Int. J. Heat Mass Transfer. Vol. 4, pp. 47–62. Pergamon Press 1961. Printed in Great Britain.

HEAT AND MASS TRANSFER BETWEEN THE GASEOUS AND LIQUID PHASES OF A BINARY MIXTURE

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Abstract—A rigorous theoretical analysis is presented of the heat and mass transfer occurring at an element of the interface separating the liquid and gaseous phases of a binary mixture. Solutions of the equations are presented for ethanol–water mixtures, three separate cases being considered, namely—(i) the bulk liquid and gas states are not saturated, and both Lewis numbers equal to unity; (ii) the bulk states are saturated and both Lewis numbers equal unity; and (iii) the liquid Lewis number is close to zero, while the gaseous one equals unity, the bulk states being either saturated or not. Results are compared with the predictions of the approximate (equi-molal transfer) treatment conventionally used (e.g. [1]).

It is shown that the conventional theory only gives tolerable accuracy for case (ii); in the other cases its prediction bears almost no relation to those of the rigorous theory.

The rigorous theory shows that, in the examples considered, either net condensation or net vaporization may occur, depending on the conductance values and the bulk states. In some cases the more volatile component is caused to condense despite having a higher gas-phase concentration at the interface than in the bulk of the gas.

NOMENCLATURE

B,	driving force for mass transfer (equation 1) (Dimensionless);
f,	mass of one of the components per mass of mixture (equation 3) (Dimensionless);
g,	mass-transfer conductance (equation 1) (kg/m^{2}h);
g^*,	value of g corresponding to zero mass transfer (equation 9) (kg/m^{2}h);
h,	specific enthalpy of mixture (equation 4) (kcal/kg);
Δh_i,	latent heat of vaporization of component i (equation 16a) (kcal/kg);
$\dot{m}''$,	net mass transfer rate (equation 1) (kg/m^{2}h);
m_i'',	mass transfer rate of component i (equation 19) (kg/m^{2}h);
M_i,	molecular weight of component i (equation 16) (kg/kg mole);
P,	any conserved property (equation 2) (various);
t,	temperature (equation 10) (°C).

Subscripts

f, h,	pertaining respectively to concentration and to enthalpy;
I, II,	respectively the gaseous and the liquid phases;
i, C_2H_5OH, H_2O,	Mixture components;
G, S, T, L, F, G_S, T_S, F_L, T_L,	Mixture states.

1. INTRODUCTION

1.1. *The problem considered*

We shall consider the interactions which occur across the interface between a liquid and a gaseous phase, when each consists of a mixture of the same two chemical compounds. Such liquid–gas contact of binary mixtures occurs in many situations of engineering importance, for example: in the rectification column of a plant producing liquid air; in the de-aerator of a steam power plant; and in the rectification column of an absorption-type refrigeration plant employing ammonia–water mixtures.

The questions to be asked are: How can we predict the rates of heat and mass transfer across an element of the interface when the bulk states of the liquid and of the gas are given? What is the nature of the material which is transferred? And how are the answers to these questions dependent on the "conductances" of the liquid and gas boundary layers?

Answers to the questions are needed for three

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reasons. Firstly, a knowledge of the answers might facilitate the design of continuous-contact rectification columns in the future. Secondly, such knowledge throws light on the transfer processes which occur between the vapour bubbles and the liquid on the trays of a plate-type column. Thirdly, although many of the most important rectification processes, for example those occurring in the petroleum industry, involve multicomponent mixtures, it seems certain that a full understanding of the processes in binary mixtures must precede that of the more general case.

It should be stressed that attention is confined to local and instantaneous conditions: we shall not here consider how our findings influence the variations with position of the bulk liquid and gas states throughout the tower or the variations with time of these states in an unsteady-state experiment. However, the present study is a necessary preliminary to the solution of the latter problems, which it is hoped to deal with in later publications.

1.2. *Earlier treatments of the problem*

Despite the crucial importance of the process under consideration, no rigorous treatments of it appear to have been published,† at least in the Western literature. Instead, textbooks on mass transfer, distillation, absorption, etc. [1–3] present an approximate treatment similar to that described in section 3 below.

However, the approximate treatment, though satisfactory in many cases, sometimes predicts mass transfer rates which are incorrect, not only in magnitude but also in sign. Moreover, it obscures some aspects of the phenomenon which must be clearly perceived if understanding of the efficiency of bubble-cap plates, for example, is to advance.

1.3. *Purposes of present work*

The aim of the present paper is therefore to provide a rigorous treatment of the problem, i.e. to provide, for the questions indicated above, answers which are consistent with the laws of heat and mass transfer. This purpose could be fulfilled simply by writing down the complete set of governing equations and indicating a suitable numerical solution procedure; the more extended discussion presented below must therefore be justified by reference to two further aims.

The first of these is to provide *insight* into what governs the heat and mass transfer processes; it is for this purpose that graphical methods are employed. The second aim is to see whether these processes can be adequately described and calculated by fitting them into the framework of a recently developed standard formulation of the convective mass-transfer problem [4].

2. THEORY

2.1. *The system considered*

Figure 1 illustrates an element of the interface separating the gas from the liquid. It will be supposed that gradients of composition and temperature are confined to relatively thin boundary layers on either side of the interface, and that outside these regions it is meaningful to speak of the "bulk" states of the gas and of the liquid. These will be designated the G- and F-states respectively.

The state of the gas immediately adjacent the interface is generally different in both composition and temperature from that of the bulk of

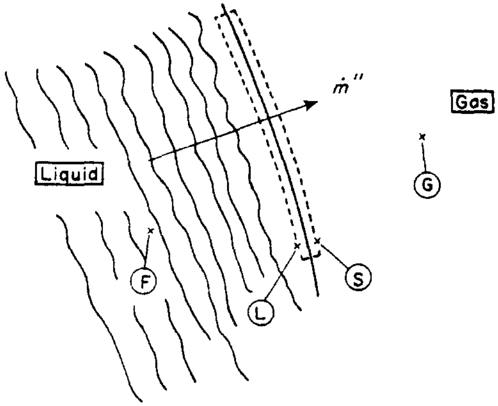

FIG. 1. Illustrating an element of the interface between a liquid and a gaseous phase.

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† The most complete treatment known to the writer is that of Colburn and Drew [6]. These authors were probably aware of all the qualitative features of binary mixture interphase transfer which are described in the present report. However, their paper paid most attention to differential condensation on a dry wall and did not explore the general problem treated here.

the gas; it will here be called the S-state. The liquid immediately adjacent the interface can be taken as in thermodynamic equilibrium with the gas in state S; this liquid state will be denoted by the letter L.

In addition to the G-, F-, S- and L-states, one further state will require consideration; this is the "transferred-substance" or T-state. However, this state is not normally *possessed by* the mixture at any particular location; discussion of its significance will therefore be deferred.

Practical relevance. Figures 2(a) and 2(b) illustrate the relevance of the elementary situation of Fig. 1 to practical equipment. In the former, the interface element lies between a film of liquid, running over the surface of an irregularly shaped solid in a packed tower, and a stream of gas which flows upward through the interstices of the packing. In Fig. 2(b), the G-state is the instantaneous average state of a gas bubble which rises up through liquid which flows towards the downspout of a bubble-cap plate.

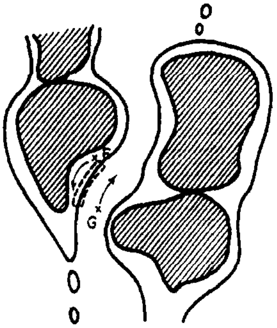

FIG. 2(a). Illustrating the interface element, and the F and G streams, in the context of packed-bed transfer equipment.

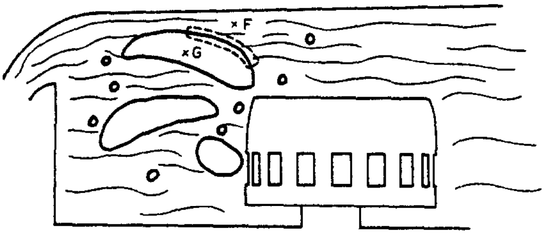

FIG. 2(b). Illustrating the interface element, and the F and G streams in the context of bubble-cap-tray transfer equipment.

Thermodynamic description. It will be supposed that only two chemical substances are present, and that these may mix in any proportions in both the gaseous and the liquid phases. For example, the two materials might be water and ethanol (C_2H_5OH), the thermodynamic properties of which, for a total pressure of 1 atm, are represented in Fig. 3 [5]. The latter is a diagram with enthalpy as ordinate and mass fraction as abscissa; such diagrams will prove to be extremely helpful in the following discussion.

As an example, four state-points have been marked on Fig. 3: G, F, S and L. These correspond to four states discussed above. It will be noticed that S and L each lie on their respective saturation line, at opposite ends of a mixed-phase isotherm (92°C). The G and F points have been placed in typical positions in relation to the L and S points.

In most problems, the G- and F-states are given, whereas the L- and S-states are not; we shall shortly have to consider ways of determining the locations of points L and S.

2.2. *Equations*

The "Ohm's Law" equations. In the standard formulation referred to above [4], the net rate of mass transfer into the phase under consideration, $\dot{m}''$ (kg/m²h), is expressed by:

$$m'' = g \cdot B \tag{1}$$

where g = a "conductance", mainly determined by aerodynamic factors (kg/m²h), and B = a "driving force" (dimensionless), determined by the values of a conserved property P in the G-, S- and T-states, usually in accordance with:

$$B \equiv \frac{P_G - P_S}{P_S - P_T} \tag{2}$$

wherein the subscript denotes the state referred to.

We shall use the same formulation here, with the following additional distinctions:

(ii) The vapour phase will be designated I, and the liquid phase II. The conductances g_I and g_{II} consequently refer to the gaseous and the liquid boundary layers respectively.

(ii) The conserved properties which will be

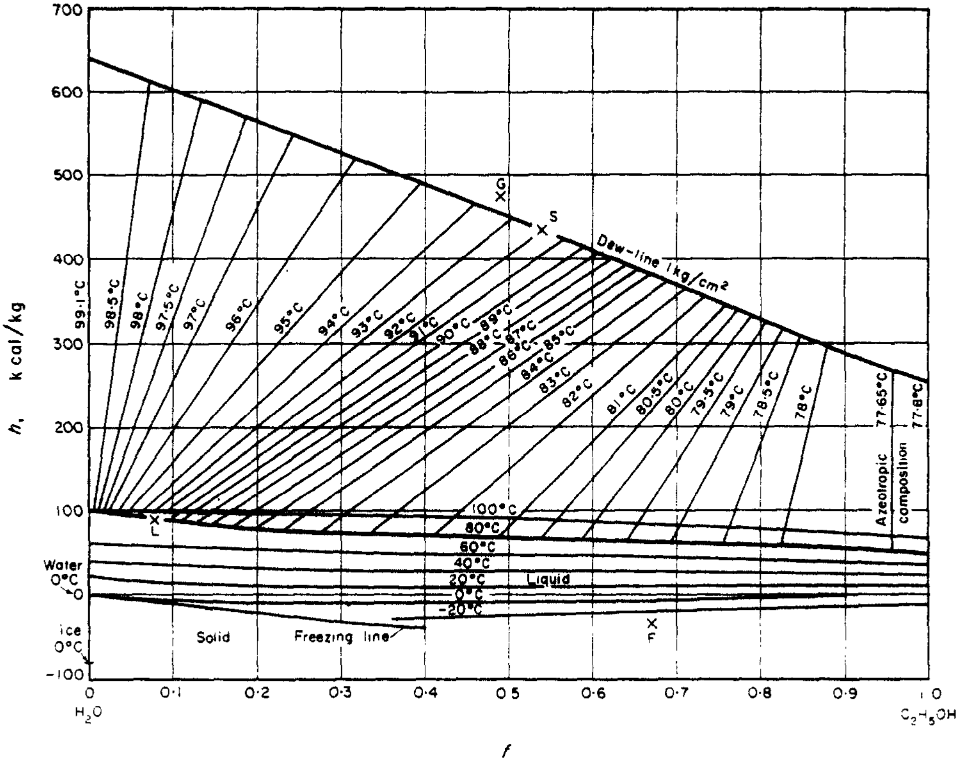

FIG. 3. Enthalpy-composition (h-f) diagram for mixtures of ethyl-alcohol (C_2H_5OH) and water at 1 atm pressure [5].

used are h and f, respectively the ordinate and abscissa of diagrams such as Fig. 3.

h stands for the specific enthalpy of the mixture (kcal/kg), while f stands for the mass of one component of the mixture (ethanol in Fig. 3) per unit mass of mixture.

We may therefore distinguish two forms of the driving force appropriate to the gas phase, based respectively on f and on h. These are:

$$B_{I,f} \equiv \frac{f_G - f_S}{f_S - f_T} \tag{3}$$

$$B_{I,h} \equiv \frac{h_G - h_{G_S}}{h_{T_S} - h_T} \tag{4}$$

wherein state G_S is that of material having the composition of G but the temperature, phase and state of molecular aggregation of S, while state T_S similarly has the composition of T and the temperature, phase and state of molecular aggregation of S.

Corresponding equations may be written for the liquid phase, introducing the states F_L and T_L, defined in a similar fashion. All the states† referred to are represented by state-points in Fig. 4, wherein the broken lines G_SST_S and LF_LT_L are prolongations of pure-phase isotherms.

(iii) Since the exchange coefficients governing

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† Equation (4) has the same form as equation (2) provided that the convention is adopted that all substances having the temperature, phase and state of aggregation of S have zero enthalpy. Since it is often inconvenient to adopt this convention, equation (4) should be used; its use corresponds to case (vi) of section 2.3 of [4].

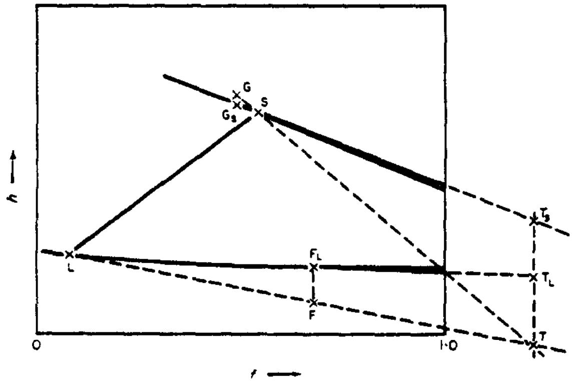

FIG. 4. Illustrating the locations of the state-points G_S, T_S, T and T_L. The diagram is drawn for the case in which GST and FLT are straight lines. (Lewis numbers equal to unity.)

the diffusion of matter and heat (respectively the diffusion coefficient times the mixture density, and the mixture thermal conductivity divided by the mixture specific heat at constant pressure) normally have different values, the conductances appropriate to B_f and B_h will differ. We therefore distinguish the two conductances for the gas phase: $g_{I,f}$ and $g_{I,h}$.

(iv) In the standard formulation of [4], it was possible to focus attention on one of the two phases, namely that for which G was the bulk state. Now that two phases are present, the phase containing mixtures F and L is of equal importance. However, to avoid introduction of further notation, we allow a certain asymmetry to enter, by retaining the convention that $\dot{m}''$ is positive when the net mass transfer is towards the phase designated G.

We are now in a position to write down the four "Ohm's Law" equations, corresponding to the four "resistances" to transfer, two of which reside in phase I (gas) and two in phase II (liquid). The equations run:

$$\dot{m}'' = g_{I,f}(f_G - f_S)/(f_S - f_T) \quad (5)$$

$$= g_{I,h}(h_G - h_{G_S})/(h_{T_S} - h_T) \quad (6)$$

$$= - g_{II,f}(f_F - f_L)/(f_L - f_T) \quad (7)$$

$$= - g_{II,h}(h_F - h_{F_L})/(h_{T_L} - h_T). \quad (8)$$

How the conductances are determined. It will be assumed that sufficient information is available for the values of the g's to be determined; for example, knowledge of the liquid-film thickness and velocity and of the appropriate exchange coefficients could lead to a determination of the g_{II}'s. More precisely, such knowledge could enable a g^* to be calculated, this being the value of the g which prevails as B tends to zero. g and g^* are related to B by an equation which has the general characteristics of:

$$\frac{g}{g^*} = \frac{\ln(1 + B)}{B} \quad (9)$$

to the symbols of which the appropriate I, II, h and f subscripts can be added; the exact form of the relation depends on the flow conditions [4]. For the present, it will be helpful to regard the g's as easily determined quantities, and to confine attention to the $g(B)$ relation of equation (9).

Thermodynamic-property relations. In addition to equations (5), (6), (7) and (8), relations exist between the S and L properties. These express, among other things, the requirement of thermodynamic equilibrium at the interface and may be written in terms of the interface temperature t_S (which is equal to t_L) as:

$$f_S = f_S(t_S) \quad (10)$$

$$h_{G_S} = h_{G_S}(t_S, f_G) \quad (11)$$

$$h_{TS} = h_{TS}(t_S, f_T) \quad (12)$$

$$f_L = f_L(t_S) \quad (13)$$

$$h_{F_L} = h_{F_L}(t_S, f_F) \quad (14)$$

$$h_{T_L} = h_{T_S}(t_S, f_{T_S}). \quad (15)$$

Here the bracket denotes " is a function of ".

The transferred-substance state T. It is necessary to refer to [4] for a full discussion of the significance of this state. Here it may suffice to state:

(i) That the T-state is the state which a single fluid stream must possess if, in flowing from the F to the G phase at a mass rate $\dot{m}''$, it is to have the same effects as the totality of mass and heat fluxes which actually cross control surfaces at either the S or the L locations.

(ii) The T-state can be represented by a state-point on an enthalpy–composition diagram, but this point is not constrained to lie between the lines $f = 0$ and $f = 1$. Fig. 4 in fact illustrates the situation in which f_T is greater than unity.†

2.3. *The mathematical problem*

The data. As has been indicated already, the mathematical problem is specified in terms of given bulk-fluid states and given conductances; thus all the g's and h_G, f_G, h_F and f_F, can be regarded as known.

The required information. We normally require to find out the net mass transfer rates, $\dot{m}''$, and the composition of the transferred substance, e.g. f_T. The latter quantity gives the rate of transfer of the substance whose mass fraction is measured by f: for this is equal to $\dot{m}''f_T$. The transfer rate of the other component is of course $\dot{m}''(1 - f_T)$.

Equations and unknowns. The equations to be solved are (5)–(8) and (10)–(15); there are ten of them. There are also ten unknowns, namely: f_S, f_T, f_L, h_{G_S}, h_{T_S}, h_T, h_{F_L}, h_{T_L}, t_S and $\dot{m}''$. The problem is evidently soluble.

Since the equations are non-linear, and since the relations contained in equations (10)–(15) may not be expressible through simple functions, trial-and-error procedures will ordinarily be necessary. However there is no need to discuss such prosaic matters here.

Discussion of the problem in graphical terms. It is helpful to interpret the mathematical problem by reference to Fig. 4. Two facts stand out: the locations of points G and F are known; and the locations of T, S and L are sought. With the latter points located, G_S, T_S, F_L and T_L can be found immediately; indeed, since S and L are tied together, only one of these need be regarded as an independent unknown. Graphical representation of the problem on an enthalpy–composition chart thus suggests that attention should be concentrated at first on establishing the interface temperature t_S (hence S and L) and the transferred-substance state T; with these known, everything else follows quickly.

3. THE CONVENTIONAL APPROXIMATE PROCEDURE

3.1. *Simplification of the mathematical problem*

The basic assumption. The mathematical problem displayed in the last section is rarely solved rigorously; at any rate, no rigorous solutions appear to have been published. Instead, the problem is usually simplified by making an assumption about the transferred substance. This assumption contains the following elements:

(i) The rate of vaporization of the more volatile compound bears a known ratio to the rate of condensation of the less volatile component. In the present terms, this means: f_T is known.

(ii) The above ratio is equal to the inverse ratio of the latent heats of vaporization of the respective pure components. This implies that the mixtures are ideal.

(iii) *The molal* latent heats of vaporization are assumed to be equal.

(iv) Consequently *the molal condensation rate of the less volatile component is equal to the molal vaporization rate of the more volatile component.* The last statement is the basic assumption referred to in the title.‡ It may be expressed symbolically as:

$$f_T = 1/(1 - M_j/M_i) \qquad (16)$$

where

M_i = molecular weight of the substance i, the one whose concentration is measured by f, and

M_j = molecular weight of the other component of the mixture.

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† In the work of Colburn and Drew [6], f_T is represented (in molal units) by the symbol z. The authors made it clear that z could lie outside the region between 0 and 1.

‡ Of course there is no need to make step (iii), which involves a further approximation; instead, equation (16) could be replaced by the more correct equation:

$$f_T = 1/(1 - \Delta h_i/\Delta h_j) \qquad (16a)$$

where Δh is the latent heat of vaporization. Something of this kind is done when "fictitious molecular weights" [3] are employed; the direct use of equation (16a) is less devious and renders the mention of molecular weights entirely unnecessary.

Consequences. The main consequence of equation (16) is that it permits further considerations of the equations involving h to be dispensed with. The remaining equations are:

$$\dot m'' = g_{\mathrm{I},f}\,(f_{\mathrm{G}} - f_{\mathrm{S}})/(f_{\mathrm{S}} - f_{\mathrm{T}}) \tag{5}$$

$$\dot m'' = -\,g_{\mathrm{II},f}\,(f_{\mathrm{F}} - f_{\mathrm{L}})/(f_{\mathrm{L}} - f_{\mathrm{T}}) \tag{7}$$

and

$$f_{\mathrm{S}} = f_{\mathrm{S}}\,(f_{\mathrm{L}}) \tag{20}$$

the last equation resulting from the elimination of t_{S} between (10) and (13).

In these three equations there are only three unknowns, viz. f_{S}, f_{L} and $\dot m''$; for f_{T} is given by (16). The problem is therefore soluble; it is moreover considerably simpler than the full problem outlined in section 2.3.

3.2. *Method of solution*

Despite the simplicity of the reduced mathematical problem, graphical methods are often employed. Fig. 5 illustrates the type of diagram used, with f_{S} as ordinate and f_{L} as abscissa. The full curve represents the equilibrium relation (20), while the broken curve represents the equation resulting from the elimination of $\dot m''$ between equations (5) and (7), namely:

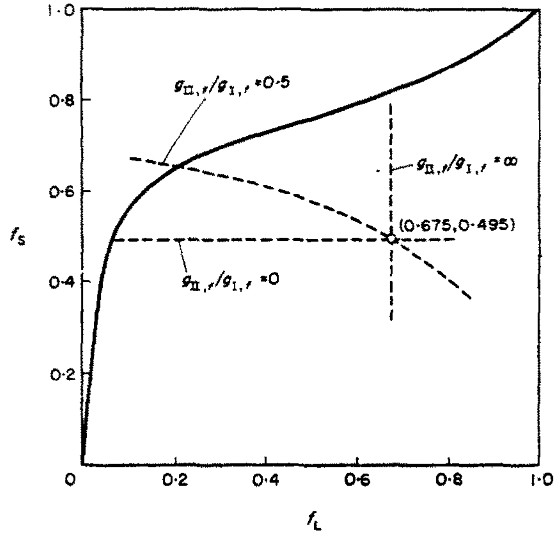

FIG. 5. Equilibrium-concentration diagram for mixtures of ethyl-alcohol and water at 1 atm pressure, showing construction lines for the example shown in the text, according to equation (21).

$$f_{\mathrm{S}} - f_{\mathrm{G}} = \frac{(f_{\mathrm{L}} - f_{\mathrm{F}})\,(f_{\mathrm{T}} - f_{\mathrm{G}})\,g_{\mathrm{II},f}/g_{\mathrm{I},f}}{(f_{\mathrm{L}} - f_{\mathrm{F}})\,(1 + g_{\mathrm{II},f}/g_{\mathrm{I},f}) + (f_{\mathrm{F}} - f_{\mathrm{T}})}. \tag{21}$$

When $g_{\mathrm{II},f}/g_{\mathrm{I},f} = 0$, this equation represents a horizontal straight line on Fig. 5; when $g_{\mathrm{II},f}/g_{\mathrm{I},f} = \infty$ the equation represents a vertical straight line; for all other values of $g_{\mathrm{II},f}/g_{\mathrm{I},f}$, the equation represents a curve unless f_{T} happens to be infinite (equal molecular weights), in which case it represents a line of slope $-g_{\mathrm{II},f}/g_{\mathrm{I},f}$.

If *molal* concentrations are used, in place of f, for Fig. 5, equation (21) is always represented by a straight line.

The values of f_{S} and f_{L} can be determined from the intersection of the equilibrium line in Fig. 5 with the curve representing equation (21) for a particular value of the conductance ratio $g_{\mathrm{II},f}/g_{\mathrm{I},f}$; thereafter $\dot m''$ is easily evaluated from equation (5) or (7). The value of the mass transfer rate of a particular component, say $\dot m_i''$, is subsequently found from the definition of f_{T}, namely:

$$\dot m_i'' = f_{\mathrm{T}}\dot m''. \tag{22}$$

Numerical example. The above procedure has been applied to the ethanol–water example illustrated by Fig. 3, for which $f_{\mathrm{G}} = 0{\cdot}495$ and $f_{\mathrm{F}} = 0{\cdot}675$. Since it is conventional to ignore the influence of the mass-transfer rate on the conductance, g_f and g_f^* have been taken to be identical; inspection of equation (9) shows that this amounts to assuming that B is close to zero. The molecular weights are such that $f_{\mathrm{T}} = 1{\cdot}643$.

Figure 6 represents the results of the calculation in the form of curves of the quantities t_{S}, $\dot m''_{\mathrm{C_2H_5OH}}/g^*_{\mathrm{I},f}$, $\dot m''/g^*_{\mathrm{I},f}$ and $\dot m''_{\mathrm{H_2O}}/g^*_{\mathrm{I},f}$. The abscissa quantity is $g^*_{\mathrm{I},f}/(g^*_{\mathrm{I},f} + g^*_{\mathrm{II},f})$, this being chosen in preference to the conductance ratio because it represents all physically realisable conditions in the finite range 0 to 1; the sum $(g^*_{\mathrm{I},f} + g^*_{\mathrm{II},f})$ has no particular physical significance.

Inspection of the curves of Fig. 6 shows that the process is one of net vaporization; for $\dot m''$ is always positive. However the rate of vaporization of ethanol is even greater than $\dot m''$; water on the other hand condenses, for $\dot m''_{\mathrm{H_2O}}$ is negative

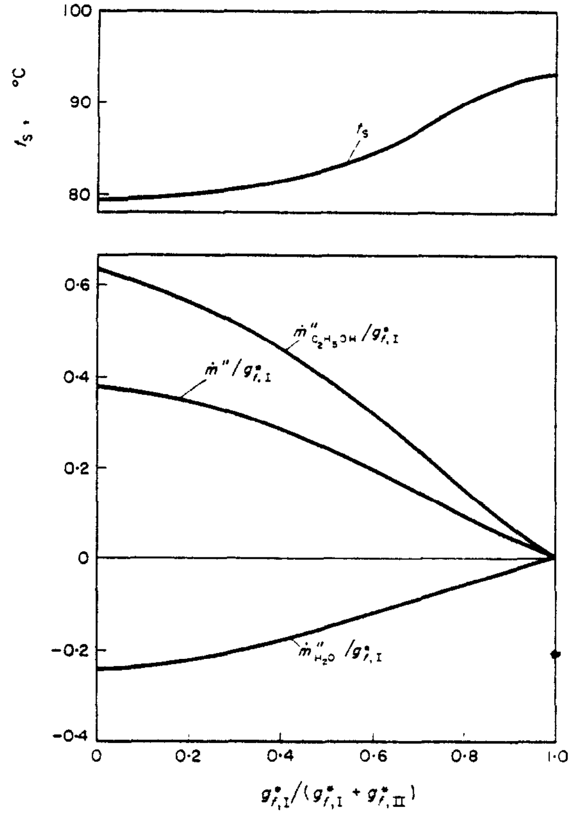

FIG. 6. Results of the approximate calculation method when applied to the example in section 3.2 of the text.

These results are qualitatively in accordance with conventional expectations and are an expression of the rectifying action of the interphase contact.

The shapes of the curves of Fig. 6 are such that the transfer rates are proportional to $g^*_{\mathrm{I},f}$ when this quantity is small (gas-phase control); when $g^*_{\mathrm{I},f}$ is much larger than $g^*_{\mathrm{II},f}$ however, the transfer rates depend only on the liquid-phase conductance. These results are also well known.

The curves of Fig. 6 have been presented primarily for comparison with the curves expressing the results of more rigorous theoretical predictions (Figs. 8, 10 and 12).

3.3. *Discussion*

The calculation method just described is easy to perform, and provides definite answers to most of the questions which interest the equipment designer. Why then should we look further?

There are several answers to this question. Firstly, as will be shown below, the predictions of the conventional theory, though definite and easy to obtain, are often entirely incorrect; this at any rate is the conclusion which follows from the analysis given below, although it must be admitted that experimental data which bear on the matter are hard to come by. Secondly, the procedure described is quite different from that which is used in, for example, air-conditioning or cooling-tower design; yet the water–air system is merely a particularly simple binary-mixture system, so should be amenable to the present treatment. Thirdly, the disappearance of the enthalpies from the calculation occasions justifiable misgivings: the conventional theory predicts the same rates of material transfer, for fixed gas and liquid compositions, regardless of whether the gas is superheated; can this be correct?

In the following sections a rigorous treatment of the problem will be presented: here we shall no longer *assume* the value of f_{T} in the manner of section 3.1, but shall solve the general problem described in section 2.3. Three examples will be studied; these are chosen so as to have the same gas and liquid bulk compositions as in the example just considered; comparison of their solutions with that displayed in Fig. 6 will therefore enable the correctness of the conventional method to be assessed.

4. RIGOROUS SOLUTION OF THE MATHEMATICAL PROBLEM WHEN THE LEWIS NUMBERS ARE UNITY

4.1. *The implications of the Lewis number restriction*

Definition. The Lewis number is here understood to be the material exchange coefficient (i.e. diffusion coefficient times density) divided by the thermal exchange coefficient (thermal conductivity divided by constant-pressure specific heat). Its value is usually close to unity in gases and in all turbulent fluids; it is however much less than unity in most non-turbulent liquids. In the present section we consider the case in which the Lewis number is equal to unity in both the liquid and the gaseous phase.

Influence on conductances. It is shown in [4] (and, of course, in many other places as well) that when the Lewis number is unity for a phase, the g_h and g_f conductances for the phase in question are equal.

Influence on the location of the state points. Inspection of equations (5) and (6), for example, together with interpretation of the f- and h-differences appearing there as lengths on Fig. 4, quickly reveals that, if $g_{\mathrm{I},f}$ and $g_{\mathrm{I},h}$ are equal, the state-points G, S and T must lie on a straight line. For similar reasons, F, L and T are also co-linear.

Incidentally, in this case it is permissible to write the driving force $B_{\mathrm{I},h}$, for example, as $(h_{\mathrm{G}} - h_{\mathrm{S}})/(h_{\mathrm{S}} - h_{\mathrm{T}})$; this is in accord with simplification (ii) to the differential equations of [4].

The co-linearities of G, S and T and of F, L and T ensure that there is only one state-point on the diagram h–f which has to be established: for with G and F fixed, specification of the location of any one of F, L or T immediately fixed the other two. Fig. 4 illustrates this.

4.2. *Possible and impossible conditions*

The length ratios representing B_{I} and B_{II}. It is evident that if g_f and g_h are equal, we may drop the h and f subscripts from the B's, as well as from the g's. Further, the B's can be represented by length ratios on an h–f diagram, by reason of equations (5)–(8); we have:

$$B_{\mathrm{I}} = \overline{\mathrm{GS}}/\overline{\mathrm{ST}} \tag{23}$$

and

$$B_{\mathrm{II}} = \overline{\mathrm{FL}}/\overline{\mathrm{LT}} \tag{24}$$

where $\overline{\mathrm{GS}}$, $\overline{\mathrm{ST}}$ etc. stand for the lengths of the corresponding lines on the h–f diagram.

Now not all possible pairs of values of B_{I} and B_{II} correspond to physical reality. There are two restrictions: firstly, no B value can be less than -1, for this would contravene the Second Law of Thermodynamics; secondly, when B_{I} is positive, B_{II} is negative for reasons of continuity. It follows that the points S and L cannot range at will along the saturation lines on the h–f chart.

Permissible locations for S, L *and* T. The above reflections lead to the conclusion that S, L and T may only lie on the loci indicated by heavy lines in Fig. 7. Here the S and L loci are restricted by

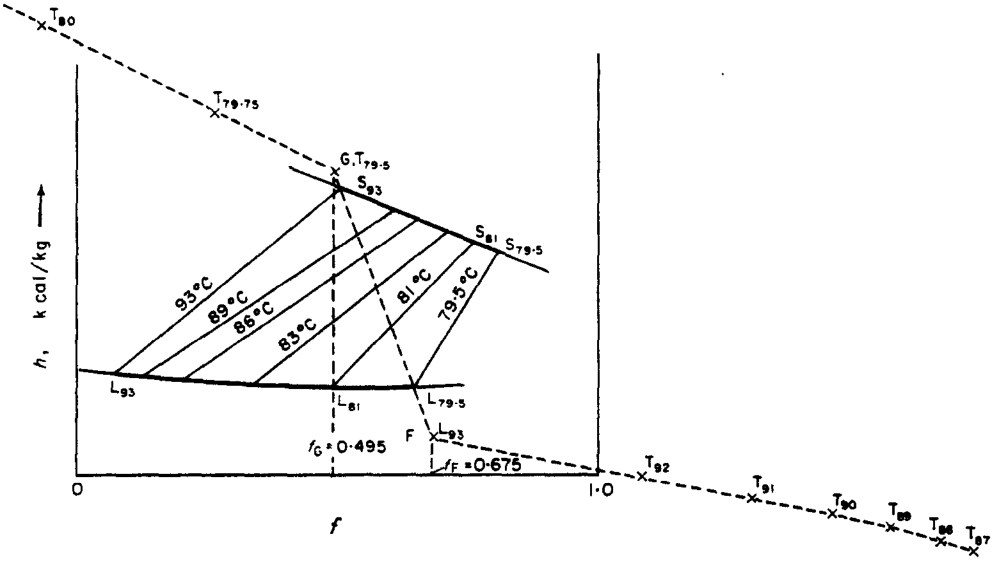

FIG. 7. Illustrating the permissible loci of S, L and T when G and F are fixed. The positions of G and F, and the shape of the h–f diagram, correspond to the C_2H_5OH–water example discussed in section 4 of the text.

the mixed-phase isotherms which pass through the intersections of the saturation curves with the straight line GF; the T loci can be deduced from this requirement. If for example the point S were to lie elsewhere on its saturation line, it can be easily verified that one of the restrictions on B would be contravened.

The lengths of the permissible loci of S and L clearly depend greatly on the positions of G and F: if f_G is close to zero and f_F is close to unity, for example, S and L each has the freedom of almost the whole length of its saturation curve; on the other hand, if the line GF happened to coincide with a mixed-phase isotherm, only one pair of surface states would be possible.

4.3. *Determination of the actual interface conditions*

The equation. We have seen that S and L, and so t_S, can only vary within certain limits; we now determine where within these limits they actually lie in a given case. To do this we equate two quantities derived from equations (5) to (8), equation (9) and equations (23) and (24); there results:

$$g^*_{II}/g^*_I = -\frac{\ln(1+\overline{GS}/\overline{ST})}{\ln(1+\overline{FL}/\overline{LT})} \qquad (25)$$

wherein the h- and f-subscripts have been omitted as redundant.

The role of the conductance ratio. Now $\overline{GS}/\overline{ST}$ and $\overline{FL}/\overline{LT}$ are functions of t_S alone, once G and F are fixed, as has been seen. It is therefore possible to evaluate for every value of t_S, the quantity:

$$-\ln(1+\overline{GS}/\overline{ST})/\ln(1+\overline{FL}/\overline{LT});$$

according to equation (25) this is equal to the ratio of the zero-mass-transfer conductances of the two phases, i.e. g^*_{II}/g^*_I.

The influence of the conductance ratio is brought out by the top curve of Fig. 8 which has been derived in the way just indicated for the situation illustrated in Fig. 7. This shows the interface temperature, t_S, plotted versus the quantity $g^*_I/(g^*_I + g^*_{II})$, in the same manner as for Fig. 6. We see that the interface temperature is highest, in the present case, when the gas-side conductance is the larger; low interface temperatures are associated with large liquid-side conductances.

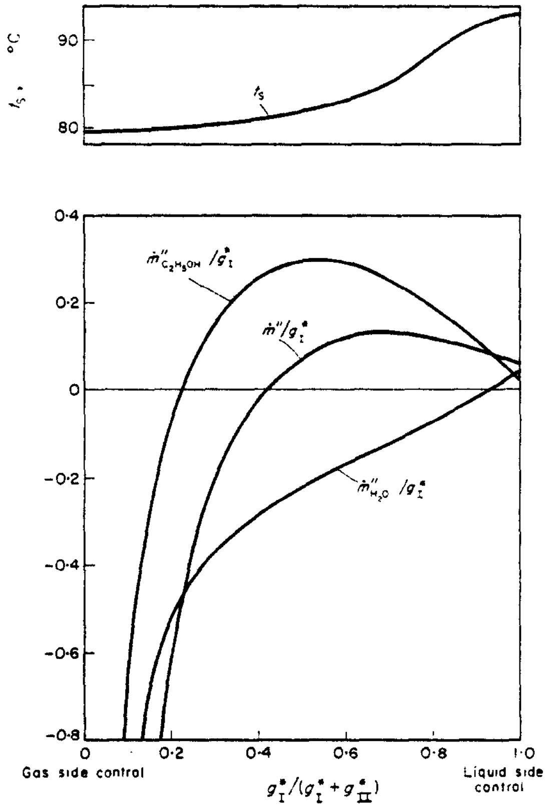

FIG. 8. Results of the rigorous calculation indicated in Fig. 7 (G superheated and F supercooled).

Comparison with the approximate treatment. Qualitatively, the interface-temperature variation just described accords with that predicted by the approximate treatment of section 3. Comparison of the t_S curves of Figs. 6 and 8 reveals slight quantitative differences between the results of the approximate and of the rigorous treatments, but these are of little account in the present case. It is easy to see that the differences would be larger if the G and F states of our problem lay further from their respective saturation lines (highly superheated vapour, highly sub-cooled liquid).

4.4. *The mass transfer rates*

Net mass transfer rate. Now that the interface condition has been established, we may evaluate the mass transfer rate $\dot{m}''$, for given values of the conductances by way of equations (5) to (8). Fig. 8 exhibits a curve containing this information valid for the example specified in Fig. 7; it is the curve with co-ordinate $\dot{m}''/g_{\mathrm{I}}^*$. Inspection of this curve shows that $\dot{m}''$ is positive when g_{I}^* is greater than $(0{\cdot}42/0{\cdot}58)g_{\mathrm{II}}^*$; then the process is one of net vaporization. When g_{II}^* is larger than $(0{\cdot}58/0{\cdot}42)g_{\mathrm{I}}^*$ on the other hand, $\dot{m}''$ is negative, signifying that there is a net condensation. As is easy to understand, vaporization thus occurs when the interface temperature is high, and condensation when it is low.

Comparison of the $\dot{m}''$ curve of Fig. 8 with that of Fig. 6 shows some startling differences. The conventional theory is correct (i.e. Fig. 6 gives the same value of $\dot{m}''/g_{\mathrm{I},f}^*$ as in Fig. 8) only for a value of the abscissa around 0·73; when the abscissa quantity is less than 0·42, however, the conventional theory is wrong even as to the sign of the net mass-transfer rate.

Ethanol vaporization rate. The curve for $\dot{m}''_{\mathrm{C_2H_5OH}}/g_{\mathrm{I},f}^*$ shown in Fig. 8 has been obtained by multiplying values of $\dot{m}''/g_{f,\mathrm{I}}^*$ by f_{T}, which is of course the abscissa of T on Fig. 7; it lies above that for the net mass transfer rate over almost the whole of the conductance range; in this respect it accords with the curve obtained from the conventional theory, in Fig. 6. The curves scarcely agree in any other respect however: the rigorous theory shows that even ethanol condenses when the gas-side conductance is low enough.

It is worth noting that the ratio $\dot{m}''_{\mathrm{C_2H_5OH}}/\dot{m}''$, i.e. f_{T}, is shown by Fig. 7 to be capable of taking any value, positive or negative, outside the range from 0·495 to 0·695. It has the value assumed in the conventional theory (namely 1·643, given by evaluating equation (16) with $M_i = 46$ and $M_j = 18$) for only one value of the interface temperature, namely 85·8°C. The corresponding value of $g_{\mathrm{I},f}^*/(g_{\mathrm{I},f}^* + g_{\mathrm{II},f}^*)$ is 0·67; this is of course near[†] the condition, noted above, at which the net mass-transfer rates predicted by the conventional and the exact theories are equal.

Water vaporization rate. The rate of water vaporization is obtained from the foregoing results by way of the equation:

$$\dot{m}''_{\mathrm{H_2O}} = \dot{m}'' - \dot{m}''_{\mathrm{C_2H_5OH}}. \tag{26}$$

The corresponding curve is also plotted in Fig. 8; it shows that, except at very large values of the gas-phase conductance, the water vaporization rate is negative; i.e. steam *condenses.*

Though qualitatively similar to the prediction of the conventional theory (Fig. 6), large quantitative discrepancies exist, particularly when the gas-side conductance is controlling ($g_{\mathrm{I},f}^*$ small).

Discussion. It is evident that the conventional theory totally fails to provide an acceptable prediction of the mass-transfer phenomena for the case in question. However, practical problems often differ from the one studied in two respects, namely: (i) the G- and F-states usually lie on the saturation lines, and (ii) the Lewis number of the liquid phase is usually nearer to zero than to unity.

Before condemning the conventional theory, it is therefore necessary to examine whether its predictions are equally at fault under the conditions just indicated.

4.5. *When the bulk fluid states are saturated*

Relation to the previous problem. Fig. 9 illustrates the new situation that is analysed; the values of f_{G} and of f_{F} are the same as before, 0·495 and 0·675 respectively, but the enthalpies of the G- and F-states are respectively lowered and raised so that their state-points lie on the saturation lines.

Since there has been no change in f_{G} or f_{F}, the predictions of the conventional theory about this new situation are identical with its predictions for the situation of Fig. 7: according to the conventional theory the enthalpies of the G- and F-states are unimportant.

Graphical solution of the problem. The procedure for determining the properties of the transferred substance is the same as before: S and L lie at opposite ends of an isotherm; T lies on GS, produced if necessary, and also on FL; therefore T is found, for a given interface temperature, as the intersection of the corresponding GS and FL lines.

Inspection of Fig. 9 shows that, since G and F

[†] The agreement would be precise did not the conventional theory also include the approximation: $g_f = g_f^*$.

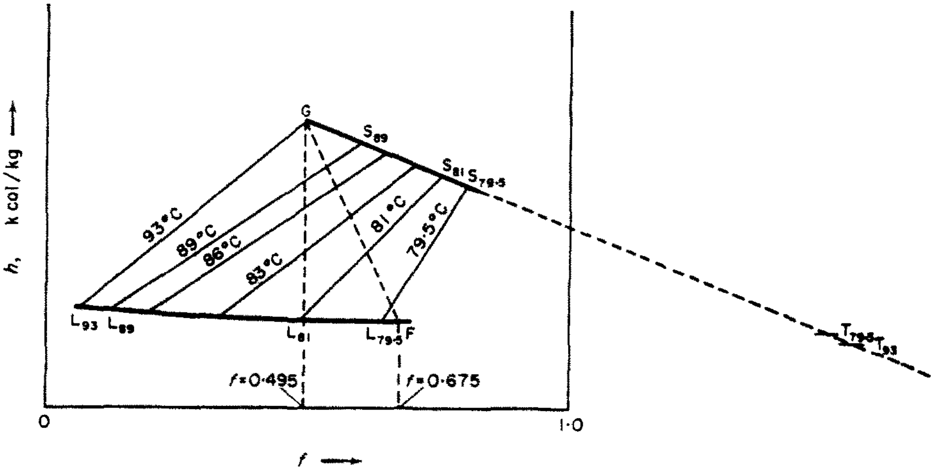

FIG. 9. Illustrating the locations of G and F (on the saturation lines) and of S, L and T, for the example discussed in section 4.5 of the text. Results of calculations are shown in Fig. 10.

now lie on the (approximately straight) saturation lines, the directions of GS and FL can no longer vary much; the consequence is that the locus of T is now extremely short: f_T has the practically constant value of 1·5.

Results. The net rate of mass transfer, and the rates of vaporization of ethanol and water, have been determined in the manner indicated above; they are displayed graphically in Fig. 10. Comparison with Fig. 6 shows a much greater similarity to exist than for the previous case: qualitatively the conventional theory yields good predictions over the whole range of conditions, although there are small quantitative disagreements. The latter spring from two facts: firstly, the conventional theory presumes that $f_T = 1{\cdot}643$, whereas we find $f_T = 1{\cdot}5$ approximately; secondly, the conventional theory neglects the difference between g and g^*.

Discussion. Evidently the conventional theory is not nearly so unreliable when G and F lie on the saturation lines as when they do not. Indeed, if the conventional theory were modified so as to use equation (16a) of the footnote to section 3.1, and $\Delta h_i/\Delta h_j$ were calculated with proper allowance for the non-ideality of the mixtures, its prediction would be quite good.

It should not be forgotten that, in the examples considered rigorously so far, the Lewis numbers have been assumed to equal unity for both the gaseous and the liquid phases. In the next section an example will be worked out for which this condition does not hold.

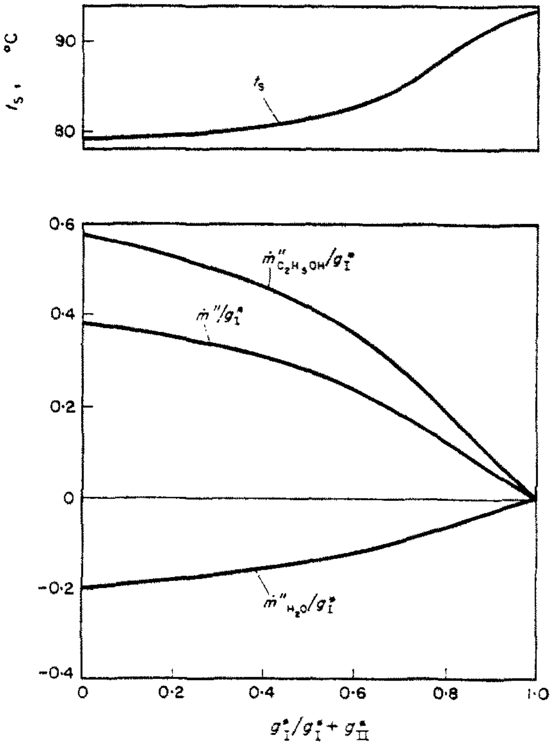

FIG. 10. Results for the rigorous calculation indicated in Fig. 9 (F and G on the saturation line).

5. RIGOROUS SOLUTION WHEN THE LIQUID PHASE LEWIS NUMBER IS ZERO

5.1. *The problem considered*

The diffusion coefficient of a binary liquid mixture is often one or two orders of magnitude lower than its thermal diffusivity; the Lewis number of the liquid phase may therefore be as low as 0·01. A consequence is that, if the liquid is entirely free of turbulence, the conductance of equation (7) is very much less than that of equation (8).

In order to investigate the influence of this tendency on the nature of the transfer processes, we shall now study an extreme case, that for which the conductance ratio is practically zero in the liquid phase:

$$\frac{g_{II,f}}{g_{II,h}} \ll 1. \tag{27}$$

In other respects, the problem will be similar to that first studied: the G- and F-states will be as illustrated in Figs. 3, 4 and 7; and the gas-phase conductances, $g^*_{I,h}$ and $g^*_{I,f}$, will be taken as equal once more. We shall investigate the influence of the relative values of the gas-side and liquid-side conductances on the surface temperature and on the directions and magnitudes of the mass transfers. Both conventional and rigorous procedures will be used.

5.2. *Predictions of the conventional procedure*

Influence of $g^*_{I,f}/(g^*_{I,f} + g^*_{II,f})$. The fact represented by equation (27) exerts no influence on the conventional theory of mass transfer in a binary mixture; the prediction described in section 3 and displayed in Fig. 6 therefore applies equally well to the present problem.

Influence of the heat-conductance ratio. Now equation (27), taken together with the fact that $g^*_{I,f}$ and $g^*_{I,h}$ are equal, implies that, whenever $g^*_{II,h}$ is of the same order as $g^*_{I,h}$, $g^*_{II,f}$ is very much less than $g^*_{I,f}$. We shall be studying the influence of $g^*_{I,h}/(g^*_{I,h} + g^*_{II,h})$ below; we should therefore remember that, for all values of this quantity greater than zero, the conventional theory predicts that $g^*_{II,f}/g^*_{I,f}$ is zero, and so (Fig. 5) that:

$$f_S = f_G. \tag{28}$$

The intersection of the horizontal line represented in Fig. 5 by equation (28) with the curve representing the equilibrium condition gives the value of f_L; it is 0·07. Since f_T is assumed to equal 1·643, and f_F is equal to 0·675, equations (7) and (22) can be evaluated; thus:

$$\frac{\dot{m}''}{g^*_{II,f}} = -\frac{(0{\cdot}675 - 0{\cdot}07)}{(0{\cdot}07 - 1{\cdot}643)} = 0{\cdot}384 \tag{29}$$

and

$$\frac{\dot{m}''_{C_2H_5OH}}{g^*_{II,f}} = 0{\cdot}32 \times 1{\cdot}643 = 0{\cdot}627. \tag{30}$$

Consequently, $\dot{m}''/g^*_{II,h}$ and $\dot{m}''_{C_2H_5OH}/g^*_{II,h}$ are then positive but *close to zero*, by reason of equation (27); it is this result which will be compared with predictions of the rigorous theory, which will now be developed.

5.3. *Rigorous determination of the interface temperature and transferred-substance state*

The transferred-substance composition. Inspection of equations (5) to (8), with particular attention to equation (7), shows that, when $g_{II,f}$ is very much smaller than all the other g's, it is only possible for the transfer rates to be finite if:

$$f_L = f_T. \tag{31}$$

Expressed verbally, this important equation signifies that ethanol and water cross the phase boundary in precisely the same proportion as that which exists between their concentrations in the gas adjacent the interface.

A corollary of equation (31) is that the directions of transfer of both ethanol and water must be the same; for f_L is constrained to lie between 0 and 1, so now f_T must do likewise.

The location of T. Equation (31) implies that the state-point T on the enthalpy–composition diagram must lie on the vertical line through the point L. This condition, replacing the previous one that F, L and T were co-linear, now enables the location of T to be fixed for any value of the interface temperature, for G, S and T still are co-linear, the Lewis number being unity in the gas phase; T therefore lies on the intersection of GS with the vertical through L. This is shown in Fig. 11.

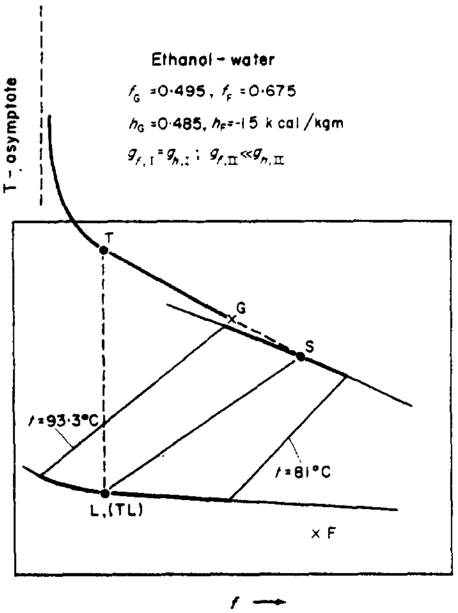

FIG. 11. Illustrating the loci of S and T for the case discussed in section 5 of the text when Lewis number equals to zero for liquid and to unity for gaseous phase. Results of calculations are shown in Fig. 12.

Possible positions of S, L *and* T. The limitations on the values of B, which were mentioned in section 4.2, still prevail. It is therefore easily seen that S, L and T are confined to the loci indicated in Fig. 11 by heavy lines: S cannot lie to the left of G, while L cannot lie to the right of it.

These dispositions ensure that G always lies between S and T so, that $\overline{GS}/\overline{ST}$ is invariably negative. This implies that the direction of net mass transfer is always negative: only condensation occurs.

As has already been seen, f_T lies between 0 and 1. An additional implication of Fig. 11 is therefore that $\dot{m}''_{C_2H_5OH}$ and $\dot{m}''_{H_2O}$ are also invariably negative.

5.4. *Results of the calculation*

Clearly Fig. 11 displays a one-parameter family of situations, for each of which it is possible to determine t_S, $\dot{m}''/g^*_{I,h}$, $\dot{m}''/g^*_{II,h}$, $g^*_{I,h}/(g^*_{I,h}+g^*_{II,h})$, etc. These evaluations have been made; the results are contained in Fig. 12, which has $g^*_{I,h}/(g^*_{I,h}+g^*_{II,h})$ as abscissa.

As already predicted, the curves show that only condensation occurs, the rate increasing as $g^*_{I,h}$ falls relative to $g^*_{II,h}$.

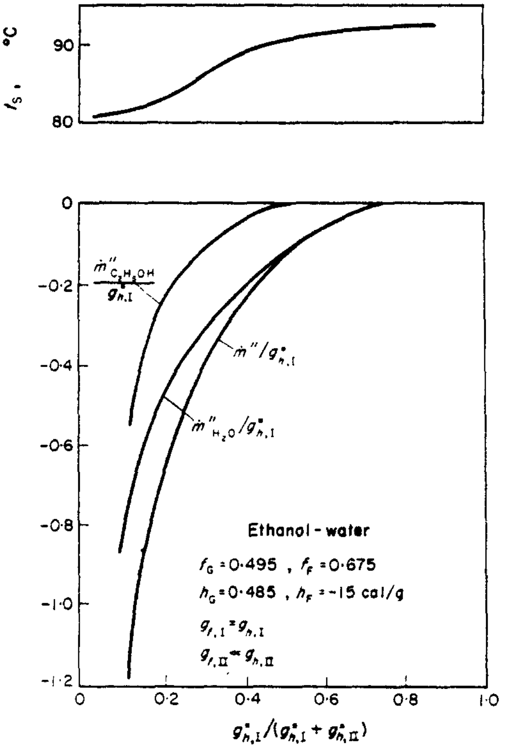

FIG. 12. Results for the example discussed in section 5 of text.

Comparison with the case with a Lewis number of unity for the liquid (*section* 4.1). Fig. 12 is directly comparable with Fig. 8; the only difference in the situations is that $g_{II,f}$ and $g_{II,h}$ are equal for Fig. 8 but obey the inequality (27) for Fig. 12. Any differences between the two sets of curves are therefore purely the consequence of the change of the Lewis number in the liquid.

Inspection of Figs. 8 and 12 shows that the differences are profound. The main one is that the vanishing of $g^*_{II,f}$ suppresses vaporization of ethanol: for it "cannot get out" of the liquid phase. Only at low values of $g^*_{I,h}/(g^*_{I,h}+g^*_{II,h})$

do the two sets of curves have approximately the same course.†

Comparison with the predictions of the conventional theory. We have already noted that, according to the conventional theory, $\dot{m}''/g^*_{\mathrm{I},h}$, $\dot{m}_{C_2H_5OH}/g^*_{\mathrm{I},h}$ and $\dot{m}_{H_2O}/g^*_{\mathrm{I},h}$ are all zero when $g^*_{\mathrm{I},h}/(g^*_{\mathrm{I},h} + g^*_{\mathrm{II},h})$ is finite; consequently the conventional theory predicts that, on a plot such as that of Fig. 8, all three curves should collapse into the base line.

The conventional theory is therefore totally incorrect: it predicts that, because $g^*_{\mathrm{II},f}$ happens to be very small, only a small amount of mass transfer will occur. Yet, with hot vapour in contact with cold liquid, no mere suppression of liquid-phase diffusion can prevent condensation from occurring; indeed, liquid would condense from the vapour onto a cold metal wall, so why should it not also do so onto the surface of the cold F-state liquid? Of course, the condensate will not mix with the bulk of the liquid but will form a layer on its surface, of thickness increasing with time.

5.5. *Case in which the* G- *and* F-*states are saturated*

When the Lewis numbers were unity, it was seen that the conventional theory gave tolerable results when the bulk states of the liquid and vapour were saturated; it is therefore necessary to check whether this is the case for a zero Lewis number in the liquid.

Inspection of Fig. 12 yields the answer, so rendering a detailed calculation unnecessary. We see that the movement of G and F to the saturation lines merely results in a slight change in the shape of the T-locus, which however still has the same asymptote and still terminates at G on the right; all the above qualitative conclusions therefore remain. The conventional theory is still totally wrong.

6. CONCLUSIONS

(i) Theoretical examination of the heat and mass transfers which occur at the interface separating the two phases of an ethanol–water mixture has shown that the conventional calculation procedure (e.g. [1]) makes tolerably good predictions if the bulk states are saturated *and* the Lewis numbers of liquid and gas are unity.

(ii) If the bulk states are not saturated, even though the Lewis numbers are still unity, the conventional method gives very unreliable predictions; the *directions* of the transfer of the components may be incorrectly predicted.

(iii) When the liquid Lewis number is very small, as often occurs in practice, the conventional theory again makes totally incorrect predictions whether the bulk states are saturated or not.

(iv) Although ten simultaneous equations have to be solved in the rigorous theory, the use of graphical constructions on an enthalpy–composition diagram renders this a relatively simple task. The diagram also provides considerable insight into the processes of mass transfer.

(v) Experimental data which could confirm or deny the above conclusions do not appear to be available; the process in question is of sufficiently central importance in chemical engineering to deserve further study.

(vi) The standard formulation for mass-transfer problems [4] appears to be flexible enough to accommodate all the phenomena of binary-mixture mass transfer, provided that subscripts are introduced to distinguish the two phases. In particular, the concept of the "transferred substance" (T-state) is a helpful one.

ACKNOWLEDGEMENT

The author wishes to thank Miss M. P. Steele for assistance in the preparation of the diagrams for this paper.

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† There appears to be no physically realistic solution to the equations possible when $g^*_{\mathrm{I},h}/(g^*_{\mathrm{I},h} + g^*_{\mathrm{II},h})$ exceeds the value 0·81. The author is not sure how to interpret this, since it is physically possible to arrange the flow patterns of liquid and gas streams so that this ratio *is* exceeded. This matter requires further study.

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Résumé—Cet article présente une analyse théorique rigoureuse du transport de chaleur et de masse qui intervient sur un élément de la surface de séparation des phases liquide et gazeuse d'un mélange binaire. Des solutions des équations sont présentées pour des mélanges eau–alcool éthylique dans les troise cas suivants: (1) Les milieux gazeux et liquide ne sont pas saturés et les deux nombres de Lewis sont égaux à l'unité; (2) Les phases sont saturés et les deux nombres de Lewis sont égaux à l'unité; (3) Le nombre de Lewis du liquide est voisin de zéro tandis que celui du gaz ést égal à l'unité, les milieux étant saturés ou non. Les résultats sont comparés aux prévisions des solutions approchées habituellement utilisées (transport équimoléculaire).

La théorie habituelle ne donne des résultats dont la précision est acceptable que dans le cas 2; dans les autres cas ses solutions n'ont presque pas de rapport avec celles de la théorie rigoureuse.

La théorie rigoureuse montre que, dans les exemples étudiés, il peut se produire une condensation ou une vaporisation très nette suivant les valeurs de la conductance et les états des milieux. Dans quelques cas, le composant le plus volatil se condense bien qu'il ait une concentration en phase gazeuse plus élevée à la surface de séparation que dans le milieu continu gazeux.

Zusammenfassung—Für den Wärme- und Stoffübergang an einem Element der Trennschicht zwischen Flüssigkeits- und Gasphase eines binären Gemisches wird eine strenge theoretische Analyse angegeben. Die Lösungen der Gleichungen erstrecken sich auf Äthanol–Wasser Gemische für drei verschiedene Fälle, nämlich—(i) die Flüssigkeits und Gasströme sind nicht gesättigt und beide Lewiszahlen haben die Grösse eins; (ii) Flüssigkeits- und Gasströme sind gesättigt, beide Lewiszahlen sind gleich eins; (iii) die Lewiszahl der Flüssigkeit ist nahezu Null, während die des Gases gleich eins ist und die Ströme entweder gesättigt sind oder nicht. Die Ergebnisse werden mit jenen verglichen, die aus gewöhnlich verwendeten Näherungsbetrachtungen (äquimolare Übertragung) gewonnen werden (z.B. [1]). Die konventielle Theorie ergibt nur im Falle (ii) leidliche Genauigkeit; in den anderen Fällen stehen ihre Ergebnisse in nahezu keinem Zusammenhang mit denen der strengen Theorie. Nach der strengen Theorie kann in den betrachteten Beispielen—abhängig von den Leitfähigkeitswerten und den Zuständen im Innern der Flüssigkeit bzw. des Gases—entweder reine Kondensation oder reine Verdampfung auftreten. In einigen Fällen kondensiert die flüchtigere Komponente, obwohl an der Trennfläche eine höhere Gasphasenkonzentration vorliegt als im Innern des Gases.

Аннотация—Предложена совместная система уравнений, описывающая установившийся тепло-и массоперенос через промежуточный элемент, отделяющий жидкую фазу от газообразной, состоящей из паров той же жидкости. Описан графический метод решения предложенной системы уравнений. Приведены численные примеры расчётов по предложенному методу. Полученные результаты сопоставляются с общепринятым методом расчёта.