the absence of cellular convection. This value is higher than the actual experimental value

when cells are present, because of the mixing of the liquid phase caused by the existence of any finite cellular convection.

There were several reasons for ignoring the effect of the cellular motion on the interfacial concentration and on the predictions of Equations ^{16,} 17, 18 and 19 for the computation of the Thompson and Rayleigh numbers. First of all, these properties are not altered by cellular motion at or below the critical Rayleigh or Thompson number where the motion first begins. One important reason for neglecting the cell effect above the critical Rayleigh or Thompson number is that one would prefer to determine the influence of the cellular convection from a direct and non-iterative calculation based upon known or easily predicted quantities. A second reason is based upon the assumption that the magnitude of the cellular convection effect is a function of the driving force, or the ratio of the Thompson or Rayleigh group to the critical value. If this is a correct assumption, then it is only necessary to employ values of temperature and concentration gradients, h and interfacial concentration uniquely related to the true value. The proposed method is a convenient approach for obtaining such a value.

Upon calculation of the Thompson or Rayleigh numbers for each of the four possible situations, it was discovered that the surface tension-driven, concentration gradient-induced mechanism yielded a value of the Thompson number which was two orders of magnitude larger in relation to the critical Th or R than occurred for the other mechanisms. To illustrate the values of Th and R in the four situations, the results of a

sample calculation carried out for n-pentane/tridecane at a pentane mole fraction of 0.05 are given below.

(1) For the concentration gradient-induced case:

$$Th_{avg} = 13,900$$

$$R_{avg} = 26$$

(2) For the temperature gradient-induced case:

$$Th_{avg} = 93$$

$$R_{avg} = 155$$

These values of the Rayleigh and Thompson groups are averaged along the entire channel length; since R and Th vary as $x^{\frac{1}{2}}$, the average is 2/3 of the value at the exit probe.

Of the four mechanisms, two tend to predominate, the concentration gradient-induced, surface tension-driven instability and the temperature gradient-induced, density-driven instability. This is primarily due to the dependence of the groups on h, which is h^2 for Th and h^4 for R. Because of the extremely low value of the liquid-phase diffusivities, h tends to be quite small for the concentration profile; thus the value of Th tends to be much larger than the value of R for the concentration-dependent situation. For the temperature-dependent forms the reverse is true. The penetration depths for the temperature profiles tend to be fairly large, making the density-driven situation relatively more important than the surface tension-driven one.

The CS_2/n -tridecane system should not exhibit concentration gradient-induced cellular convection, since both the density

and the surface tension of CS_2 lie in the wrong direction from that of tridecane. The results for this system shown in Figure 1 support this conclusion, with the agreement between experiment and interphase theory remaining quite good at values of XL_A up to 0.30 or more. This good agreement for the CS_2 system serves to substantiate the validity of the approach used for the prediction of interphase mass transfer rates in the absence of cellular convection.

The deviation which finally begins to occur in the CS_2 /tridecane data at the higher concentration levels can be attributed to temperature gradient-induced, density-driven cells. This hypothesis is supported by the calculated value of the Rayleigh number for the carbon disulfide/tridecane system at $\text{XL}_A = 0.30$. R_{avg} is 1600, a value which is significantly larger than the theoretical critical value of approximately 650. To show that the cellular convection in the three other experimental systems was apparently not strongly influenced by density-driven cells, the values of XL_A which yield a calculated value of $R_{\text{avg}} = 1600$ are $\text{XL}_A = 0.24$ for n-pentane/tridecane, $\text{XL}_A = 0.27$ for cyclopentane/tridecane, and $\text{XL}_A = 0.22$ for ethyl ether/tridecane.

Convection cells in the liquid near the interface were also noticed for the evaporation of pure liquids discussed in Part I. This occurred at high liquid volatilities and resulted in a noticeable lessening of the interfacial temperature depression. Presumably these cells resulted from the temperature gradient-induced, density-driven mechanism.

Since the majority of the cellular convection appeared to

be attributable to the concentration gradient-induced, surface tension-driven mechanism, an effort was made to correlate the mass transfer behavior of the liquid phase with the physical parameters which lead to this type of cellular convection. It was found that a single value of $Th_{cr} = 8000$ was sufficient to predict the point of instability of all the experimental systems studied. A table of the values of XL_A which corresponds to $Th_{cr} = 8000$ is given below.

n-pentane/tridecane	$XL_{A,cr} = 0.029$
ethyl ether/tridecane	$XL_{A,cr} = 0.014$
cyclopentane/tridecane	$XL_{A,cr} = 0.071$

At present the most promising theoretical approach towards predicting the effect of surface tension-driven cellular convection upon the mass transfer behavior of a system appears to lie in the solution of the nonlinear flow equations. An approach similar to the one used by Malkus and Veronis¹⁷ or that due to Kuo¹⁴ should at least predict the behavior in the region near the critical point for flow instability. Unfortunately, as was pointed out earlier, such a solution does not presently exist. An alternative procedure is to use the approach of dimensional analysis, which leads to the following expressions:

$$Sh = f(Th, Sc, Re) \quad \text{above } Th_{cr} \quad (20)$$

and

$$Sh = f'(Sc, Re) \quad \text{at or below } Th_{cr} \quad (21)$$

From the above two expressions, and in view of the results obtained by Kuo and others for the somewhat analogous heat transfer problem, it appears that a reasonable form for correlation of the experimental data is:

$$k'_{\phi} / k'_{\phi, CD} = f \left[\frac{Th}{Th_{cr}}, Sc, Re \right] \quad (22)$$

The variable $k'_{\phi, CD}$ is the value of the liquid-phase mass transfer coefficient which is predicted theoretically by simple convective diffusion theory, the value at or below the point where the flow instability is first observed, with concentration, flux and physical property corrections to the actual concentration level taken into account.

A correlation of the type given by Equation 22 has the advantage of giving the increase in mass transfer due to cellular convection effect alone. Thus the resistance to mass transfer in the presence of cellular convection is obtained by simply multiplying the expected liquid-phase mass transfer coefficient by a correction factor to obtain the actual mass transfer coefficient.

The experimental results of this study are shown in Figure 6, plotted in the form suggested by Equation 22. As can be seen, the agreement between the three different systems -- n-pentane, cyclopentane, and ethyl ether -- is quite good when placed on this basis. It is interesting to note that the increase in the mass transfer coefficient due to cellular convection can be quite large for some systems, such as the ethyl ether/tridecane mixture where the observed value of $k_{\phi, avg}$ reached 10 to 20 times the expected value. Another fact which may be observed from Figure 6 is that the initial slope is approximately the same as indicated by the nonlinear heat transfer analysis for density-driven cells, a $\frac{1}{4}$ -power dependence upon

the Thompson (or Rayleigh) number ratio.¹⁴ The dashed straight line in Figure 6 indicates the $\frac{1}{4}$ -power dependence, and can be seen to be tangent to the results obtained experimentally in the vicinity of the critical value of the Thompson number.

An examination of the quantities entering into the correlation given by Figure 6 shows that the correlation is essentially one of $k'_{\phi} / k'_{\phi,cr}$ versus $\Delta\phi / \Delta\phi_{cr}$, since the other quantities in the Thompson number are only weak functions of concentration. There are several other factors which need to be explored in more detail experimentally and theoretically. Among these are the effect of the ratio of gas-phase to liquid-phase mass transfer coefficient, k_x / k_{ϕ} , which was varied only slightly during this work. Substantial changes in this ratio could invalidate the procedure used to calculate $\phi_{A\infty} - \phi_{A0}$ for use in the Thompson number. A second point is that the liquid depths utilized in this study were rather large; therefore any application of these results to systems having very small liquid depths, or differing flow characteristics, should be made with caution. Because of the similar physical constants of the liquid systems involved, the Sc variation was not large, and therefore the effect of Schmidt number, if any, could not be determined. Also, the effect of different liquid-phase Reynolds numbers was not explored in this work. Further experimental work with more diverse systems at widely different flow rates should be carried out to define the effects of these two groups. Finally, minute concentrations of surface-active impurities could radically affect the flow characteristics of the surface

tension-driven cellular convection. This type of situation would be most likely to occur in an aqueous system, usually bringing about a large reduction in the quantity of cellular convection from that which would be predicted for such a system.

CONCLUSIONS

Part I:

1. A high flux solution has been obtained for the case of a linear velocity gradient in a semi-infinite flowing fluid (the Leveque model).

2. The high flux and high concentration level correction factors proposed in this work have been confirmed experimentally for the case of evaporation of pure volatile liquids into a flowing gas stream.

3. A simple calculational approach has been developed for the prediction of the effect of mass transfer upon the interfacial temperature of a liquid (or liquid mixture) evaporating into a laminar gas stream. This method was confirmed experimentally.

Part II:

4. A trial and error, addition of resistances technique has been developed to predict interphase, high flux and high concentration level mass transfer rates. This procedure was also confirmed experimentally for the evaporation of CS_2 from n-tridecane into nitrogen.

5. An experimental correlation has been developed which accurately predicts the effect of surface tension-driven

cellular convection upon the average liquid-phase mass transfer coefficient, provided the Reynolds number and Schmidt number variation is not large.

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REFERENCES

1. American Chemical Society, "Physical Properties of Chemical Compounds," Advances in Chemistry, No. 22, Vol. 2 (1959).
2. Bakker, C. A. P., P. M. Buytenen, and W. J. Beek, Chem. Eng. Sci., 21, 1039 (1966).
3. Berg, J. C., A. Acrivos and M. Boudart, Advances in Chemical Engineering, Vol. 6, Academic Press, New York (1966).
4. Berg, J. C., Dissertation, University of California, Berkeley, 1964.
5. Bidlack, D. L., and D. K. Anderson, J. Phys. Chem., 68, 3790 (1964).
6. Byers, C. H., Dissertation, University of California, Berkeley, 1966.
7. Byers, C. H., and C. J. King, A.I.Ch.E. Journal, 13, 628 (1967).
8. ———, ibid., p. 637.
9. Clark, M. W., and C. J. King, U.S. Atomic Energy Commission Report UCRL-17527 (1967).
10. Jakob, M., "Heat Transfer," Vol. 1, John Wiley & Sons, New York, 1949.

11. King, C. J., A.I.Ch.E. Journal, 10, 671 (1964).
12. King, C. J., L. Hsueh and K. Mao, J. Chem. Eng. Data, 10, 348 (1965).
13. Koefoed, J., and J. V. Villadsen, Acta Chem. Scand., 12, 1124 (1958).
14. Kuo, H. L., J. Fluid Mech., 10, 611 (1961).
15. Lewis, W. K., Mech. Eng., 44, 445 (1922).
16. Low, A. R., Proc. Roy. Soc. (London), A125, 180 (1929).
17. Malkus, W. V. R., and G. Veronis, J. Fluid Mech., 4, 225 (1958).
18. Maroudas, N. G., and H. Sawistowski, Chem. Eng. Sci., 19, 919 (1964).
19. Merson, R. L., and J. A. Quinn, A.I.Ch.E. Journal, 11, 391 (1965).
20. ———, ibid., 10, 804 (1964).
21. Muenz, K., and J. M. Marchello, ibid., 12, 249 (1966).
22. Pearson, J. R. A., J. Fluid Mech., 4, 225 (1958).
23. Pellew, A., and R. V. Southwell, Proc. Roy. Soc. (London), A176, 312 (1940).
24. Perry, R. H., "Chemical Engineers Handbook," 4th ed., McGraw-Hill Book Co., Inc., New York, 1963.
25. Pillow, A. F., Aeronaut. Res. Rept. Australia, A79, 1 (1952).
26. Rayleigh, Lord, Phil. Mag. (6) 32, 529 (1916).
27. Sparrow, E. M., R. J. Goldstein, and V. K. Johnson, J. Fluid Mech., 18, 513 (1964).
28. Timmermans, J., "Physico-chemical Constants of Pure Organic Compounds," Elsevier, New York, 1950.

29. Ward, W. K., and J. A. Quinn, A.I.Ch.E. Journal, 11, 1005 (1965).
30. Westkaemper, L. E., and R. R. White, ibid., 3, 69 (1957).
31. Whitman, W. G., Chem. Met. Eng., 29, 146 (1923).

NOMENCLATURE

c	total concentration (gmoles/cm ³)
C _A	concentration of species A (gmoles/cm ³)
D _{AB}	diffusion coefficient in the binary system A-B (cm ² /sec)
Gr	Grashof number (dimensionless)
g	acceleration due to gravity (cm/sec ²)
H	Henry's law constant (atm cm ³ /gmoles)
h	depth of a liquid layer (cm); also used in this study as the penetration depth of a concentration or temperature profile in the liquid phase.
k	mass transfer coefficient at low flux conditions (gmoles/cm ² sec)
k'	mass transfer coefficient (applicable at high flux conditions) (gmoles/cm ² sec)
N _A	molar flux of component A relative to stationary coordinates (gmoles/cm ² sec)
P	pressure (atm)
R	Rayleigh number (dimensionless)
R _{AB}	dimensionless flux ratio
Re	Reynolds number (dimensionless)
Sc	Schmidt number (dimensionless)
Sh	Sherwood number (dimensionless)
T	temperature (°C)
Th	Thompson number (dimensionless)

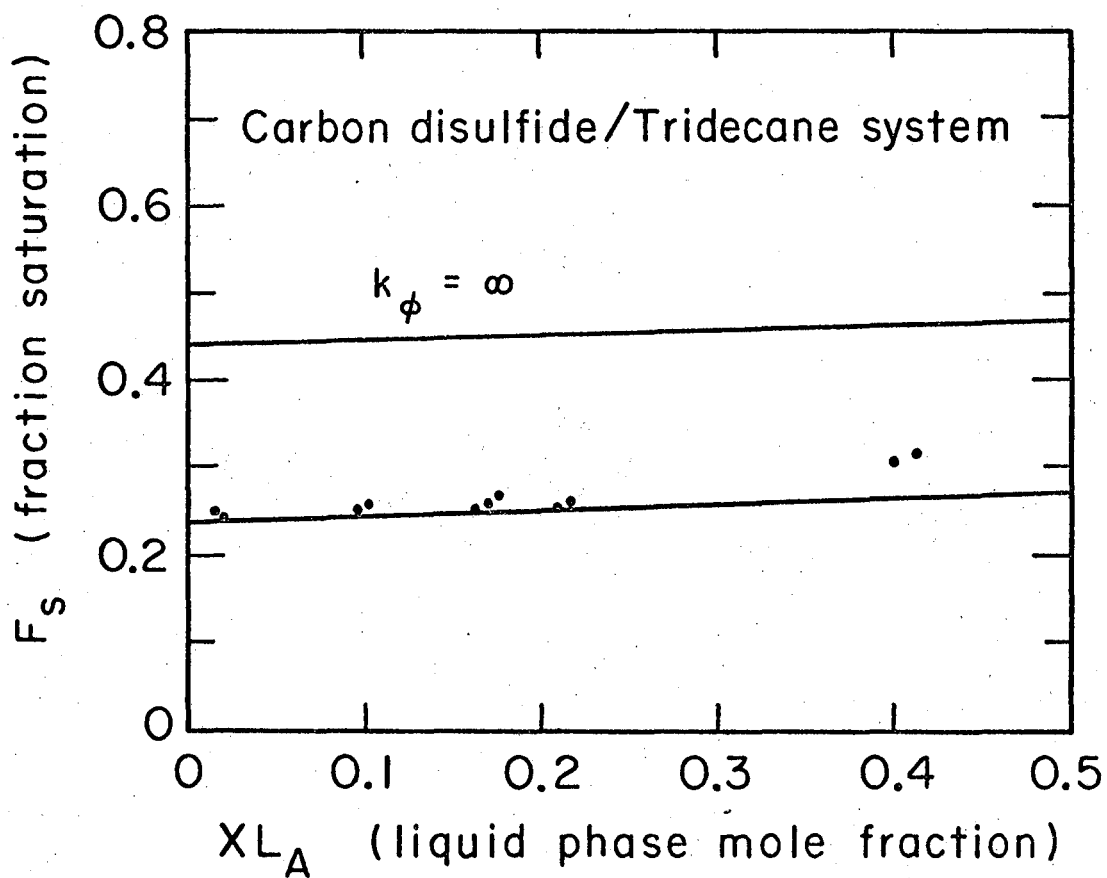
U_{int}	interfacial x-direction velocity (cm/sec)
\tilde{V}	partial molal volume (cm^3/gmole)
x	horizontal distance variable (cm)
x_A	mole fraction of component A (used in gas phase)
XL_A	liquid-phase mole fraction of component A (volatile solute)
y	vertical distance variable (cm)
α	thermal diffusivity (cm^2/sec)
β	coefficient of thermal expansion ($^{\circ}\text{C}^{-1}$)
γ	surface tension (dynes/cm)
Δ	difference in quantity between interfacial and bulk conditions
θ_{AB}	dimensionless flux correction factor
μ	viscosity (poises)
ν	kinematic viscosity (stokes)
φ_A	volume fraction of component A (used in liquid phase)

Variable Subscripts

A,B	refers to components A, B, etc.
AB	refers to the binary system composed of components A and B
avg	average of a quantity
CD	predicted by simple convection diffusion theory
cr	at the critical point for cellular flow instability
G	gas
int	quantity evaluated at the interfacial position
L	liquid
loc	a local or point value
o	quantity evaluated at the interfacial position
x	based upon mole fractions (used for gas phase)
φ	based upon volume fractions (used for liquid phase)
∞	quantity evaluated at a large distance from the gas-liquid interface, equivalent to inlet conditions

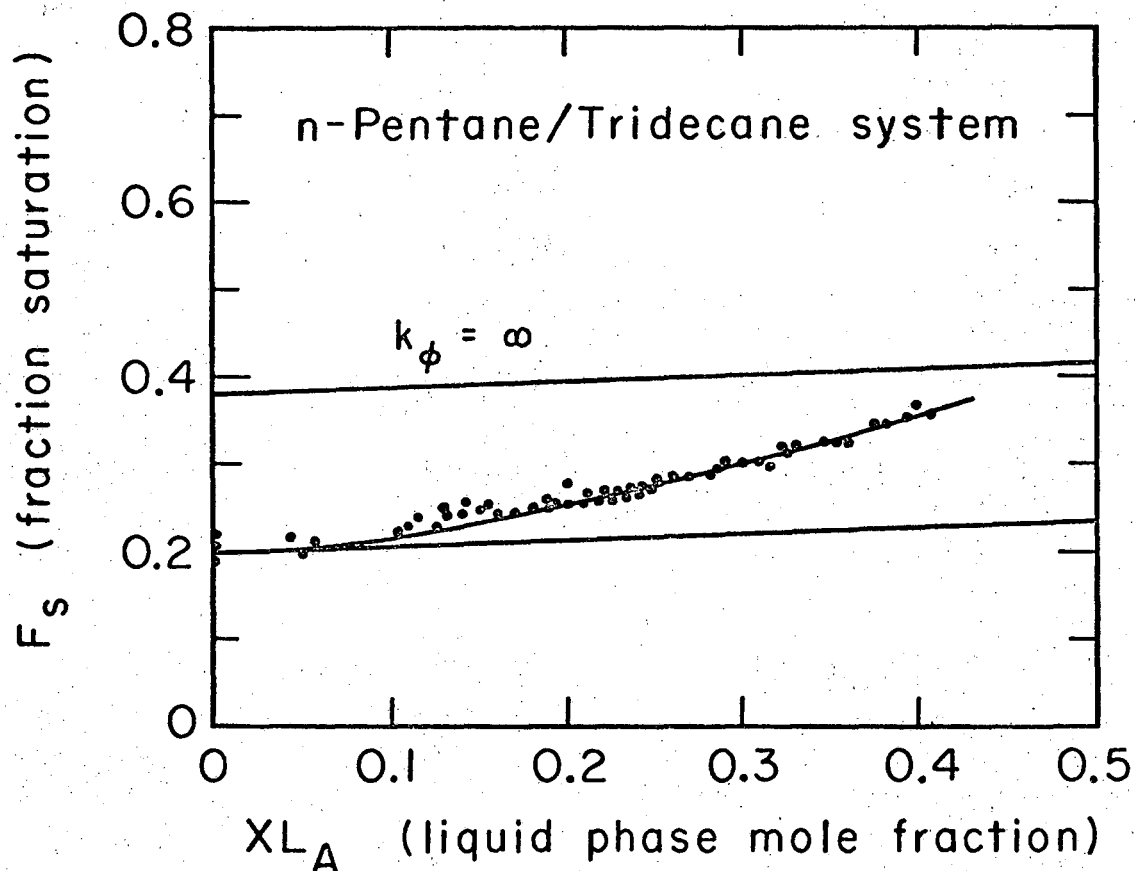
Table 1. Physical Properties for Different Solutes

	<u>n-Pentane</u>	<u>Cyclo pentane</u>	<u>Ethyl ether</u>	<u>Carbon disulfide</u>
T_0 (°C)	20	25	25	30
Vapor pressure at T_0 (mm Hg)	418.8	314.9	535.1	426.4
Surface tension (dyne/cm)				
20°C	16.00	22.57	17.06	33.07
30°C	-	21.17	15.95	32.25
Density (g/ml)				
20°C	0.626	0.745	0.714	1.263
30°C	0.616	0.735	0.702	1.250
Gas phase diffusivity with N_2 at T_0 (cm^2/sec)	0.0882	0.0943	0.0975	0.1112
Viscosity constants at T_0 for mixtures with n-tridecane				
A	1.92	1.730	1.730	-
B	-2.74	-1.323	-2.332	-
C	1.06	0	0.824	-
Diffusivities at T_0 at high dilution ^o ($cm^2/sec \times 10^5$)				
a. Solute in n-tridecane	1.10	1.16	1.17	1.33
b. n-Tridecane in solute	3.71	1.97	3.82	2.88



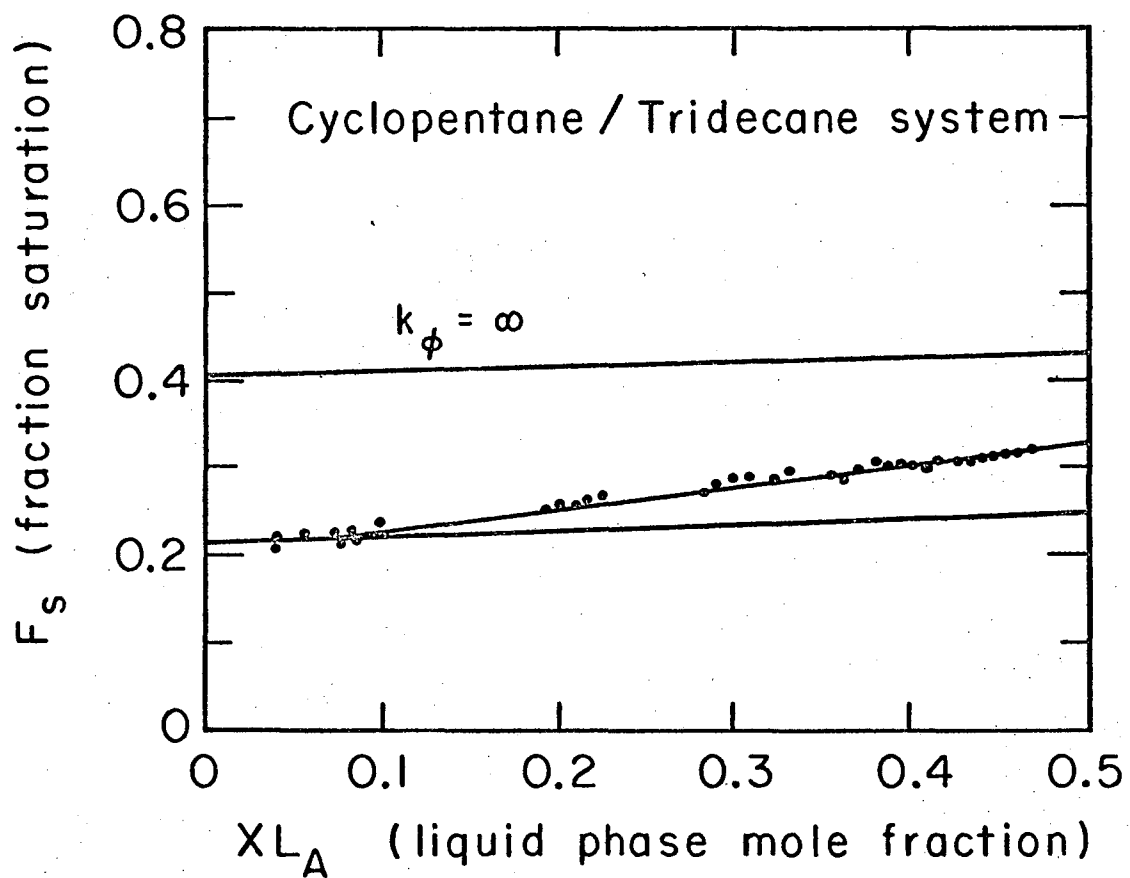
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Figure 1. Evaporation of carbon disulfide from n-tridecane.



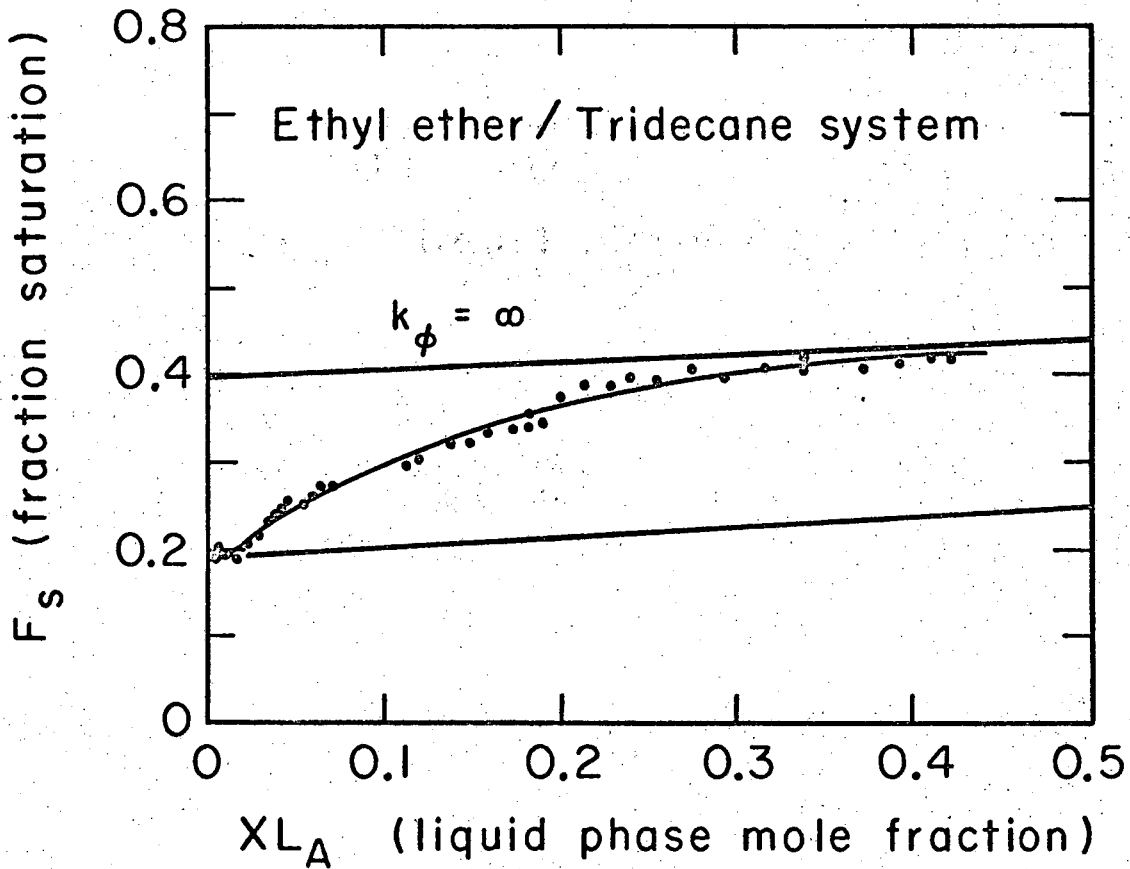
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Figure 2. Evaporation of n-pentane from n-tridecane. $T_o = 20^\circ\text{C}$.



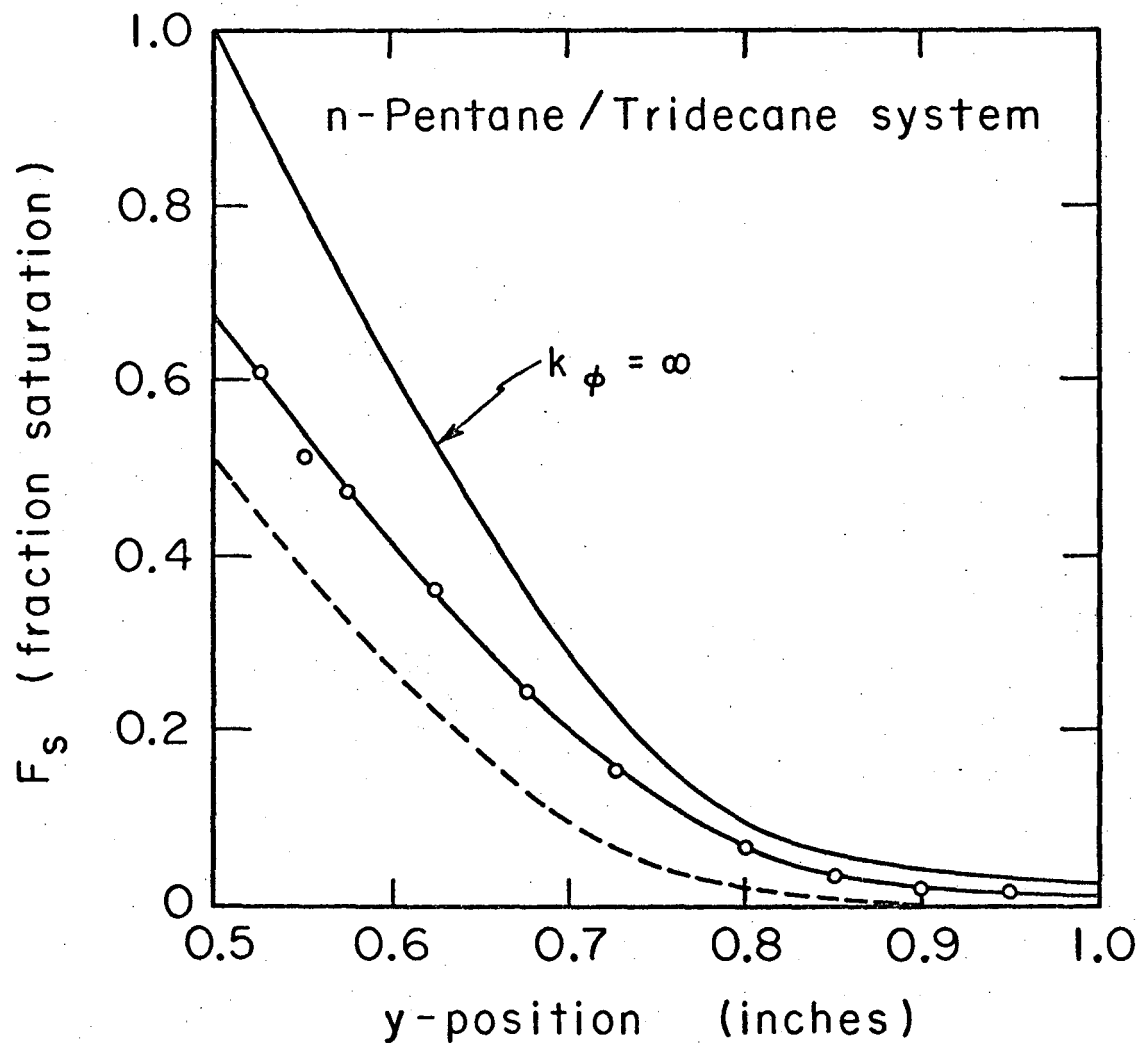
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Figure 3. Evaporation of Cyclopentane from n-tridecane. $T_o = 25^\circ\text{C}$.



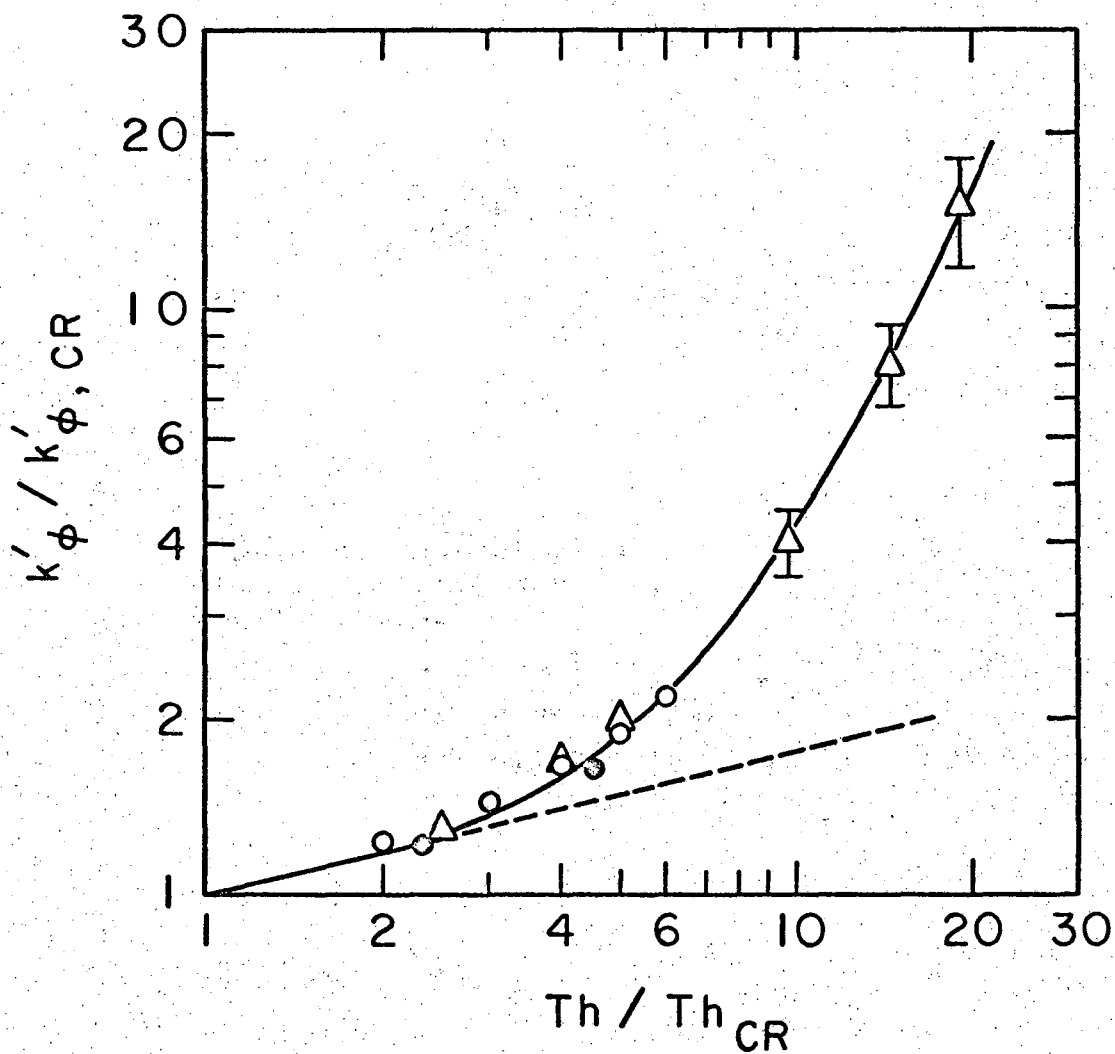
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Figure 4. Evaporation of ethyl ether from n-tridecane. $T_0 = 25^\circ\text{C}$.



XBL675-3126

Figure 5. Gas-phase concentration profile at channel exit for evaporation of n-pentane from n-tridecane. $XL_A = 0.185$; $T_o = 20^\circ\text{C}$.



XBL675-3133

Figure 6. Correlation of the effect of surface tension-driven cellular convection upon liquid-phase mass transfer coefficients.

- Δ - ethyl ether/tridecane system
- o - n-pentane/tridecane system
- \bullet - cyclopentane/tridecane system

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