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CALCULATION MANUAL FOR LIQUID-LIQUID EXTRACTION

By
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CALCULATION MANUAL FOR LIQUID-LIQUID EXTRACTION

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1.0 Abstract

A calculation manual for liquid-liquid extraction processes is presented, providing the background for, and the development of, a consistent mathematical picture covering the rate of extraction. The basis for the treatment is the idea that diffusion is the controlling process, and that the resistances to diffusion reside in two liquid films adjacent to an interface.

The analysis leads to methods of interpretation and correlation of experimental data, to procedures for equipment design, and to suggestions on the planning and conduct of experimental work.

2.0 Introduction

Liquid-liquid extraction, as a unit operation, is very old. Many procedures and many equipment details were developed long before any extensive theoretical work was begun. Nonetheless, extraction as an engineering tool is comparatively so recent that even now the theoretical aspects have not been developed and understood to a satisfactory degree. There is no adequate text on the subject. The technical literature is widely scattered and is confused by differing nomenclature and by conflicting basic assumptions. Consequently, need was seen for a summarization of extraction theory that is complete, up-to-date, and consistent in regard to viewpoint and nomenclature.

The slow development of extraction theory reflects the fact that in the past the process of extraction has not been particularly effective. In turn, this is because the known solvents were hardly ever very selective in their action. But in recent years, it has developed that for many inorganic compounds there exist organic "solvents" that react to form loosely-bound complexes whose formation is so specific and so selective that new realms of possibility have been opened up for solvent extraction.

A serious deterrent to the development of extraction as a unit operation has been the overuse of the analogy between the usual countercurrent process and a succession of equilibrium stages. It has been customary to express the behavior of a countercurrent process in terms of so many equivalent equilibrium stages, by use of the HETS, height equivalent to a theoretical stage. The

Introduction (continued)

analogy is easy to employ, is useful, and will always have a place. But the analogy is basically incorrect in any actual case excepting that of mixer-settlers, and beyond a point in its use is actually harmful. It does not supply a true picture of the actual processes, yet by appearing to do so, the analogy operates as a mental block to a more complete understanding. In any actual countercurrent system equilibrium is never attained at any point. Indeed, if equilibrium were attained, the extraction process would stop because it depends for its progress on a driving force which is exactly the degree by which equilibrium is not attained.

A basic, and more suitable, approach to extraction problems comes from consideration of the actual diffusional behavior. Material diffuses in response to a gradient in chemical potential which, for engineering purposes, is adequately expressed as a concentration gradient. Suitable differential equations embodying this fact have been integrated across the two-film resistances of a liquid-liquid contact, and from one equipment terminal to the other. The resulting equations are expressive of the diffusional character of the process. This procedure leads to the concept of a transfer unit which represents a definite amount of progress in a diffusional transfer. The HTU, height of a transfer unit, bears a definite relation to the older concept of HETS.

The diffusional approach has not yet been widely applied to liquid-liquid extraction, mainly because of its newness. One of the most successful instances has been the work of Colburn and Welsh, who planned their experimental work in

Introduction (continued)

such a manner that the individual film resistances were separately measured. This is a distinct advance over previous work which always measured the combined resistance of the two adjacent films, and left uncertain the contribution of each. This technique, if properly exploited, could supply the detailed information on the behavior of individual film resistances, without which no general advance in the state of extraction theory is possible.

The diffusional approach to extraction processes requires for its best use a considerable body of physical data on liquid diffusion coefficients. Very little of the required physical data is at hand. Therefore, some attention should be paid now to the problems of obtaining such data.

This work was done while the author was a Research Participant at Oak Ridge National Laboratory, on loan from North Carolina State College.

3.0 Mass Transfer Through Fluid Films

3.10 Film Concept of Mass Transfer

In the development of the diffusional theory, a prominent part is given in this report to mass transfer through gaseous films. For the purposes of building up a diffusional theory for liquid-liquid extraction, this might appear somewhat strange. Actually, there is good reason for this. Historically, the diffusional approach was first applied to gaseous systems. In so doing, a large body of terminology, numerous equations, many assumptions, and many manners of approach were developed and are in constant use today. Many of these ideas and forms are applied directly to liquid-liquid extraction cases by mere substitution or redefinition of symbols. Or, at other times, a method of approach for the gaseous case is carried to an arbitrary stage, then additional assumptions are made to apply to the liquid case, and the development continued. As a result, it is quite difficult to follow many papers on extraction unless one is familiar with the work on gaseous mass transfer.

The diffusional approach emphasizes the fact that there are similarities between heat transfer, mass transfer and momentum transfer (involved in friction losses). While the analogies between the three processes are still incomplete, it is clear that the effective films involved in mass transfer are substantially the same as the ones postulated in heat transfer and momentum transfer. This means that there is a close similarity between distillation, absorption, heat transfer, extraction, leaching, dialysis, crystallation, humidification and drying operations. The realization of these facts has greatly accelerated both

Film Concept of Mass Transfer (continued)

theoretical and experimental work in extraction, as witness the recent "Absorption and Extraction Symposium" in the June, 1950, issue of Industrial and Engineering Chemistry.

3.11 Basic Picture

Consider an object immersed in a flowing stream, either gaseous or liquid. Notwithstanding turbulence in the main body of flow, some of the fluid forms into a thin film-like layer that hugs the object tightly, covering it completely, and following its contours. This film is remarkably like a skin of variable thickness. The fluid that comprises this skin-like layer is not stagnant, for it possesses motion. But the motion within the film is always streamline, or laminar, meaning that the lines of flow are parallel to each other and follow smoothly the contours of the object. It has been shown that the velocity of flow decreases through the film as a phase boundary is approached, and that the velocity reaches exactly zero at a solid-fluid boundary.

Wherever a fluid possesses a phase boundary, there the fluid also possesses this film. Even when two fluids are in contact, such as a vapor and a liquid, or a liquid and another liquid, each fluid possesses a film at the boundary.

3.12 Relation of the Film to the Main Body of Flow

In the usual case, the fluid beyond the film is found to be in a state of turbulent flow. The slower the average flow the less the turbulence and the thicker the film, until finally in the end the film extends throughout the fluid space. But the reverse does not take place. While the laminar film does decrease in thickness as the main body turbulence increases, never does the film disappear entirely (except perhaps at some supersonic velocity).

The transition from the film to the main body is never abrupt, there being an ill-defined transition region which fluctuates with time in its behavior and which smooths out the turbulent swirls and diminishes their violence so that they grade imperceptibly into the two main patterns. This makes it difficult to define the film thickness with precision, and has led to the use of the terminology of an "effective film thickness", or a "fictitious film".

3.13 Evidence for the Film's Existence

The evidence in favor of the film is overwhelming. Theories and deductions based upon the film concept have had remarkable success. It has been demonstrated physically by photographic techniques and has even been explored for its velocity profile. One such velocity profile for an air film of about 0.015" thickness on a flat plate is shown in Figures 39 and 40, pages 102 and 103, McAdams, "Heat Transmission", 2nd edition. The velocity profile for films inside smooth, round pipes is shown in Figures 49 and 50, page 110 of the same reference.

Evidence for the Film's Existence (continued)

The order of magnitude of the film thickness is from 0.01 to 1.0 millimeter. This makes it very much thicker than the "films" of which the physical chemist speaks in connection with adsorption and catalysis.

3.14 Importance of the Film

To the engineer, these fluid films are of tremendous importance because they are barriers, or resistances, to flow toward and away from phase boundaries. Since the only fluid flow in the film is streamline flow parallel to the phase boundary, any transport perpendicular to the phase boundary must be by diffusion. Transport by diffusion is a very much slower process than is transport by fluid flow or turbulence (in the usual case). Hence, while the fluid film may form only a fraction of a percent of the thickness of total fluid, it usually represents virtually all of the resistance to transport to and from a boundary.

Strictly speaking, three resistances to transport to and from a phase boundary can be distinguished. One is the film resistance, one is the resistance in the boundary or transition zone, and one is the resistance in the main body of the fluid. Of these, the film resistance is at least 80 percent of the total for most chemical engineering applications. Because of this, it is customary to imagine a fictitious film whose thickness is sufficient to provide in effect the total resistance of all the classes. Practically all chemical engineering calculations are made in terms of this "effective film".

Importance of the Film (continued)

There are some who consider it desirable to treat the system as consisting of two resistances, one as effective film resistance and the other an "eddy" or "core" resistance to make up the total. But no general system of ideas, methods and correlations has yet been built on the use of two classes of resistance. On pages 541 to 543 of Chemical Engineering Handbook, 3rd edition, can be found a discussion involving these points, and a guide to the most pertinent literature.

3.20 Single Film Mass Transfer

3.21 Gaseous Diffusion (Binary Case)

3.21.1 Stephan Equation

For the diffusion of gaseous molecules A in a mixture of A and B, the classical kinetic theory plus the assumption of steady state behavior (no acceleration) leads to the Stephan equation.

$$-dC_A = \alpha_{AB} C_A C_B (U_A - U_B) dB$$

where

C = concentration in lb mols/ft^3

U = velocity, in ft/hr

B = "effective" film thickness, feet

Since we have a binary gas case, $C_A + C_B = C$ = constant, and

$dC_A + dC_B = 0$. We can show that

$$\alpha_{AB} = \alpha_{BA} = \alpha$$

Stephan Equation (continued)

In other words, for a binary case there is only one diffusion coefficient. Molecule B diffuses exactly as fast as molecule A, the driving forces being equal. The diffusivity of H_2 is the same as that of Hg in a mixture of H_2 and Hg, but this diffusivity value is different from that of H_2 in H_2 and air. For a binary system, the diffusivity is a common property of both phases, somewhat like the case of interfacial tension between two liquids. For examples of this effect, see Figures 4 and 5, page 21, "Absorption and Extraction", by T. K. Sherwood.

With liquids, the case is sufficiently similar in this regard to say that the diffusivity is the same for both components of a binary mixture. If one has a multicomponent mixture, then the individual components acquire individual diffusivities. Similarly, for multicomponent ionic solutions.

We define the volumetric diffusivity for the vapor phase, D_V as lb mols of A per hour per square foot per unit of concentration driving force in lb mols A per cubic foot per foot of travel. If the concentration driving force is expressed as lb mols of A per lb mol of phase, per foot of travel, the diffusivity is written D_M and called the diffusivity in mass units. Since, in a binary system the total concentration, $C_A + C_B$, is constant and we have previously seen that $\alpha_{AB} = \alpha_{BA} = \alpha$

we may then write $D_V = \frac{1}{\alpha C}$, where $C = C_A + C_B$ = total concentration

The diffusivity, D_V, may have the units of $\frac{ft^2}{hr}$, $\frac{cm^2}{sec}$ or any $Length^2/Time$.

3.21.2 Conversion to Common Units

Let N_A = lb mols of A diffusing per hour per sq. ft.

Then, $N_A = U_A C_A = \frac{(ft)}{(hr)} \frac{(lb\ mols)}{(ft^3)} = \frac{lb\ mols}{(hr)(ft)^2}$

Substituting into the Stephan equation,

$$-dC_A = \frac{C_A C_B}{D_v C} \left[\frac{N_A}{C_A} - \frac{N_B}{C_B}\right] dB$$

If we express in terms of mol fraction,

$C_B = y_B C$ $\qquad dC_B = C dy_B$

$C_A = y_A C$ $\qquad dC_A = C dy_A$

Then

$$-dy_A = \frac{y_A y_B}{D_v C} \left[\frac{N_A}{y_A} - \frac{N_B}{y_B}\right] dB$$

$$-dy_A = \frac{1}{D_v C} \left[N_A y_B - N_B y_A\right] dB$$

Similarly, in terms of partial pressure, and

because $C = \frac{n}{v} = \frac{x}{RT}$, $C_A = \frac{p_A}{RT}$, $C_B = \frac{p_B}{RT}$

$$-dp_A = \frac{RT}{Dvx} \left[N_A p_B - N_B p_A\right] dB$$

3.21.3 Single Component Diffusing Through a Film

Examples of a single component diffusing through a gaseous film may be found in humidification, absorption, and adsorption. Diffusion through liquid films is found among crystallization, dialysis, leaching, and extraction processes.

Refer to the accompanying Fig. 1. In this case, $U_B = 0$, $N_B = 0$, and

$$-dC_A = \frac{N_A \; C_B}{D_v \; C} \; dB$$

$$N_A = \frac{D_v C}{C_B} \left(-\frac{dC_A}{dB}\right) = \frac{D_v C}{C_B} \; \frac{dC_B}{dB} = D_v C \left(\frac{d\ln C_B}{dB}\right)$$

Compare these equations with equation 49, page 538, Chemical Engineering Handbook, 3rd edition, which, in our symbols, is

$$N_A = -D_v \left(\frac{dC_A}{dB}\right)$$

The above equation is for equimolar counter diffusion, a slightly different case. Converting to mol fraction, we get

$$N_A = \frac{D_v C}{y_B} \; \frac{dy_B}{dB} = D_v C \; \frac{d\ln y_B}{dB}$$

$$\int_{y_{BG}}^{y_{Bi}} d \ln y_B = \frac{N_A}{D_v C} \int_0^{B_G} dB$$

$$\ln \frac{y_{Bi}}{y_{BG}} = \frac{N_A}{D_v C} \; B_G$$

$$\text{Since } (y_B) \text{ log mean} = \frac{y_{Bi} - y_{BG}}{\ln \frac{y_{Bi}}{y_{BG}}} = \frac{y_{AG} - y_{Ai}}{\ln \frac{y_{Bi}}{y_{BG}}}$$

SINGLE COMPONENT DIFFUSION

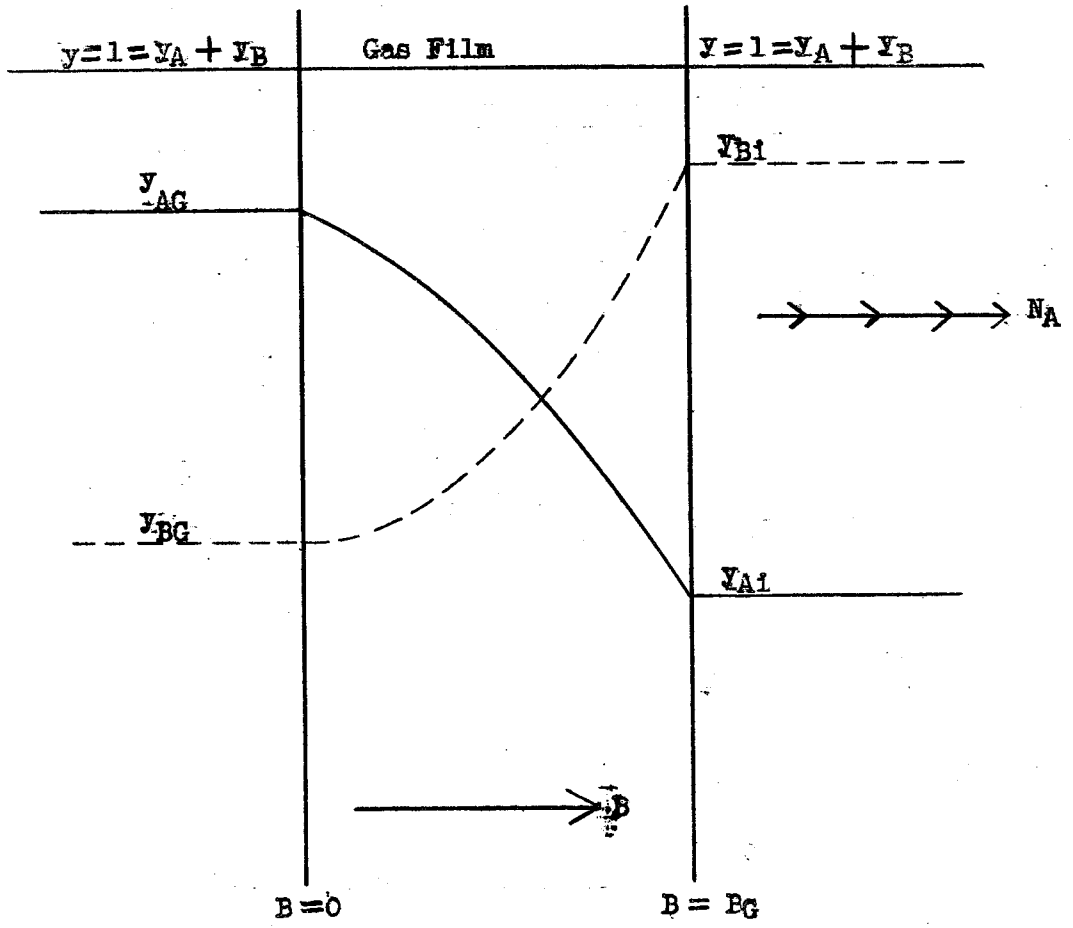

Figure 1

Single Component Diffusing Through a Film (continued)

$$N_A = \frac{D_v C}{B_G} \quad \frac{y_{AG} - y_{Ai}}{(y_B)_{lm}} = \frac{D_v \pi}{RTB_G} \quad \frac{y_{AG} - y_{Ai}}{(y_B)_{lm}}$$

This is equation 55, page 539, Chemical Engineering Handbook, 3rd edition.

Note that while the B molecules have no net diffusion rate, they nevertheless end up with a concentration gradient that apparently should give them a diffusion rate opposite that of A (See Figure 1). The answer is that in a sense, the B molecules are diffusing to the left, but their velocity of travel is just enough to keep them where they are. Obviously, then, the faster the transport rate of A, the steeper the concentration gradient of B, and the more the gas film changes towards just B molecules. This effect in turn chokes down on the flow of A. It is because of this manner of build-up of B in the film that the devised equation has the term $(y_B)_{lm}$.

3.21.4 Two Components in Equimolar Counter Diffusion

The only case in counter diffusion that it is practical to handle is the one wherein the two counter-diffusion rates are exactly equal. This situation is closely true for both the vapor and liquid films in distillation, and is approached sometimes in liquid-liquid extraction.

Our basic assumption, then, is that $N_A = -N_B$.

Then since $$-dC_A = \frac{C_A C_B}{D_v C}\left[\frac{N_A}{C_A} - \frac{N_B}{C_B}\right] dB$$

$$-dC_A = \frac{1}{D_v C}\left[N_A C_B + C_A N_A\right] dB = \frac{N_A}{D_v}\, dB$$

and $$N_A = -D_v \frac{dC_A}{dB} = D_v \frac{dC_B}{dB} = -\left(\frac{D_v \pi}{RT}\right)\frac{dy_A}{dB}$$

This is apparently equation 49, page 538, Chemical Engineers Handbook, 3rd Edition.

In this case the gradient across the film is straight (see Figure 2). The integration leads to

$$N_A = \frac{D_v C}{B_G}\left(y_{AG} - y_{Ai}\right) = \frac{D_v \pi}{RTB_G}\left(y_{AG} - y_{Ai}\right)$$

This is equation 52, page 539, Chemical Engineers Handbook, 3rd Edition. Note that the log mean inert gas concentration is absent.

3.21.5 Two Components Diffusing Through a Third Component

This situation arises frequently in such cases as the absorption of NH_3 from air by H_2O. If one takes into consideration the simultaneous movement of both NH_3 and H_2O vapor through the stagnent air, the case is somewhat different from the movement of NH_3 alone.

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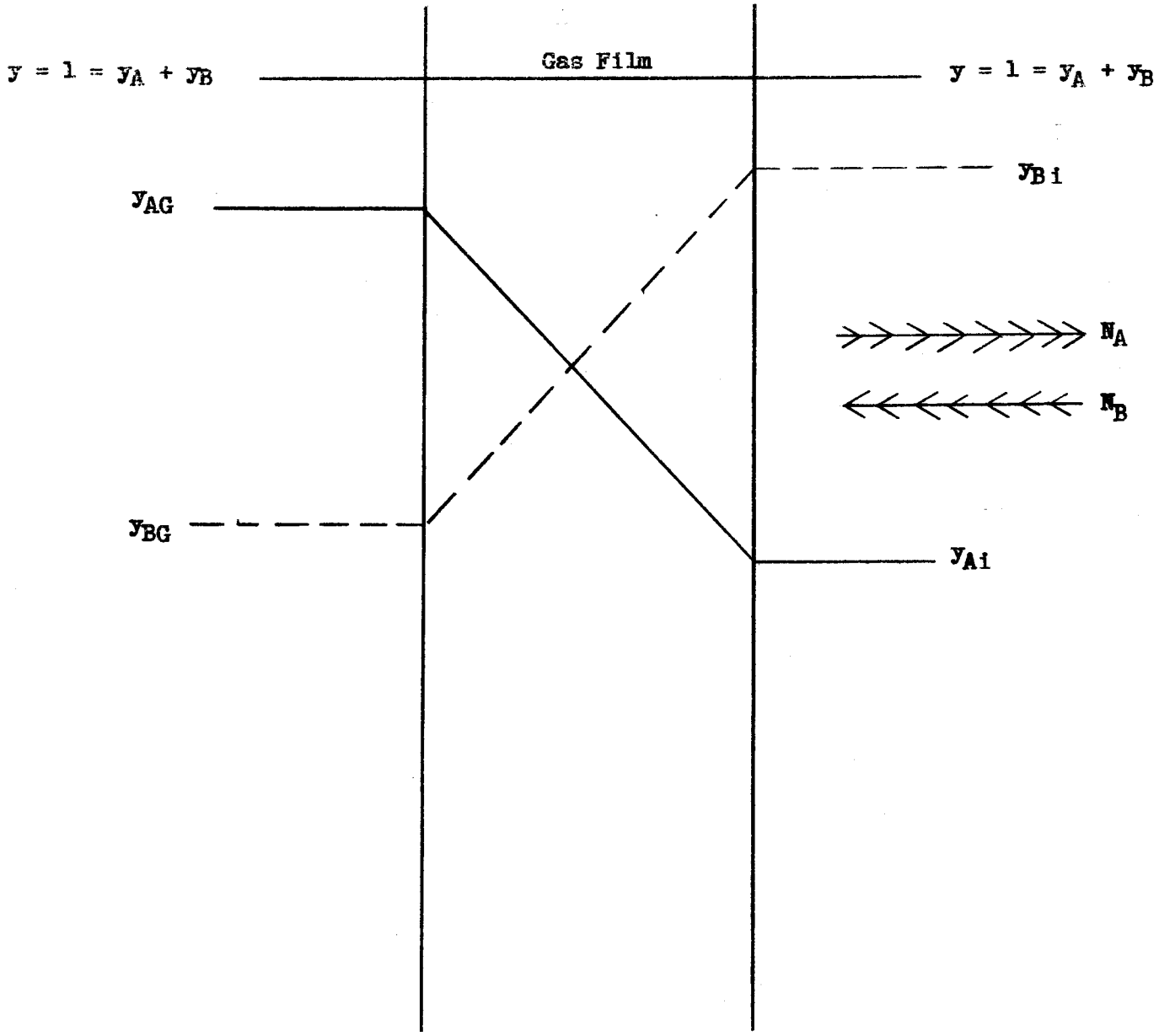
Figure 2

EQUIMOLAR COUNTER DIFFUSION



Two Components Diffusing Through a Third Component (continued)

The exact solution for this case has been worked out by E. R. Gilliland and is presented by T. K. Sherwood, "Absorption and Extraction", page 10-14. Fortunately, the movement of the extra component can be neglected within about 10% error.

3.21.6 Concept of k_G

In the past it has been customary, for a single component diffusing in a steady state, to set up equations as follows (or sometimes in terms of partial pressures).

$$N_A = k_G (y_{AG} - y_{Ai}) = \frac{\text{lbmols A}}{(\text{hr})(\text{ft})^2}$$

$$\text{Since } N_A = \frac{D_V \pi}{RTB_G} \frac{(y_{AG} - y_{Ai})}{(y_B)_{lm}}$$

$$k_G = \frac{D_V \pi}{RTB_G (y_B)_{lm}} \frac{D_V C}{B_G (y_B)_{lm}}$$

For the case of equimolar counter diffusion, we define a slightly different k_G' and get

$$k_G' = \frac{D_V \pi}{RTB_G} = \frac{D_V C}{B_G}$$

$$k'_G = (y_B)_{lm} \; k_G$$

3.21.7 Concept of H_G

Consider a vapor-liquid contacting tower, with vapor flowing upward and liquid downward. Focus attention on a differential height of tower, dZ, in which is exposed dA units of interfacial area available for mass transfer (see Figure 3). First the equations will be worked out for the case of one component diffusing. The amount of material transferred across dA is as follows:

$$N_A dA = \frac{\text{lbmols}}{(\text{hr})} = \frac{D_V \pi \ (y_{AG} - y_{Ai})\ dA}{RT\ B_G\ (y_B)_{lm}} = k_G\ (y_{AG} - y_{Ai})\ dA$$

$$N_A dA = SV_i dY = (\text{ft})^2 \left(\frac{\text{lbmols inert}}{(\text{hr})(\text{ft})^2}\right) \left(\frac{\text{lbmols A}}{\text{lbmols inert}}\right)$$

S = superficial tower cross-section

$$Y = \frac{y_A}{y_B} = \frac{\text{lbmols A}}{\text{lbmol inert}}$$

$$dY = d\ (y_A/y_B) = \frac{dy_A}{y_B^{\,2}}$$

$$\text{Thus} \quad \frac{D_V \pi \ (y_{AG} - y_{Ai})\ dA}{RTB_G\ (y_B)_{lm}} = SV_i \ \frac{dy_A}{y_B^{\,2}}$$

Rearranging, and defining $V_M\ y_B = V_i$

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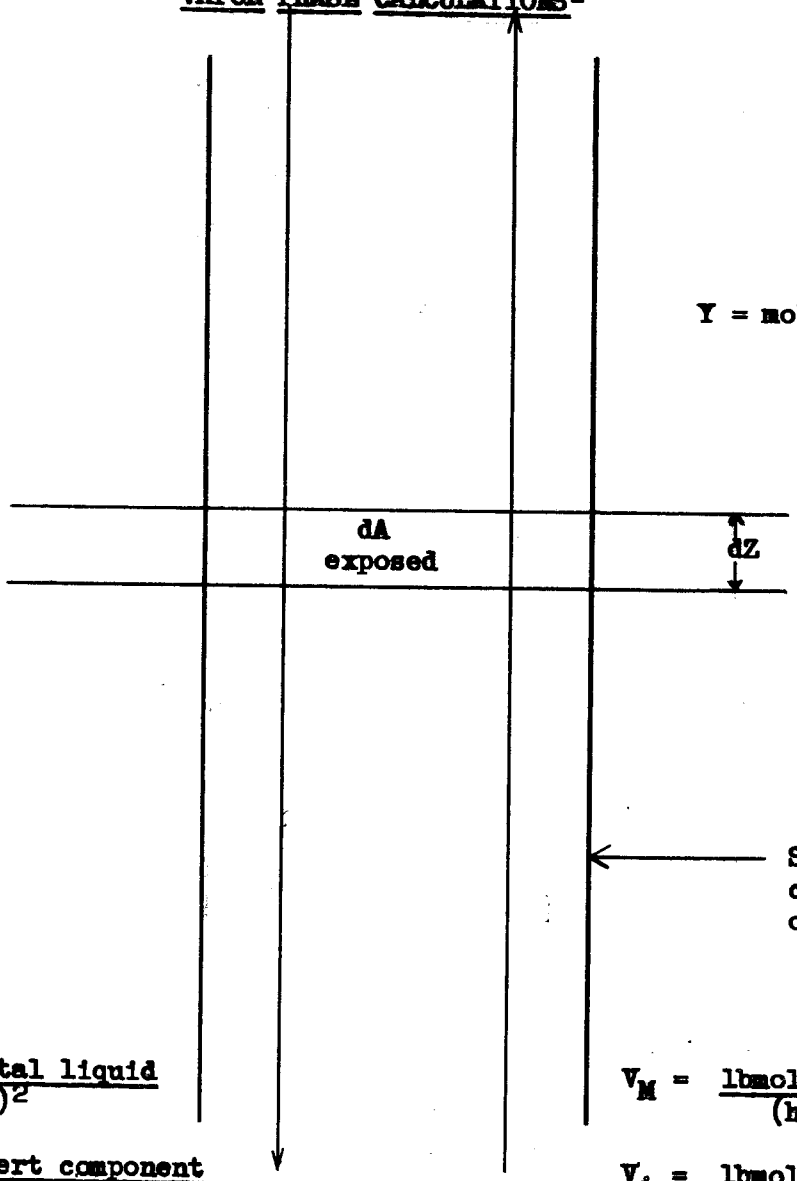
Figure 3

COUNTERCURRENT CONTACT IN A TOWER
-VAPOR PHASE CALCULATIONS-



Y = mol ratio = $\frac{\text{lbmols A}}{\text{lbmol inert}}$

S = superficial cross-section area of tower.

L_M = $\frac{\text{lbmols of total liquid}}{(\text{hr})\ (\text{ft})^2}$

L_i = $\frac{\text{lbmols of inert component}}{(\text{hr})\ (\text{ft})^2}$

V_M = $\frac{\text{lbmols of total vapor}}{(\text{hr})\ (\text{ft})^2}$

V_i = $\frac{\text{lbmols of inert component}}{(\text{hr})\ (\text{ft})^2}$

Concept of H_G (continued)

$$\frac{(y_B)_{lm}\ dy_A}{(y_B)(y_{AG} - y_{Ai})} = \left(\frac{D_V \pi}{RTB_G}\right)\left(\frac{y_B dA}{V_i^3}\right) = \frac{D_V \pi\ dA}{RTB_G V_M S}$$

Now, for any given packing material, or spray nozzle, the square feet of interfacial area exposed per cubic foot of tower is a constant. In other words,

$A = aV_T$, V_T being the tower volume,

and $dA = adV_T$

Furthermore, $\frac{V_T}{S} = Z$

Hence, $\frac{(y_B)_{lm}\ dy_A}{(y_B)(y_{AG}-y_{Ai})} = \frac{D_V \pi\ a\ d\ Z}{RTB_G V_M} = \frac{k_G\ a\ (y_B)_{lm}\ dZ}{V_M}$

The concept of the height of a transfer unit, and the number of transfer units arose from two aspects of the above equations.

(1) The left hand member is a function of y_A alone, contains in itself (practically) all of the y terms, and moreover is dimensionless. Furthermore, changes in y_A have little effect on the right-hand terms. As a consequence, for any given circumstance, all the changes that take place in y are reflected only in the left term. This term, then varies with the required changes in concentration across the tower. The more the y values must change to give greater adsorption, the bigger the expression gets, and vice versa. It is, therefore, logical to say that the left term measures the difficulty of carrying out a given separation. The units in which this difficulty is expressed are called transfer units.

Concept of H_G (continued)

Thus $$N_G = \int \frac{(y_B)_{lm}\, dy_A}{(y_B)(y_{AG} - y_{A1})}$$

N_G = number of transfer units, based upon gas film concentration units

At this stage, we can say $$N_G = \int \frac{D_V \pi a}{RTB_G V_M}\, dZ$$

(2) For a gas film, the expression $\frac{D_V \pi a}{RTB_G V_M}$ taken as a whole, can be shown theoretically to be independent of π, practically independent of y, dependent upon absolute temperature only to the 0.06 power ($T^{0.06}$), and dependent only upon $V^{0.2}$. The net result is that for any reasonable changes within a tower

$$\frac{D_V \pi a}{RTB_G V_M} = \text{constant} = \frac{1}{H_G}$$

Then $$N_G = \frac{1}{H_G} \int dZ = \frac{Z}{H_G}$$

Writing thus, $Z = N_G H_G$

H_G is seen to be the height of a transfer unit, N_G.

In accordance with these ideas, Gilliland and Sherwood, I.E.C., 26, 516 (1934) showed experimentally that H_G is independent of total pressure. Colburn, A.I.Ch.E., 35, 219 (1939) showed that H_G varied as $V_M^{0.1}$ to $V_m^{0.2}$. The effect of temperature has not been proven, but apparently is slight.

Summarizing, for one component diffusing

$$N_G = \int \frac{(y_B)_{lm}\, dy_A}{(y_B)\,(y_{AG} - y_{Ai})} = \frac{Z}{H_G}$$

$$H_G = \frac{RTB_G\, V_M}{D_V \pi a} = \frac{V_M}{k_G a (y_B)_{lm}} = \frac{(B\ )\ (\text{Superficial Vapor Velocity, ft/hr})}{D_V\ a}$$

If we treat the case of equimolar counter-diffusion, we get

$$N_G = \int \frac{dy_A}{y_{AG} - y_{Ai}} \qquad \frac{Z}{H_G}$$

$$H_G = \frac{RTB_G V_M}{D_V \pi\ a y_B} = \frac{V_M}{k'_G\ a\ y_B} = \frac{(B_G)(\text{Superficial Vapor Velocity, ft/hr})}{D_V\ a\ y_B}$$

3.21.8 Correlations for Gas Diffusion Coefficients

The equations usually derived treat only the case of one component diffusing through a mixture with another component, as H_2O through H_2O-air. The best correlation is that of Gilliland, reported as equation 50, page 538, Chemical Engineers Handbook, 3rd Edition. With this equation, the D_V values for binary systems can be calculated just about as accurately as they usually are determined experimentally.

The case of one gas diffusing through a multicomponent stagnant gas mixture has been treated by C. R. Wilke, Chem. Eng. Prog., 46, 95-103, 1950. Rules are given for the calculation of the proper diffusivity coefficient.

For gases, kinetic theory indicates that the Schmidt number, $\frac{\mu}{\rho\, D_V}$, is constant for self diffusion of a molecule among its own kind. This idea is sometimes extended to a multicomponent system to estimate the effects of temperature, pressure, and density changes upon D_V.

3.22 Liquid Diffusion

3.22.1 Approach Used

Liquid diffusion is more complicated than gaseous diffusion, since molecular interactions are much stronger in the condensed phase. Lacking any sound fundamental approach, we are left with nothing better to do than to assume the same basic form, the Stephan equation, that we used for the gaseous case, and to assume further that the diffusivity term, D_L, takes into consideration all that is necessary. The result is that D_L frequently varies more with concentration than we would like, and in regard to the derivations of equations, some confusion can arise as the result of various workers making different assumptions as to what to do with various minor terms they do not feel justified in carrying along.

3.22.2 Single Component Diffusing

Strictly by analogy with the case for gaseous diffusion of a single component, we write

$$N_A = D_L\, C \left(\frac{d \ln C_s}{dB}\right)$$

where the subscript s denotes solvent

Usually we can say that C = total conc. = $mC_s + b$, in which case the integration leads to

$$N_A = \frac{D_L\, C_{avg}}{B_L} \ln \frac{C_{sL}}{C_{si}}$$

Single Component Diffusing (continued)

Where $C_{avg} = m\,(C_s)_{lm} + b$

Now $C_{sL} = x_{sL}\,C_L$

$C_{si} = x_{si}\,C_i \cong x_{si}\,C_L$

Carrying these substitutions through, we get

$$N_A = \frac{D_L\ C_{avg}\ (x_{Ai} - x_{AL})}{B_L\ (X_s)_{lm}}$$

3.22.3 Two Components in Equi-molar Counter Diffusion

Again, by analogy with the gaseous case, we start with

$$N_A = D_L\ \frac{dC_s}{dB}$$

Proceeding as above, we quickly get

$$N = \frac{D_L\ C_{avg}\ (x_{Ai} - x_{AL})}{B_L}$$

3.22.4 Concept of k_L

Formerly, we said $N_A = k_L\ C_{avg}\ (x_{Ai} - x_{AL})$ (This differs from equation 84, page 549, Chemical Engineers Handbook, 3rd Edition), from which we get

$$k_L = \frac{D_L}{B_L(x_s)_{lm}}, \text{ for single component diffusion}$$

$$k_L' = \frac{D_L}{B_L}, \text{ for equimolar counter diffusion}$$

$$k_L' = (x_s)_{lm}\ k_L$$

3.22.5 Concept of H_L

Take first the case of one component diffusing. Refer to Figure 4. The amount of material transferred across dA is as follows.

$$N_A dA = \frac{D_L C_{avg} (x_{Ai} - x_{AL})\, dA}{B_L (x_s)_{lm}}$$

$$N_A dA = SL_s\, d\, x$$

$$X = \frac{x_A}{x_s}, \quad dX = \frac{dx_A}{x_s^2}$$

By substitution and rearrangement,

$$\frac{(x_s)_{lm}\, dx_A}{x_s (x_{Ai} - x_{AL})} = \frac{D_L C_{avg}\, dA}{L_M B_L S} = \frac{k_L (x_s)_{lm} C_{avg}\, dA}{L_M S}$$

Strictly by analogy with the gas case, we define

$$N_L = \int \frac{(x_s)_{lm}\, dx_A}{x_s (x_{Ai} - x_{AL})} = \frac{Z}{H_L}$$

and $$H_L = \frac{L_M B_L}{D_L C_{avg} a} = \frac{L_M}{k_L a (x_s)_{lm} C_{avg}} = \frac{\text{(Superficial Liquid Velocity ft/hr)}}{k_L a (x_s)_{lm}}$$

In the case of equimolar counter diffusion, we get

$$N_L = \int \frac{dx_A}{(x_{Ai} - x_{AL})}$$

$$H_L = \frac{L_M B_L}{D_L C_{avg} x_s} = \frac{L_M}{k_L' a x_s C_{avg}} = \frac{\text{(Superficial Liquid Velocity ft/hr)}}{k_L' a x_s}$$

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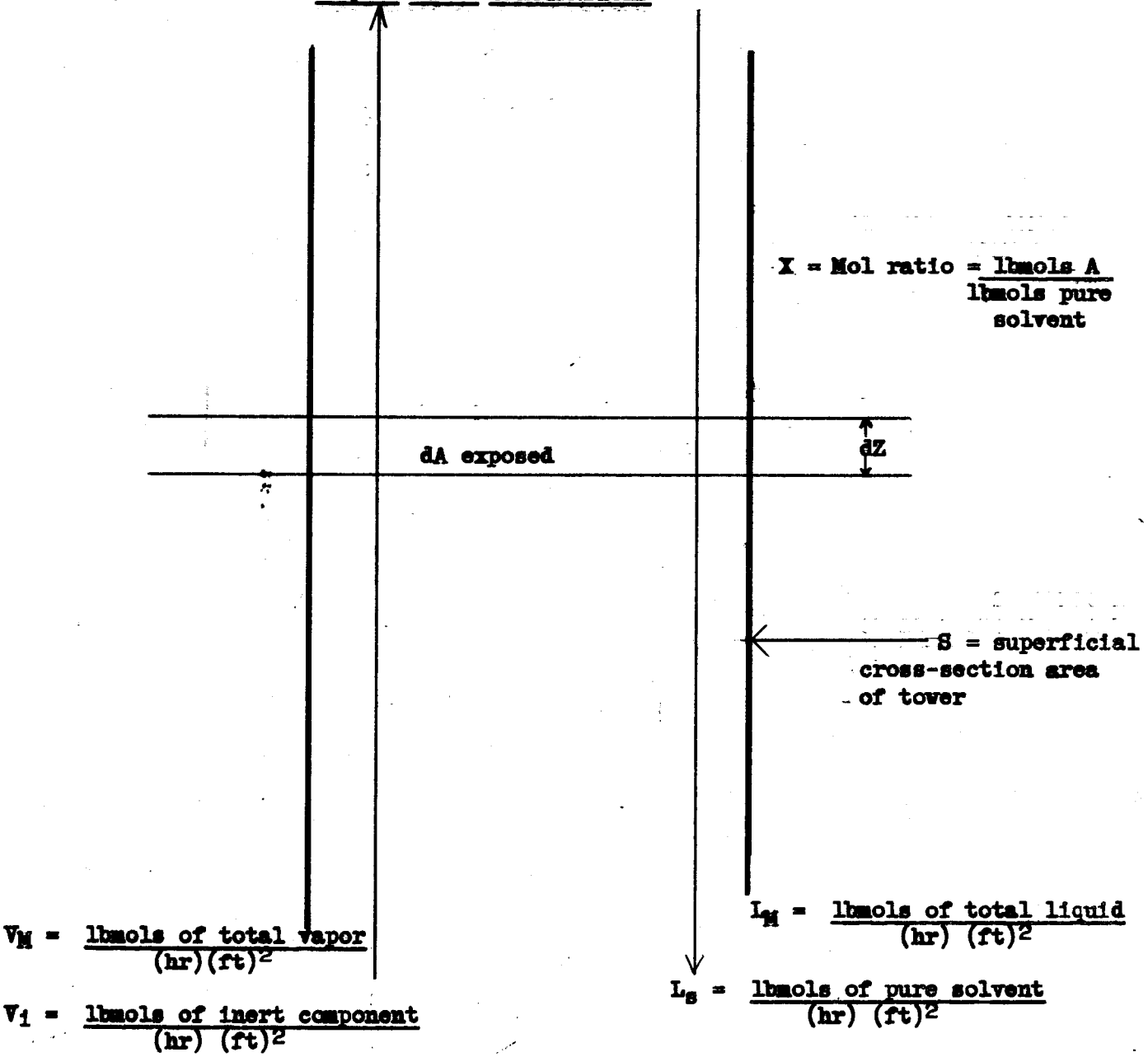
Figure 4

COUNTERCURRENT CONTACT IN A TOWER
-LIQUID PHASE CALCULATIONS-



3.22.6 Correlation for Liquid Diffusion Coefficient

In a recent article, "Estimation of Liquid Diffision Coefficients", Chem. Eng. Prog., 45 , 218-24, 1949, C. R. Wilke presents the only generally useful procedure for estimating liquid film diffusivities. He demonstrates that for liquid system the grouping $\left(\frac{T}{D_L \mu}\right)$ is substantially constant. He correlates the value of this grouping against the solute molal volume (used also in gas diffusivity correlations) for various solvents.

3.30 Two Film Transfer Theory

3.30.1 Physical Picture

According to the theory of Whitman, W. G., Chem. Met. Eng., 29, 146 (1923), when two fluid phases are in contact, there exists for each fluid at the phase boundary a fluid film with properties similar to those found when a fluid contacts a solid. These films are indeterminate in their thickness, each blending gradually in properties with the main body, and in addition, the phase boundary itself is not stable. Nevertheless, considerable success has been had with the theory that the resistance of each fluid film region can be treated like that due to an effective film thickness.

Mass is transferred across these two effective films at a rate which is the same for both when the steady state has been reached. The two films constitute two resistances in series.

Physical Picture (continued)

It is assumed that at the interface between the phases, the boundary concentrations are in equilibrium with each other. This equilibrium relationship is bound to hold unless there is a resistance at the interface. No such resistance has yet been found or even postulated for the conventional case. It is now known that if interfacial tension depressants are added or present they concentrate at the interface and constitute a third and additional resistance. Also, in the similar case of crystallization, there is an additional resistance at the interface due to the orientation necessary before the average molecule can fit into the crystal lattice. We shall assume no resistance at the interface.

A schematic drawing of two idealized adjacent fluid films is shown in Figure 5.

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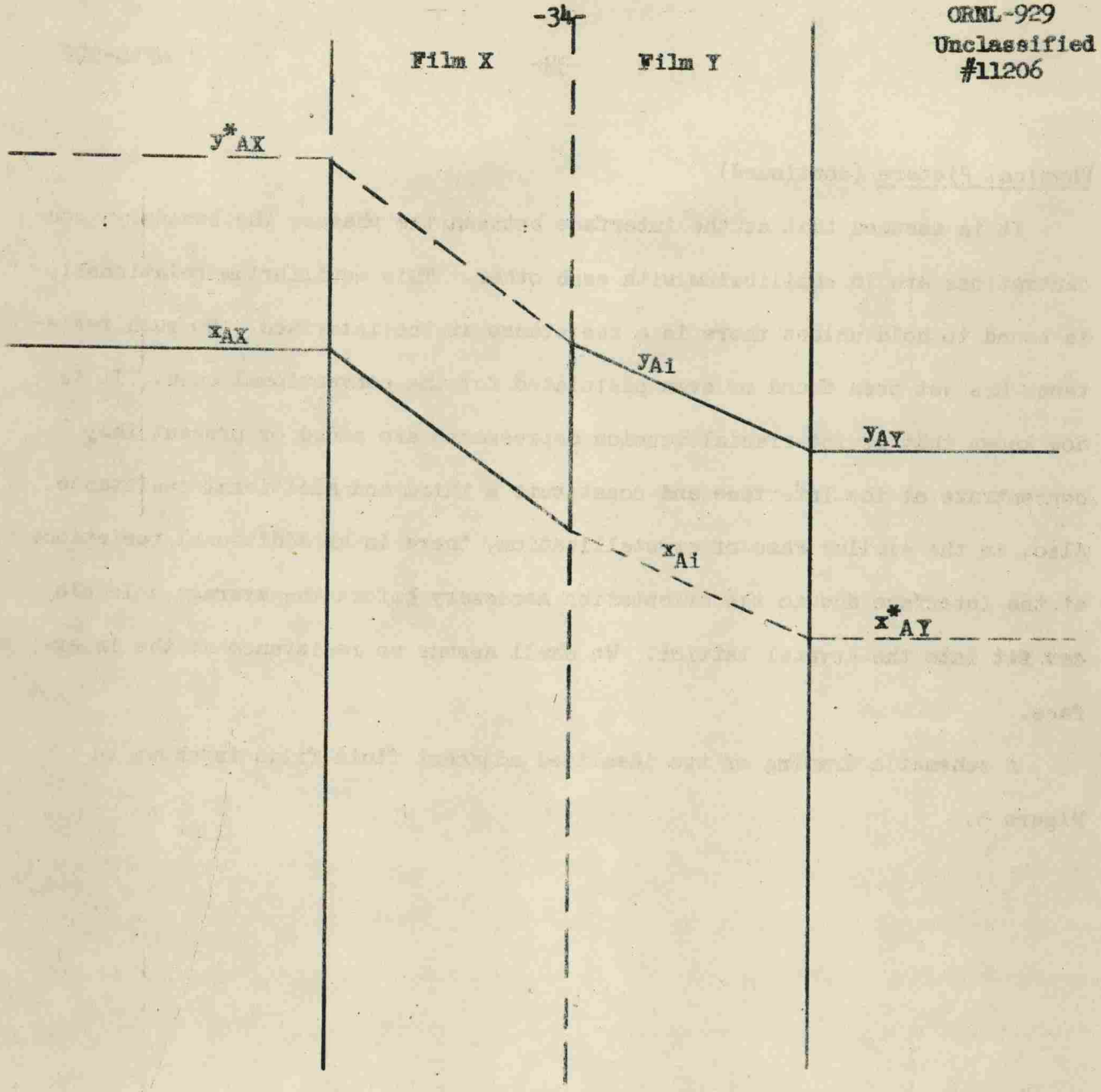

Figure 5

CONCENTRATION GRADIENTS FOR TWO ADJACENT FILMS

Physical Picture (continued)

Note the discontinuity at the interface. This arises from the fact that the liquid diffusion equations, founded as they are on the simple gas theory, are basically incorrect. The driving forces for mass transfer are certainly not concentration gradients, such as Δy and Δx, but probably are chemical potential gradients, $\frac{d\mu}{dB}$. At least when $d\mu = 0$, no mass transfer takes place, but the same cannot be said about concentration gradients.

Because we have stated our driving forces incorrectly and moreover since we use, in y and x, two different sets of concentration driving force units, we have two equally valid ways of setting up overall driving forces across the two film resistances.

Consider first the driving forces in y units. Across the y film we have the driving force y_{Ai} and y_{Ay}. Across the x film there is really no Δy. But we can proceed as follows. Suppose the x film were replaced by a y film that maintained an identity separate from the first y film. Next adjust the outer concentration of this imaginary y film to that composition, y_{AX}^*, which is in equilibrium with the x_{AX} composition. The y^*_{AX} composition has the same escaping tendency as the x_{AX}, and so serves as its counterpart. The result is that the effective driving force across the x film, in y units, is $y_{AX}^* - y_{Ai}$, and the overall driving force across both films is $y_{AX}^* - y_{AY}$.

Similarly, driving forces in x units may be postulated as $x_{Ai} - x_{AY}^*$ across the y film, $x_{AX} - y_{Ai}$ across the x film, and $x_{AX} - x_{AY}^*$ across both resistances.

3.30.2 Definitions for Single Component Diffusion

Based upon the two film theory of Whitman, and proceeding strictly by analogy with our previous definitions of H_Y and H_X, we define overall coefficients as follows:

$$N_{OY} = \int \frac{(y_B)_{OM}\ dy_A}{(y_B)\ (y_{AC}^* - y_{AY})} = \int \frac{(1-y)_{OM}\ dy}{(1-y)\ (y^* - y)} = \int \frac{(1-y)_f\ dy}{(1-y)\ (y^* - y)}$$

$$\text{where } (1-y)_{OM} = (1-y)_f = (y_B)_{OM} = \frac{(1-y) - (1-y^*)}{\ln \frac{(1-y)}{(1-y^*)}}$$

$$N_{OX} = \int \frac{(x_s)_{OM}\ dx_A}{(x_s)\ (x_{AL} - x^*_{AY})} = \int \frac{(1-x)_{OM}\ dx}{(1-x)\ (x-x^*)} = \int \frac{(1-x)_f\ dx}{(1-x)\ (x-x^*)}$$

$$\text{where } (1-x)_{OM} = (1-x)_f = (x_s)_{OM} = \frac{(1-x^*) - (1-x)}{\ln \frac{(1-x^*)}{(1-x)}}$$

$$H_{OY} = \frac{V_M}{K_G a\ (1-y)_{OM}} = \frac{(\text{Superficial Vapor Velocity, ft/hr})\left(\frac{\text{lbmols A}}{\text{ft}^3\ \text{phase}}\right)}{K_G\ a\ (1-y)_{OM}}$$

$$H_{OM} = \frac{L_M}{K_L\ a\ (1-x)_{OM}\ C_{avg}} = \frac{(\text{Superficial Liquid Velocity, ft/hr})}{K_L\ a\ (1-x)_{OM}}$$

where $N_A = K_G\ (y^*_{AX} - y_{AY}) = K_L\ C_{avg}\ (x_{AX} - x^*_{AY})$ for single component diffusion. Compare with equations 84, 98, and 100, pages 549 and 550, Chemical Engineers Handbook, 3rd Edition.

3.30.3 Definitions for Equimolar Counter-Diffusion

In a fashion similar to that above, we define the following

$$N_{OY} = \int \frac{dy_A}{(y^*_{Ax} - y_{AY})} = \int \frac{dy}{(y^* - y)}$$

Definitions for Equimolar Counter-Diffusion (continued)

$$N_{OX} = \int \frac{dx}{x_{AX} - x^*_{AY}} = \int \frac{dx}{(x - x^*)}$$

$$H_{OY} = \frac{V_M}{K'_G a\, y_{BM}} = \frac{V_M}{K'_G a\, (1-y)_{OM}} = \frac{\left(\text{Vapor Velocity, ft/hr}\right)\left(\frac{\text{lbmols A}}{\text{ft}^3}\right)}{K'_G a\, (1-y)_{OM}}$$

$$H_{OX} = \frac{L_M}{K_L a\, X_{sM} C_{avg}} = \frac{(\text{Liquid Velocity, ft/hr})}{K'_L a\, X_{sM}}$$

Where $N_A = K'_G (y^*_{AX} - y_{AY}) = K'_L C_{avg} (x^*_{AX} - x_{AY})$

For equimolar counter diffusion, compare with equations 84, 98, and 100, pages 549 and 550, Chemical Engineers Handbook, 3rd Edition.

3.30.4 Relations Between Individual and Overall HTU's

Take the case of one component diffusing. Here it just happens that y is greater than y*. Consider a section of differential tower height.

$$\frac{dZ}{dy} = \frac{H_{OG}\ (1-y)_{OM}}{(1-y)(y-y^*)} = \frac{H_G\ (1-y)_M}{(1-y)(y-y_i)}$$

From which $H_{OG} = H_G\left(\frac{y-y^*}{y-y_i}\right)\frac{(1-y)_M}{(1-y)_{OM}}$

also: $\frac{dz}{dx} = \frac{H_{OL}\ (1-x)_{OM}}{(1-x)(x^*-x)} = \frac{H_L\ (1-x)_M}{(1-x)\ (x_i-x)}$

From which $H_{OL} = H_L\ \frac{(x^*-x)}{(x_i-x)}\ \frac{(1-x)_M}{(1-x)_{OM}}$

We make this rearrangement,

$$\frac{y-y^*}{y-y_i} = \frac{y-y_i\ +\ y_i\ -\ y^*}{y\ -\ y_i} = 1\ +\ \frac{y_i\ -\ y^*}{y\ -\ y_i}$$

Relations Between Individual and Overall HTU's (continued)

Substituting, we get

$$H_{OG} = H_G \frac{(1-y)_M}{(1-y)_{OM}} + H_G \frac{(y_i - y^*)}{(y - y_i)} \frac{(1-y)_M}{(1-y)_{OM}}$$

We can relate H_G and H_L

$$\frac{H_G}{H_L} = \frac{(1-y)(y-y_i)}{(1-y)_M \, dy} \times \frac{(1-x)_M \, dy}{(1-x)(x_i-x)}$$

Substituting, we get

$$H_{OG} = H_G \frac{(1-y)_M}{(1-y)} + H_L \frac{dx \, (1-y)(1-x)_M (y_i - y^*)}{dy \, (1-x)(1-y)_{OM} \, (x_i-x)}$$

Now a material balance gives

$$V_i \, d \, Y = L_i \, d \, X$$

From which comes

$$\frac{V_M}{L_M} = \frac{dx \, (1-y)}{dy \, (1-x)}$$

Substituting further

$$H_{OG} = H_G \frac{(1-y)_M}{(1-y)_{OM}} + H_L \left(\frac{V_M}{L_M} \right) \frac{(1-x)_M}{(1-y)_{OM}} \frac{(y_i - y^*)}{(x_i - x)}$$

Consider now, Figure 6, a plot of the equilibrium curve and the operating line, and the compositions y and x at some point in a tower.

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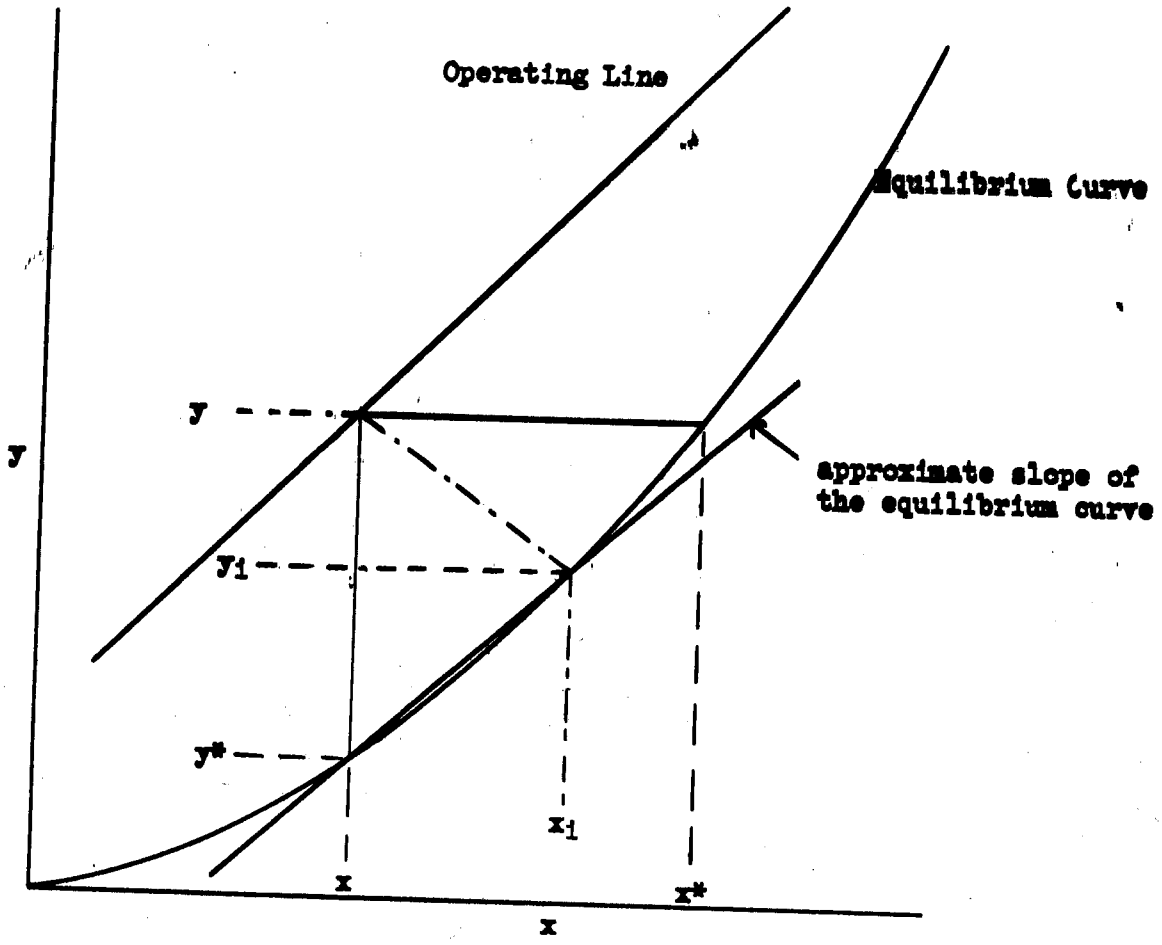
Figure 6

TOWER CONDITIONS



Relations Between Individual and Overall HTU's (continued)

The average slope of the equilibrium curve over the pertinent section of the curve is,

$$m = \text{slope} = \frac{y_i - y^*}{x_i - x}$$

Using this m value

$$H_{OG} = H_G \frac{(1-y)_M}{(1-y)_{OM}} + \left(\frac{mV_M}{L_M}\right) H_L \frac{(1-x)_M}{(1-y)_{OM}}$$

If the gas film controls, $x_i \rightarrow x$, $y_i \longrightarrow y^*$

The equation then simplifies to

$$H_{OG} = H_G + \frac{mV_M}{L_M} H_L \frac{(1-x)_{OM}}{(1-y)_{OM}}$$

This is equation 97a, page 550, Chemical Engineers Handbook, 3rd Edition. By similar rearrangements, it can be shown that

$$H_{OL} = H_L \frac{(1-x)_M}{(1-x)_{OM}} + H_G \frac{L_M}{mV_M} \frac{(1-y)_M}{(1-x)_{OM}}$$

and if the liquid film controls, this reduces to

$$H_{OL} = H_L + \left(\frac{L_M}{mV_M}\right) H_G \frac{(1-y)_{OM}}{(1-x)_{OM}}$$

This is equation 97b, page 500, Chemical Engineers Handbook, 3rd Edition. For the case of equimolar counter diffusion, the following equations are obtained. The opportunity for further simplification in accordance to which film controls does not exist for this case.

$$H_{OG} = H_G + H_L \frac{mV_M}{L_M} \frac{(1-x)}{(1-y)}$$

Relations Between Individual and Overall HTU's (continued)

$$H_{OL} = H_L + H_G \frac{L_M}{mV_M} \frac{(1-y)}{(1-x)}$$

It is implied in the section under equation 97b, page 550, Chemical Engineers Handbook, 3rd Edition, that the $\frac{(1-x)}{(1-y)}$ terms should not be there. But the derivations lead to them.

3.30.5 Expressions Specifically for Liquid-Liquid Extraction

The equations derived above can be used directly for liquid-liquid extraction, merely by defining one of the liquid phases to carry the symbols ascribes to the vapor phase.

However, they are readily converted to more standard extraction terminology. If we speak of extract and raffinate phases, we can write

$$H_{OE} = H_E \frac{(1-x^E)_M}{(1-x^E)_{OM}} + H_R \left(\frac{L^E_M}{mL^R_M}\right) \frac{(1-x^R)_M}{(1-x^E)_{OM}}$$

If we can say that the raffinate film controls, then

$$H_{OE} = H_E + H_R \left(\frac{L^E_M}{mL^R_M}\right) \frac{(1-x^R)_{OM}}{(1-x^E)_{OM}}$$

Similarly,

$$H_{OR} = H_R \frac{(1-x^R)_M}{(1-x^R)_{OM}} + H_E \frac{mL^R_M}{L^E_M} \frac{(1-x^E)_M}{(1-x^R)_{OM}}$$

If we can say that the extract film controls,

$$H_{OR} = H_R + H_E \frac{mL^R_M}{L^E_M} \frac{(1-x^E)_{OM}}{(1-x^R)_{OM}}$$

In the above equations $m = \frac{dx^R}{dx^E}$

Expressions Specifically for Liquid-Liquid Extraction (continued)

Compare these equations with equation 93, 94, 95, and 96, page 744, Chemical Engineers Handbook, 3rd Edition.

It is more pertinent, however, to speak in terms of the discontinuous and the continuous phases. Let us use y to denote concentrations in the discontinuous phase, and use x for the continuous phase. Here $m = \frac{dy^*}{dx}$

$$H_{OD} = H_D \frac{(1-y)_M}{(1-y)_{OM}} + H_C \left(\frac{mV_D}{V_C}\right) \frac{(1-x)_M}{(1-y)_{OM}}$$

If the discontinuous film controls,

$$H_{OD} = H_D + H_C \left(\frac{mV_D}{V_C}\right) \frac{(1-x)_{OM}}{(1-y)_{OM}}$$

Similarly,

$$H_{OC} = H_C \frac{(1-x)_M}{(1-x)_{OM}} + H_D \left(\frac{V_C}{mV_D}\right) \frac{(1-y)_M}{(1-x)_{OM}}$$

If the continuous film controls

$$H_{OC} = H_C + H_D \left(\frac{V_C}{mV_D}\right) \frac{(1-y)_{OM}}{(1-x)_{OM}}$$

4.0 Calculation Methods

4.10 Operating Lines

4.11 Phases are Mutually Insoluble

In practically all industrial cases, the phases are only slightly soluble in each other. Otherwise, the solvent losses would be quite high, perhaps requiring extra equipment for recovery purposes.

An operating line is a material balance made around a terminal end of a tower, as a fixed point, and through some generalized intermediate tower section. The material balance may be made to include either, but not both, ends of the tower, as convenient.

The material balance is rigorous, the phases being insoluble, when made in terms of the mol ratios, Y and X. Thus, as pictured in Figure 7,

$$V_i (Y_n - Y_2) = L_i (X_n - X_2) = \frac{\text{lb. mols of A}}{(\text{hr})(\text{ft})^2}$$

and

$$Y_n = \left(\frac{L_i}{V_i}\right) X_n + \left[Y_2 - \frac{L_i}{V_i} X_2\right] = \left(\frac{L_i}{V_i}\right) X_n + b$$

If the material balance is made around the lower end,

$$Y_n = \left(\frac{L_i}{V_i}\right) X_n + \left[Y_1 - \frac{L_i}{V_i} X_1\right] = \left(\frac{L_i}{V_i}\right) X_n + b$$

Since these equations are straight lines regardless of the dilution (as long as V_i and L_i are constant), they are highly desirable forms. By virtue of their straightness, the task of evaluating N_{OD}, N_{OC} and M_{avg} is frequently greatly facilitated. To make use of this situation, often the equilibrium data are recalculated into terms of Y and X.

Phases are Mutually Insoluble (continued)

If the equilibrium data are in terms of y and x, mol fractions, it may be desirable to have the operating line in those same terms. Starting with the operating line in Y and X, and remembering that

$$Y = \frac{y}{1-y} \qquad X = \frac{x}{1-x}$$

We get

$$V_i \left[\frac{y}{1-y} - \frac{y_2}{1-y_2} \right] = L_i \left[\frac{x}{1-x} - \frac{x_2}{1-x_2} \right]$$

Setting $r = \frac{y_2}{1-y_2}$, $s = \frac{x_2}{1-x_2}$, $t = \left(r - \frac{L_i}{V_i} s \right)$

$$y = \frac{\left[\frac{L_i}{V_i} - r + \frac{L_i}{V_i} s \right] x + \left[r - \frac{L_i}{V_i} s \right]}{\left[\frac{L_i}{V_i} - r + \frac{L_i}{V_i} s - 1 \right] x + \left[1 + r - \frac{L_i}{V_i} s \right]}$$

$$y = \frac{\left[\frac{L_i}{V_i} - t \right] x + \left[t \right]}{\left[\frac{L_i}{V_i} - t - 1 \right] x + \left[t + 1 \right]}$$

This is definitely not a straight line equation, yet not often does the line deviate much from straightness.

If the solutions are dilute, then $1 - y = 1 - y_2 = (1-y)_{avg}$ and $1 - x = 1 - x_2 = (1-x)_{avg}$

then

$$\frac{V_i}{(1-y)_{avg}} \left[y - y_2 \right] = \frac{L_i}{(1-x)_{avg}} \left[x - x_2 \right]$$

$$V_M \left[y - y_2 \right] = L_M \left[x - x_2 \right]$$

$$y = \left(\frac{L_M}{V_M} \right) X + \left[y_2 - \frac{L_M}{V_M} x_2 \right]$$

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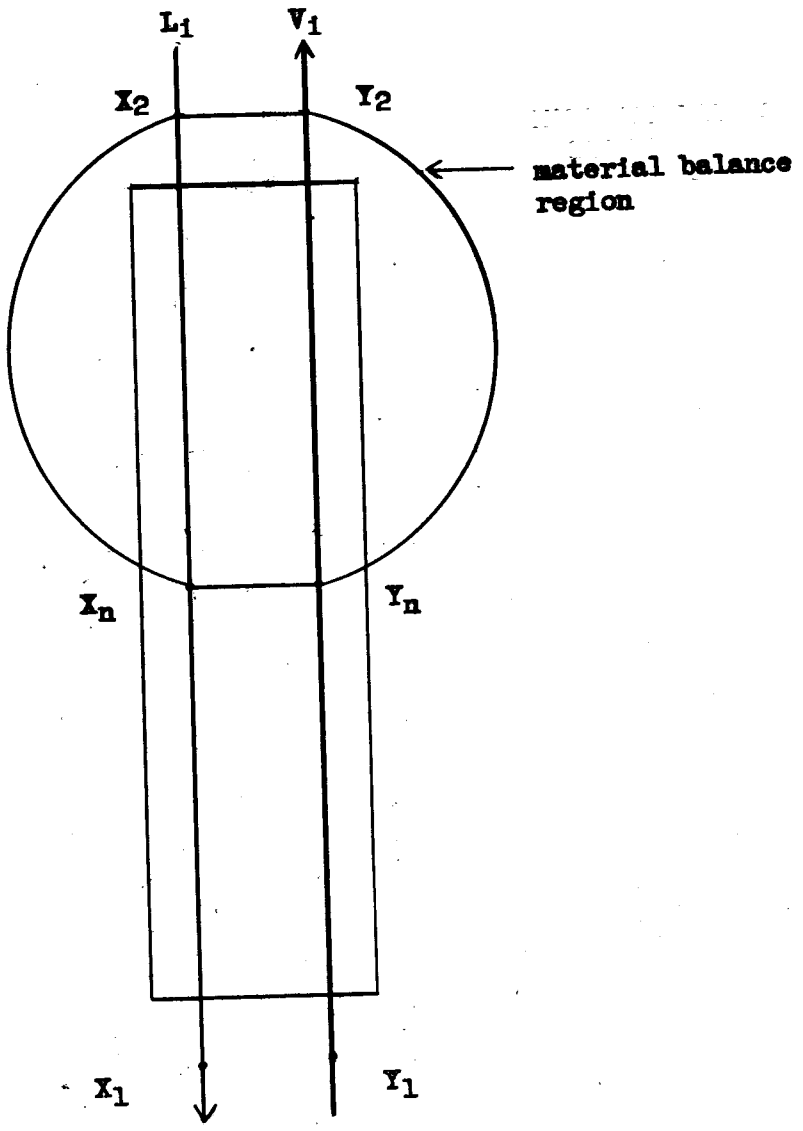
Figure 7

EXHIBIT OF A MATERIAL BALANCE



Phases are Mutually Insoluble (continued)

If we used the material balance around the bottom section, we get

$$y = \frac{L_M}{V_M} x + \left[y_1 - \frac{L_M}{V_M} x_1 \right]$$

Both of these operating lines are straight. If the solutions are dilute enough, they can be used.

4.12 Phases are Somewhat Soluble

If it is felt that the two phases are so soluble in each other that this fact must be taken into consideration, use can be made of a number of calculation procedures. All require knowledge of the mutual solubility of the two phases as a function of solute concentration. Reference should be made to the 2nd and 3rd edition of Chemical Engineer's Handbook, or "Graphical Methods as Applied to Extraction Problems", by Bull and Coli, Bulletin 72, Virginia Polytechnic Institute.

4.20 The Group (m V/L)

The group (m V/L) turns out to be a factor of very great importance in all cases of mass transfer between two phases. This importance has been realized by many workers, and at various times this ratio, or its equivalent, has been termed the "extraction" factor, the "absorption" factor, the "performance" factor, or other similar titles.

The magnitude of this factor determines whether or not the transfer process is controlled by one or the other of the films present. For instance, we have these simplified equations for the overall HTU values. Here $mV/L = \frac{mV_D}{V_C}$.

$$HTU_{OD} = H_D + H_C\left(\frac{mV_D}{V_C}\right)\frac{(1-x)_{OM}}{(1-y)_{OM}} \quad \text{(Discontinuous film controlling)}$$

$$HTU_{OC} = H_C + H_D\left(\frac{V_C}{mV_D}\right)\frac{(1-y)_{OM}}{(1-x)_{OM}} \quad \text{(Continuous film controlling)}$$

The Group (mV/L) (continued)

If $\frac{mV_D}{V_C}$ is small enough

$$HTU_{OD} = H_D \text{ closely}$$

$$HTU_{OC} = (H_D) \frac{V_C}{mV_D} \frac{(1-y)_{OM}}{(1-x)_{OM}} \text{ closely.}$$

In this case, the H_C for the continuous film plays very little part in the transfer, and practically all of the resistance to transfer lies in the discontinuous film. One would know in that case that any changes to speed up transport would have to be changes that affected the discontinuous film.

The group $\frac{mV}{L}$ is dimensionless, and must always be so formulated. It is, in fact, a ratio of two dimensional quantities which are in themselves ratios. For instance, $\frac{V}{L}$ is the ratio of the flow rates of the two phases. Appearing thus as a ratio, it is immaterial where V is expressed as a simple velocity (quantity per hour) or as a space velocity (quantity per hour per square foot) as long as L is treated the same way with the same sized units as is V.

The units can readily be checked, e. g.,

$$\frac{mV}{L} = \frac{\frac{\text{lb. mols. A}}{\text{lb. mols total V}}}{\frac{\text{lb. mols. A}}{\text{lb. mols. total L}}} \times \frac{\frac{\text{lb. mols total V}}{(\text{hr})(\text{ft})^2}}{\frac{\text{lb. mols. total L}}{(\text{hr})\ (\text{ft})^2}} = \text{Dimensionless}$$

The Group (mV/L) (continued)

Many different formulations of mV/L have been used. A number of typical ones are given in a table in the appendix. A procedure for assuring a correct formulation is shown as follows. Assuming that it is desired to measure and correlate values of the overall HTU based upon a certain organic phase. The laboratory furnishes measurements of concentration in terms of gram mols of A per gram of sample, and flow measurements in pounds of total phase per hour per square foot. First, one should specify which phase is the equivalent of V, which the equivalent of L, in mV/L. It is a matter of convenience, not necessity, which choice is made, since the final result is readily inverted to provide the other alternate formulation. However, that choice is better which derives from the following form, which shows a common use of mV/L.

$$HTU_{OY} = HTU_Y + HTU_X \left(\frac{mV}{L}\right) \frac{(1-x)_{OM}}{(1-y)_{OM}}$$

Note that Y and V refer to the same phase, as do X and L. If we define the certain organic phase as the Y phase then HTU_{OY} is the desired HTU. Since V goes with Y, V is now the designation for the organic phase. Hence V/L is obtained from the flow ratio of the organic to the other phase. A check on dimensions shows that $m = \frac{dC^*_V}{dC_L}$, where C_V is the concentration in the V phase, now the organic phase. The final result will be dimensionless if

C_V and C_L = lbmols A/lb. of total phase = gm. mol. A/gm. of total phase

W_V and W_L = lbmols total phase/ $(hr)(ft)^2$

$$\frac{mV}{L} = \left(\frac{dC^*_V}{dC_L}\right)\left(\frac{W_V}{W_L}\right)$$

The Group (mV/L) (continued)

The range of value of (mV/L) in industrial processes is really quite small, usually varying from 0.5 to 0.8, with an extreme range of perhaps 0.2 to 0.95. The industrial optimum for either vapor-liquid or liquid-liquid operations is stated by Colburn to be close to 0.7, or somewhat higher if the solute is of relatively little value. Here it is assumed that the direction of transfer is from the V phase to the L phase. If the direction is reversed, the values of mV/L quoted above should be inverted. The typical range of mV/L then becomes 1/0.5 to 1/0.8, or 2 to 1.25.

The small variations encountered in the (mV/L) term in practice is amazing, since differing cases can easily vary a thousand fold in m or V/L.

Another reason for the importance of the group mV/L is that in recent years it has been shown that the efficiencies of phase contacting devices, such as bubble trays or packed columns, is a function of (mV/L), decreasing as (mV/L) increases.

For absorption and stripping columns, and also extraction columns, Colburn presents on pages 708 and 709 of Chemical Engineers Handbook, 3rd edition, a series of equations relating the optimum operation of the tower as a function of mV/L and cost factors.

4.30 The Average Slope, M_{avg}

There has been considerable confusion concerning the correct value to assign m in the case of an experiment in which m varies considerably over the tower. Such cases arise frequently in practice.

Furnas and Taylor, Trans. A.I.Ch.E., 36, 135-171 (1940) suggest, but do not prove, that the average m be calculated as follows:

$$M_{avg} = \frac{\int m dy}{y_1 - y_2}$$

This definition has been used by Duncan, Koffolt and Withrow, Trans. A.I.Ch.E., 28, 259-81, (1942), by O. S. Knight, Trans. A.I.Ch.E., 39, 450, (1943) and others. However, it apparently gives poor results.

The following derivation appears rigorous for a countercurrent tower (by the author):

$$dZ = (H_{OY})(d\ N_{OY})$$

Assuming one component diffusing,

$$dN_{OY} = \frac{(1-y)_{OM}\ dy}{(1-y)(y^*-y)}$$

$$H_{OY} = H_Y \frac{(1-y)_M}{(1-y)_{OM}} + \frac{mV_M}{L_M} H_X \frac{(1-x)_M}{(1-y)_{OM}}$$

$$\text{Then } dZ = H_Y \frac{(1-y)_M}{(1-y)} \frac{dy}{y^* - y} + m \frac{V_M}{L_M} H_X \frac{(1-x)_M}{(1-y)} \frac{dy}{y^* - y}$$

The Average Slope, M_{avg} (continued)

$$\text{and } Z = \int H_Y \frac{(1-y)_M}{(1-y)} \frac{dy}{y^* - y} + \int m \frac{V_M}{L_M} H_X \frac{(1-x)_M}{(1-y)} \frac{dy}{y^* - y}$$

The term M_{avg} is always interpreted to be a single value applicable to an entire tower. Since it is a constant, its definition comes from this equation.

$$Z = H_Y \frac{(1-y)_M}{(1-y)} \frac{dy}{y^* - y} + \int M_{avg} \frac{V_M}{L_M} H_X \frac{(1-x)_M}{(1-y)} \frac{dy}{y^* - y}$$

Comparing, we see that

$$M_{avg} = \frac{\int m \frac{V_M}{L_M} H_X \frac{(1-x)_M}{(1-y)} \frac{dy}{y^*-y}}{\int \frac{V_M}{L_M} H_X \frac{(1-x)_M}{(1-y)} \frac{dy}{y^*-y}}$$

This definition is quickly simplified. For a given run (V_M/L_M) is usually constant. And the ratio $\frac{(1-x)_M}{(1-y)}$ has an average value close to 1.0 for any practical case. Hence, these terms can readily be taken outside of the integral sign, whereupon they cancel out, as follows.

$$M_{avg} = \frac{\int H_X \frac{m dy}{y^* - y}}{\int H_X \frac{dy}{y^* - y}}$$

Now the systems involved may be either vapor-liquid or liquid-liquid. For each case, for any type of equipment studies so far, and regardless of which phase H_X is defined for, experience shows that H_X is either a constant or a function of V or L, or both. Therefore, for a given test condition, H_X is substantially constant and can be eliminated.

$$\text{Hence} \quad M_{avg} = \frac{\int \frac{m dy}{y^*-y}}{\int \frac{dy}{y^*-y}}$$

The Average Slope, M_{avg} (continued)

To evaluate this equation, it is necessary to be able to specify m as a function of y, as m = f (y). With the present state of knowledge, this is impossible to do in the general case. If the equilibrium line is only gently curved, m is usually evaluated at the y* values. If the curvature is appreciable, it is suggested that m be evaluated at the points which are 3/4 of the way from y to y*. If the curvature is great, information on the relative values of the two film resistances is required.

4.40 Relations Between HETP and HTU

4.41 $$HETP = HTU_{OD} \frac{\ln\left(\frac{mV_D}{V_C}\right)}{\left[\frac{mV_D}{V_C} - 1\right]} = \frac{\ln \frac{V_C}{mV_D}}{\left[1 - \frac{mV_D}{V_C}\right]} HTU_{OD}$$

$$HETP = HTU_{OD} \frac{\ln \frac{mV_i}{L_i}}{\left[\frac{mV_i}{L_i} - 1\right]} = \frac{\ln \frac{L_i}{mV_i}}{\left[1 - \frac{mV_i}{L_i}\right]} HTU_{OD}$$

If we assume that $Y^* = m X + b$

and $$Y = \left(\frac{L_i}{V_i}\right) X + \left[Y_2 - \frac{L_i}{V_i} X_2\right]$$

We can calculate up a column step by step and show that

$$N_P = \frac{1}{\ln\left(\frac{mV_i}{L_i}\right)} \ln \frac{Y^*_2 - Y_2}{Y^*_1 - Y_1}$$

But $N_{OY} = \frac{1}{\left[\frac{mV_i}{L_i} - 1\right]} \ln \frac{Y^*_2 - Y_2}{Y^*_1 - Y_1}$ (by integration)

Comparing,

$$N_P = \frac{\left(\frac{mV_i}{L_i} - 1\right)}{\ln\left(\frac{mV_i}{L_i}\right)} \qquad N_{OY} = \frac{\left[1 - \frac{mV_i}{L_i}\right]}{\ln\left(\frac{L_i}{mV_i}\right)} N_{OY}$$

$$HETP = \frac{\ln \frac{mV_i}{L_i}}{\left[\frac{mV_i}{L_i} - 1\right]} HTU_{OY} = \frac{\ln \frac{L_i}{mV_i}}{\left[1 - \frac{mV_i}{L_i}\right]} HTU_{CY}$$

Here $m = \frac{dY^*}{dX}$

If we deal in mol fractions, $y^* = mx + b$, and $y = \frac{L}{V} x + (y_2 - L/V\ x_2)$, then we get

$$N_P = \frac{\left(\frac{mV_M}{L_M} - 1\right)}{\ln\left(\frac{mV_M}{L_M}\right)} N_{OY} = \frac{\left(1 - \frac{mV_M}{L_M}\right)}{\ln\left(\frac{L_M}{m\ V_M}\right)} N_{OY}$$

$$HETP = \frac{\ln \frac{mV_M}{L_M}}{\left(\frac{mV_M}{L_M} - 1\right)} HTU_{OY} = \frac{\ln \frac{L_M}{mV_M}}{\left(1 - \frac{mV_M}{L_M}\right)}$$

These equations check those of Colburn, Ind. Eng. Chem., 33, 462, 1941. They disagree, however, with equation 102, page 550, Chemical Engineer's Handbook, 3rd Edition.

$$4.42 \quad N_{OX} = N_{OY}\left(\frac{mV_M}{L_M}\right)\left(\frac{1-x}{1-y}\right) \simeq N_{OY}\left(\frac{mV_M}{L_M}\right)$$

$$N_{OX} = \left(\frac{mV_i}{L_i}\right) N_{OY}$$

Usually we can use the simplified forms

$$N_{OY} = \int \frac{dy}{y^* - y} \quad \text{and} \quad N_{OX} = \int \frac{dx}{x - x^*}$$

Assume that the two phases are relatively insoluble, then by a material balance

$$V_i \; dY = L_i \; dX$$

$$V_i \; \frac{dy}{(1-y)^2} = L_i \; \frac{dx}{(1-x)^2}$$

$$\frac{dy}{dx} = \frac{L_M}{V_M} \; \frac{(1-y)}{(1-x)}$$

Assume further that the used portion of the equilibrium curve is straight enough to allow substitution by $y^* = m\,x + b$.

$$N_{OX} = \int \frac{dx}{x-x^*} = \int \frac{\frac{V_M}{L_M}\,\frac{1-x}{1-y}\,dy}{x - x^*} = \left(\frac{1-x}{1-y}\right)\left(\frac{V_M}{L_M}\right) \int \frac{dy}{x - \frac{y-b}{m}}$$

$$N_{OX} = \frac{(1-x)}{(1-y)}\,\frac{mV_M}{L_M} \int \frac{dy}{mx + b - y} = \frac{(1-x)}{(1-y)}\,\frac{V_M}{L_M} \int \frac{dy}{y^* - y}$$

$$N_{OX} = \frac{(1-x)}{(1-y)}\left(\frac{mV_M}{L_M}\right) N_{OY} \simeq \left(\frac{mV_M}{L_M}\right) N_{OY} \quad \text{if dilute}$$

$$\text{and } H_{OY} = \frac{(1-x)}{(1-y)}\left(\frac{mV_M}{L_M}\right) H_{OX} \simeq \left(\frac{mV_M}{L_M}\right) H_{OX} \quad \text{if dilute}$$

If the symbols Y and X are used, and if $Y^* = mX + b$, then the derivation leads to

$$N_{OX} = \left(\frac{mV_i}{L_i}\right) N_{OY}$$

$$H_{OY} = \left(\frac{mV_i}{L_i}\right) H_{OX}$$

$$4.43 \quad M_{avg} = \frac{(\Delta y)_{lm}}{(\Delta x)_{lm}} \simeq \frac{(\Delta y)_{am}}{(\Delta x)_{am}}$$

If the equilibrium curve can be approximated by a straight line, and if the operating line is fairly straight, it can be shown that

$$N_{OY} = \int \frac{dy}{y^* - y} = \frac{Y_1 - Y_2}{(\Delta y)_{lm}}$$

$$N_{OX} = \int \frac{dx}{x - x^*} = \frac{x_1 - x_2}{(\Delta x)_{lm}}$$

Now from the material balance, we can derive (see section 4.42)

$$\frac{dx}{dx} = \frac{L_M}{V_M} \quad \frac{(1-y)}{(1-x)} \simeq \frac{y_1 - y_2}{x_1 - x_2}$$

and from section 4.42 above,

$$N_{OX} = \frac{(1-x)}{(1-y)} \left(\frac{mV_M}{L_M}\right) N_{OY}$$

Substituting, we get

$$M_{avg} = \frac{(\Delta y)_{lm}}{(\Delta x)_{lm}} = \frac{(\Delta y)_{\text{arithmetic mean}}}{(\Delta x)_{\text{arithmetic mean}}}$$

4.44 N_{Plates} = log mean of N_{OY} and N_{OX}

This derivation follows the derivation of R. N. Lyon, July 15, 1946 (unpublished).

Assume that $Y^* = mX + b$, and that the operating line is $V_i (Y-Y_1) = L_i (X - X_1)$.

$$\text{Then} \quad N_{OY} = \int_1^2 \frac{dY}{Y^* - Y} \quad \left(\frac{1}{\frac{mV_i}{L_i} - 1}\right) \ln \frac{Y_2^* - Y_2}{Y^*_1 - Y_1}$$

$$\text{Since} \quad N_{OX} = \left(\frac{mV_i}{L_i}\right) N_{OY}$$

$$N_{OX} = \frac{\frac{mV_i}{L_i}}{\left(\frac{mV_i}{L_i} - 1\right)} \ln \frac{Y_2^* - Y_2}{Y_1^* - Y_1}$$

The log mean of these two expressions is:

$$(N_{OX}, N_{OY})_{lm} = \frac{1}{\ln \frac{mV_i}{L_i}} \ln \frac{Y_2^* - Y_2}{Y_1^* - Y_1}$$

With the aid of the same assumptions as above, we can calculate up the column step by step to get

$$N_P = \text{number of plates} = \frac{1}{\ln \frac{mV_i}{L_i}} \ln \frac{Y_2^* - Y_2}{Y_1^* - Y_1}$$

Comparing the two expressions, we see that

$$N_P = (N_{OY}, N_{OX})_{\text{lg mean}}$$

It is easy to show that

$$\left(\frac{1}{\text{HETS}}\right) \quad \text{lg mean of} \quad \frac{1}{HTU_{OY}} \quad \text{and} \quad \frac{1}{HTU_{OX}}$$

4.45 The Loss Ratio, L

The loss ratio, L, has been used a number of times by various people. It is, however, only valid when both the equilibrium curve is a straight line through the origin, $Y^* = m X$, and the operating line is straight, meaning the phases are insoluble, so that $Y_n = \left(\frac{L_i}{V_i}\right) X_n + \left[Y_1 - \frac{L}{V} X_2\right]$

It can be shown that

$$L = \text{loss ratio} = \frac{(R - 1) + \frac{VY_1}{LX_2} (R^N - 1)}{\left(R^{N+1} - 1\right)} = \frac{X_1}{X_2}$$

Where, $R = \frac{mV_i}{L_i} = \left(\frac{dY^*}{dX}\right) \frac{V_i}{L_i}$

N = number of theoretical stages

Y_1 = entering composition in the V_i stream

X_2 = entering composition in the L_i stream

X_1 = leaving composition in the L_i stream.

If appropriate, these terms can be replaced by L_M, V_M, $m = dy^*/dx$, and y and x, in mol fractions.

This equation differs from the one quoted as equation 69, page 741, Chemical Engineers Handbook, 3rd Edition, which is this one.

$$L = \text{loss ratio} = \frac{(R-1) + \frac{Y_1}{Y_2} (R - 1)}{\left(R^{N+1} - 1\right)}$$

The difference has not been reconciled at the time of writing.

The Loss Ratio, L (continued)

When $Y_1 = 0$, both equations reduce to

$$L = \frac{(R-1)}{R^{N+1} - 1} = \frac{X_1}{X_2}$$

A plot of this equation is given as Figure 41, page 741, Chemical Engineers Handbook, 3rd Edition.

4.46 Stage Efficiency

Frequently, the equipment for contacting two phases simulates the idea of a theoretical stage or step. Such extraction equipment includes the conventional bubble cap contactor, sieve plate extractors, mixer-settlers, disc and donut units, the Scheibel column, and other types of stage extractors. It seems quite natural to interpret the data in terms of the HETS. But it must be remembered that the HETS is function of (mV_D/V_C), as well as the usual factors of flow velocities and properties.

For the case of bubble plate distillation columns, Gerster and others, Chem. Eng. Prog., 45, 716 - 24 (1949), derived equations relating the local efficiency E_{OG} with mV/L as follows

$$\frac{1}{\ln\left(\frac{1}{1-E}\right)} = \frac{1}{N_G} + \frac{1}{N_L}\left(\frac{mV}{L}\right)$$

Stage Efficiency (continued)

It can be seen that when mV/L becomes high, E_{OG} becomes low. Gerster uses this correlation (plotted on page 611, Chemical Engineer's Handbook, 3rd Edition) as a means of predicting plate efficiencies for various systems, by comparison with experimental data on air - H_2O systems.

This general method has been applied once so far, in the literature, for liquid-liquid extraction. Pyle, Colburn, and Duffey, Ind. Eng. Chem., 42, 1042-7 (1950), show on their Figure 7 a plot of $\frac{1}{-\ln(1-E)}$ versus $m\, W_E/W_W$ for the system acetic acid - ethyl ether - water.

4.50 Calculations for Tower Height

4.51 Conventional Use of HTU_{OY} and HTU_{OX}

It can be shown that:

$$Z = \text{height} = \left[H_Y \frac{(1-y)_M}{(1-y)_{OM}} + \left(\frac{mV_M}{L_M}\right)_{avg} H_X \frac{(1-x)_M}{(1-y)_{OM}} \right] \int \frac{(1-y)_{OM}\, dy}{(1-y)(y^*-y)}$$

This is usually treated as

$$Z = \left[H_Y + \left(\frac{mV_M}{L_M}\right)_{avg} H_X \frac{(1-x)_{OM}}{(1-y)_{OM}} \right] \int \frac{(1-y)_{OM}\, dy}{(1-y)(y^*-y)}$$

$$Z = (H_{OY})_{avg} \int \frac{(1-y)_{OM}\, dy}{(1-y)(y^*-y)} = (H_{OY})_{avg}\ N_{OY}$$

Conventional Use of HTU_{OY} and HTU_{OX} (continued)

The HTU_{OY} is evaluated at the average value of $(m V_M/L_M)$ and the N_{OY} is evaluation by any one of several methods.

If (mV_M/L_M) varies greatly over the tower, the tower can be considered to be made up of several sections, over each of which (mV_M/L_M) does not vary more than a permissible amount, and the total height is calculated as the sum of the section heights.

Another, more exact procedure is to set up this expression, where $HTU_{OY} = f(y)$.

$$dZ = HTU_{OY}\ dN_{OY} = \frac{HTU_{OY}\ (1-y)_{OM}}{(1-y)(y^*-y)}\ dy$$

Integration of the area indicated supplies the height Z. See Figure 8.

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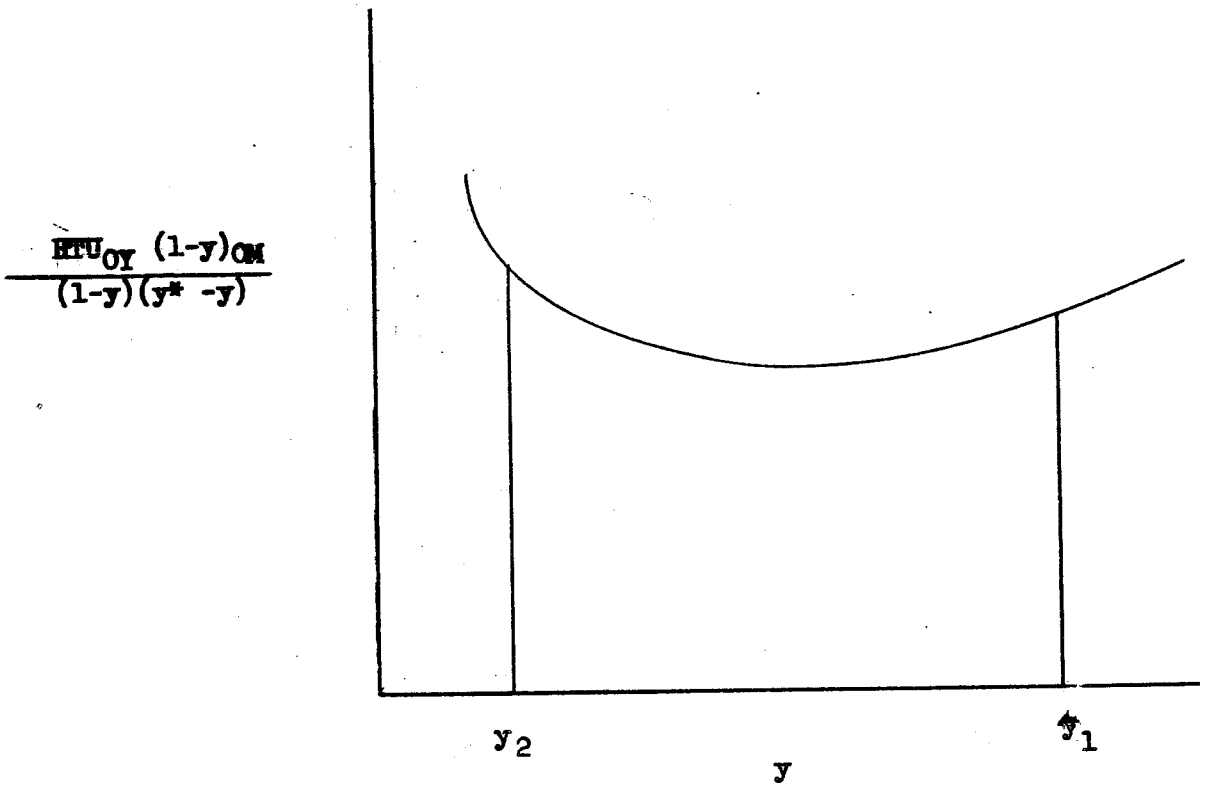
Figure 8

INTEGRATION FOR TOWER HEIGHT



4.52 Method of Simon and Rau

References: Ind. Eng. Chem., 40, 93-6 (1948)

We start with $dZ = HTU_{OY}\ dN_{OY}$

where $HTU_{OY} = HTU_Y \frac{(1-y)_M}{(1-y)_{OM}} + \frac{mV_M}{L_M}\ HTU_X \frac{(1-x)_M}{(1-y)_{OM}}$

$$dN_{OY} = \frac{(1-y)_{OM}\ dy}{(1-y)(y^* - y)}$$

Substituting,

$$dZ = HTU_Y \frac{(1-y)_M}{(1-y)} \frac{dy}{y^*-y} + \frac{mV_M}{L_M}\ HTU_X \frac{(1-x)_M}{(1-y)}\ \frac{dy}{y^*-y}$$

Now according to Simon and Rau,

$$m = \frac{y^* - y_i}{x_i - x} = \frac{dy^*}{dx} \quad \text{in the limit}$$

The material balance is

$$V_i\ (Y - Y_2) = L_i\ (X - X_2)$$

where $Y = \frac{y}{1-y}$ and $X = \frac{x}{1-x}$

Assuming V_i and L_i are constant, differentiating, we get

$$\frac{dy}{dx} = \frac{L_M}{V_M}\ \frac{(1-y)}{(1-x)}$$

Therefore,

$$\left(\frac{dy}{dx}\right)\left(\frac{dx}{dy^*}\right) = \frac{L_M\ (1-y)}{V_M(1-x)}\ \frac{1}{m} = \frac{dy}{dy^*}$$

Method of Simon and Rau (continued)

Substituting,

$$dZ = HTU_Y \frac{(1-y)_M}{(1-y)} \frac{dy}{y^*-y} + HTU_X \frac{\cancel{V_M}}{\cancel{L_M}} \frac{\cancel{L_M}}{\cancel{V_M}} \frac{dy^*}{\cancel{dy}} \frac{\cancel{(1-y)}\ (1-x)_M}{(1-x)\ \cancel{(1-y)}} \frac{\cancel{dy}}{y^*-y}$$

$$dZ = HTU_Y \frac{(1-y)_M}{(1-y)} \frac{dy}{y^*-y} + HTU_X \frac{(1-x)_M}{(1-x)} \frac{dy^*}{y^*-y}$$

For a given design condition,

$$HTU_Y = \text{constant}, \quad HTU_X = \text{constant}$$

$$\frac{(1-y)_M}{(1-y)} \simeq \text{constant}, \qquad \frac{(1-x)_M}{(1-x)} \simeq \text{constant}$$

Therefore,

$$Z = HTU_Y \frac{(1-y)_M}{(1-y)} \int \frac{dy}{y^*-y} + HTU_X \frac{(1-x)_M}{(1-x)} \int \frac{dy^*}{y^*-y}$$

Almost always,

$$\frac{(1-y)_M}{(1-y)} \simeq 1 \simeq \frac{(1-x)_M}{(1-x)}$$

So $$Z = HTU_Y \int \frac{dy}{y^*-y} + HTU_X \int \frac{dy^*}{y^*-y}$$

Simon and Rau interpret this to mean

Z = Z_Y, (resulting from the resistance of the y film) + Z_X, (resulting from the resistance of the x film)

4.60 Evaluation of Overall Coefficients

4.61 Graphical Integration

It is, of course, always possible to graphically integrate the forms

$$\int \frac{(1-y)_{OM}\, dy}{(1-y)(y^*-y)} \qquad \text{and} \qquad \int \frac{dy}{y^*-y}$$

These integrals are in the form $\int f(y)\, dy$. To integrate graphically, plot $f(y)$ against y and measure the area under the curve from y_2 to y_1. This procedure always gives an answer as exact as the method of plotting will permit.

4.62 Wiegand's Approximation

Reference: J. H. Wiegand, Trans, A.I.Ch.E., 36, 679-81 (1940)

Consider the form

$$N_{OY} = \int \frac{(1-y)_{OM}\, dy}{(1-y)(y^*-y)}$$

$$\text{where } (1-y)_{OM} = \frac{(1-y) - (1-y^*)}{\ln\left(\frac{1-y}{1-y^*}\right)}$$

By replacing the log mean average by the arithmetic average,

$$(1-y)_{OM} \simeq \frac{(1-y) + (1-y^*)}{2}$$

We get

$$N_{OY} = \int_2^1 \frac{dy}{y^*-y} - 1/2 \ln\left(\frac{1-y_1}{1-y_2}\right) = \int_2^1 \frac{dy}{y^*-y} + 1/2 \ln\left(\frac{1-y_2}{1-y_1}\right)$$

4.63 Conversion to Other Units

1. Units of Y

$$Y = \frac{y}{1-y}, \qquad dY = \frac{dy}{(1-y)^2}, \qquad 1-y = \frac{1}{1+Y}$$

$$N_{OY} = \int \frac{(1+Y)_{OM}\, dY}{(1+Y)\,(Y^*-Y)}$$

Using Wiegand's approximation,

$$N_{OY} = \int_2^1 \frac{dY}{Y^*-Y} + 1/2 \ln \frac{1+Y_2}{1+Y_1}$$

2. Units of X

$$X = \frac{x}{1-x}, \qquad dX = \frac{dx}{(1-x)^2}, \qquad 1-x = \frac{1}{1+X}$$

$$N_{OX} = \int \frac{(1+X)_{OM}\, dX}{(1+X)\,(X-X^*)}$$

Using Wiegand's approximation

$$N_{OX} = \int_2^1 \frac{dX}{X-X^*} + 1/2 \ln \frac{1+X_1}{1+X_2}$$

3. Weight Fractions

Let w = weight fraction of A

1-w = weight fraction of B

$$r = \frac{\text{molecular weight of B}}{\text{molecular weight of A}} = \frac{M_B}{M_A}$$

Conversion to Other Units (continued)

Using Wiegand's approximations,

$$N_{OY} = \int_2^1 \frac{dw}{w^* - w} + 1/2 \ln \frac{1 - (1-r)\, w_2}{1 - (1-r)\, w_1} + 1/2 \ln \frac{(1-w_2)}{(1-w_1)}$$

This equation differs slightly from that of A. P. Colburn, Ind. Eng. Chem., 33, 461, 1941.

4. Weight Ratios

Let $H = \frac{w}{1-w}$, $r = \frac{M_B}{M_A}$ (see above)

Using Wiegand's approximation,

$$N_{OY} = \int_2^1 \frac{dH}{H^* - H} - 1/2 \ln \frac{1 + r H_1}{1 + r H_2}$$

4.64 Evaluation of $\int \frac{dy}{y^*-y}$

If (y^*-y) is a straight line function of y, then the integration can be made very simply. This assumption is usually true only when the equilibrium curve and the operating lines are both straight.

$$\int_2^1 \frac{dy}{y^*-y} = \frac{y_1 - y_2}{(y^*-y)_{lm}} = \frac{y_1 - y_2}{(\Delta y)_{lm}}$$

$$(\Delta y)_{lm} = \frac{(y_1^* - y_1) - (y_2^* - y_2)}{\ln\left(\frac{y_1^* - y_1}{y_2^* - y_2}\right)}$$

Similarly, $$\int_2^1 \frac{dx}{x - x^*} = \frac{x_1 - x_2}{(\Delta x)_{lm}}$$

Evaluation of $\int \frac{dy}{y^*-y}$ (continued)

Even when it is not possible to say, for a given case, that the equilibrium and the operating lines are straight, it is always possible to consider the tower as being made up of several sections, each chosen so that over it the equilibrium curve and the operating lines are substantially straight. The number of transfer units for the entire tower is the sum of those for each individual section.

4.65 Colburn's Equation

If we can assume that

$$Y^* = bX + c$$

$$\text{and } Y_n = (L_1/V_1)\, X_n + \left[Y_1 - L_1/V_1\, X_1 \right]$$

$$\text{then } N_{OY} = \int \frac{dY}{Y^*-Y} = \frac{1}{\left(1 - \frac{mV_1}{L_1}\right)} \ln \left[\left(1 - \frac{mV_1}{L_1}\right) \left(\frac{Y_1 - mX_2}{Y_1 - mX_2} \right) + mV_1/L_1 \right]$$

This equation can be used directly. It has been particularly useful in providing an equation for transfer units in a tower terminal region, for use in economic balances.

A plot of (essentially) this equation is shown as Figure 28, page 554, Chemical Engineers Handbook, 3rd Edition.

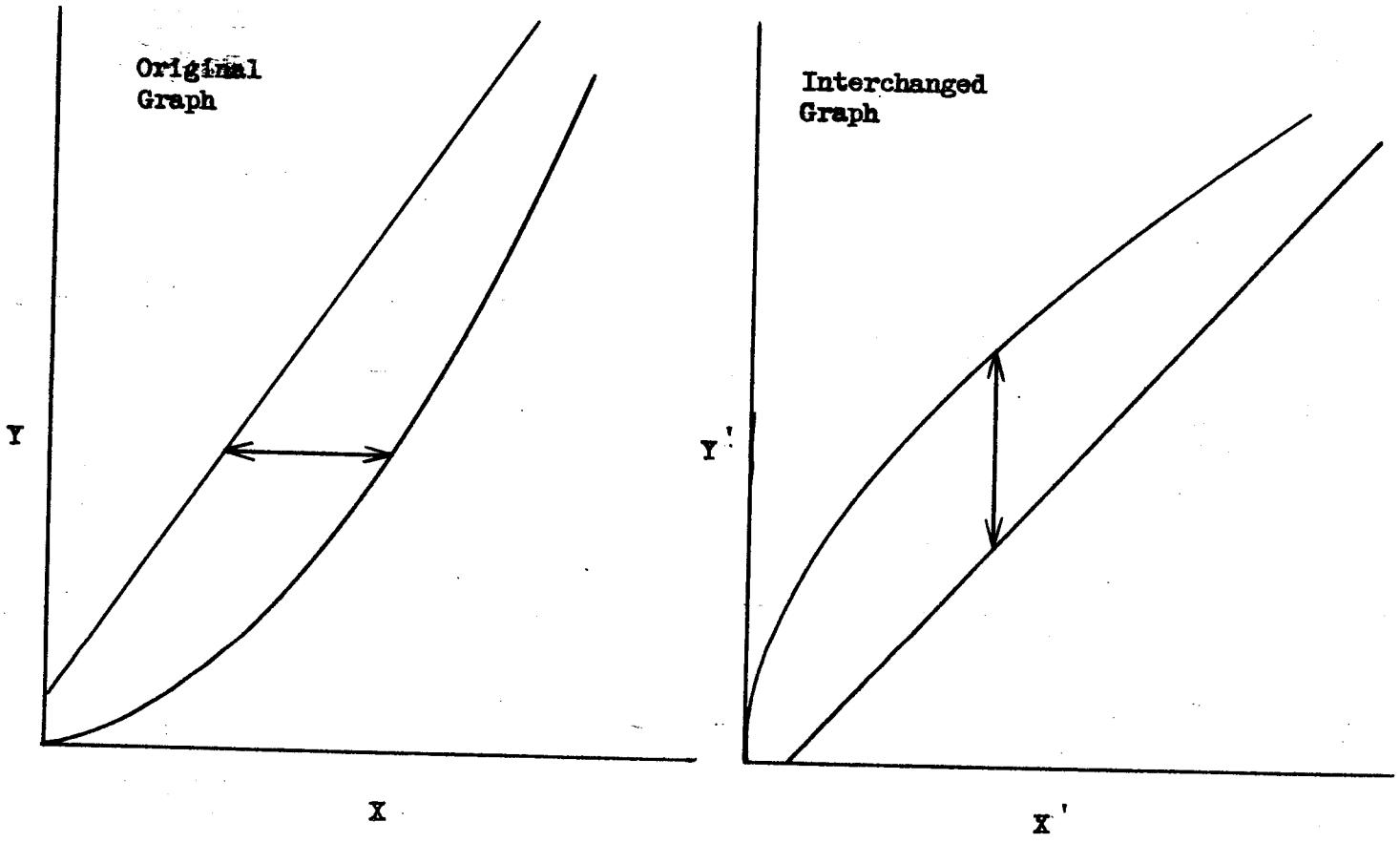
Colburn's Equation (continued)

If, when attempting to use this equation or the plot based upon it, you get a negative value for $\frac{Y_1 - mX_2}{Y_2 - mX_2}$, it means that the terminology of Colburn and that which you are using are reversed. It is entirely arbitary whether an operation is to be called an absorption or a stripping operation. It is possible to use the graph or the equation to get the answer desired anyway.

First, consider Figure 9 in which the left situation is the one in mind, and which gives negative $\frac{Y_1 - mX_2}{Y_2 - mX_2}$ values, and the one on the right is made from the left one by interchanging the definition, Y for X and V_i for L_i.

Figure 9

EXAMPLE FOR COLBURN'S EQUATION



Colburn's Equation (continued)

An N_{OY} defined for the right hand chart, using $Y'^{*} - Y'$ values, is exactly the same as an N_{OX} for the left chart, using $X^{*} - X$ values. Colburn's equation and chart can be used to obtain N_{OY} for the right hand scheme, and that value will be N_{OX} in the left hand scheme. But we know that

$$N_{OY} = \left(\frac{L_i}{mV_i}\right) \quad N_{OX}$$

In this manner, we get the N_{OY} desired.

Many times one works in mol fractions, y and x. If the solutions are sufficiently dilute $y_n = L_M/V_M\, x_n + y_1 - L_M/V_M\, x_1$ and the equation becomes

$$N_{OY} = \int \frac{dy}{y^{*}-y} = \frac{1}{\left(1 - \frac{mV_M}{L_M}\right)} \ln\left[\left(1 - \frac{mV_M}{L_M}\right)\left(\frac{y_1 - mX_2}{y_1 - mX_2}\right) + \frac{mV_M}{L_M}\right]$$

4.66 Colburn's Equation for Two Tower Sections

In case the equilibrium line is not straight enough for the use of the above equation, it may yet be possible to approximate the equilibrium curve by two straight lines. Colburn found that if the break in the two straight line sections is made at $y_a = \sqrt{y_1\, y_2}$ then an integration could be made. In such a case, y_2 being the dilute end, the equilibrium curve between y_2 and y_a is assumed to be $y^{*} = m_2\, x$. This dilute region has $\left(\frac{m_2 L_M}{V_M}\right)_2$.

Colburn's Equation for Two Tower Sections (continued)

The summation for both sections of the tower together gave

$$\int_{y_2}^{y_1} \frac{dy}{y - y^*} = \frac{1}{\left[1 - \left(\frac{m_2V_M}{L_M}\right)_2\right]} \ln \left[1 - \left(\frac{m_2V_M}{L_M}\right)_2 \left\{ \frac{\left(y_1 - m_2x_2\right)\left(1 - \left(\frac{m_2V_M}{L_M}\right)_2\right)}{\left(y_2 - m_2x_2\right)\left(1 - y_1^*/x_1\right)} \right\} + \left(\frac{m_2V_M}{L_M}\right)_2 \right]$$

The plot of Colburn's first equation can be used to solve this equation if the group

$$\left\{ \frac{\left(y_1 - m_2x_2\right)\left(1 - \left(\frac{m_2V_M}{L_M}\right)_2\right)}{\left(y_2 - m_2x_2\right)\left(1 - y_1^*/x_1\right)} \right\}$$ is used as abscissa

to replace $\left\{ \frac{\left(y_1 - mx_2\right)}{\left(y_1 - mx_2\right)} \right\}$.

If mV/L is greater than 1.0, this equation breaks down.

4.67 Method of Scheibel and Othmer

Reference: E. G. Scheibel and D. F. Othmer, Trans A.I.Ch.E., 38, 339 - 364 (1942)

Scheibel and Othmer assume that the equilibrium curve is a parabola of the form $y^* = mx^2 + bx$. This is basically a much better assumption than that $y^* = mx + b$. The resulting integrated form, however, is cumbersome to use. The authors discuss the use of their equations in a number of cases, and supply a chart to facilitate numerical solutions.

4.68 Method of G. E. White

Reference: G. E. White, Trans. A.I.Ch.E., 46, 363 - 368 (1950)

White focuses attention upon the two terminal driving forces and a "central" driving force taken at the arithmetic concentration average of the terminal concentration values. This method assumes that a parabola is passed through the three points envolved on the equilibrium curve. This parabola need not pass through the origin of the xy diagram, but rather is set up to fit best the region of the equilibrium curve that is pertinent to the specific problem at hand. White derives equations to evaluate $N_{OY} = \int \frac{dy}{y^* - y}$ and supplies a nomograph to facilitate numerical solutions to his equations.

4.70 Evaluation of Single Film Coefficients

4.71 Experimental Technique of Colburn and Welsh

References:

1. A. P. Colburn and D. G. Welsh, Trans. A.I.Ch.E., 38, 179-202 (1942)

2. G. S. Laddha, and J. M. Smith, Chem. Eng. Prog., 46, 195-202 (1950)

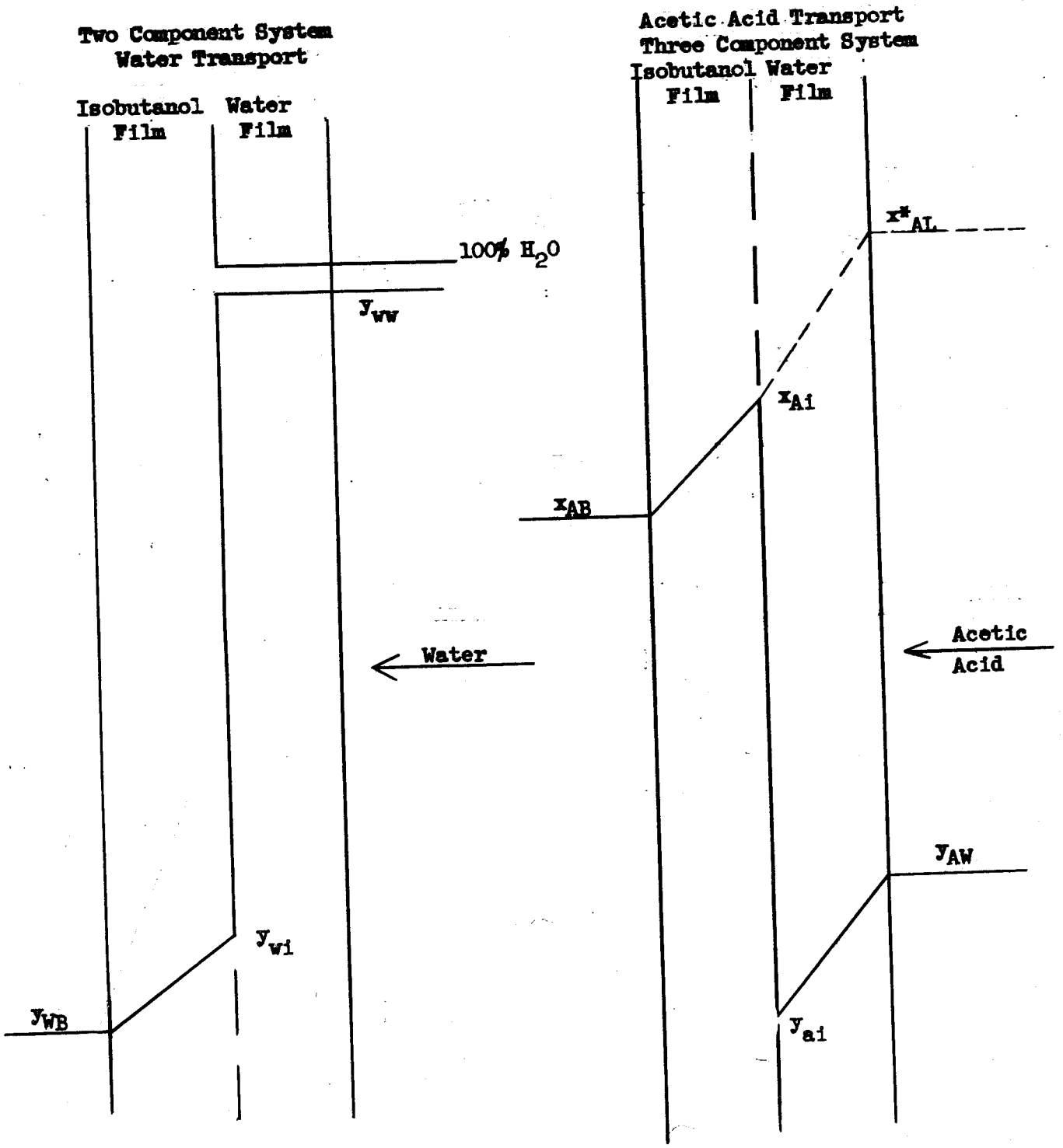
Experimental Technique of Colburn and Welsh (continued)

Ordinarily, when a person thinks of a mass transfer process between two phases, he thinks of a three phase system. A typical case for a vapor-liquid system would be the absorption of NH_3 from an air phase to an aqueous phase. A typical case for a liquid-liquid system would be the extraction of acetic acid from an aqueous phase by diisopropyl ether. Such ternary systems are the customary ones for study even to this date, although, as it turns out, it is quite difficult in this case to disentangle and evaluate the resistances of the individual films (which is highly desirable).

A much better technique is to use a binary system, wherein the diffusing substance is one of the phase components itself. The advantages of doing this can be made apparent by the study of an actual case involving acetic acid, isobutanol, and water. If we study the transport of acetic acid from water to isobutanol, we get concentration gradients across the two film which are schematically shown on the right hand diagram of Figure 10. On the other hand, if we study the transport of water itself into the isobutanol, we get a situation as in the schematic diagram on the left of Figure 10.

Figure 10

CONCENTRATION GRADIENTS FOR MASS TRANSPORT



Experimental Technique of Colburn and Welsh (continued)

Consider first the three component case, with acetic acid. There is a decided concentration drop, in general, across both films. In each film acetic acid is an alien component and appears in a molal concentration which is small compared to 1.00. In each film, acetic acid must travel by diffusion alone across two definite and distinct films. Direct measurements give only the overall concentration driving forces, never the interfacial concentration, hence the capacity coefficients obtained relate to two resistances in series.

In the second case, that of water pickup by isobutanol, the situation is quite different. For one thing, the first film encountered is comprised mainly of the same component, water, that diffuses into the isobutanol. In the limiting case of no isobutanol solubility in water, the film would be 100% H_2O, and there would be no diffusion problems across the water film. It would be simply that at the phase boundary the water film would furnish H_2O molecules to travel through the isobutanol film, but as these boundary H_2O molecules were used up, they would be replenished by having the water film as a whole physically move toward the boundary, adding to itself on the other side by a fluid flow process. Actually, of course, there is some isobutanol solubility in the water phase and the water film is not quite 100% H_2O , so a slight diffusion gradient is set up to combine its process with the "melting away" process mentioned above. The net result is that the interface value y_{wi} is closely approximated as the equilibrium value for the solubility of water in isobutanol. Therefore, the concentration gradient is known specifically for the isobutanol film, and the resistance of that one film can be obtained from the transport measurements.

Experimental Technique of Colburn and Welsh (continued)

This trick of using a two-component, two-phase system to isolate specific film resistances is an old one, having been used a number of times to evaluate the gas film resistance in humidification and dehumidification experiments with air and water. But Colburn and Welsh were the first to apply it to liquid-liquid extraction systems.

Obviously, the basic idea becomes more exact the more nearly insoluble are the two phases. But then the more difficult the analytical problems become. The experimenter faces the problem of compromising between the ideal approach and the practical problems. To my thinking, Colburn and Welsh chose a system (isobutanol-water) with too high a mutual solubility.

4.72 From Overall Coefficients

We start with

$$H_{OD} = H_D + \frac{mV_D}{V_C} H_C \frac{(1 - x_C)_{OM}}{(1-y_D)_{OM}}$$

Colburn and Welsh, and Laddha and Smith showed for packed and spray towers that for a given system and equipment, that

H_D = constant = C_1

$H_C = C_2 (V_C/V_D)^{0.75}$ by Colburn and Welsh

$H_C = C_2 (V_C/V_D)^{0.54 \text{ to } 0.96}$ by Laddha and Smith

From Overall Coefficients (continued)

Colburn and Welsh had difficulty in deciding upon their exponent of 0.75 for instance stating that 0.67 would fit the data about as well. Laddha and Smith reported different values for three different systems, the averages for the three being 0.57, 0.86, and 0.96. However, an inspection of their data shows that these values are not well established, and that an overall average of 0.75 would serve quite well.

Using these correlations, we get

$$H_{OD} = C_1 + C_2\left[m\,(V_D/V_C)^{1/4}\right]\frac{(1-x_C)_{OM}}{(1-y_D)_{OM}}$$

and $$H_{OC} = C\,(V_C/V_D)^{0.75} + C_1\left(\frac{V_C}{mV_D}\right)\frac{(1-y_D)_{OM}}{(1-x_C)_{OM}}$$

It is obvious that is H_{OD} if plotted against $m\,(V_D/V_C)^{1/4}\,\frac{(1-x_C)_{OM}}{(1-y_D)_{OM}}$, or simply $m\,(V_D/V_C)^{1/4}$ if the solutions are dilute enough, a straight line should result, with slope of C_2 and intercept of C_1. In this manner the individual film coefficients are obtained from measurements on the overall coefficient.

On the other hand, it is quite common to see plots made of H_{OC} versus $\left(\frac{V_C}{mV_D}\right)\left[\text{or}\quad\frac{V_C}{mV_D}\,\frac{(1-y_D)_{OM}}{(1-x_C)_{OM}}\right]$. This is done because of a loose analogy with vapor-liquid systems. From the derivations above, one would not expect a correlation of this type because the intercept is not constant. However, in practically all cases, correlations are apparently obtained. This anomaly is due to the fact that (1) the data are invariably poor, (2) the experiments are

From Overall Coefficients (continued)

almost always poorly planned and do not cover a wide range of V_C/mV_D, and (2) the intercept is a small number compared to the H_{OD} values, is quite difficult to locate precisely, and variations in the intercept value have little or no influence on the upper reaches of the "correlation". In spite of its apparent success in some cases, this correlation procedure is not sound and is not recommended. If H_{OC} is used, the relation $(HTU_{OC})\ (V_D/V_C)^{0.75} = C_2 + C_1$ times $(1/m)(V_C/V_D)^{1/4}\ \frac{(1-y_D)_{OM}}{(1-x_C)_{OM}}$ suggests that it is more profitable to plot $(HTU_{OC})(V_D/V_C)^{0.75}$ versus $(1/m)(V_C/V_D)^{1/4}$, with perhaps the minor correction terms included.

4.73 From Overall Coefficients, Special Case

By judicious selection of the systems being studied, it is possible to minimize the influence of one film, hence have the measurable overall coefficient be roughly equivalent to a single film coefficient. The gist of this procedure lies in the control, by selection, of the value of m.

There are two ways to develop this procedure theoretically. One way is as follows:

$$H_{OD} = H_D + H_C \left(\frac{mV_D}{V_C}\right)\frac{(1-x_C)_{OM}}{(1-y_D)_{OM}}$$

If m is chosen to be very small, the second term on the right becomes negligible, unless excessively large V_D/V_C ratios are used, and

$$H_{OD} \simeq H_D$$

From Overall Coefficients, Special Case (continued)

Similarly, if m is made very large,

$$H_{OC} \simeq H_C$$

A second way to develop this idea is based upon a graphical picture. Consider Figure 11 showing the driving force gradients across the two films of a two phase system.

Take the case when m is quite small. From the graph, we see that $y-y^*$ is a close approximation for $y-y_i$. Hence

$$N_{OY} = \int \frac{dy}{y-y^*} \simeq \int \frac{dy}{y-y_i} = N_Y$$

$$H_{OY} \simeq H_Y$$

Similarly, when m is large, $x^* - x$ becomes an approximation for $x_i - x$, and

$$N_{OX} \simeq N_X = \int \frac{dx}{x_i-x}$$

This idea has been much used in the past, but there always arises the question about how high or how low m must be in order for the approximation to be satisfactory. For this reason, the method has been losing its popularity as a means for measuring individual film coefficients.

In special cases, however, the method can be made much more effective. Take the case of the extraction of acetic acid from benzene by an aqueous phase. If some NaOH is introduced into the aqueous phase, it will react immediately with the acetic acid as it comes into the aqueous film from the benzene film. The reaction product, Na Acetate, is not soluble in benzene, hence does not complicate diffusion in the benzene phase.

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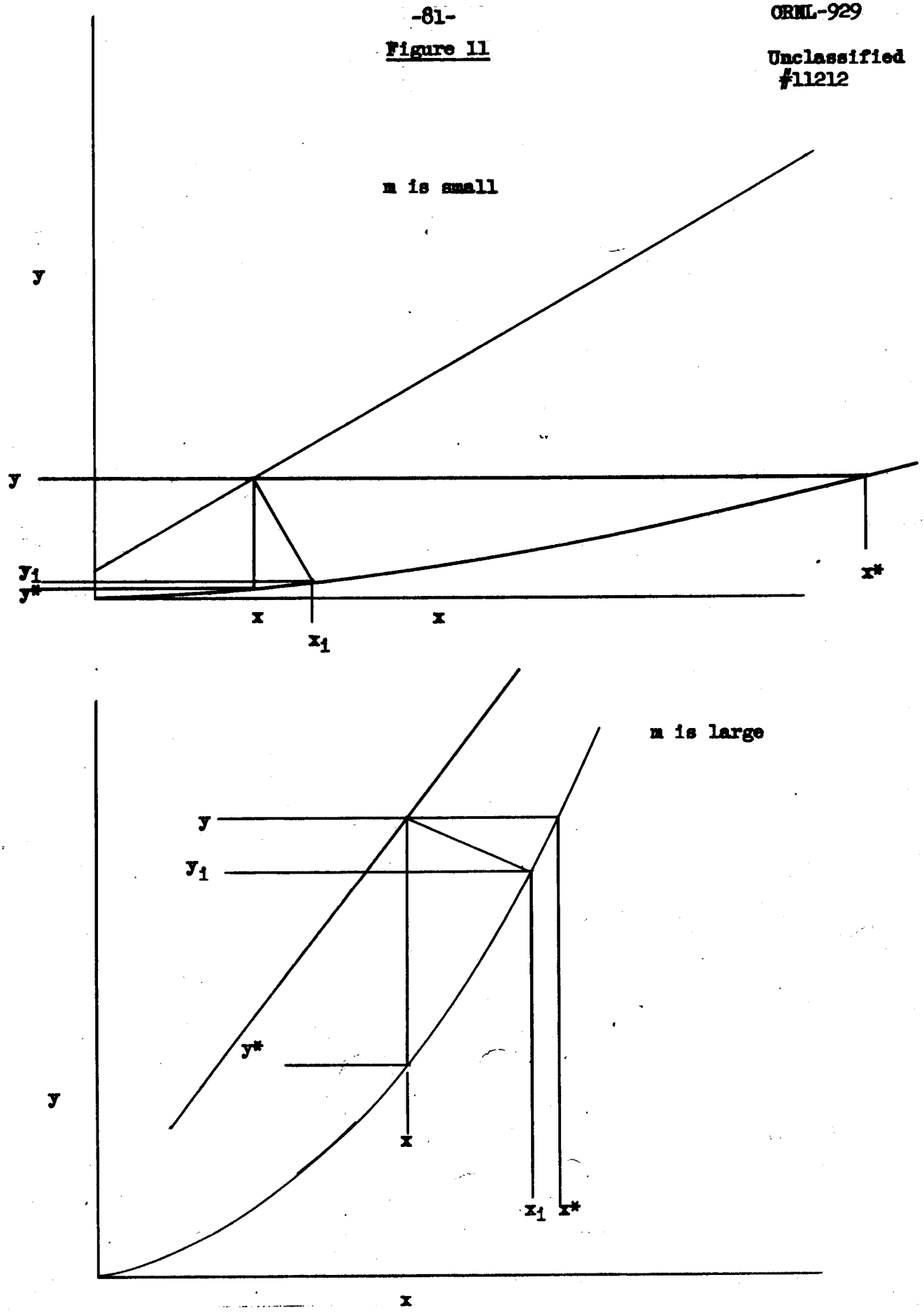
Figure 11



From Overall Coefficients, Special Case (continued)

Effectively, by the addition of Na OH, the value of $m = dy^*/dx$ has been reduced to zero. This technique has been used by W. S. Farmer (among others) in his work reported in ORNL-635. T. B. Drew, Trans. A.I.Ch.E., 36, 681-682 (1940), has shown that, if $y_1 \longrightarrow 0$,

$$N_G = \int_1^2 \frac{(1-y)_f \, dy}{(1-y)(y-y_1)} = \ln \left[\frac{\ln(1-y_1)}{\ln(1-y_2)} \right]$$

Drew's equation is valid only if the reaction rate is fast enough to maintain the film concentration of solute at zero. If the reaction rate is slower, the solute builds up a back pressure and eventually some diffuses into the main body. Where the reactions are ionic, such as the absorption of NH_3 by H_2SO_4, or HA_c by NaOH, Drew's equation is valid.

5.0 Correlation Information

5.1 Discontinuous vs. Continuous Phase Behavior

Two facts of great importance have become apparent over the years.

(1) There are two major ways of operating a liquid-liquid extraction column. A given phase can be fed either as the continuous phase or the discontinuous phase, with considerable difference in behavior. This effect can be attributed to the fact that the discontinuous phase resistance is constant when once established, but the continuous phase resistance is a function of turbulence within the tower.

(2) For each of the above methods of operation, there are two sub-classes of behavior. Either one or the other of the phases may be the one that wets the packing. This difference shows up markedly in the performance. In practically all cases the aqueous phase wets the packing.

Consequently, for a given column and packing, and a given two-phase system, there are 4 modes of operation, each of which gives different answers.

The work of Colburn and Welsh, and Laddha and Smith indicate that one should talk and correlate in terms of the discontinuous phase and the continuous phase, noting which wets the packing, and not in terms of the specific phases, such as benzene and water.

Most of the available data are on systems in which the aqueous phase is the continuous one.

5.2 End Effects

At the entrance and at the exit of a tower there are turbulence effects above and beyond those obtaining further inside the tower. In most careful work, this excess turbulence is minimized by calming sections. In addition to this effect, there is always exposed at the tower ends some interfacial area available for transport that is not included in the tower area proper. These terminal area effects can also be minimized by careful design, if such is desired for purposes of experimental evaluation.

The total effect of these terminal conditions is called the end effect. In this term is usually lumped both terminal effects as if they were alike, which may not be true. The end effect is usually in the neighborhood of 2" to 5" for packed towers. Such a height is quite important for short experimental columns, say from 1/2 to 1 feet in height.

For spray columns, Sherwood, Evans, and Longcor, Trans. A.I.Ch.E., 35, 597 - 622 (1939), found that the end effect, which was located in the drops as they formed, caused 40-45% of the extraction for their towers. Farmer, ORNL-635, found an effect of the same magnitude for his spray columns. Shulman and Molstad, Ind. Eng. Chem., 42, 1058-70 (1950), reported end effect data on gas-bubble columns. Geankopolis and Hixson, Ind. Eng. Chem., 42, 1141-51 (1950) in their Figure 11 show that the end effect increases as the flowrate increases. Licht and Conway, Ind. Eng. Chem., 42, 1151-7 (1950) provide similar data.

End Effects (continued)

For mass transfer in packed columns, information can be found in the following sources. The end effect will vary as the tower details vary.

McAdams, Pohlenz, and St. John — 7" end effect

Chem. Eng. Prog., 45, 241-52 (1949)

Weisman and Bonilla — 4.5" end effect

Ind. Eng. Chem., 42, 1099 - 1105 (1950)

5.3 Wetted Area of Packing (For Packed Towers)

Consider these expressions, for a single component diffusing,

$$H_{OG} = \frac{RTB_G V_M}{D_V \pi a} \quad \text{and} \quad H_L = \frac{L_M B_L}{D_L C_{avg} a}$$

Those quantities, the ignorance of which prevents us from predicting the heights of transfer units, are the film thickness, B, the diffusivity, D, and the square feet of transport area per cubic foot of packing, a. In time the basic physical data on diffusivities (D) are certain to be obtained. It is almost certain that we will come to be able to relate film thickness (B) to turbulence and physical property factors. Therefore, an important uncertainty lies in the problems of determining the value of "a".

End Effects (continued)

The first major work along this line is that of Weisman and Bonilla, Ind. Eng. Chem., 45, 1099-1105 (1950). They show that for vapor-liquid mass transfer over spherical packing that

$$\frac{a_d}{a_t} = 0.00067 \left(\frac{D_p G}{\mu_G}\right)^{0.31} L^{0.5} \qquad \text{(Equation 19)}$$

for the experimental ranges of flow rates.

where a_d = area effective for diffusion

a_t = total surface area of the spheres

L = lbs. per hour per square foot of tower cross section.

They speculate that the expression could be generalized somewhat to

$$\frac{a_d}{a_t} = 0.00508 \left(\frac{D_p G}{\mu_G}\right)^{0.31} \left(\frac{D_p L}{\mu_L}\right)^{0.5}$$

For 1" Raschig Rings under certain limits, they found that

$$\frac{a_d}{a_t} = 0.044 \quad G^{0.31} \quad L^{0.07}$$

These results show that at higher rates of flow of either phase, more area of the packing is made available for the transport process. This is as to be expected. No information is yet available on liquid-liquid extractors.

5.4 Effect of Reynolds Number of the Continuous Phase

For flow inside smooth round pipes, the situation is as follows; a vast amount of heat transfer work leads to $\left(\frac{d}{H_t}\right)_c = f\left(Re_c^{0.8}\right)$ where H_t = heat transfer unit. Fallah, Hunter, and Nash, J. Soc. Chem. Ind., 54, 49T (1935) and Gilliland and Sherwood, Ind. Eng. Chem., 26, 516 (1934) found that $\left(\frac{d}{H_d}\right)_c = f\left(Re_c^{n}\right)$ where H_d = mass transfer unit, and n = 0.8 and 0.83, respectively. It is true that Brinsmade and Bliss, Trans. A.I.Ch.E., 39, 679 (1943) found n = 0.67, but most workers have accepted n = 0.8 for this case for either heat or mass transfer.

For flow over packing material (with an immobile surface) sometimes n has been taken to be 0.8 in a mistaken analogy to the case of round pipes. But McAdams has shown for heat transfer that n = 0.6. In recent years the following workers have shown that n = 0.6 for mass transfer within the range of their correlations.

Molstad and Parsly, Chem. Eng. Prog., 46, 20-8 (1950)

Taecker and Hougen, Chem. Eng. Prog., 45, 188 (1949)

Riggle and Tepe (they found n = 0.7), Ind. Eng. Chem., 42, 1036-41 (1950)

Bedinfield and Drew, Ind. Eng. Chem., 42, 1164-73 (1950)

Parekh, M, PhD. Thesis, M.I.T., 1941
Reported on page 289, "Heat Transmission", McAdams

Maisel and Sherwood, Chem. Eng. Prog., 46, 131-8 (1950)

Attempts at a more general correlation have also been made by a graphical presentation without using an exponent on the Reynold's number. See Figure 16, page 546, Chemical Engineers Handbook, 3rd Edition, and Figure 6 by Gaffney and Drew, Ind. Eng. Chem., 42, 1120-7 (1950).

5.5 Effect of the Schmidt Number of the Continuous Phase

By analogy with some restricted work on heat transfer, Chilton and Colburn, Ind. Eng. Chem., 26, 1183 (1934) suggest that the Schmidt number should enter to the 2/3 power. This suggestion has come into general use, but now appears to be incorrect. Bedinfield and Drew in the foregoing reference, analyzed available mass transfer data for vapor-liquid systems and found the proper exponent to be 0.56. Gaffney and Drew in the foregoing reference obtained data on liquid systems in which the Schmidt number was varied from 150 to 13,000, and found that the exponent should be 0.58. The 2/3 value should be abandoned in place of 0.58.

5.6 Effect of Mobile Interface

When a fluid flows past a solid, the interface between the fluid and the solid is stationary and a characteristic amount of stability exists for the fluid films. Even the case of a solid surface covered with a liquid-soaked layer of paper comes in this class. But when two liquid films, or a gas and a liquid film, exist side by side, the interface acquires a mobility that is frequently visible as ripples and other movements. Through such mobility, another factor affecting the transport is generated.

Effect of Mobile Interface (continued)

The case for transport at immobile interfaces is covered on pages 546 and 547 Chemical Engineers Handbook, 3rd Edition, with the use of the incorrect Schmidt exponent of 2/3. It is claimed there that in the case of mass transfer to droplets, less than about 1 mm in diameter, the surface is practically immobile. Bedinfield and Drew (loc. cit.) give a good theoretical treatment of this case and obtained a good general correlation for gas films. Gaffney and Drew (loc. cit.) claim that liquid films and gas films at immobile surfaces give different correlations. However, these investigators worked with very short towers, some less than 3", but made no correction for end effects. Their work is important, though, in showing that at low values of Reynold's numbers some free convection takes place which introduces a Grashof number as in heat transfer.

The work on two adjacent films with a "mobile" interface leads to much more complications. O'Brien and Stutzman, Ind. Eng. Chem., 42, 1181-7 (1950) summarized the information for gas-liquid films in contact and arrived at a complicated correlation for the continuous film coefficient, involving the Reynolds number and the Schmidt number of the continuous phase but no property of the liquid phase. At least they concluded that the case of the mobile interface is quite different from that of the immobile interface.

Effect of Mobile Interface (continued)

The best evidence for behavior of a mobile interface as a variable in itself is the comparison between a wetted wall tower operated with a vapor core, and one with a fluid core. Gilliland and Sherwood, Ind. Eng. Chem., 26, 516 (1934) found a relation for the gaseous core that can be expressed as

$$\left(\frac{d}{H_G}\right) = 3.76\left(\frac{dV\rho}{\mu}\right)^{0.83}\left(\frac{\mu}{\rho D_V}\right)^{0.56}$$

While Fallah, Hunter, and Nash, J. Soc. Chem. Ind., 54, 49T (1935) found for a liquid core an expression equivalent to

$$\left(\frac{d}{H_L}\right) = 0.00921\left(\frac{dV\rho}{\mu}\right)^{0.80}\left(\frac{\mu}{\rho D_L}\right)^{0.46}$$

The "constant" terms, 3.76 and 0.0921, are so different considering that the equipment employed and the exponents used are so similar, that it is evident that some factor has been neglected. This factor is logically related to the physical properties of the two contacting phases. Since the mobility of the interface can be observed visually under many conditions of flow, it is a logical suspect for the difference. Some day this mobility effect will be properly expressed in a function of the physical properties of the two phases.

5.7 Effect of Interfacial Tension Depressants

In experiments in which the interfacial area was maintained constant, E. Hutchinson, J Phys. and Colloid Chem., 52, 897-908 (1948), found that adsorbed films at benzene-water interfaces usually, but not always, greatly retarded diffusion across the interface. However, the retarding effect of a given adsorbed layer was a function of the configuration and structure of the diffusing molecule. Hence, it was concluded that the retardation was not merely that of a mechanical obstruction, but included some kind of interaction between the diffuser and the adsorbed layer.

Chu, Taylor, and Levy, Ind. Eng. Chem., 42, 1157-63 (1950) extended the study of the effect of interfacial tension depressants to packed extraction towers. They interpreted their results to mean that the presence of an adsorbed layer at the interface caused an additional transfer resistance that retarded diffusion, but at the same time the lowered interfacial tension decreased the droplet size, increased the exposed interfacial area, and increased diffusional transfer. If the agent were exceptionally effective, the increase in area overbalanced the increased resistance of the adsorbed layer, and a net advantage was obtained. The maximum increase they obtained in extraction rate was 46%. With less effective agents, and particularly with relatively high concentrations of addition agent, the net effect was a decrease in extraction rate.

Effect of Interfacial Tension Depressants (continued)

A general conclusion is that interfacial tension depressants are quite specific in their action, and that most show a range of concentration wherein they aid extraction in commercial equipment, and a range of concentration wherein they retard extraction.

5.8 Treatment with Dimensionless Groups

For liquid-liquid extraction, there exists a discontinuous phase film and a continuous phase film, for which the correlations are different. For each film, there are two correlations, depending upon which film wets the packing.

For the continuous film that wets the packing, the present information is that the group $\left(\frac{d_p}{H_c}\right)$, where d_p = packing diameter, is a function of the following groups.

1. Reynolds number, $\frac{(d_p V \rho)}{\mu}$.

   The evidence is that for packed towers, the Reynold's number enters to the 0.6 power.

2. Schmidt number $\left(\frac{\mu}{\rho D}\right)$

   The evidence is that the Schmidt number enters to the 0.58 power. Many use the 2/3 power tentatively proposed some time ago by Chilton And Colburn.

Treatment with Dimensionless Groups (continued)

3. End Effect Number, $\left(\frac{Z}{d_p}\right)$

Heat transfer work indicated that the end effect is a function of this group. In most cases the effect is equivalent to an additional tower height of from 2 to 5 inches.

4. Grashof Number

Analogy with heat transfer, and the work of Gaffney and Drew indicates that at low Reynold's numbers free convection, represented by the Grashof number, plays a part.

5. Groups (or group) Related to Interface Mobility

This group has not yet been formulated. It seems to me that it would contain only the physical properties of the two adjacent films, such as densities, viscosities, and interfacial tension.

A general correlation for all two phase systems would include all groups above. For a specific liquid-liquid system in the usual flow range, a good correlation could probably be obtained with only the Reynolds and Schmidt number.

For the wall fluid of a wetted wall column, which corresponds roughly to the discontinuous film that wets the packing, the Schmidt and the Reynolds numbers are the only firmly established groups. See Brinsmade and Bliss, Trans. A.I.Ch.E., 39, 679 (1943). For the discontinuous film that does not wet the packing, the usual case for packed towers, no studies have yet been made, but a Schmidt number reliance has frequently been assumed.

5.9 Simultaneous Mass Transfer and Chemical Reaction

No generally useful treatment for problems in this class has been developed. In practice, the desired answers are sought by experimental techniques.

If the reaction is extremely fast and irreversible, such as are many ionic reactions, and if the reaction products are soluble in one phase only, the rate of transfer is governed only by the film of the non-reacting phase. The extraction of the acetic acid from benzene by aqueous NaOH is a typical case. Drew, Trans. A.I.Ch.E, 35, 681 (1939) has performed the integration for this case to allow the calculation of the number of transfer units.

A general treatment for combined mass transfer and chemical reaction has been proposed by Hatta, and extended by T. K. Sherwood, "Absorption and Extraction", page 200-205. R. N. Wilhelm, Chem. Eng. Progress, 45, 208 (1949) has also treated this case. These theoretical treatments are so far useful only in special cases, and for general deduction.

If the reaction is reversible, and if it is slow enough for the diffusing molecules to penetrate, on the average, through or a good way through the "reacting" film before they are converted, then there ought to be a different extraction rate correlation, depending upon the direction of extraction from phase to phase. Farmer, ORNL-635, has shown that acetic acid, which associates to a large extent into double molecules in CCl_4, gives different extraction rates (under comparable conditions) depending upon whether the acetic acid is extracted into or away from the CCl_4 phase. Because of this behavior, every system being

Simultaneous Mass Transfer and Chemical Reaction (continued)

studied should, if possible, be tested under both directions of diffusion to see if the same behavior is obtained.

6.0 Recommendations

In order to take advantage of the diffusional approach to solvent extraction, and in order to make the most out of the experiences of others, the following recommendations are made for basic studies in liquid-liquid extraction.

6.10 Experimental Programs

6.11 Equipment

1. The contacting towers should be as short as possible in order to avoid great changes in the property of the system over the tower. Otherwise, it may be quite difficult to pick average conditions, particularly the average slope of the equilibrium curve, to characterize the entire tower. On the other hand, the tower should not be so short that end effects become large. Tentatively, packed tower heights should be 2 to 3 feet. If possible, the end effects should be determined for the equipment used.

Equipment (continued)

2. The details of distributors, entrances, packing supports, method of dumping the packing, etc. should be standardized with some care. If this is done, information on different towers of the same approximate size should be comparable, and the correlation of information on towers of different sizes should be greatly facilitated.

6.12 Systems Used

1. If possible, systems should be chosen in which the distribution ratio is as near constant as possible with changes in concentration. It is also desirable to have little change with temperature.
2. The equilibrium curve should be determined with care, if not already available. The number of data points should be enough to permit an evaluation of the accuracy of the data.
3. Where possible, the system should be so chosen that the diffusing substances has the same molecular weight in both phases.
4. Experiments made to study single film coefficients should be made on a binary system having a mutual molar solubility of less that about 5 percent.

6.13 Operation of Equipment

1. The equipment should be run to provide a wide variation in the term $m\ (V_D/V_C)^{1/4}$.
2. As an aid to correlations, and to allow comparisons with future correlations, measurements should be made of temperature, flow rates of each stream (not just their sum), and the densities, viscosities and interfacial tension applicable to both phases, for at least certain key runs.
3. A record should be kept concerning which phase was made discontinuous, which phase wet the packing and walls, and to what extent.
4. Enough measurements should be made to permit, for each run, a weight balance of all pertinent material flows.
5. The tests should include runs, under comparable flow conditions, covering both possible directions of diffusion.

6.2 In Working Up Test Data

1. Material balances, in weight units, should be made for each run as sosn as possible, so that corrections can be applied judiciously.
2. The height of a transfer unit, based upon the discontinuous phase calculations, should be calculated.

In Working Up Test Data (continued)

3. The HTU_{OD} should be correlated against $m_{avg} (V_D/V_C)^{1/4}$, at least for packed and spray columns.
4. The HETS should be calculated.
5. For each run, and for each correlation, one should state clearly which phase was discontinuous, and which phase wet the packing.

6.3 Diffusion Coefficient Determination

The knowledge of the inherent diffusivity of a component is one of the most important single properties that can be specified for a given extraction case. The task of formulating a general correlation for the prediction of extraction rates will never be completed without knowledge of this property. Therefore, it is important that work on the thoery of liquid-liquid extraction include also a program of determining liquid diffusivities.

7.0 Appendix

7.1 Nomenclature

Symbol	Description	Engineering Units
A	Interfacial area exposed for diffusion transport	$ft.^2$
a	Ratio of interfacial area exposed to cubic foot of equipment volume	$\frac{ft.^2}{ft.^3} = \frac{1}{ft.}$
B	Effective film thickness	ft.
C	Concentration	$\frac{lb.\ mol.}{ft.^3}$
d	Diameter, as of a pipe	ft.
D_V	Volumetric diffusivity, lb. mols of A per hour per square foot per unit of concentration gradient in lb. mols of A per cubic foot of phase per foot	$\frac{ft.^2}{hr.}$
D_M	Mass diffusivity, same as above except concentration in lb. mols of A per lb. mol of phase	$\frac{lb.\ mols}{(hr.)(ft.)}$
H HTU	Height of a transfer unit, usually with a subscript for a special case	ft.
H	Weight ratio	$\frac{lbs.\ A}{lb.\ non\ A}$
k_G	Gas phase capacity coefficient, lb. mols of A diffusing per hour per square foot per unit of concentration gradient in mol fraction of gas phase, for single component diffusion	$\frac{lb.\ mols\ A}{(hr)(ft)^2(\Delta y)}$
k'_G	Gas phase capacity coefficient for equimolar counter diffusion. $k'_G = k_G\ (y_{BM})$	$\frac{lb.\ mols\ A}{(hr)(ft)^2(\Delta y)}$
k_L	Liquid phase capacity coefficient, lb. mols A diffusing per hour per square foot per unit of concentration gradient in lb. mols of A per cubic foot of phase, for single component diffusion	$\frac{ft.}{hr.}$

Nomenclature (continued)

Symbol	Description	Engineering Units
k'_L	Liquid phase capacity coefficient for equimolar counter diffusion. $k'_L = k_L x_{SM}$	$\frac{ft.}{hr.}$
L	Lb. mols of liquid phase per hour per square foot of superficial equipment cross section.	$\frac{lb.\ mols}{(hr.)(ft.)^2}$
L	Loss ratio, exit concentration over inlet concentration	None
M	Molecular weight	$\frac{lbs.}{lb.\ mols}$
m	Slope of equilibrium curve	y^*/x
N	Lb. mols diffusing per hour per square foot	$\frac{lb.\ mols}{(hr)(ft)^2}$
N NTU	Number of transfer units, usually with a subscript for a special case	None
N_p	Number of theoretical steps (plates or stages)	None
n	Number of lb. mols	lb. mols
p	Partial pressure	atm.
R	Gas constant	$\frac{(ft.^3)(atm)}{(lb.mol)(^oR)}$
R	The dimensionless group mV/L	None
S	Square feet of superficial equipment cross section	$ft.^2$
T	Absolute temperature	^oR
U	Velocity	ft./hr.
V	Lb. mols of a phase, often vapor, per hour per square foot of superficial equipment cross section	$\frac{lb.\ mols}{(hr)(ft)^2}$

Nomenclature (continued)

Symbol	Description	Engineering Units
V_T	Volume of tower	$ft.^3$
V	Velocity; volume of flow	ft./hr.; $ft.^3/hr.$
v	volume	$ft.^3$
W	Lbs. of total phase per hour per square foot	$\frac{\text{lb. mols}}{(\text{hr})(\text{ft})^2}$
w	Weight fraction	$\frac{\text{lbs. A}}{\text{lb. total}}$
x	Mol fraction, usually in a liquid phase	$\frac{\text{lb. mols A}}{\text{lb. mols total}}$
X	Mol ratio	$\frac{\text{lb. mols A}}{\text{lb. mol non A}}$
y	Mol fraction, often in a vapor phase	$\frac{\text{lb. mol A}}{\text{lb. mols total}}$
Y	Mol ratio	$\frac{\text{lb. mol A}}{\text{lb. mol non A}}$
Z	Tower height	ft.

Greek Alphabet

α	Diffusivity coefficient	
ρ	Density	$\frac{\text{lbs.}}{ft.^3}$
μ	Viscosity	$\frac{\text{lbs.}}{(\text{ft.})(\text{hr.})}$
μ	Chemical Potential	energy/lb. mol
π	Total pressure	atm.

Nomenclature (continued)

Subscripts

Symbol	Description
A,B	Components A and B
D,C	Discontinuous and continuous phase
E,R	Extract and raffinate phase
L,G	Liquid and gas, or one liquid and another liquid
Y,X	Y and X components or conditions
avg.	Average
am	Arithmetic average
lm, lgm	Logarithmic average
M	Logarithmic average across a single film
OM	Logarithmic average across two films
M	Mol units
S	Solvent
i	Interface; inert components
f	Film quantity
1,2	Terminal ends of a tower, 2 usually the dilute end

Superscripts

*	Equilibrium value
E	Extract phase
R	Raffinate phase

7.2 Summary of Equations

a. Number of Transfer Units (NTU)

	Single Component Diffusion	Equimolar Counter Diffusion
N_G =	$\int \frac{(1-y)_M \, dy}{(1-y)(y_i-y)}$	N_G = $\int \frac{dy}{y_i - y}$
N_{OG} =	$\int \frac{(1-y)_{OM} dy}{(1-y)(y^*-y)}$	N_{OG} = $\int \frac{dy}{y^*-y}$
N_L =	$\int \frac{(1-x)_M \, dx}{(1-x)(x-x_i)}$	N_L = $\int \frac{dx}{x - x_i}$
N_{OL} =	$\int \frac{(1-x)_{OM} \, dx}{(1-x)(x-x^*)}$	N_{OL} = $\int \frac{dx}{x - x^*}$

The driving force terms may have the sign reversed.

b. Height of Transfer Unit (HTU)

H_G =	$\frac{RTB_G \, V_M}{D_V \pi \, a} = \frac{V_M}{k_G \, a (y_B)_M}$	H_G =	$\frac{RTB_G V_M}{D_V \pi a y_B} = \frac{V_M}{k'_G \, a y_B}$
H_{OG} =	$\frac{V_M}{K_G \, a \, (1-y)_{OM}}$	H_{OG} =	$\frac{V_M}{K'_G \, a (1-y)_{OM}}$
$H_x = H_L$ =	$\frac{L_M B_L}{D_L \, C_{avg} \, a} = \frac{L_M}{k_L \, a \, C_{avg} (x_s)_M}$	$H_x = H_L$ =	$\frac{L_M B_L}{D_L C_{avg} a x_s} = \frac{L_M}{k'_L \, a x_s C_{avg}}$
$H_{OX} = H_{OL}$ =	$\frac{L_M}{K_L \, a \, C_{avg} (1-x)_{OM}}$	$H_{OX} = H_{OL}$ =	$\frac{L_M}{K'_L \, a \, C_{avg} (1-x)_{OM}}$

$(1-y)_M$ = log mean of $(1-y)$ and $1-y_i$)

$(1-y)_{OM}$ = log mean of $(1-y)$ and $1-y^*$)

Similar definitions hold for $(1-x)_M$ and $(1-x)_{OM}$.

c. Overall HTU's as a Function of Individual HTU's

$$H_{OG} = H_G \frac{(1-y)_M}{(1-y)_{OM}} + H_L \frac{mV_M}{L_M} \frac{(1-x)_M}{(1-y)_{OM}}$$

If the G film controls

$$H_{OG} \cong H_G + H_L \frac{mV_M}{L_M} \frac{(1-x)_{OM}}{(1-y)_{OM}}$$

$$H_{OL} = H_L \frac{(1-x)_M}{(1-x)_{OM}} + H_G \frac{L_M}{mV_M} \frac{(1-y)_M}{(1-x)_{OM}}$$

If the L film controls,

$$H_{OL} \cong H_L + H_G \frac{L_M}{mV_M} \frac{(1-y)_{OM}}{(1-x)_{OM}}$$

$m = dy^*/dx$

y refers to G film

x refers to L film

Single component diffusing

$$H_{OD} = H_D \frac{(1-y)_M}{(1-y)_{OM}} + H_C \frac{mV_D}{V_C} \frac{(1-x)_M}{(1-y)_{OM}}$$

If the D film controls

$$H_{OD} \cong H_D + H_C \frac{mV_D}{V_C} \frac{(1-x)_{OM}}{(1-y)_{OM}}$$

$$H_{OC} = H_C \frac{(1-x)_M}{(1-x)_{OM}} + H_D \frac{V_C}{mV_D} \frac{(1-y)_M}{(1-x)_{OM}}$$

If the C film controls

$$H_{OC} \cong H_C + H_D \frac{V_C}{mV_D} \frac{(1-y)_{OM}}{(1-x)_{OM}}$$

$m = \frac{dy^*}{dx}$

y refers to D film

x refers to C film

Single component diffusing

For equimolar counter diffusion, drop the subscripts on the (1-y) and (1-x) terms. Some terms will then cancel.

d. Capacity Coefficients

Single Component Diffusion	Equimolar Counter Diffusion
$k_G = \frac{N_A}{(y_{Ai} - y_{AG})}$	$k'_G = \frac{N_A}{(y_{A1} - y_{AG})}$
$k_G = \frac{D_V \alpha}{RTB_G (y_B)_{lm}}$	$k'_G = \frac{D_V \alpha}{RTB_G}$
$k_L = \frac{N_A}{C_{avg} (x_{AL} - x_{Ai})}$	$k'_L = \frac{N_A}{C_{avg}(x_{AL} - x_{Ai})}$
$k_L = \frac{D_L}{B_L (x_s)_{lm}}$	$k'_L = \frac{D_L}{B_L}$
$K_G = K_Y = \frac{N_A}{y_{AL}^* - y_{AS}}$	$K'_G = K'_Y = \frac{N_A}{(y_{AL}^* - y_{AG})}$
$K_L = K_X = \frac{N_A}{C_{avg} (x_{AL} - x_{AG}^*)}$	$K'_L = K'_Y = \frac{N_A}{C_{avg} (x_{AL} - x_{AG}^*)}$

Other definitions have appeared in the literature, among which are the following.

$$k_G = \frac{N_A}{(p_{Ai} - p_{AG})}$$

$$k_L = \frac{N_A}{(x_{AL} - x_{Ai})}$$

e. Some Formulations of the Group (mV_M/L_M)

Designation	Group	Definition of Terms
mol fractions	$\left(\frac{dy^*}{dx}\right)\left(\frac{V_M}{L_M}\right)$	y and x = mol fractions of A V and L = lbmols total phase per hr per ft.^{2}

Some Formulations of the Group (mV_M/L_M) (continued)

Designation	Group	Definition of Terms
mol ratios	$\left(\frac{dY^*}{dX}\right)\left(\frac{V_i}{L_i}\right)$	Y and X = mols A/mol non A V_i and L_i = lbmols non A per hr per $ft.^2$
weight fractions	$\left(\frac{dW^*_V}{dW_L}\right)\left(\frac{V}{L}\right)$	w_V and w_L = weight fractions of A V and L = lbs total phase per hr per ft^2
weight ratios	$\left(\frac{dH^*_V}{dH_L}\right)\left(\frac{V_i}{L_i}\right)$	H_V and H_L = lbs A/lb. non A V_i and L_i = lbs non A per hr per ft^2
molar-volumetric	$\left(\frac{dC^*_V}{dC_L}\right)\left(\frac{V_V}{V_L}\right)$	C_V and C_L = lbmols A/cubic foot of phase V_V and V_L = $ft.^3$ of phase per hr per ft^2
weight-volumetric	$\left(\frac{d\rho^*_V}{d\rho_L}\right)\left(\frac{V_V}{V_L}\right)$	ρ_V and ρ_L = lbs A/$ft.^3$ of phase V_V and V_L = $ft.^3$ of phase per hr per ft^2
molar-weight	$\left(\frac{dC^*_V}{dC_L}\right)\left(\frac{W_V}{W_L}\right)$	C_V and C_L = lbmols A/lb. total phase W_V and W_L = lb total phase per hr per ft^2

The m term is the slope of the equilibrium curve. The flow rates can be expressed in any time and area units, just so the result is dimensionless.

Some Formulations of the Group (mV_M/L_M) (continued)

f. Miscellaneous

$$m_{avg} = \frac{\int \frac{m\,dy}{y^* - y}}{\int \frac{dy}{y^* - y}} = \text{average slope}$$

Z = height of tower = NH = (number of transfer units) x (height of a transfer unit)

Colburn's equation

$$N_{OY} = \int_2^1 \frac{dy}{y^* - y} = \frac{1}{(1 - mV_M/L_M)} \ln \left[(1 - mV_M/L_M) \left(\frac{y_1 - mx_2}{y_2 - mx_2} \right) + \frac{mV_M}{L_M} \right]$$

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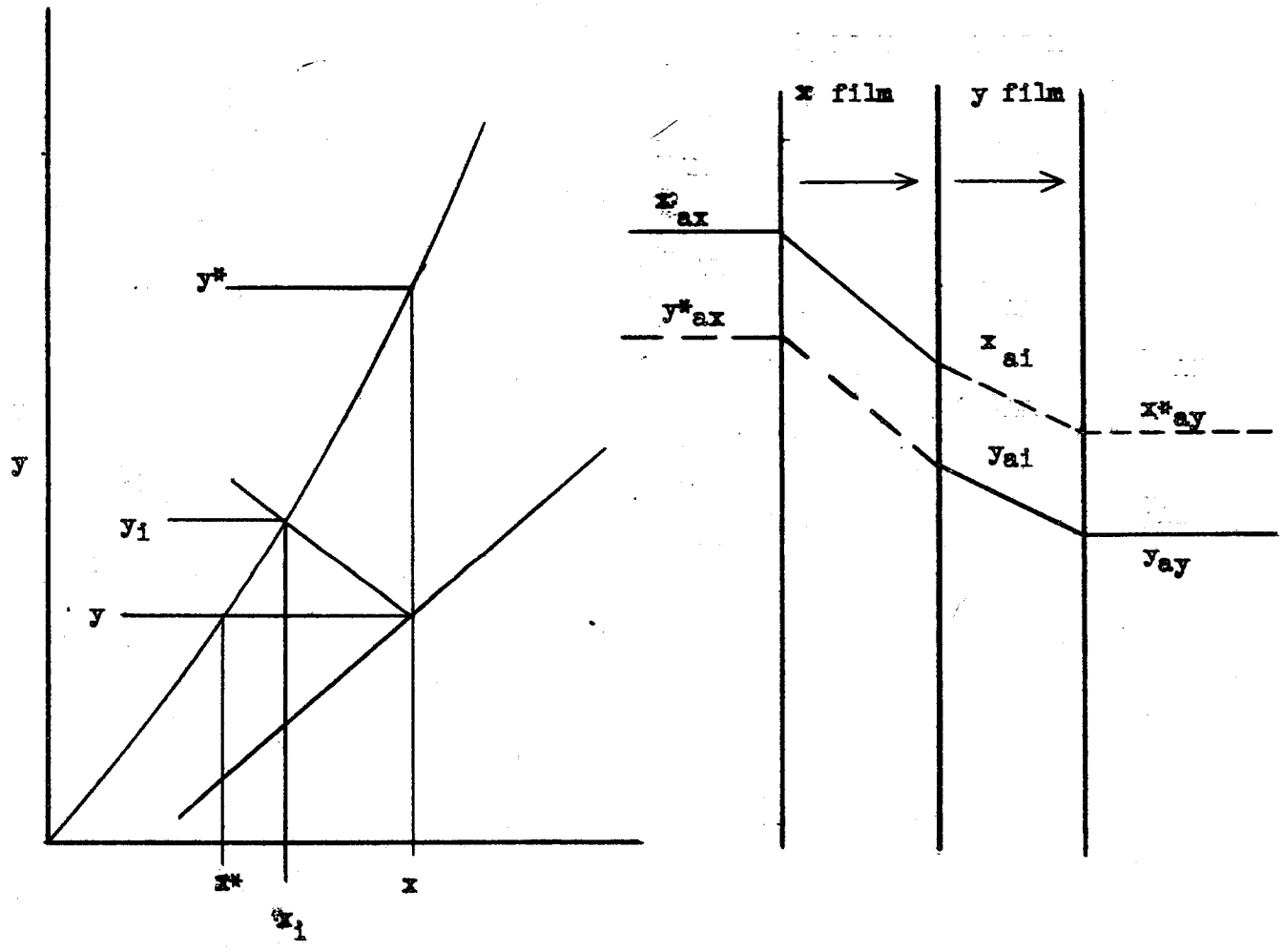
Figure 12

Pictorial Relation of Terms



7.3 Sample Calculation

A 3.2 mol percent solution of propionic acid in water is to be extracted at 30°C with CCl_4 in a packed tower to take the acid concentration down to 0.2 mol percent. For each 100 pound mols of entering aqueous phase, 104.3 pound mols of CCl_4 is to be used. Water is the continuous phase.

Physical data for the system at 30°C are as follows:

Carbon Tetrachloride Phase		Aqueous Phase	
30°C Density gm/ml	Mol Percent Acid	30°C Density gm/ml	Mol Percent Acid
1.5743	0.0000	0.9958	0.0000
1.5743	0.0068	0.9959	0.048
1.5744	0.0782	0.9965	0.214
1.5687	1.201	0.9989	0.965
1.5579	3.361	1.0010	1.742
1.5341	8.174	1.0048	3.08
1.4832	17.58	1.0101	5.38

(a) Calculate the number of theoretical stages required for this separation.

(b) Calculate the number of overall transfer units for the discontinuous phase.

(c) Calculate the value of m_{avg}.

(d) Calculate the value of $(m_{avg}\ V/L)$

Sample Calculation (continued)

(e) What is the minimum theoretical amount of CCl_4 that could be used, in pound mols per hour, and still maintain to tower top conditions, and treat the same feed? What would be the new value of y_2? How tall would the tower be?

(a) Basis: 1 hour

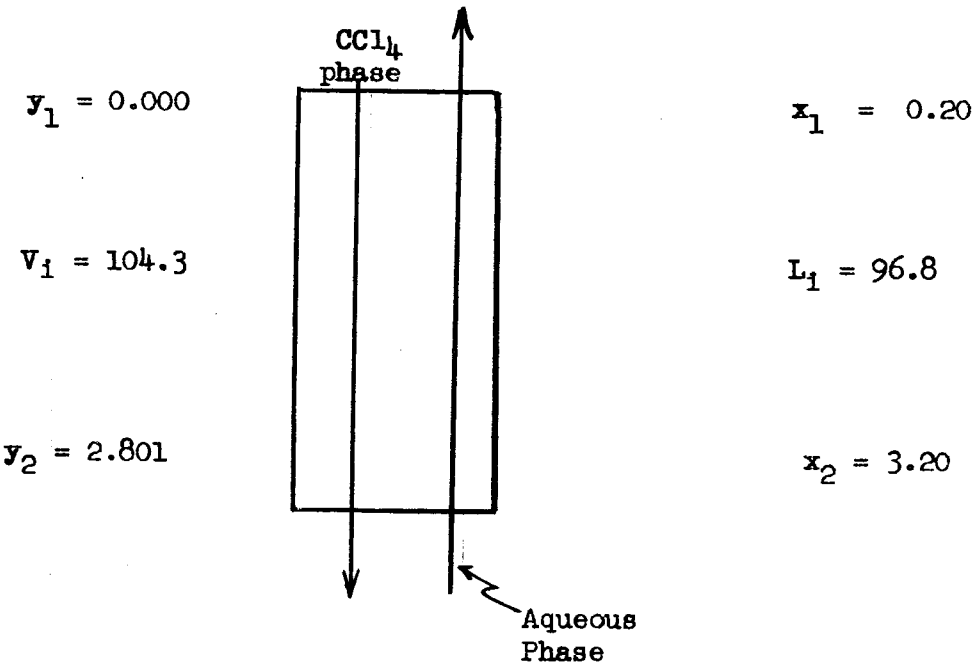
Let L_i = lbmols of pure H_2O = 100 (0.968) = 96.8

V_i = lbmols of pure CCl_4 = 104.3

x = conc. in the aqueous phase, mol percent

y = conc. in the CCl_4 phase, mol percent

The flow sheet is as follows:



Sample Calculation (continued)

The overall material balance is as follows:

$$L_1 \left(\frac{x_2}{100 - x_2} - \frac{x_1}{100 - x_1}\right) = V_i \left(\frac{y_2}{100 - y_2} - \frac{y_1}{100 - y_1}\right)$$

$$96.8 \left(\frac{3.2}{96.8} - \frac{0.20}{99.8}\right) = 104.3 \left(\frac{x_2}{100 - x_2} - 0\right)$$

$$3.2 - 0.1940 = 3.0060 = 104.3 \left(\frac{x_2}{100 - x_2}\right)$$

$$x_2 = 2.801$$

The operating line is as follows:

$$L_i \left(\frac{x}{100 - x} - \frac{x_1}{100 - x_1}\right) = V_i \left(\frac{y}{100 - y} - \frac{y_1}{100 - y_1}\right)$$

$$\left(\frac{x}{100 - x} - 0.002004\right) = 1.0776 \left(\frac{y}{100 - y}\right)$$

Points calculated on this operating line are as follows:

y	x	y	x
0.0000	0.20	0.5596	0.80
0.0093	0.21	0.7458	1.00
0.0186	0.22	1.212	1.5
0.0466	0.25	1.679	2.0
0.0931	0.30	2.142	2.5
0.1864	0.40	2.801	3.2
0.2796	0.50	3.082	3.5
0.3736	0.60	9.195	10.0

In order to step off the theoretical stages, it is customary to employ ordinary rectilinear graph paper. Accordingly, Figure 11 is such a plot made of the equilibrium curve and of the operating line (which is practically straight). The number of theoretical stages comes out to be 7.67 to go from y = 0 to y = 2.801.

Sample Calculation (continued)

Frequently, a plot on logarithmic paper provides an easier spacing of the stages, and allows a better evaluation of how the equilibrium curve should be drawn to fit the data points. Such a plot is shown as Figure 12. On it the theoretical stages is 7.92. The difference from the other answer is the result of the sensitivity of the graphical work. Let the answer be 7.8 stages.

(b) The general equation is as follows:

$$N_{OY} = \frac{(1-y)_{OM}\, dy}{(1-y)(y^*-y)}$$

Since we have defined y to be the composition of the discontinuous phase, this equation fits our case exactly. To use it we need a plot of y versus x, which we have in Figure 12.

Using Wiegand's approximation,

$$N_{OD} = \int \frac{dy}{y^* - y} + 1/2 \ln \frac{(1-y_2)}{(1-y_1)}$$

$$1/2 \ln \frac{1-y_2}{1-y_1} = 1/2 \ln \frac{0.972}{1.000} = 1/2 \ln/0.0295 =$$

$$- 1/2 (0.0290) = - 0.015$$

Thus $N_{OD} = \frac{dy}{y^* - y} - 0.015$

The integral is evaluated by graphical integration as follows. Values are taken from the logarithmic plot. They can be followed on the rectilinear plot readily.

Sample Calculation (continued)

y	y*	y* - y	$\frac{1}{y^* - y}$
0.000	0.084	0.084	11.90
0.050	0.129	0.079	12.67
0.100	0.174	0.074	13.51
0.150	0.229	0.079	12.67
0.200	0.292	0.092	10.9
0.250	0.363	0.113	8.85
0.300	0.439	0.139	7.19
0.400	0.605	0.205	4.88
0.60	0.97	0.37	2.70
0.80	1.41	0.61	1.64
1.00	1.90	0.90	1.11
1.5	3.38	1.88	0.53
2.0	5.15	3.15	0.32
2.5	7.3	4.8	0.21
2.801	8.7	5.9	0.17
3.0	9.7	6.7	0.15

A plot of $\frac{1}{y^* - y}$ versus y is shown on Figure 13.

By graphical integration

$$\int_2^1 \frac{dy}{y^* - y} = 6.20$$

Thus N_{OD} = 6.18 transfer units = 6.20 - 0.02

(c) $$M_{avg} = \frac{\int_2^1 \frac{m\,dy}{y^*-y}}{\int_1 \frac{dy}{y^*-y}} = \frac{\int_2^1 \frac{m\,dy}{y^*-y}}{6.20}$$

To evaluate the integral we need values of m as a function of y. Not having any better information, let us assume that m can be evaluated as the slope of the equilibrium curve at the y* values associated with the x, y values. Consider the logarithmic plot. Let the slope of the log plot be s.

Sample Calculation (continued)

$$s = \frac{d \ln y^*}{d \ln x} = \frac{dy^*}{y^*}\frac{x}{dx} = \frac{dy^*}{dx}\frac{x}{y^*} = m\,(x/y^*)$$

$$m = \frac{y^*}{x}\,(s)$$

y	x	y*	s	m
- 0.09	0.1	0.0245	0.577	0.142
- 0.04	0.15	0.051	0.566	0.192
0.00	0.20	0.084	0.575	0.242
0.093	0.30	0.169	0.578	0.325
0.186	0.40	0.277	0.587	0.407
0.280	0.50	0.405	0.589	0.477
0.374	0.60	0.555	0.591	0.547
0.560	0.80	0.90	0.595	0.669
0.746	1.0	1.30	0.598	0.777
1.22	1.4	2.26	0.604	0.975
1.679	2.0	4.0	0.606	1.212
2.142	2.5	5.8	0.607	1.409
2.62	3.0	7.9	0.607	1.600
3.00	3.42	9.7	0.607	1.72

A plot of the instantaneous slope, m, is shown on Figure 14. Values of m as needed are interpolated from this graph.

We can now formulate $\frac{m}{y^*-y}$

y	y*	y* - y	m	$\frac{m}{y^* - y}$
0.000	0.084	0.084	0.238	2.83
0.050	0.129	0.079	0.283	3.58
0.100	0.174	0.074	0.328	4.43
0.150	0.229	0.079	0.370	4.68
0.200	0.292	0.092	0.410	4.46
0.250	0.363	0.113	0.451	3.99
0.300	0.439	0.139	0.488	3.51
0.400	0.605	0.205	0.558	2.72
0.60	0.97	0.37	0.683	1.85
0.80	1.41	0.61	0.796	1.31
1.00	1.90	0.90	0.899	1.00
1.5	3.38	1.88	1.131	0.60
2.0	5.15	2.15	1.340	0.425
2.5	7.3	4.8	1.540	0.32
2.801	8.7	5.9	1.658	0.28
3.0	9.7	6.7	1.731	0.26

Sample Calculation (continued)

On Figure 13, $\frac{m}{y^*-y}$ is plotted against y

Graphical integration gives

$$\int_2^1 \frac{m\,dy}{y^* - y} = 3.41$$

Hence, $M_{avg} = \frac{3.41}{6.20} = 0.550$

The instantaneous m = 0.550 occurs at y = 0.39

(d) At the top of the column

V = 104.3 lb. mols total

L = (96.8)(100/99.8) = 97 lb. mols. total

V/L = 1.075

At the bottom of the column

V = (104.3)(100.0/97.2) = 107.3 lb. mols. total

L = (96.8)(100/96.8) = 100 lb. mols. total

(V/L) = 1.073

Therefore, $(V/L)_{avg} = 1.074$

$(m_{avg}\ V/L) = (0.550)(1.074) = 0.591$

$(m_{avg}\ V/L)^{1/4} = (0.550)\ (1.018) = 0.560$

Sample Calculation (continued)

(e) The minimum reflux ratio is best obtained graphically on Figure 11. Since the tower top conditions are maintained, the operating will always pass through the point $y_1 = 0.0$, $x_1 = 0.20$. Assume that the operating line is straight with slope L/V. As V, the CCl_4 phase, is decreased the operating line swings upward, pivoting on the top concentration point. When the line becomes tangent to the equilibrium curve, the V is a minimum. The tangent value of L/V is found to be 1.333. The average value of (L/V) was previously 1.074, when 104.3 pound mols of CCl_4 were required.

Therefore, $V_{min} = (104.3)\ \frac{1.074}{1.333} = 84.0$

The height required is an infinite height. The y_2 max. = 3.98 mol percent, from Figure 11.

7.4 Problems in Mass Transfer Related to Solvent Extraction

1. The individual film coefficient for heat transfer for air at 100°C and 760 mm Hg. pressure is 20 in a particular case. What is the effective film thickness, in millimeters? For kerosene at 68°F providing a heat transfer coefficient of 150, what is the film thickness in millimeters? Are these film thicknesses comparable to those effective for mass transfer?
2. Calculate the value of Dv in cm^2/sec. at 25°C and 1 atm. for methyl isobutyl ketone in air, by Gilliland equation. Convert to $ft.^2$/hr.
3. Calculate the diffusivity of methyl isobutyl ketone in dilute aqueous solution at 25°C, using the correlation of C. R. Wilke, Chem. Eng. Prog., 45, 219 - 24 (1949).
4. Calculate the atomic volume of uranium from literature data on UF_6. Using this value, calculate the diffusivity of $UO_2(NO_3)_2$ and $UO_2(NO_3)_2$ $(TBP)_2$ at 25°C. TBP = tributyl phosphate. The solution is dilute aqueous.
5. Gilliland found that for a gas film mass transfer coefficient inside a round pipe that

$$\left(\frac{d}{B_G}\right) = 0.023\left(\frac{dV\rho}{\mu}\right)^{0.83}\left(\frac{\mu}{\rho D_v}\right)^{0.44}$$

where d = diameter of the pipe.

In comparison, Fallah, Hunter, and Nash found that the liquid film coefficient for the core liquid in a wetted wall column could be correlated by the equation

Problems in Mass Transfer Related to Solvent Extraction (continued)

$$\frac{kd}{D_L} = 0.94 \left(\frac{dV\rho}{\mu}\right)^{0.8} \left(\frac{\mu}{\rho D_L}\right)^{0.46}$$

Convert these two equations to give an expression for $\left(\frac{Hg}{d}\right)$ and $\left(\frac{H_L}{d}\right)$ respectively, and compare them.

6. Starting with the equation for a binary gas system.

$$- dC_A = \frac{1}{D_V C} \left[N_A C_B - N_B C_A\right] dB$$

where D_V = diffusivity in ft.^{2}/hr.

C = concentration in lb. mols. per cubic foot.

N = lb. mols. per hour per sq. ft.

B = film thickness in feet.

For the case of a single component diffusing across a single film and assuming that $C = \frac{\pi}{RT}$ and $C_A = \frac{p}{RT}$, derive the following formula.

$$N_A = \frac{D_V \pi \left(p_{AG} - p_{Ai}\right)}{RT\, B_G \left(p_B\right)_{lm}}$$

where the subscripts G and i refer to values at the main gas side of the film and at the other interface, respectively. The term $(p_B)_{lm}$ is the log mean of the two bounding values.

Problems in Mass Transfer Related to Solvent Extraction (continued)

7. For one component diffusing through a gas film, the Stephan equation reduces readily to

$$-dC_A = \frac{N_A C_B}{D_V C} dB$$

Assuming that this equation can be applied to liquid diffusion, and further assuming that $C_A + C_B = m C_B + b$, derive the meaning for the C_{avg} term that appears in the usual integrated form which is as follows:

$$N_A = \frac{D_L C_{avg} (x_{Ai} - x_{AL})}{B_L x_{SM}}$$

x_{SM} = lg mean of the boundary values for the solvent.

8. (a) Make an idealized drawing of a two phase contacting system, indicating schematically thereon two adjacent vertical films and the terminal and intermediate main body and interface compositions. Use these compositions to make clear the definition of $(1-y)_{OM}$, $(1-y)_M$, $(1-y)$, $(1-x)_{OM}$, $(1-x)_M$, and $(1-x)$.

(b) On a rectilinear plot, draw an operating line and an equilibrium curve. Indicate on this plot a value of y, yi, y*, x, xi, and x*. Define m in terms of these symbols, and contrast with the value of m in y = m x.

9. Starting with

$$H_{OG} = H_G \frac{(1-y)_M}{(1-y)_{OM}} + H_L \left(\frac{mV_m}{Lm}\right) \frac{(1-x)_M}{(1-y)_{OM}}$$

Derive the following relationship,

$$\frac{1}{K_G a} = \frac{1}{k_G a} + \frac{H'}{k_L a}$$

10. A certain chemical reaction produces as a by-product an aqueous phase containing on the average 0.60 mol percent propionic acid. It is proposed that this propionic acid concentration be reduced to 5% of its original value by extraction with diisopropyl ether at 30°C. The solvent is distilled from the acid and returned water-saturated to the extraction column. In the extraction column, the ratio of mols of entering water phase to mols of entering ether phase will be 5.5.

(a) Calculate the exit concentration of the diisopropyl ether phase.

(b) To what percentage of the planned amount would it be possible to reduce the flow of the DIPE phase, as an absolute minimum?

(c) Determine the number of transfer units required, based upon DIPE concentrations, by graphical integration.

(d) Determine the number of transfer units by the use of Colburn's charts.

(e) Determine the number of transfer units by the appropriate use of an integrated equation involving the log mean driving face.

(f) How many theoretical stages are required?

Problems in Mass Transfer Related to Solvent Extraction (continued)

The equilibrium data for the system diisopropyl ether-propionic acid-water at 30°C is as follows:

Water Phase Mol Percent			Diisopropyl Ether Phase Mol Percent		
DIPE	P. A.	H_2O	DIPE	P. A.	H_2O
0.131	0.0000	99.87	96.58	0.000	3.42
0.132	0.0299	99.84	96.35	0.175	3.47
0.133	0.0853	99.78	95.86	0.511	3.63
0.135	0.1378	99.73	95.35	0.873	3.78
0.138	0.2277	99.63	94.53	1.425	4.04
0.142	0.3914	99.47	92.84	2.600	4.56
0.148	0.6184	99.23	90.46	4.24	5.30
0.155	0.8003	99.05	88.38	5.68	5.94

11. A mixture of air containing 21% of SO_2 by volume is to be scrubbed isothermally at 20°C in an 18 inch diameter tower packed with 3 inch spiral rings. The pressure is 760 mm Hg, the exit gas strength is 2% SO_2, and the entering water contains no SO_2. Equilibrium data are given on page 1129, Perry, 2nd Edition. (Other somewhat different data are given on page 396.) The ratio of entering pure water to entering pure air, in lb.-mols., is 56.2. Neglect the pressure drop across the tower, and assume no water vapor in the air.

    (a) Calculate the equation of the operating line in terms of y and x, mol fractions. Check the accuracy of your equation by demonstrating that when y = 0.21, x = 0.00435.

Problems in Mass Transfer Related to Solvent Extraction (continued)

(b) Plot on the same graph the operating line and the equilibrium curve in terms of y and x.

(c) Calculate, for the tower top and the tower bottom conditions, the slope of a line passing through a point y, x on the operating line and yi, xi on the equilibrium curve. The requisite data may be taken from Figure 30, page 1191, Perry, 2nd Edition.

(d) Calculate the number of transfer units for the gas film itself, N_G.

(e) Calculate the tower height, in feet.

12. The data of O. S. Knight, Trans. A.I.Ch.E., 39, 439-56 (1943) have been recalculated by J. I. Stevens to provide values of the overall HTU's for the dispersed phase, and values for $M_{avg}\left(V_D/V_C\right)^{1/4}$. The M_{avg} was calculated from the relationship

$$M_{avg} = \frac{\int \frac{m\,dy}{y^* - y}}{\int \frac{dy}{y^* - y}}$$

Run Number	HTU_{OD}	HTU_{OC}	HETS	M_{avg}	V_D/V_C	$M_{avg}\left(V_D/V_C\right)^{1/4}$
1	12.37	5.31	4.77	7.92	0.62	7.02
2	21.2	3.01	7.0	8.23	1.052	8.34
6	18.3	1.96	9.42	10.61	1.19	11.08
7	56.7	11.92	28.	29.89	0.295	22.05
8	47.4	8.49	19.9	27.29	0.1575	17.2
9	47.3	9.50	20.4	26.33	0.328	19.4
10	48.3	7.04	15.0	22.49	0.481	18.74
11	34.9	12.35	17.5	29.63	0.1872	19.48
12	46.2	5.71	12.8	22.61	0.495	18.95
13	43.1	6.20	13.3	23.95	0.437	19.46

Problems in Mass Transfer Related to Solvent Extraction (continued)

(a) Plot the data as HTU_{OC} versus $\frac{1}{M_{avg}} \left(\frac{V_C}{V_D}\right)$
Compare with the original plot by O. S. Knight, where M_{avg} was calculated by the method of Dodge, and Furnes. Note that Knight omitted two points from his plot.

(b) Plot as HTU_{OD} versus $M_{avg} \left(V_D/V_C\right)^{1/4}$

(c) Estimate HTU_{OD} from the papers of Colburn and Welsh, A.I.Ch.E., 38, 179-202 (1942), and Laddha and Smith, Chem. Eng. Progress, 46, 195-202 (1950).

(d) Draw a straight line through the points of (b), using the information of (c).

13. A certain countercurrent extraction process is operated under conditions such that the equilibrium and operating line relations are as follows.

Y_2 = 0.0000 and Y_1 = 0.0200

X	Y*		X	Y*	Y
0.00	0.0000		0.08	0.0320	0.0120
0.01	0.0005		0.09	0.0405	0.0140
0.02	0.0020	0.0000	0.10	0.0500	0.0160
0.03	0.0045	0.0020	0.11	0.0605	0.0180
0.04	0.0080	0.0040	0.12	0.0720	0.0200
0.05	0.0125	0.0060	0.13	0.0845	
0.06	0.0180	0.0080	0.14	0.980	
0.07	0.0245	0.0100			

Evaluate the integral $\int_2^1 \frac{dY}{Y^*-Y}$ by the following means

Problems in Mass Transfer Related to Solvent Extraction (continued)

(a) Exact integration, knowing that

$Y^* = 5X^2$

$Y = 0.2X - 0.004$

(b) The use of Figure 28, page 554, Chemical Engineers' Handbook, 3rd Edition. This figure and the equation upon which it is based assumes that both the operating line and the equilibrium curve are straight. When the equilibrium line is curved, frequently the slope utilized is that for the tower end where the most transfer units are required, usually the more dilute end.

(c) Colburn has derived an equation for a tower broken into two sections, the break occurring at $Y_a = \sqrt{Y_1 Y_2}$. This equation is presented as equation 13, Ind. Eng. Chem. 33, 461 (1941) and is quoted by Elgin as equation 108, page 745, Chemical Engineers' Handbook, 3rd Edition. A certain procedure is advocated whereby the equation can be solved graphically by the use of Figure 28, page 554, Chemical Engineers' Handbook, 3rd Edition. Note that the procedure breaks down when mV/L is greater than 1.0, so the value of m must be chosen carefully.

(d) The method of Scheibel and Othmer, Trans. Amer. Inst. Chem. Engrs. 38, 339-64 (1942). Note carefully the definitions of m, and m_2 as illustrated in figure 1, page 341.

(e) The method of G. E. White, Chem. Eng. Progress 46, 363-8 (1950).

Problems in Mass Transfer Related to Solvent Extraction (continued)

14. Given

$$N_{OY} = \int_2^1 \frac{(1-y)_{OM}\, dy}{(1-y)\,(y^*-y)}$$

Where

$$(1-y)_{OM} = \frac{(1-y) - (1-y^*)}{\ln \frac{(1-y)}{(1-y^*)}}$$

Convert to the symbol Y, the mol ratio such that

$$Y = \frac{y}{1-y}$$

Then assume that the lg mean (1-y) can be replaced by the arithmetic mean (1-y), which is Wiegand's approximation, and show that

$$N_{OY} = \int_2^1 \frac{dY}{Y^* - Y} + \frac{1}{2} \ln \frac{1 + Y_1}{1 + Y_2}$$

15. A certain extraction operation is carried out in a 4" i.d., 25 foot column packed with 3/8" metal Raschig rings. Aqueous feed containing 60 mg of the component A per mg of solution is feed to the top of the column as the continuous phase. The content of A in this phase is reduced to 0.01 mg/ml at the tower exit. The extracting solution is a dispersed organic phase entering with no content of A. The ratio of the flow rates of the discontinuous phase to the continuous phase is 3 to 2. Equilibrium data for this system are as follows:

Problems in Mass Transfer Related to Solvent Extraction (continued)

Mg A per ml solution		Mg A per ml solution	
Organic	Aqueous	Organic	Aqueous
0.00010	0.0013	14.0	1.5
0.00025	0.0015	20.0	3.0
0.00060	0.0020	35	6.0
0.0025	0.0025	35	10
0.020	0.005	45	20
0.060	0.010	60	25
0.50	0.040	58	40
1.5	0.15	60	60
3.5	0.60	60	80
6.0	0.50	60	100

The molecular weight of A is over 200.

The molecular weight of the solvent is about 85.

(a) Plot the equlibrium data on logarithmic paper (6 cycles by 5 cycles) so that the number of overall transfer units may be most readily calculated for the dispersed phase.

(b) Show that it is satisfactory to treat the system as dilute. Then calculate the exit organic phase concentration.

(c) Formulate the equation for the operating line, and plot on the graph with the equilibrium data.

(d) Prove that the slope (s) of the equilibrium curve on logarithmic paper equals x/y times the slope (m) of the same curve on rectilinear paper, y being the ordinate.

Problems in Mass Transfer Related to Solvent Extraction (continued)

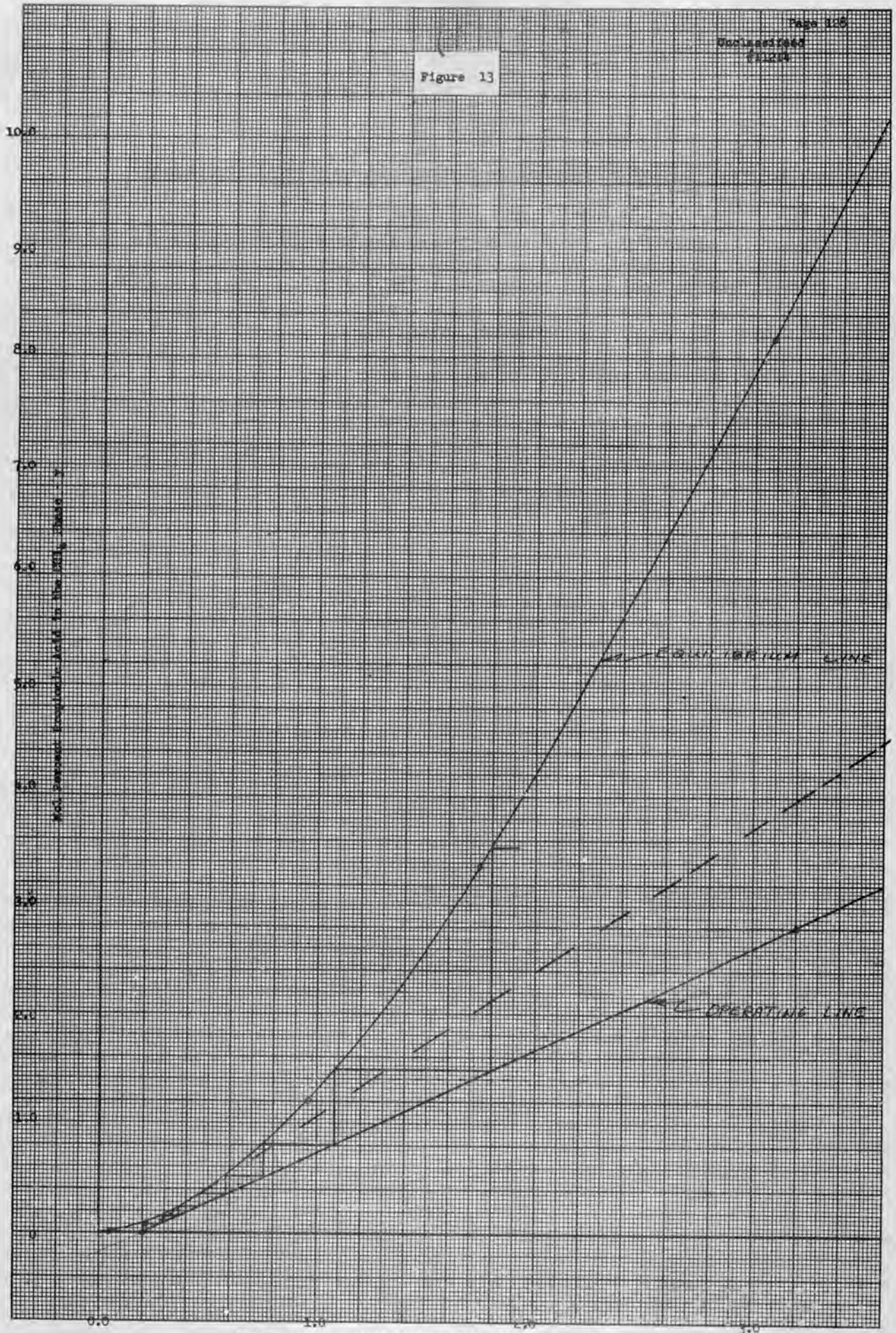
(e) Prepare a logarithmic plot of m versus the concentration in the dispersed phase. Assume that m is evaluated at y^*.

(f) Calculate the number of transfer units, N_{OD}.

(g) Calculate the average value of m.

(h) Calculate $(M_{avg}\ V_D/V_C)$ for this test case.

FPP/rcp


10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
0.0
1.0
2.0
3.0
Wt. Percent Propionic Acid in the Ether Phase - y
EQUILIBRIUM CURVE
OPERATING LINE
Mol Percent Propionic Acid in the Water Phase - x

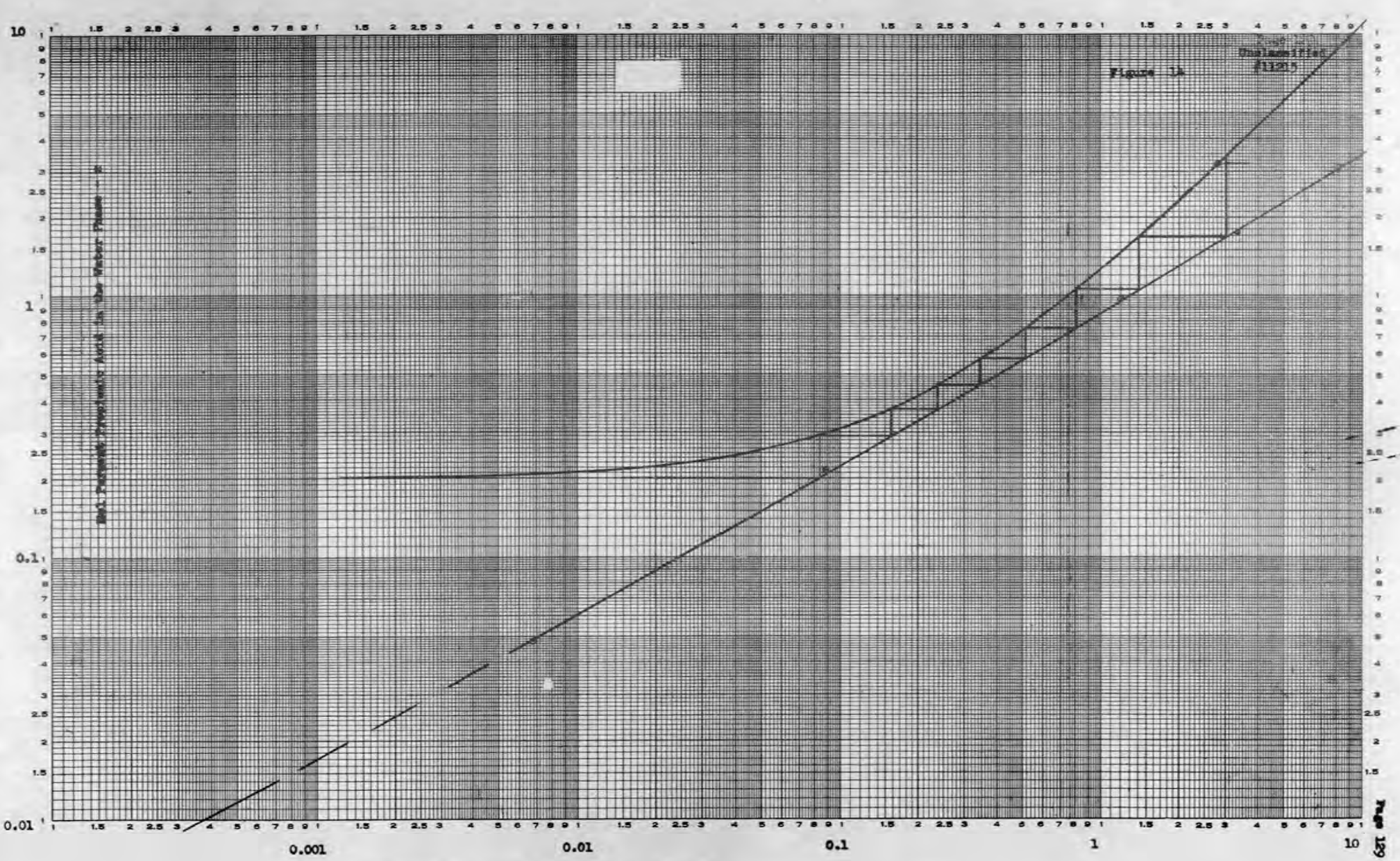


Figure 1A
Mol Percent Propionic Acid in the Water Phase - x
Mol Percent Propionic Acid in the CCl4 Phase - y
10
1
0.1
0.01
0.001
0.01
0.1
1
10

Figure 15

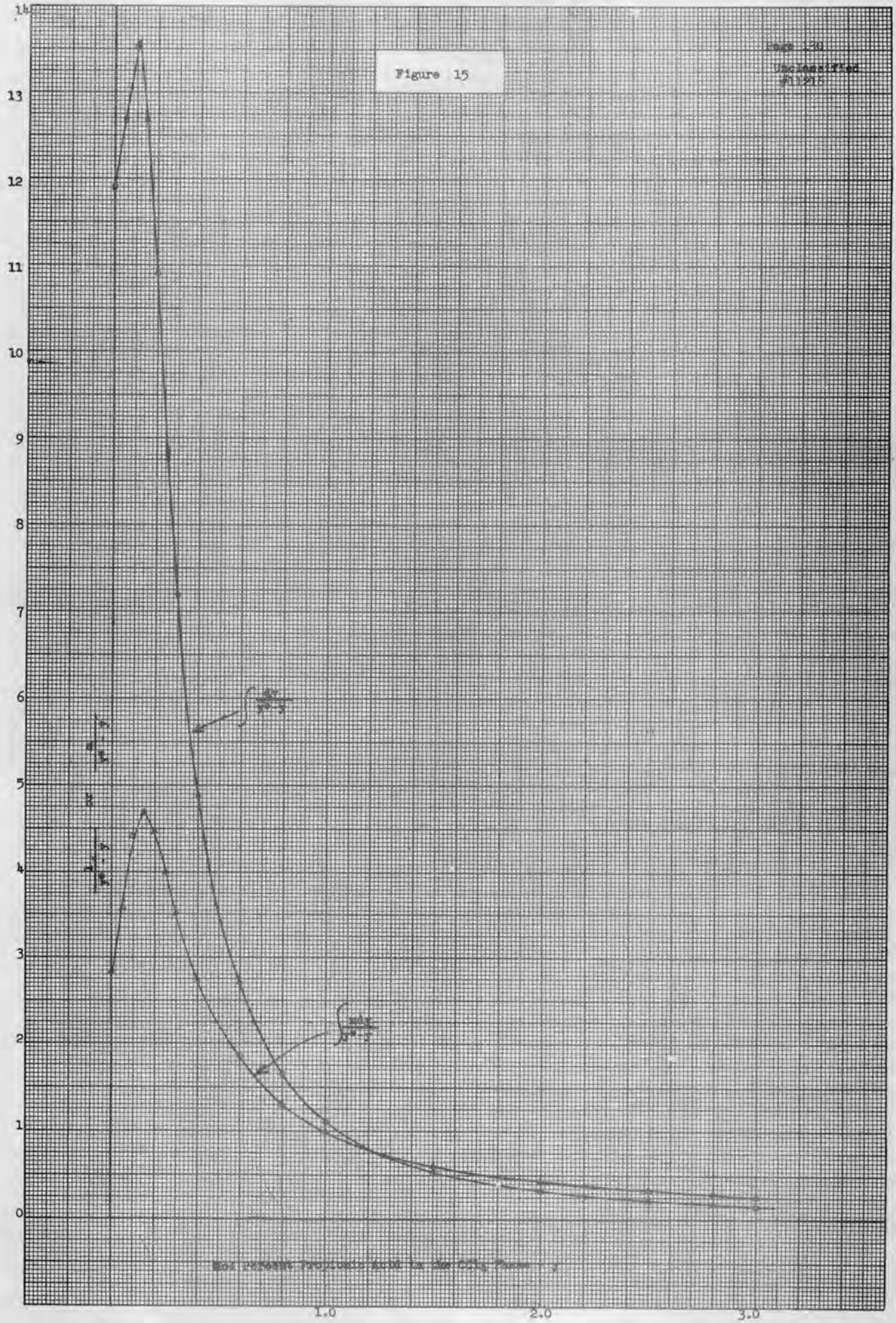


Figure 16