MASS TRANSFER STUDIES ON A SIEVE PLATE

A Thesis submitted to the University of Glasgow in fulfillment of the requirements of the Degree of Doctor of Philosophy

by

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Mass Transfer Studies on a Sieve Plate.

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SUMMARY

The mass transfer and hydraulic characteristics of a 9 in diameter sieve plate have been studied using three gas phase controlled systems, (a) the adiabatic evaporation of water into air, (b) the non-adiabatic evaporation of carbon tetrachloride into air and (c) the absorption from air of carbon tetrachloride by decahydronaphthalene (decalin). The object was to investigate the variation of plate efficiency with gas and liquid rate, due to the effect of these variables on the hydraulic behaviour of the plate, i.e. on froth density, gas residence time etc., under these three different systems. It was also intended to investigate the correlation of the mass transfer data.

The mass transfer behaviour of the plate during evaporation of water, was studied by examining the rate of change of a very dilute dye i.e. concentrations less than .01%. Gas rates varied from 1 to 4.5 ft/sec through the bubbling area and liquid rates from 70 to 800 gal/hr ft^2 of column cross sectional area. It was found that the relationship between the Murphree plate efficiency, E_{MV} and the gas rate was more complicated than has been previously reported for this system. Consideration of the hydraulic characteristics of the aqueous system studied, which included the froth density, fractional gas hold up and gas residence time, showed that the relationship found is to be expected under the conditions studied and a mechanism is proposed to explain the variations in plate efficiency with gas rate.

The mass transfer characteristics of the air/carbon tetrachloride evaporation system were studied by measuring the change in enthalpy of the air before and after mass transfer took place. The gas rates studied were in the range 1-3.5ft/sec

and liquid rates from 80 to 310 gal/hr ft^2 of column area. The Murphree plate efficiency, E_{MV}, was found to fall with gas rate and rise with liquid rate as expected from the hydraulic characteristics of the system, but the magnitude of the efficiencies was found to be lower than expected. An explanation is suggested.

The mass transfer characteristics of the absorption system were studied by measuring the changes in concentration of gas and liquid across the plate. The gas rates studied were from 1.4 to 3.0 ft/sec and the liquid rates studied varied from 110 to 560 gal/hr ft^2. The Murphree plate efficiency, E_{MV}, was found to fall with gas rate and rise with liquid rate approximately as predicted from the examination of the hydraulic behaviour of the system.

Comparison of the hydraulic characteristics of the three systems showed that properties such as froth density and gas residence time, considered at similar gas and liquid rates, were not independent of the system properties. The fractional gas hold up could be predicted, for the three systems by the equation

$$H_G = .25\,F - .0087\,\gamma\,\dot{\rho}_L + .55$$

where F is the gas rate F factor, γ is the surface tension dyne / cm^2 and $\dot{\rho}_L$ is the liquid density gm / cm^3.

Attempts were made to correlate the mass transfer results by Gerster's method i.e. by relating the numbers of transfer units for different systems by the ratio of the square roots of the respective Schmidt numbers, the comparison of transfer units being made at similar gas and liquid rates. No satisfactory correlation was obtained as was expected from the results of the hydraulic studies which showed that at similar gas and liquid

rates, the factors which govern mass transfer such as gas residence time and froth density were different for different systems.

When comparisons were made at similar gas residence times more satisfactory correlations were obtained and it was concluded that while Gerster's method is basically correct, more knowledge of the structure and properties of gas/liquid foams and froths on commercially operating sieve plates is necessary before the method can be applied with confidence in this field.

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1. INTRODUCTION

1.1. GENERAL

Prior to the industrial revolution, man's interest in mass transfer between the liquid and the gas phase was limited to the distillation of certain flower extracts to obtain perfumes, certain alchemical purification processes, for example the preparation of quicksilver, and, above all, the preparation of alcoholic drinks by the concentration of wine and other weak, naturally brewed, alcoholic solutions. After the revolution, this interest spread and continues to spread to more and more new applications and these new applications needed more efficient methods of contacting the vapour and liquid phases than the early type of still in which the vapour and liquid met each other on only one stage. To satisfy this need, two types of improved equipment were developed, the packed tower and the plate tower, the former being the more useful over a widespread range of applications.

Commercially,
The most ~~commercially~~ successful of the plate devices has been the bubble-cap plate, invented by Cellier-Blumenthal in 1818, but recently the supremacy of this plate has been challenged by the perforated or sieve plate which was first introduced in the Coffey still (although a still containing a sieve plate is described by Demokritos in the second century A.D.) a piece of equipment used in the manufacture of whisky and gin, invented in 1830 by a Dublin exciseman Aeneas Coffey.

Demands for more efficient contacting devices have inevitably been coupled with demands for accurate design procedures and it is along these two directions that most of the research lies in this field of chemical engineering.

1.2. COMPARISON OF FRACTIONATING PLATES

Several standard text books [1,2,3], give descriptions of the most common types of distillation plate, and their performances have been compared by Garner, Ellis and Freshwater [4], Stanislas and Smith [5] and others,[6,7,8,9].

A brief account of the principal devices is given here with a comparison of some of their properties.

1.2.1. The bubble-cap plate

As has already been stated, the bubble-cap plate has been the most popular commercial device used in vapour liquid mass transfer. The basic design consists of circular caps mounted on short vertical tubes or risers which project through the plate floor. There are vertical slots in the skirts of the caps to allow the vapour which passes through the risers to be broken into bubbles. Liquid, which is sealed on the plate by the height of the risers, passes across the plate between or over the bubble caps and through one or more downcomer pipes to the plate below. The downcomers project below the liquid level on the plate below to prevent vapour entering. Weirs may be fitted at the entry to and exit from the downcomers to ensure a greater liquid depth on the plate. In plates up to about 6 ft in diameter, the downcomers are placed on alternate sides of the plates in a column so that the liquid must traverse the full width of the tray in contact with the rising vapour. In trays of larger diameters, the flow is split and may be from centre to the periphery or vice versa.

1.2.2. The sieve plate

This plate is simpler than the bubble-cap tray and consists of a horizontal plate with perforations. It is fitted with downcomers similar to the bubble cap, and the flow pattern of the liquid is usually the same except that the flow is not obstructed

by any caps. The vapour contacts the liquid by rising through the holes, the velocity of the vapour being sufficient to prevent weeping of the liquid through them. This means that the plate must be operated above a certain velocity and hence for many years did not receive much attention as it was thought to have too narrow an operating range [10], and its use was limited to industries whose preference was for a plate that was very easy to clean. In 1952, Mayfield et al. [11] gave an account of studies of sieve trays which led to their widespread acceptance by the Celanese Chemical Corporation on the grounds of the higher efficiency, higher capacity and lower cost. Since then other workers, [4,6,12,13,14,15,16], have studied the sieve plate and have endorsed and amplified these conclusions. The narrower range of operating conditions has ceased to be a major disadvantage ~~due to the use of~~ owing to improved methods of design, and the sieve plate is beginning to become more popular than the bubble-cap plate.

1.2.3. The floating-cap or valve tray

This design is an improvement on the sieve plate in that it will function over a much wider range of operating conditions, and it retains some of the advantages of the sieve over the bubble cap plate, namely reduced pressure drop, lower hydraulic gradient and cheaper construction, [9,17,18]. It consists of a flat plate perforated with holes of 1 to 2 in diameter and with a free area of about 15%. The holes are covered with metal caps, held in position by cages. The design feature claimed for this plate is that as the gas rate increases the metal caps rise to keep the orifice velocity approximately constant. This has not been found to be the case in practice as discussed by Norman and Grocott [19].

The greater operational flexibility of this type of tray does not confer overwhelming advantages with its use, as most distillation and absorption columns are designed to operate between fairly narrow limits of flow rates.

1.2.4. The APV-West plate

This tray functions as a sieve plate superimposed on a bubble cap tray and combines the performance of a sieve plate with the stability of a bubble-cap tray at low vapour velocities. The capacity of the plate is greater than that of a bubble-cap plate, but less than that of a sieve plate? The pressure drop can be less than that of a sieve plate.[5]

1.2.5. The Kittel plate

This plate consists of pairs of trays fabricated in expanded metal. The inclination of the slots of the expanded metal imparts transverse motion to the liquid, which is centripetal on one tray and centrifugal on the other. This ensures stable flow and excellent distribution of the liquid. There are no downcomers, the liquid travelling downwards by leakage at the centre and periphery. The free cross sectional area of the plate is greater than that of a sieve plate with a consequent low pressure drop which makes it particularly suitable for vacuum distillation [5,8].

1.2.6. Downcomerless or dualflow plates

These plates may be sieve plates with extremely large perforations or composed of parallel bars of metal, as in the case of the Turbogrid plate.[9,20,21,22]. The liquid falls through the perforations or slots, through which the vapour also rises. The operating range of these trays is smaller than that of the sieve plate, but the pressure drop is lower. The efficiency is also lower.

1.2.7. Conclusion

All workers agree that the perforated or sieve plate is the most suitable for the majority of uses. Where special considerations apply other plates may be more suitable such as the valve tray for operation over a wide range of conditions or the Turbogrid type trays for high vacuum functions.

1.3 INTRODUCTION TO PLATE EFFICIENCY

The efficiency of a plate as a mass transfer device can be defined in the following ways.

1.3.1 Overall column efficiency, E.

An absorption or distillation column can be considered to function as a number of stages at which mass transfer takes place with the vapour and liquid at equilibrium. As a plate can theoretically do no more than bring the liquid and vapour on it to equilibrium, and in practice cannot accomplish this, the performance of the column can be expressed as the ratio of the number of theoretical plates or stages to the number of actual plates. Methods such as that by McCabe and Thiele [23] for obtaining the number of theoretical plates in a column are described in many text books.

1.3.2 Murphree plate efficiency - E_{MV} or E_{ML}

In 1925 Murphree [24] defined the efficiency of a single plate as the ratio of the actual change in composition of the vapour or liquid to the change which would have taken place if equilibrium had been attained. In terms of vapour composition, the efficiency of plate n is:

$$E_{MV} = \frac{y_n - y_{n-1}}{y_n^* - y_{n-1}} \qquad \text{(1.1)}$$

where y_n and y_{n-1} are the average vapour compositions leaving plates n and n-1 and y_n^* is the composition of the vapour in equilibrium with the liquid of composition x_n leaving plate n.

In terms of the liquid concentrations:-

$$E_{ML} = \frac{x_{n+1} - x_n}{x_{n+1} - x_n^*} \qquad \text{(1.2)}$$

where x_{n+1} and x_n are the average liquid compositions leaving plates n+1 and n and x_n^* is the composition of the liquid in equilibrium with the vapour of composition y_n leaving plate n.

The Murphree plate efficiency is equal to the overall column efficiency when the operating and the equilibrium lines for the system are straight and parallel on a McCabe Thiele diagram. When this is not the case, the relationship between them is given by

$$E = \frac{\ln \left[1 + E_{MV} \left(\frac{mG_M}{L_M} - 1 \right) \right]}{\ln \frac{mG_M}{L_M}} \qquad \text{——(1.3)}$$

where G_M and L_M are the molal vapour and liquid flows and m is the gradient of the equilibrium curve.

1.3.3 The Murphree point efficiency E_{OG}, E_{OL}

This is the efficiency at a specific point on the plate and is defined in terms of concentration similar to the Murphree plate efficiency.

The Murphree point efficiency and plate efficiency are only equal when the concentrations are uniform across the plate.

$$E_{MV} = E_{OG} \qquad \text{——} \quad (1.4)$$

This is the case in evaporation of single substances, and on plates of small diameter,[25,26] although it is claimed that even on very small plates the mixing is still not perfect.[27] As the length of the liquid flow path increases, the effectiveness of mixing is reduced and a concentration gradient exists across the plate. This means that the value of the plate efficiency E_{MV} will be greater than the average point efficiency as the value of the liquid composition on which the equilibrium concentration is based will, for average conditions on the plate, be less than the liquid composition at the exit. For no mixing, the plate efficiency is related to the point efficiency by the relationship,[28]

$$E_{MV} = \frac{1}{\lambda} \left(e^{\lambda E_{OG}} - 1 \right) \qquad \text{——} \quad (1.5)$$

where $$\lambda = \frac{m G_M}{L_M}$$

In practice all plates, with the possible exception of very small plates, operate between the two extremes of complete mixing and non-mixing.

1.3.4 Other expressions of plate efficiency

The plate efficiency can also be expressed in terms of chemical potential driving forces and expressed as $E_{dif.}$ the diffusional efficiency. Vigdorov and Kafarov [29] indicate that the Murphree efficiency is a particular case of a general expression for plate efficiency based on the difference in chemical potentials and that its use is not correct when the difference between equilibrium and operating conditions is large and the departure from ideality is great.

In practice, however, the concept of the Murphree efficiency appears to be entirely adequate and is in widespread use theoretically and practically.

1.4 THE EFFECT OF PROCESS VARIABLES ON SIEVE PLATE EFFICIENCY

The factors which might affect the performance of a plate can be divided into three groups.

(a) Mechanical design of the plate e.g. free area, weir height, downcomer design.

(b) Operating conditions e.g. vapour and liquid flow rates, temperature and pressure.

(c) System properties e.g. density of gas and liquid, viscosity of gas and liquid, interfacial surface tension, diffusion coefficients and relative volatility or solubility.

It is not possible here to describe all the work done in this field, but the effects of the more important variables are summarised.

1.4.1 Free area

The literature is sometimes in conflict as to the effect of this variable. Ellis and Moyade [30] found the plate efficiency increased whereas English and Van Winkle [31] found it decreased as the free area was increased. It seems, however, that the smaller hole diameters give greater efficiency but at the cost of higher pressure drops. Also the efficiency increases as the number of holes increases, but there is a maximum value above which weeping through the holes seriously impairs the efficiency. The recommended values [3] usually are a free area of about 10% with the holes between 1/8 and 3/8 in diameter on equilateral triangular spacing.

1.4.2 Weir height

Raising the weir height causes an increase in liquid hold up on the plate which has been found to cause an increase in efficiency. This has been found by many workers including Ellis and Moyade, [30] English and Van Winkle, [31] Finch and Van Winkle, [32] and Gerster et al. [33]

Increase in weir height also causes increase in pressure drop and above a certain value, the increased efficiency may be offset economically by the increased pressure drop.

1.4.3 Downcomer design

It is necessary to ensure that the downcomer is capable of allowing disengagement of vapour from the froth as the liquid flows to the next plate. Mass transfer can also occur in the downcomer.

1.4.4 Vapour rate

Increase in vapour rate causes greater turbulence on the plate but has been found to have either no effect or a detrimental effect on the plate efficiency.[32,33,34,35] Low air rates cause liquid to weep through the perforations, but this does not have a great effect on efficiency, although at very low air rates when the liquid rains through the plate or "dumps", the performance is seriously impaired. Very high vapour rates cause heavy entrainment[36], which also has a detrimental effect on the plate efficiency.

1.4.5 Liquid rate

Increase in liquid rate results in increased liquid hold up on the plate which increases the efficiency.[30,32,33,34,35,37] Above a certain value however, the downcomers may not be able to cope with the froth of vapour and liquid and the plate floods.

1.4.6 Temperature and pressure

The influence of temperature and pressure is reflected mostly in the effects these variables have on the properties of the materials used. Ellis, Barker and Contractor[38] found the effect of pressure on efficiency to be very small.

1.4.7 System properties

The main effect of viscosity and density in the gas phase is on molecular diffusion and hence on efficiency. Similarly viscosity and density of the liquid also affect efficiency of mass transfer through their effect on liquid phase molecular diffusion.[34] The effects of these variables on the hold up of gas and liquid on the plate has not been clearly established as is discussed in Section 1.5. Interfacial surface tension has been found to affect efficiency as this has a critical effect on gas hold up and froth heights.[39,40,41,42].

1.5. MASS TRANSFER THEORY

1.5.1. The two film theory

The mass transfer relationships which describe the behaviour on bubble plates are described in standard textbooks[3], [43,44], and are only briefly summarised here. The basis of most theoretical equations is the "two-film" theory due to Whitman[45] who postulated that there was a laminar film on either side of a phase boundary, and a molecule, travelling from one phase to another, would encounter resistance only in penetrating the two laminar films. It was assumed that the two laminar films would be in equilibrium and that, accordingly, there would be no resistance to mass transfer crossing the phase boundary. Fick's first law was assumed to apply, the rate of mass transfer being proportional to the concentration difference and the molecular diffusivity, and inversely proportional to the film thickness.

From this, the rate at which one component A, of a gas mixture of A and B, transfers to a liquid across a phase boundary can be written as

$$N_A = \frac{D_{AB}}{Z} (y - y_i) \qquad \text{——————} \qquad (1.6)$$

where N_A is mass transfer rate of diffusing component A (lb mol/hr ft^2)

D_{AB} is diffusion coefficient of A through B (ft^2/hr)

Z is thickness of laminar film (ft)

y is concentration of diffusing component in bulk of gas phase (lb mol/ft^3)

and y_i is concentration of diffusing component in gas film at phase boundary (lb mol/ft^3)

This may also be written as:-

$$N_A = k_G (y - y_i) \qquad \text{——————} \qquad (1.7)$$

where k_G is the gas film mass transfer coefficient (ft/hr)

and for mass transfer through the liquid film:-

$$N_A = k_L (x_i - x) \qquad \text{(1.8)}$$

where k_L is the liquid-film mass transfer coefficient (ft/hr)

and x_i is concentration of diffusing component in liquid film at phase boundary (lb mol/ft^3)

and x is concentration of diffusing component in bulk of liquid phase (lb mol/ft^3)

As it is not possible to measure concentrations at the phase boundary, it is more convenient to describe the process in terms of overall mass transfer coefficients.

i.e. $$N_A = K_{OG} (y - y^*) = K_{OL} (x^* - x) \qquad \text{(1.9)}$$

where y^* is the concentration of diffusing component in equilibrium with concentration x (lb mol/ft^3)

and x^* is the concentration of diffusing component in equilibrium with concentration y (lb mol/ft^3)

and K_{OG} and K_{OL} are overall gas- and liquid-phase mass transfer coefficients (ft/hr)

If it is assumed that Henry's Law is obeyed over the short range of concentrations considered,

then $y^* = \bar{m}x$, $y = \bar{m}x^*$ and $y_i = \bar{m}x_i$

where $\bar{m}$ is the dimensionless Henry's law constant.

Equation (1.9) may be written as,

$$\frac{1}{K_{OG}} = \frac{y - y^*}{N_A} = \frac{y - y_i}{N_A} + \frac{\bar{m}(x_i - x)}{N_A}$$

$$= \frac{1}{k_G} + \frac{\bar{m}}{k_L} \qquad \text{(1.10)}$$

and $$\frac{1}{K_{OL}} = \frac{x^* - x}{N_A} = \frac{y - y_i}{\bar{m} N_A} + \frac{x_i - x}{N_A}$$

$$= \frac{1}{\bar{m} k_G} + \frac{1}{k_L} \qquad \text{(1.11)}$$

hence, $$K_{OL} = \bar{m} K_{OG}$$

If the gaseous concentrations are expressed in partial pressures, the Henry's law constant has the dimensions atm ft^3/lb mol and the gas-film mass transfer coefficients are expressed in lb mol/ ft^2 hr atm.

For a small portion of gas rising through a liquid on a bubble plate, the mass of one component transferring to the liquid during a small increment of time and a small increment of vertical travel may be described by the equation,

$$V dy = K_{OG} a (y^* - y) dt \qquad (1.12)$$

where V is the volume of the portion of gas (ft^3)

a is the surface area available for mass transfer (ft^2)

dt is the time of contact (hr)

y^* is the concentration of the transferring component in the gas phase, at equilibrium with the liquid on the plate (lb mol/ft^3)

This equation may be integrated between the limits of contact time and concentration, i.e. between $t = 0$, and $t = t_G$, and between $y = y_1$ and $y = y_2$, where t_G, is the gas residence time on the plate (hr).

y_1 is the concentration of gas entering the plate (lb mol/ft^3)

y_2 is the concentration of gas leaving the plate (lb mol/ft^3)

i.e.
$$\int_{y_1}^{y_2} \frac{dy}{y^* - y} = \int_0^t \frac{K_{OG} a}{V} dt.$$

$$= - \ln \frac{y^* - y_2}{y^* - y_1} = \frac{K_{OG} a t_G}{V} \qquad (1.13)$$

The right hand side of the equation is defined as the number of transfer units, N_{OG}

$$N_{OG} = - \ln \frac{y^* - y_2}{y^* - y_1} = \frac{K_{OG} a t_G}{V} \qquad (1.14)$$

$$= - \ln \left(1 - \frac{y_2 - y_1}{y^* - y_1}\right)$$

$$= - \ln \left(1 - E_{OG}\right) \qquad \text{——————} \qquad (1.15)$$

where E_{OG} is the Murphree point efficiency for the gas phase. A similar expression may be derived for N_{OL},

$$N_{OL} = - \ln \left(1 - E_{OL}\right) \qquad \text{——————} \qquad (1.16)$$

These are overall transfer units and may be related to the numbers of transfer units for each phase by substitution of equation (1.14) in equation (1.11) to give

$$\frac{1}{N_{OG}} = \frac{1}{N_G} + \frac{\lambda}{N_L} \qquad \text{——————} \qquad (1.17)$$

and

$$\frac{1}{N_{OL}} = \frac{1}{N_L} + \frac{1}{\lambda N_G} \qquad \text{——————} \qquad (1.18)$$

1.5.2 The Penetration theory

As can be seen from equation (1.6) the Whitman two-film theory predicts that the rate of mass transfer should be directly proportional to the diffusivity. Experimental studies of the gas-film controlled mass transfer on wetted-wall columns by Gilliland and Sherwood [46] and others,[47,48,49], showed that this was not the case and that

$$k_g \propto D_G^x$$

where x varies from 0.4 to 0.5 and D_G is the gas diffusivity, (cm^2/sec) Studies of liquid-controlled mass transfer also showed that the liquid-phase mass transfer coefficient was not directly proportional to the diffusivity. Calderbank and Moo Young[50] give

$$K_L \propto D_L^{0.67}$$

and Norman and Sammak[51] give

$$K_L \propto D_L^{0.5}$$

It has been found that the "penetration theory" more accurately describes mass transfer at a phase boundary. This theory was first proposed by Higbie [52] to describe mass transfer through liquid films. This model supposes that the laminar layer at the phase boundary is systematically renewed, and each element of liquid surface is exposed to the gas for the same length of time. The relation between mass transfer coefficient and diffusity is

$$K_L \propto \sqrt{\frac{D_L}{t_e}}$$

where t_e is the time of exposure.
Danckwerts [53], suggested that there should be no correlation between the time for which an element of liquid surface has been exposed and its chance of being remixed, and that the time of exposure be replaced by the rate of surface renewal, S,

i.e. $$K_L \propto \sqrt{D_L S}$$

The prediction of the penetration theory that the mass transfer coefficient is proportional to the square root of the diffusivity is more in agreement with experimental evidence

both for the liquid- and the gas-phase mass transfer coefficients. However Toor and Marchello [54] suggest that if the unsteady-state build up of material at the phase boundary continues for a sufficiently long period, a steady concentration gradient will build up as described by the two film theory and the mass transfer coefficient will be proportional to the diffusivity to a power greater than 0.67. Harriot [55] does not agree with this model, and proposes one in which eddies of bulk composition approach the phase boundary, but do not penetrate it.

It has also been found that under very turbulent conditions such as on bubble plates, eddy diffusivity becomes important in determining mass transfer rates. Garner and Porter [56] showed that at high velocities effective diffusivities of three or more times the molecular diffusivity were required to explain some reported plate efficiencies.

Although the penetration theory explains experimental evidence better than the original two film theory, it seems that the former complements and amplifies the two-film theory, rather than replaces it,[57] and that the calculation of overall mass transfer coefficients and mass transfer units, by the addition of the individual film coefficients and transfer units as in equations (1.11) (1.17) and (1.18) is still justified. It is on a basis of these equations that the methods described in the next section for predicting the efficiencies of mass transfer behaviour on bubble plates have been developed.

1.6 PREDICTION OF PLATE EFFICIENCY

Of the formidable quantity of publications on bubble plate efficiencies, a great deal is devoted to their prediction by empirical or semitheoretical means. Many empirical correlations give reasonable results when applied to systems and conditions similar to those used in their development, but give erroneous and misleading results when applied to situations where these conditions are not fulfulled. Very often this is due to lack of appreciation of all the factors which affect the mass transfer processes which occur on a plate. Recent developments in the theory of mass transfer and an increase in understanding of factors which affect plate efficiency, for example liquid mixing, have resulted in correlations which appear to be much more satisfactory.

An account of the principal correlations is given below.

1.6.1 Expressions for plate efficiency derived empirically

Walter and Sherwood[25] studied various absorption, desorption, humidification and rectification systems on bubble cap plates and were able to correlate their results by an empirical relation relating Murphree vapour efficiency to gas solubility, total pressure, liquid viscosity, slot width and the effective liquid depth on the plate. The principal variable was found to be the gas solubility. The largest column used was 18 in diameter, the smallest a 2 in diameter column. Drickamer and Bradford[58] derived a correlation developed from test data on 54 refinery fractionating columns equipped with bubble-cap plates,

$$E_{MV} = 0.17 - 0.616 \log \mu_L \qquad \text{(1.19)}$$

where μ_L is the feed viscosity at the average tower temperature. The correlation applied mainly to hydrocarbon systems of low relative volatility and to a narrow range of column designs, and was in considerable error for large diameter towers. The range of viscosities

studied was fairly small, 0.07 to 1.40 cP O'Connell [59] modified the correlation by introducing a gas solubility term to the equation, thereby extending it to systems of considerably differing relative volatilities, but the correlation still did not take into account differences in plate or column design. Chu, Donovan, Bosewell and Furmeister [60] modified O'Connell's correlation to include the effect of the liquid and vapour flows and the effective liquid depth. Chaiyavech and Van Winkle [61] obtained a correlation for sieve plates for plate efficiencies based on work done on a 1 in diameter perforated plate column using 8 different systems of widely differing physical properties. This work was extended by English and Van Winkle [31] and combined with data of other workers to obtain another correlation

$$E_{MV} = 10.84 \ (\beta)^{-0.28} \left(\frac{L}{V}\right)^{0.024} (h_w)^{0.241-0.013\,G^{0.044}} \left(\frac{\gamma}{\mu_L V_g}\right) \times \left(\frac{\mu_L}{\rho_L D_L}\right)^{0.137} \alpha - 0.028 \qquad \text{——— (1.20)}$$

where β is free area fraction of the column cross section

$\frac{L}{V}$ is the reflux ratio

h_w is the weir height, (in).

G is the mass vapour flow based on column cross section ($lb/ft^2 hr$).

γ is surface tension, (dynes/cm).

μ_L is viscosity of liquid, (cP).

V_g is vapour velocity through column, (cm/sec).

ρ_L is liquid density, (g/cm^3).

D_L is liquid molecular diffusivity, (cm^2/sec).

α is relative volatility.

Recently, Finch and Van Winkle [32] described a method for design of commercial-scale perforated plates based on scale up of small-column data. Operating and design variables were related to the residence times of gas and liquid upon a plate, and these were combined to give the plate efficiency by the equation

$$E_{MV} = A_G t_G + A_L t_L \qquad \text{——— (1.21)}$$

where A_G and A_L are functions of the diffusive properties of the gas and liquid phases of the system and can be obtained from small column experiments. Factors t_{G_0} and t_L for commercial systems are calculated from correlations similar to those developed by the A.I.Ch.E. study [27,33,69], on bubble-caps.

1.6.2 Expressions for plate efficiency derived from examination of bubble dynamics

The approach of Geddes[62] was based on a consideration of the mass transfer to a stream of rising bubbles. It was assumed that the bubble diameter was determined by buoyancy and surface tension as proposed by Sugden[63] and the rising velocity was as predicted by the correlation of O'Brien and Gosline[64]. From an estimate of the effective liquid height on the plate, the contact time and interfacial area were calculated. Mass transfer coefficients obtained for gas and liquid phases were combined to give an overall resistance as in equation (1.10) and the Murphree vapour point efficiency was deduced. Closer study of the bubble formation behaviour indicates that the method of obtaining the bubble diameter is not applicable at the high slot-velocities occurring in bubble caps. Chu et al.[60] revised the correlation of Geddes and gave improved methods of estimating the bubble diameter. Bakowski[65] derived a correlation based on the assumption that mass transfer on a bubble plate could be considered as mass transfer to moving channels of vapour.

West, Gilbert and Shimizu[26] used Higbie's[52] diffusion equation to calculate the mass transfer coefficients for both phases. The contact time and surface area, was calculated from values of bubble size and foam density obtained from correlations. An equation for the Murphree point efficiency for both bubble-cap and sieve plates was obtained.

Quigley, Johnson and Harris[66] obtained a correlation for the bubble size and gas hold up which enabled them to estimate the surface area of a froth formed on a plate with a single orifice. This enabled them to obtain the liquid-film coefficient and a general expression for Murphree plate efficiency for liquid controlled systems was presented. This expression agreed with the experimental results of West et al.

Planovski[67] developed a correlation between the number of gas-film transfer units and the difference between the total pressure drop and dry pressure drop across a plate. The assumption was that the rate of mass transfer on a bubble cap plate was proportional to the energy dissipated in the bubbling process.

1.6.3 Expressions for plate efficiency based on summation of individual phase contributions

As has been shown for a system involving both gas and liquid phase mass transfer, the numbers of transfer units N_G and N_L for each phase may be combined to give the overall number of transfer units N_{OG} or N_{OL} [equations (1.17) and (1.18)] and these can be related to the plate point efficiencies by equations (1.15) and (1.16). Gerster and his co-workers[34] suggested that the numbers of transfer units for each phase could be obtained by studying the performance of single-phase controlled systems and relating the information so gained by the ratio of the Schmidt numbers Sc where

$$Sc = \frac{\mu}{\rho D}$$

where μ is viscosity
ρ is density
D is diffusivity

It was suggested that the number of transfer units for each phase was proportional to the Schmidt number to the power 0.5 for the liquid phase and 0.67 for the gas phase. These values were confirmed by Calderbank[68] for the evaporation of water, ethyl alcohol and iso-propyl alcohol on a perforated plate. Difficulties were found, however, in relating the point efficiencies to the overall plate efficiencies, because of lack of knowledge of the degree of liquid mixing.

In 1952, the Research Committee of the American Institute of Chemical Engineers initiated a five year research project to study plate efficiency in distillation and absorption columns. A method for predicting plate efficiencies for both sieve and bubble caps

was developed, based on experimental data obtained at the University of Delaware[33], the University of Michigan[27] and the North Carolina State College.[69]

Gas-film controlled mass transfer was studied using the vaporisation of pure liquids into air and the absorption (or desorption) of ammonia from air by water. Liquid-film controlled mass transfer was studied by the desorption of carbon dioxide from water and organic solvents. It was found that the number of gas-film transfer units could be compared by the ratio of the Schmidt numbers to the power 0.5 and liquid-film transfer units by the ratio of the liquid diffusivities to the power 0.5.

A design manual has been published[70] as well as details of the work carried out at each establishment. The method was based on that proposed by Gerster. A brief description is given below.

Starting from a knowledge of the plate design and operating conditions, and a knowledge of the physical properties of the two phases, the calculation proceeds via the following steps.

1. The number of gas-phase transfer units N_G is obtained from a correlation with weir height, vapour rate, liquid rate and Schmidt number.
   Vapour rate is expressed as F factor $F = V_s \rho_G^{0.5}$
   V_S is velocity through bubbling area, (ft/sec)
   ρ_G is gas density, (lb/ft^3)
2. The value of the liquid residence time on the plate is calculated from a correlation of weir height, F factor, liquid rate and the distance between the weirs.
3. The value of the number of liquid-phase transfer units N_L is obtained from a correlation of liquid residence time, F factor and liquid-phase diffusivity.
4. The values of the number of phase transfer units are combined

to predict the overall point efficiency, E_{OG} :-

$$\frac{1}{-2.3 \log (1-E_{OG})} = \frac{1}{N_G} + \frac{\lambda}{N_L}$$

5. The point efficiency is corrected for mixing and entrainment to give E_{MV}, the plate efficiency.

The A.I.Ch.E. procedure has been shown to be more accurate than earlier correlations, but some criticisms have been made.

Strand[71] suggested that possible deficiencies in the A.I.Ch.E. method arose because there was no provision for assessing the effects of vapour and liquid by-passing on the plate. He introduced a modification to the A.I.Ch.E. method which took into account liquid recycling and obtained slightly more accurate predictions for the 3 systems he studied experimentally.

Dieter and Hundtermark[72] proposed a condensed version with a revised equation for mass transfer in the vapour phase which is said to give better agreement. Eduljee [73] criticised the procedure on the grounds that it was obtained from data from one University mainly, and that too much emphasis had been placed on data using aqueous systems. He proposed methods of his own based on the A.I.Ch.E. experimental work. Thorogood[74] also objected to the correlations on the grounds that no allowance had been made for mass transfer during bubble formation, and that the molecular diffusivity was used when it was necessary to include an eddy diffusion component.

Gerster[75] points out that the A.I.Ch.E. work did not cover a wide range of gas viscosities. The range studied at the University of Michigan was from .015 to .020 cP, and the systems studied at the College of North Carolina had gas viscosities all round .008 cP. This deficiency was felt not to justify completely the choice of 0.5 as the index of the gas phase Schmidt numbers but recent work[76] at the University of Delaware on the evaporation of toluene in air and propane has confirmed that the value of 0.5 is correct.

Although the above criticisms may be justified, the corrections introduced are marginal and do not detract from the importance of the method or the validity of the fundamental concepts.

1.7 EFFECT OF LIQUID MIXING ON A PLATE

As has already been noted in 1.3 and 1.6, the degree of liquid mixing on a bubble plate, and hence the distribution of concentration-difference driving forces on the plate has a considerable effect on the plate efficiencies of some systems, and it is the magnitude of this effect which controls the difference between point and plate efficiencies.

If the extent of liquid mixing is not known, complete mixing or non-mixing /Equation (1.4) and (1.5)/ must be assumed and it is known that these assumptions are justified only in certain circumstances. Rush and Stirba[35] who assumed no mixing to take place on an 18 inch diameter sieve plate found discrepancies ~~in~~ between the predicted and measured values for a liquid-phase controlled system, methyl isobutyl ketone-water. These discrepancies were attributed to the unknown effect of liquid mixing on the plate. The effect of liquid mixing is not important in gas-phase controlled systems (since it is assumed that the gas is always thoroughly mixed) but is of considerable importance in liquid-phase controlled systems.

In an attempt to describe mixing on a plate mathematically Gautreaux and O'Connell[77] adopted Kirschbaum's[78] concept of a plate containing a certain number of perfectly mixed pools, the number being proportional to the degree of mixing, and derived the relationship between the Murphree plate and point efficiencies and the number of pools n:-

$$E_{MV} = \frac{1}{\lambda} \left[\left(1 + \frac{E_{OG}\,\lambda}{n}\right)^{n} - 1 \right] \qquad (1.22)$$

n = 1, represents complete mixing; n = ∞ represents no mixing.

Although this model represented intermediate conditions, it was felt to be inadequate and other models were developed such as that of Oliver and Watson[79] which postulated the existence of liquid recycling to the entrance weir, and that of Johnson and Marangozis[80] who considered that mixing on a perforated plate was due to splashing of liquid in the froth region above the layer of clear liquid immediately above the plate, and conducted experiments to discover the factors which governed the extent of this splashing.

These models have not had the success of the eddy diffusion model suggested by Wehner and Wilhelm[81] and by Foss, Gerster and Pigford.[82] This model assumes that the rate of mixing of a component is proportional to the concentration gradient of the component across the plate and involves study of the liquid residence-time distribution on the plate. The rate of liquid mixing is characterised by an eddy diffusion coefficient. Liquid residence time distributions have been studied by several workers[82, 83, 84, 85] using injections of tracers at the liquid inlet or outlet from the plate. Theoretical considerations of the distribution of liquid residence times has led to the introduction of the dimensionless Peclet number to represent the degree of mixing.

$$Pe = \frac{Z_L U_L}{D_E} = \frac{Z_L^2}{D_E t_L} \qquad \text{——————(1.23)}$$

Z_L is distance travelled by liquid,(ft).
U_L is mean liquid velocity,based on clear liquid height,(ft/sec).
D_E is eddy diffusion coefficient,(ft^2/sec).
t_L is average residence time of liquid,(sec).

Correlations for the prediction of the eddy diffusion coefficient, and liquid residence time have been given by Gerster et al.[33] in the University of Delaware Report and Gilbert.[83] Gerster et al. derived an equation relating the plate efficiency, the point efficiency and the Peclet number and demonstrated the relationship graphically with Peclet number as the parameter. Experimental work with air-water systems showed that the eddy diffusivity was independent of liquid density, viscosity or surface tension.

While the eddy-diffusivity model is probably more realistic than that of the mixed-pool or splashing models, it still does not allow for stagnant pockets or layers of liquids or bypassing of the bubbling area. Johnson and Marangozis[80] found that mixing by eddy diffusion in the thin liquid layer which exists immediately on top of an operating sieve plate was negligible.

The model also assumes that liquid concentration gradients only exist in the direction of liquid travel and does not take into account possible gradients in the vertical or horizontal directions perpendicular to liquid flow.[85] Imperfections in hydraulic operation of the tray may cause these effects to be significant when applied to commercial fractionating towers. Furthermore, the difficulty in predicting values of the eddy diffusivity or liquid residence time renders the method less certain.

1.8 STUDY OF HYDRAULIC RELATIONSHIPS

The efficiency of a mass transfer process taking place between two phases, such as that on a perforated plate, depends upon the diffusional and the hydraulic relationships between the two phases.

The diffusional relationships generally depend upon independent variables such as molecular diffusivity, concentration etc., while the hydraulic relationships depend more on operating conditions, e.g. vapour and liquid rates. The more definitive hydraulic criteria in mass transfer are the interfacial area and the time of contact of each phase with the other.

When a perforated plate is in operation, two zones may be distinguished, a layer of liquid immediately above the plate acting as a seal, and a layer of froth or foam above, many times greater in height.

Gas, entering an orifice on the plate, forms discrete bubbles which travel through the liquid layer, and coalesce in the froth or foam, through which they pass forming a region of very intimate contact with the liquid. The gas finally leaves this area by the bursting of the bubbles at the top.

The interfacial area available for mass transfer is overwhelmingly the area of froth. Thus, Porter[86] points out that the interfacial area in a bubble-plate froth can be 100-200ft^2/ft^3 which is larger than that from all but the smallest packings. Thus the interfacial area of 1in -2in ring packing is 20-50ft^2/ft^3. The time of contact of gas on the plate, i.e. the gas residence time is the time spent travelling through the froth.

1.8.1 Formation of bubbles at orifices

The mechanism of bubble formation at orifices has received considerable attention. Spells and Bakowski[87] studied bubbling from single and multiple slots with high speed photography and witnessed that at low air rates, discrete bubbles were found which continued to grow after formation, due to ineffective closure of

the neck of the bubble. At higher air rates, chain bubbling took place with air leakage between each bubble, and if the liquid seal, or clear liquid layer, was less than 1 inch the bubble became an open channel and air "jetted" to the water surface. They also noticed that bubble size was independent of the slot dimensions studied. Van Krevelen and Hoftijzer[88] proposed the following correlation for higher gas rates:-

$$D_B = 0.0279 \; Q_G^{0.4} \left(\frac{\rho_L}{(\rho_L - \rho_G)}\right)^{0.2} \qquad \text{——— (1.24)}$$

also indicating that orifice dimensions have no effect on bubble size. Viscosity and surface tension also appear to have no effect. This correlation was based on the chain bubbling mechanism, which was not observed by Quigley, Johnson and Harris[66] who investigated the formation of bubbles at a single orifice in water, glycerine and carbon tetrachloride using a "strobotac". They agree, however, that surface tension had no effect, but observed a slight viscosity effect at a viscosity level of 417 cP. They proposed the correlation

$$D_B = 0.222 \; D_O^{.33} Q_G^{0.125} \eta^{0.02} + 3.02 \times 10^{-4} Q_G^{1.09} \qquad \text{——(1.25)}$$

Where liquid seals were in the range 0.25 to 1 ft. Siemes and Kauffmann[89] found that using small gas flow rates and low viscosity liquids, the volume of bubble formed was not affected by density or viscosity of liquid, and the controlling factors were gas flow rate and orifice diameters. The volume of bubbles formed in highly viscose liquids tends to be dependent on viscosity but the effects of surface tension and density were still negligible.

Calderbank[68] observed that the frequency of bubble formation at gas flows above 30 cc/sec was approximately constant at 15 to 20 bubbles/sec, and that the volume of the bubble depended only on gas flow rate. Orifices studied were from 1/16 in to 1/4 in diameter. Liebson et al,[90] however found that although the bubble frequency was 15/sec to 20/sec at 1/64 in to 1/16 in diameter orifices, the frequency at 1/8 in was 10/sec to 13/sec.

Davidson and Amick[91] also found bubble frequency depended on orifice diameter. Chu et al.[92] agreed with Spells and Bakowski that bubbles tended to grow after formation, but that above a liquid seal of 2.5 in, the bubble size remained constant. Below this value, the bubble size tended to increase with increasing slot area.

Johnson and Bowman [93] studying gas flow through a 1/16 in diameter orifice found that bubble frequency increased to 32 bubbles/sec at 45 cc/sec and then decreased sharply as coalescence took place. The water seal was varied from 1-6 in. Rippin [94] noted that, for large bubbles, the rising velocity was a function of size alone and that bubbles above 1.7 cm had the shape of a cap cut from the top of a sphere and tended to rock as they rose through the liquid. Davidson and Schuler [95] concluded that bubble velocity was inversely proportional to viscosity in a viscous liquid, and that bubble frequency was independent of flow rate, which, merely increased bubble size. The dimensions of the orifice at constant pressure gas flow were considered very important, but not critical for constant volume flow, which is the usual case in mass transfer devices. The Report of the Director of Warren Spring Laboratory[96] described techniques using Schlieren photography which showed the presence of very small bubbles 5-50 microns, which will contribute much to interfacial area but little to mass transfer.

To summarise the above conclusions, which in some cases are conflicting, the bubble size appears to be a function of gas rate alone over a narrow range of orifice sizes, i.e. 1/64 in to 1/4 in diameter. Viscosity and density of liquid are stated to have almost no effect at the values generally met with in practice, but have a slight effect at excessively high values. Surface tension has a slight effect at high gas rates. The mechanism of bubble formation is periodic and takes the form of chain bubbling at lower rates of flow encountered commercially, but at higher rates of flow, the bubbles coalesce and the formation is no longer periodic.

It also may be mentioned that many of the results quoted were obtained at liquid seals considerably in excess of those encountered in commercial practice, certainly in excess of those encountered on a laboratory scale.

Jackson [97] in a review of the literature on the formation and coalescence of drops and bubbles in liquid, concludes that the evidence for the effect of liquid properties is largely contradictory.

1.8.2 Foams and froths

The mechanism of bubbling has been the cause of considerable study but the mechanism of coalescence of the bubbles formed at multiple orifices to form foams and froths does not appear to have attracted the same attention. West et al.[26] studied bubble frequencies and volumes on a sieve tray with a stroboscope and found that the bubble diameter at formation was generally larger than the distance between perforations, indicating out of phase bubbling and break up of bubbles immediately on leaving the orifice. Quigley et al.[66] noted that hold up depended only on flow through orifices and was independent of orifice diameter and bubble size or system properties, and proposed the correlation

$$H_G = 2.44 \times 10^{-4}\ Q_G^{\ 0.84} \qquad \text{(1.26)}$$

They assumed that the interfacial area of the froth would be equal to the surface area of the equivalent number of bubbles which would occupy the froth. Hold up was measured by a settlement technique. Calderbank[68] also assumed that the surface area in the froth would be equal to the product of the number of bubbles formed and the surface area of each bubble. The bubble volume was calculated on the assumption that chain bubbling was the mechanism occurring. The two expressions for interfacial area per foot of foam are respectively:-

(a) $$\bar{a} = \frac{1.46 \times 10^{-3}\ Q_G^{\ 0.84}}{D_B} \qquad \text{(1.27)}$$

(b) $$\bar{a} = 9.46 \times 10^{-2}\ Q_G^{\ \frac{1}{3}} \qquad \text{(1.28)}$$

When both equations were applied to the same example in the paper by Quigley et al., the calculated interfacial areas were 0.265 and 0.275 ft^2/ft of foam per nozzle respectively, an agreement to within 5%. This agreement is very striking in view of the fact that Quigley et al. saw no chain bubbling, whereas Calderbank assumed there was. However, neither group of workers consider the effect of coalescence of bubbles and both had liquid seals of not less than 2 in.

Crozier [93] described comprehensive studies of the effect of variables on local density distribution of froth on equipment used complementary to the A.I.Ch.E. research programme. He found three distinct layers (a) sheets of gas around slots resulting in froth densities near pure liquid density, (b) break up of gas sheets above this into bubbles forming a variable density layer and (c) coagulation of the bubbles to form a layer of constant density. Bubble cap plates did not exhibit case (c) at clear liquid seals below the cap height, but the sieve plate studied always showed a constant froth layer. However, the sieve tray had a weir height of 3 in and a liquid seal of from 2.3 to 4.4 in. The froth specific gravity varied from 0.30 to 0.50, which bears out Calderbank's suggestion that a specific gravity of 0.4 corresponds to the voidage obtained with closest packing of spheres. The specific interfacial area was found to be proportional to the froth layer density rather than the average bulk froth density.

Rennie and Smith [99] in studies of air water froths on a sieve plate, noted two types of froth, a stable immobile foam of large bubbles formed at low air rates and an actively moving froth at high gas rates. Photographs also showed that physical characteristics of the froth such as density etc., remained the same whether the plate had one or many orifices and that the size of bubble or cell in the mass of the froth, was almost uniform and was independent of orifice. They also noticed with high speed cameras that when a bubble is formed at an orifice, a second bubble forms from the neck of the first bubble with which it coalesces and remains stable inside. Rennie and Evans [100]

used gamma ray absorption techniques to measure the foam density on the same sieve plate and gave the correlation

$$\rho_f = (1 - H_G)\,\rho_L$$

The gas hold up was found to vary with gas rate, rising to a maximum and then falling. Three types of froth formation were noted.

(i) at low air flow rates, the hold up increased with gas velocity and depended on number and diameter of holes on plate.

(ii) at intermediate flow rates, the fractional hold up was between 0.5 and 0.9 and the value depended on hole size and hole spacing.

(iii) at high gas rates, the hold up increased slowly with gas rate and was independent of hole size and hole spacing.

Condition (iii) resulted in the active frothy regions and the correlation for hold up proposed in this region was

$$\ln \frac{1}{1 - H_G} = 0.715\,F + 0.60$$ which compared with Crozier's

$$\ln \frac{1}{1 - H_G} = 0.715\,F + 0.45.$$ They also measured bubble size photographically at the sides of the column wall and concluded that at high Reynolds numbers, the bubbles were of nearly constant size and independent of orifice diameter. Conditions for foaming were found to be closely spaced holes, small diameter holes, low liquid rates and low orifice Reynold number. At Reynolds numbers above 2,100 the large bubbles first formed broke down to small bubbles forming an active froth of high surface area.

Calderbank and Rennie [101] used flash photography to study bubble clouds on a sieve plate and measured Sauter mean bubble size, interfacial area and the gas hold up. A comparison was made with mean bubble size measured this way and by optical reflectivity and gamma ray transmission. Good agreement was noted

at high gas rates where froths are formed. Interfacial area and gas hold up as determined photographically was invariably lower than that found using other methods, implying that the bubble sample as viewed at the column wall is unrepresentative. The following mechanism was proposed for bubbling at multiple orifices. At low gas rates, bubbles are formed at almost constant frequency and bubble volume increases with gas flow rate without much change in velocity of rise of the bubble. The closest packing of equal spheres is approached when the gas rate is increased to give a gas hold up of about 60% and then two possibilities result:

(1) The bubbles increase in size to form polyhedra and cellular foams are formed.

(2) The bubbles burst into smaller units and increasing gas velocity causes increase in velocity or rise and so gas hold up increases and froths are formed. The gas hold up was found to increase with F factor and liquid rate.

Calderbanks and Rennie propose the following method of calculating interfacial area.

1. $$\ln \frac{1}{1 - H_G} = 0.715\ F + 0.45$$

2. $$D_B = 0.713\ Re_o^{-0.05}$$

3. $$\bar{a} = \frac{6\ H_G}{D_B}$$

Equation 1 may also be written as

$$\ln \frac{1}{1 - H_G} = \ln \frac{Z_c}{Z_f}$$

using this to recalculate previous example $\bar{a} = .358\ ft^2/ft$.

In the previous three papers the same apparatus would seem to have been used and the weir height to tray length ratio seems much higher than would be encountered in commercial or even laboratory mass transfer columns. It seems fairly clear, however, that the gas hold up and consequently the interfacial area depends

only on the air rate, although Crozier suggests that some of the bad scatter of his correlation may be due to an effect of liquid rate and Barker and Choudhuri [102] suggest that a viscosity above the value of 4 cP affects the interfacial area. Of the work reviewed so far, only the air-water system has been studied, with the exception of that of Quigley et al.,whose studies however, were restricted to bubbling at single orifices.

Crozier applied his correlation to other systems but although the agreement was fair at low F factors,correlation was poor at high values.

The University of Michigan Report [27] describes a comprehensive study of the effect of liquid properties on foam density and concludes that there was no effect of liquid properties.

Zuiderweg and Harmens[39] however, have shown that structure and formation of froths on perforated plates depend very critically upon the changes in the liquid surface tension due to changes in concentration resulting from mass transfer. Zuiderweg, Verburg and Gilissen[8] noted that the tendency to foam was greatest with plate designs which caused fine dispersion of the liquid into the vapour and that there was very little difference in performance between foaming and non-foaming mixtures on bubble-cap trays. The work described in the University of Michigan Report was all on bubble-cap plates. The conclusions of Zuiderweg and Harmens have been supported by Danckwerts, Sawistowski and Smith[40], Andrew[41] and Haselden and Thorogood.[42]

Ellis and co-workers[38,103,104], also examined the efficiencies of foaming and non-foaming systems in an Oldershaw column and Ellis and Legg[105] concluded that for mixtures which do not foam, the surface tension does not effect efficiency. Danckwerts et al. suggest that the factor which controls foaming is the concentration of the more volatile component in the liquid film, separating adjacent vapour bubbles. If the more volatile component has a lower surface tension than the less volatile component, a stable foam will be formed.

It seems certain that two component mixtures will form froths which vary in structure with surface tension which, in turn, depends critically on the concentration of the two components, whereas the literature does not demonstrate clearly whether or not liquid properties have an effect on the characteristics of foams formed by single component liquids, especially foams formed on perforated plates under operating conditions.

1.9. SCOPE OF PRESENT WORK

Most of the applications of Gerster's method of prediction of plate efficiencies have been applied to distillation systems on bubble cap plates, and it was decided that to apply the method to the prediction of the values for a gas absorption system on a sieve plate would be a contribution to the knowledge of the applicability of this method.

One advantage in choosing an absorption system would be, it was hoped, the elimination or substantial reduction of the effect of liquid mixing on plate efficiency and its consequent source of error. Also it is normal commercial practice to choose a solvent in which the solute gas will have the greatest solubility (commensurate with other factors such as cost etc.) and therefore, the ideal gas absorption system should be gas phase controlled.

Most predictions of gas phase controlled systems have been based on comparisons with aqueous systems and it was thought that to base the comparison of the absorption system on information from both aqueous and organic sources would be of value.

The basis for comparison of different systems in Gerster's method is similar liquid and gas rates, the liquid rates being expressed in units of volume per time per unit area of the bubbling zone, and the gas rates as F factors, where,

$$F = \rho_G V_S^{1/2}$$

ρ_G is the density of the gas phase, lb/ft^3 and V_S is the gas velocity through the bubbling zone, ft/sec. The basic assumption in such a comparison is that the interfacial area for mass transfer and the gas residence time are equivalent at equal gas and liquid rates defined in such a manner. Differences in system properties are only corrected for in so far as they affect the diffusional properties of the system.

Since it was demonstrated(in Section 1.8) that the independence of the bubbles and froth characteristics and system

properties had not been proved conclusively, especially for sieve plates, it was decided to determine foam heights and density and gas residence time for several systems.

It was not possible in the semi-plant scale adopted in this work to use the sophisticated techniques used by many of the workers whose conclusions have been discussed in 1.8, but it was hoped that the results would have some value in explaining the mass transfer results.

2. TECHNIQUES USED FOR MASS TRANSFER STUDIES

2.1. SELECTION OF SYSTEMS FOR MASS TRANSFER

2.1.1. Selection of single phase systems

As was mentioned in 1.9, it was felt that to base the prediction of absorption efficiences on information derived from both organic and aqueous sources would be of value. The information needed was on systems in which the resistance to mass transfer was controlled only by the gas film at the mass transfer interface. It was thought that to gain information concerning liquid-film controlled mass-transfer processes would not prove so necessary, as a gas absorption system would normally be chosen in which the solute gas was very soluble. The aqueous system chosen was the adiabatic humidification of air by pure water, which has been studied by many workers (e.g. Gerster et al.[34], Garner and Freshwater[106], Rush and Stirba[35], Ellis and Moyade[30], Harris and Roper[107]) in this field. Objections have been raised to this system on the grounds of the experimental inaccuracies which can be encountered. However, modifications of procedures used by Garner and Freshwater and Ellis and Moyade were used in an attempt to eliminate some of these sources of error. Absorption of ammonia in water was used in the A.I.Ch. E. research programme with success, but the increased expense and experimental complications involved were not felt in this work to justify any possibly improved accuracy.

The organic system chosen was the humidification of air

by carbon tetrachloride. This was extremely convenient as air/carbon tetrachloride mixtures were required for the absorption studies and the same apparatus could be used. This system had also been studied by Quigley et al.[66] and Ellis and Rose[37].

2.1.2. Selection of absorption systems

The three components of a gas absorption system are the bulk vapour, or gas phase, the bulk liquid phase, called here the solvent, and the material which transfers from the gas to the liquid phase, called here the solute. For simplicity it is essential that the gas phase and solvent are inert, chemically and physically, to each other, and that the solute does not react chemically with the solvent. Air was chosen as the inert gas phase principally on the grounds of economy and convenience, ~~principally,~~ and its general inertness, especially to organic solvents. Once this was decided, more criteria were introduced in the search for a suitable solute. This material had to be easily humidified in air at room temperature and the physical properties of air/solute mixtures known, or readily calculated. Also psychrometric data for the gas/vapour system were very desirable. A further criterion was the ease of recovery of the solute from the solvent. As the most economical method of recovery is by steam stripping the solvent, it was essential that the solute should be stable at 100°C, immiscible with water and preferably have a specific gravity considerably different from unity. It was also preferable that the solute does not form

explosive mixtures with air. Carbon tetrachloride was found to fit these criteria admirably and furthermore its non-polar and perfectly symmetrical molecular shape tended to suggest that it would approach ideal behaviour. It had two principal disadvantages, one was the toxicity of air/carbon tetrachloride mixtures and the other was its tendency to hydrolyse to hydrochloric acid, which, unfortunately, was initially seriously underestimated. This confined the choice of solvent to one which was inert to air, able to dissolve carbon tetrachloride with ease, and had a very low vapour pressure at room temperature. It was also essential that the equilibrium data should be known or easily calculated. Gas oil seemed to be especially convenient for this role and was initially chosen. However, it was found that the lighter ends of the fraction tended to distil over with the carbon tetrachloride in the steam-stripping tower, thus contaminating the carbon tetrachloride and altering the physical properties of the solvent, and for this reason its use was abandoned and a search was made for a suitable material which was also homogeneous, or of one molecular type. It was also considered desirable that, in the event of the system displaying any degree of liquid-phase resistance, the diffusivity of carbon tetrachloride in the material be known, as this property is difficult to measure and the available correlations are not sufficiently accurate in all cases. After a search of the literature, tetralin emerged as a likely material, but pre-

liminary tests showed that the difference in density from water was too small to permit centrifugal separation of the emulsion leaving the steam-stripping tower.

The paper by Hammond and Stokes,[108] which led to the choice of tetralin, described a series of measurements of diffusivities of carbon tetrachloride in various materials, and from these decalin was chosen. This was perfectly acceptable on all criteria, but, at room temperature, had a slightly higher vapour pressure than gas oil or tetralin and so the inevitable losses to be expected in the steam-stripping section were slightly higher. One more disadvantage was that decalin exists in two stereo-isomeric forms and it was feasible that differential separation of one isomer in the steam stripping column could result in a change of physical properties over a period of time. It was found, however, that no such change took place to a measurable degree, and the system functioned adequately except for impositions due to the apparatus alone.

2.2. EXPERIMENTAL TECHNIQUES

2.2.1. Air/water system

The procedure usually employed by the many workers who have studied the efficiency of the humidification of air by water has been to measure directly the humidity of the air entering and leaving the contacting device. This procedure has the merit of simplicity, but has been questioned on one point,[106] namely, whether

or not the value obtained for the outlet humidity is the correct one. This doubt arises from the fact that the outgoing stream of air carries a proportion of entrained droplets, which are deposited on the outlet dry-bulb thermometer, and are then liable to further evaporation. This will bring down the dry-bulb temperature and hence give an artificially high value for the outlet humidity. The entrainment may be removed by judicious baffling, but the droplets will form a film on the baffles, which will then evaporate to give again an artificially high value for the outlet humidity (assuming the wet-bulb temperature to be correct in both cases). If the outlet wet- and dry-bulb thermometers are placed in a side neck, there is a danger that the velocity of the air sample passing the thermometer bulbs may be below the critical velocity for satisfactory use of the psychrometric equations. Some work was done here using this method, but the results were found to be unsatisfactory at gas rates above 2ft /sec.

Other workers, e.g. Garner and Freshwater[106] and Ellis and Hoyade,[30] have studied a system which involves concentrating a dilute solution of a non-volatile solute by evaporation into an air stream. A mass balance then gives the outlet humidity of the air. It was felt that this method would give the most accurate results, but, as previously used, it had two main objections. The first was the time for a run which was about 5 hours in each case. This is inconveniently long and, moreover, inlet humidity conditions are

liable to change considerably over a test of this duration. The second objection is the choice of solute. Garner and Freshwater used a 2-5% solution of sodium carbonate while Ellis and Moyade used a 5% sugar solution. Solutions with strengths of this order have vapour pressures different from that of pure water and other properties such as surface tension also differ. A 2% sodium carbonate solution was used in trial runs in the apparatus subsequently employed, and was found to give far higher foam heights than ~~those of~~ water alone at identical gas and liquid rates (see Fig. 2.1.) This in turn meant a higher gas residence time and consequently the results recorded could only apply to sodium carbonate solutions and not to water. Furthermore a 5% sugar solution has a viscosity 25% above that of water[102] and this also introduces another variable to be considered.

Accordingly it was decided that to meet the second objection, a solute would have to be selected which had the minimum effect on solution properties and could also be used in very much lower concentrations.

The first objections, i.e. the extreme length of time for a run, can be overcome in two ways, (1) by using a small initial volume of solution such that the mass of water humidified per hour is a significant proportion, and, (2) by measuring the concentration change with a high degree of accuracy.

After various other approaches were tried (see Appendix A) it was decided to use solutions of a disperse dye, Duranol Brilliant Yellow, at a concentration of below .01%.[109] The samples

chosen were analysed in a Cambridge 1500 absorptiometer which could measure the concentration to an accuracy of about 1%. A further refinement was to take samples throughout the run to give a plot of concentration change against time. This plot is a curve under certain conditions (see Appendix B) whereas Garner and Freshwater and Ellis and Moyade assumed that it was always straight.

This method allowed runs to be at the most 3 hours long and as short as 1 hour, depending on the rate of evaporation, and gave a high degree of experimental accuracy.

2.2.2. Air/carbon tetrachloride system

It was not possible to evaporate the carbon tetrachloride under adiabatic conditions using air at room temperature, as the adiabatic saturation temperature was very low. Carbon tetrachloride, cooled by partial evaporation well below room temperature, picked up a great deal of heat during the recycling process, causing a temperature drop of up to 21 deg F across the plate. This could be prevented by passing the recycling carbon tetrachloride through a cooler, but this was not economically or technically feasible and the efficiency of the mass transfer process was obtained from a heat balance across the plate. The efficiency was measured as the number of transfer units and the formula used was

$$N_{OG} = \int \frac{di_G}{i_L - i_G}$$

where i is the enthalpy.

The value of the integral was calculated using the Carey-Williamson[110] chart since the relationship between enthalpy and temperature is not linear. This method was developed for air/water systems,[110,111] and for the air/carbon tetrachloride system, a modified enthalpy had to be used.[112]

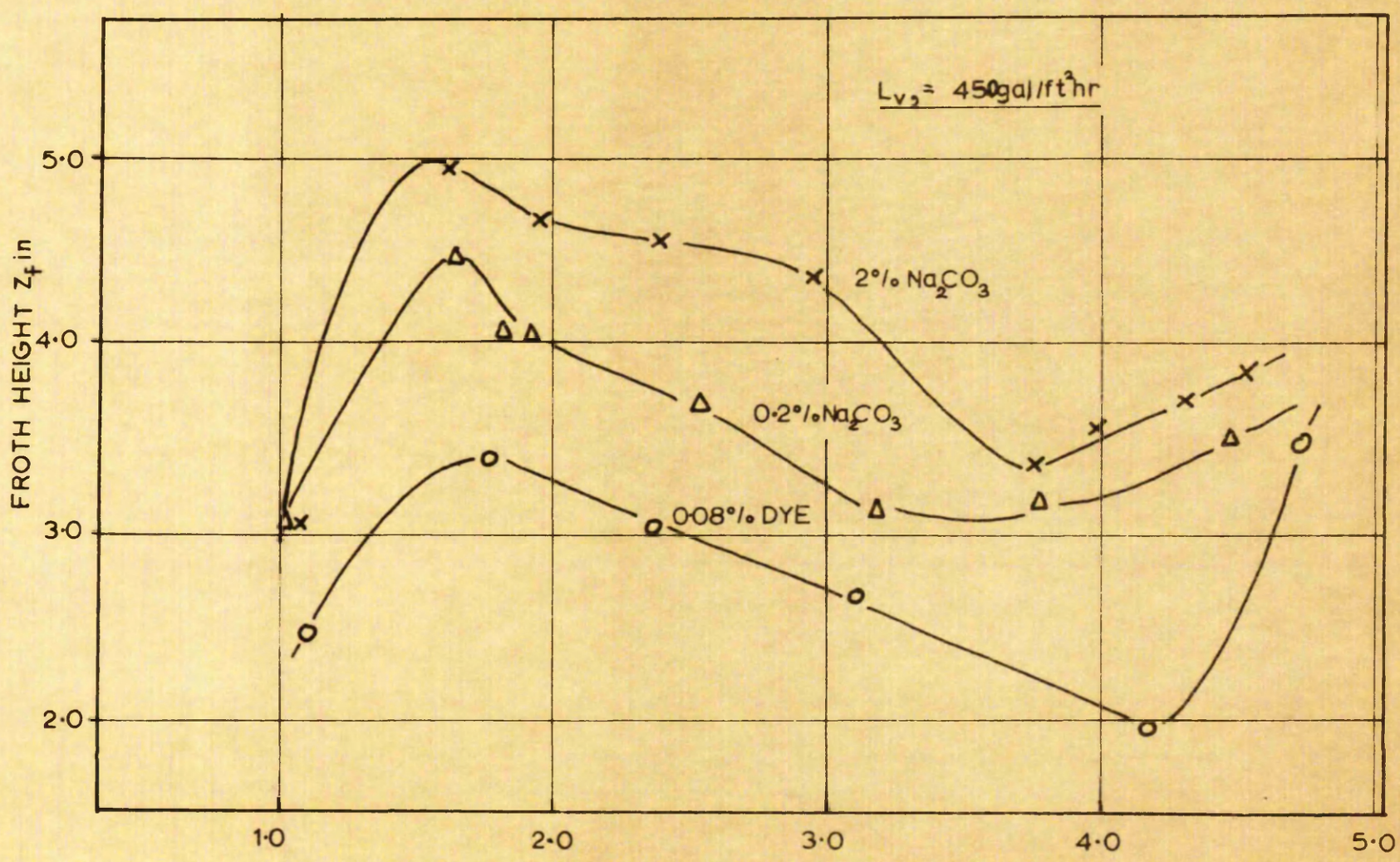
$$\text{i.e. } i = C_S r t + \lambda_o H$$

where C_S is the humid heat Btu/lb $^{\circ}F$, r is the psychrometric ratio

λ_o is the latent heat Btu/lb. H is humidity, lb vapour/lb dry gas.

2.2.3. Absorption system - general technique

The absorption was carried out by contacting a stream of air containing carbon tetrachloride with decalin on the sieve plate. The mass of carbon tetrachloride transferred from the gas phase to the liquid phase was measured by comparing the densities of the inlet and outlet decalin streams to the plate, the carbon tetrachloride being then recovered for future use.



EFFECT OF SOLUTE CONCENTRATION ON FROTH HEIGHT (air-water)

FIG. 21

3. SYSTEM PROPERTIES AND EQUILIBRIUM DATA

For calculation of the efficiencies of the three mass transfer systems used in this study, it was necessary to know the equilibrium relationships or concentration driving forces between the two phases. For comparison of the efficiencies of the three systems, it was useful to know the Schmidt numbers, Sc, of each system. To calculate Sc, the values of the interfacial diffusivity, and the density and viscosity of each phase had to be known.

Values of these various properties were either obtained from the literature, measured, or were calculated from published correlations.

3.1. SYSTEM PROPERTIES

3.1.1. Air/water system

The concentration driving force was taken as the difference between the saturated humidity and the actual humidity of the air stream at the same temperature. Information to calculate the driving force was taken from the I.H.V.E. Guide.[113] The temperatures were converted to degrees Centigrade and the data were drawn on various large scale graphs which are not reproduced here. The value of Sc was taken as .60 from Treybal[44] and Rush and Stirba.[35]

3.1.2. Air/carbon tetrachloride

Enthalpies and other psychrometric properties were taken from a chart published in Chemical & Metallurgical Engineering[114] which enabled concentration driving forces to be calculated. The density of air was taken as 1.293 gm /litre at N.T.P. which was obtained from Perry.[115] Values for the viscosity of air at various temperatures were taken from data by Johnston and McCloskey[116] obtained from the National Engineering Laboratory.

The diffusivity of carbon tetrachloride vapour through air was estimated by the method proposed by Hirschfelder, Bird and Spotz[117] using the correction suggested by Wilke and Lee.[118] Diffusivities were calculated for various temperatures and pressures. Values of the Schmidt numbers calculated from these data, were found to be relatively independent of pressure and temperature. The average value of 1.93 does not agree with the figure of 2.2 which appears in Treybal,[44] but the origin of the latter value was not stated. The tabulated values of density, viscosity, diffusivity and Schmidt numbers appear in Table 3.1.

3.1.3. Air/carbon tetrachloride/decalin

The literature was scrutinised for equilibrium data for carbon tetrachloride in decalin. Timmermans[119] quotes data at 20°C, attributed to Weissenberger et al.[120] but it was not possible to obtain the original paper, and as the intended working temperature was to be 25°C, equilibrium data were obtained for this temperature experimentally. The procedure involved is described in Section 3.2. The specific gravity of mixtures of carbon tetrachloride dissolved in decalin, was obtained over a range of concentrations at 25°C by standard density bottle techniques. Viscosity and diffusion coefficients, at 25°C, of mixtures of carbon tetrachloride in decalin have been measured by Hammond and Stokes.[108] The diffusion coefficient varied with concentration and the limiting diffusion coefficient i.e. assuming zero concentration of carbon tetrachloride, was $0.776 \times 10^{-5} cm^2/sec$ which was the value used in calculating the liquid phase Schmidt number. The viscosity of decalin was taken as 2.41 cP from International Critical Tables,[121] which also was the source of vapour pressure data.

The density of air/carbon tetrachloride mixtures was calculated for 25°C using the weighted mean of the densities

of the pure components at N.T.P. and correcting for temperature. The viscosity of air/carbon tetrachloride mixtures was calculated from the equation given by Norman[3] (see Appendix C).

The viscosity of carbon tetrachloride vapour was calculated by the procedure described by Bromley and Wilke.[122] The viscosity of the mixture fell as the concentration of carbon tetrachloride increased. Schmidt numbers were calculated from these data as necessary.

The calculated and measured properties of the air/carbon tetrachloride/decalin system are presented in Table 3.2 and Fig. 3.1. with the exception of the equilibrium data which are reported in Section 3.2.

3.2. EQUILIBRIUM DATA FOR AIR/CARBON TETRACHLORIDE/DECALIN SYSTEM

3.2.1. General

The efficiency of a mass transfer process cannot be established without an accurate knowledge of the concentration driving forces between the two phases. The literature gave data for equilibria between carbon tetrachloride and decalin at 20°C, but as the intention was to carry out the experimental work on the absorption process at 25°C, to avoid the risk of condensation of carbon tetrachloride, it was decided to ascertain experimentally the equilibrium relationships at this higher temperature. The method employed was a transpiration process in which air was blown through a train of absorption bottles containing various concentrations of carbon tetrachloride in decalin, the concentration of carbon tetrachloride in the outlet air being measured by gas analysis unit which is described in Appendix D.

3.2.2. Apparatus

Air was drawn through an absorption train sited in a thermostatic bath, and then through the gas analyser, by a

water aspirator operated by a small centrifugal pump. The absorption train consisted of three Pyrex glass bottles 5 in tall x 1¾ in diameter with ground glass stoppers. Each downcomer was fitted with a sintered glass endpiece to diffuse the gas intimately through the liquid. The final bottle in the train also had a glass thermometer pocket immersed in the liquid. The bottles were joined by vinyl plastic tubing since carbon tetrachloride and decalin both attack rubber. Before passing to the absorption train, the air was drawn through an absorption bottle containing concentrated sulphuric acid for drying purposes, and then through two copper coils to ensure that the air has the maximum time to reach bath temperature which was controlled to ± 0.1 deg C.

3.2.3. Experimental procedure

The thermostatic bath and gas analysis unit were switched on and adjusted to the working temperature, usually 25°C. Solutions of known concentration of carbon tetrachloride in decalin were made up, and about 500 cc were added to each bottle, which was then placed in the bath. The bottles were joined in to the circuit and ten minutes were allowed to elapse to permit the liquid in the bottles to come to the bath temperature. The water aspirator was then switched on and the airflow adjusted to give steady bubbling in all three bottles. As the temperature in the last bottle fell slightly, due to the entering gas stream being cooled by evaporation of carbon tetrachloride, the thermostat was set to keep the temperature in this bottle at 25°C. When the value of the outlet gas concentration was steady, conditions were held for five minutes and then the apparatus was shut off. Extending the run for a longer period resulted in a more serious evaporation of carbon tetrachloride with a consequent change in concentration of the liquid. The barometric pressure was noted after each run, and as the pressure of the gas at the outlet from the absorption train was found to be only a few inches

of water, the pressure at the outlet was assumed, in calculating the partial pressure, to be equal to atmospheric.

Although it was not expected that information would be needed above 20 mol % carbon tetrachloride in decalin, it was decided to endeavour to complete the information over the whole range of concentration. At higher concentrations however, the carbon tetrachloride vapour tended to condense on the apparatus lines and in the analysis unit itself, thus introducing a source of considerable error. To minimise this error, an electric radiator was mounted in close proximity to the apparatus.

3.2.4 Results

Expressed graphically in Figs.3.2 and 3.3, the results show a slight positive deviation from Raoult's Law. The partial pressure of carbon tetrachloride at 100% concentration was taken to be equal to the saturated vapour pressure of carbon tetrachloride and from data in Glasstone[123] a value of 111.5mm Hg was selected. The error, as was expected, was higher at the higher concentrations i.e. above 20 mol %. Below this concentration, the relationship was linear, i.e. the system obeys Henry's Law and this was the concentration range used in the mass transfer calculations.

3.2.5 Discussion - ideal mixtures

The data of Weissenberger et al.[120] appeared to show a very slight negative deviation from Raoult's Law. However the value for the equilibrium partial pressure at 100% concentration seems high. The saturated vapour pressure at 20°C from Glasstone p449 is 91 mm Hg compared with their value of 97 mm Hg. If the lower value is taken, then their data shows a linear relationship over the whole concentration (see Fig.3.3) i.e. the system, at this temperature, is ideal. Although the error very

possibly applies to the whole concentration range(and this could not be verified) this is a significant finding as this system does not appear to have been extensively reported as an ideal or near-ideal system. Also shown on Table 3.3. are the activity coefficients calculated for both the present work and that of Weissenberger et al. over the range of concentrations studied. On Table 3.4. are shown activity coefficients calculated for the system carbon tetrachloride/n heptane at 50°C, which is stated by Glasstone to show only "very small" deviations from Raoult's Law. Also shown are activity coefficients for the ethanol/water system at 25°C as an example of an accepted non ideal system. It can be seen that the approach to ideality of the carbon tetrachloride/decalin system is good in comparison, especially at 20°C.

In view of the possible importance of this system, it was decided to pursue the matter a little further, although regrettably it was not possible to repeat the work of Weissenberger et al., owing to the inaccuracy of the apparatus at high concentrations.

The conditions for the existence of an ideal solution of two materials are that they should have similar molecular behaviour, viz, they should have the same internal pressure, the same polarity, exhibit no association and be of similar structure.

The internal pressure of carbon tetrachloride relative to naphthalene is 0.81.[123] No figure for decalin is available, but, since the boiling point of naphthalene is some 30 deg C higher than that of decalin (decahydronaphthalene) and the internal pressures are approximately proportional to the absolute boiling points, in view of the similarity of molecular weights and structures, it seems reasonable to assume that the relative internal pressure will be less than 1,0 and be approximately equal to that of carbon tetrachloride. Both compounds are non-polar and consequently there will be no association, and although

the structures are dissimilar they are both symmetrical. The conditions for ideality then seem to be fairly well fulfilled. This can be verified by comparison of the predicted and measured values of specific gravity, as a consequence of the mixing of two liquids with similar molecular pressures and with no interactions, is that there will be no alteration in total volume, and hence the predicted and measured values of specific gravity should be identical. The comparison is made on Table 3.5. and as can be seen, agreement is good over the whole range considered. The corresponding values for ethanol/water solutions are also shown, to give a comparison with an accepted non-ideal system, the difference between the predicted and measured values increasing with concentration.

One further criterion of ideal mixtures is that there should be no heat of mixing and it was decided to endeavour to measure this in an approximate manner.

The method employed was very simple and merely involved mixing known weights of decalin and carbon tetrachloride and measuring the resulting temperature. The initial temperatures of the carbon tetrachloride and decalin were measured and the final temperature was calculated assuming no heat of mixing. The difference between the heat content of the mixture as calculated from the measured final temperature and the calculated temperature was expressed as a percentage of the calculated heat content. The results are shown in Table 3.6, and graphically on Fig. 3.4. They show that the heat of mixing is very small, never being greater than 3% of the calculated value, and is negative.

The above evidence and reasonable assumption seems to support the view that approximately ideal behaviour of carbon tetrachloride and decalin mixtures is to be expected thus confirming the experimental evidence.

Table 3.1

System Properties

Air/Carbon Tetrachloride System

T °C	P mm Hg	μ_G cP	D_G cm^2/sec	ρ_G gm/litre	Sc
10	760	.0177	.0737	1.247	1.93
15	"	.0179	.0757	1.225	1.93
20	"	.0182	.0777	1.205	1.94
25	"	.0184	.0810	1.184	1.92
10	780	.0177	.0716	1.284	1.93
15	"	.0179	.0735	1.262	1.93
20	"	.0182	.0754	1.241	1.94
25	"	.0184	.0786	1.219	1.92
10	740	.0177	.0757	1.214	1.93
15	"	.0179	.0777	1.193	1.93
20	"	.0182	.0798	1.174	1.93
25	"	.0184	.0832	1.153	1.92

Average value of Sc = 1.93

Table 3.2

SYSTEM PROPERTIES:- AIR/CARBON TETRACHLORIDE/DECALIN

		Source
Diffusivity of carbon tetrachloride in decalin at 25°C (D_L)	$= .776 \times 10^{-5} cm^2/sec$	Hammond[108] & Stokes
Viscosity of decalin at 25°C (μ_L)	= 2.41 cP	I.C.T.[121]

Specific gravity of carbon tetrachloride/decalin solutions at 25°C (ρ_L) — Experimental

Wt %	0	5.09	8.42	12.20	16.69	24.88	33.44	46.54
S.G.	0.8870	0.9054	0.9184	0.9346	0.9516	0.9940	1.039	1.115

Density of air/carbon tetrachloride mixtures at 25°C (ρ_G) — Calculated

Pressure mm Hg		720	740	760	780	800
Density at 0% CCl_4		0.0700	0.0720	0.0740	0.0760	0.0780
(lb/ft^3) 5	"	0.0850	0.0876	0.0899	0.0923	0.0948
10	"	0.1002	0.1030	0.1059	0.1086	0.1114
15	"	0.1153	0.1185	0.1216	0.1250	0.1280

Viscosity of air/carbon tetrachloride Mixtures (μ_G) — Calculated (see Appendix C)

Mole fraction %		0	5	10	15
Viscosity at	15°C	0.0179	0.0175	0.0169	0.0163
(cP)	20°C	0.0182	0.0178	0.0172	0.0166
	30°C	0.0184	0.0180	0.0175	0.0164

Diffusivity of carbon tetrachloride through air as in Table 2.1.

Table 3.3

SYSTEM PROPERTIES:- AIR/CARBON TETRACHLORIDE/DECALIN

1. Equilibrium Data at 25°C

Run No.	Wt.% CCl_4	Mol % of CCl_4	p.p. of CCl_4 mm.Hg.	Activity coefficient
1	2.96	2.63	3.18	1.08
2	6.06	5.42	7.73	1.27
3	9.29	8.87	11.40	1.05
4	12.20	11.10	14.83	1.19
5	16.64	15.18	20.70	1.22
6	19.34	17.75	24.62	1.23
7	22.95	21.07	30.71	1.30
8	36.80	36.34	43.54	1.06
9	45.15	42.52	52.03	1.10
10	60.95	58.32	71.58	1.10
11	75.68	73.65	96.35	1.18

2. Equilibrium Data at 20°C from Timmermans[119]

from Weissenberger, Henke and Sperling[120]

Mol %	p.p.of CCl_4 mm Hg	Activity coefficient*
25	23.7	1.04
40	36.2	0.99
50	45.7	1.00
60	54.7	1.00
75	68.0	1.00
100	97.0	-

* Calculated assuming partial pressure of pure carbon tetrachloride to be 91 mm of Hg at 20°C.

Table 3.4.

ACTIVITY COEFFICIENTS OF SYSTEMS CARBON TETRACHLORIDE/N HEPTANE AND ETHANOL/WATER.

(a) Carbon tetrachloride/n heptane at 50°C.

mol % CCl_4 in liquid	mol % CCl_4 in vapour	Pressure mm Hg	Activity coefficient
9.83	21.6	159.9	1.14
17.14	34.4	174.0	1.13
35.14	58.1	207.4	1.11
50.12	69.9	232.3	1.05
57.00	75.1	244.7	1.03
81.26	90.0	282.4	1.02

(b) Ethanol/water at 25°C.

mol % C_2H_5OH in liquid	mol % C_2H_5OH in vapour	Pressure mm Hg	Activity coefficient
5.87	57.3	34.2	5.7
17.00	70.5	45.6	3.22
32.2	7'4.6	50.6	2.00
54.3	79.6	54.4	1.35
82.5	86.9	58.4	1.04

Table 3.5.

COMPARISON OF MEASURED AND PREDICTED VALUES OF SPECIFIC GRAVITIES OF CARBON TETRACHLORIDE/DECALIN AND ETHANOL/WATER SOLUTIONS AT 25°C.

(a) Carbon tetrachloride/decalin

wt. % CCl_4 in soln.	Measured S.G.	Predicted S.G.
5.09	0.9054	0.9073
8.42	0.9184	0.9212
12.20	0.9346	0.9374
16.69	0.9516	0.9574
24.88	0.9940	0.9961
33.44	1.039	1.0402
46.54	1.115	1.1157

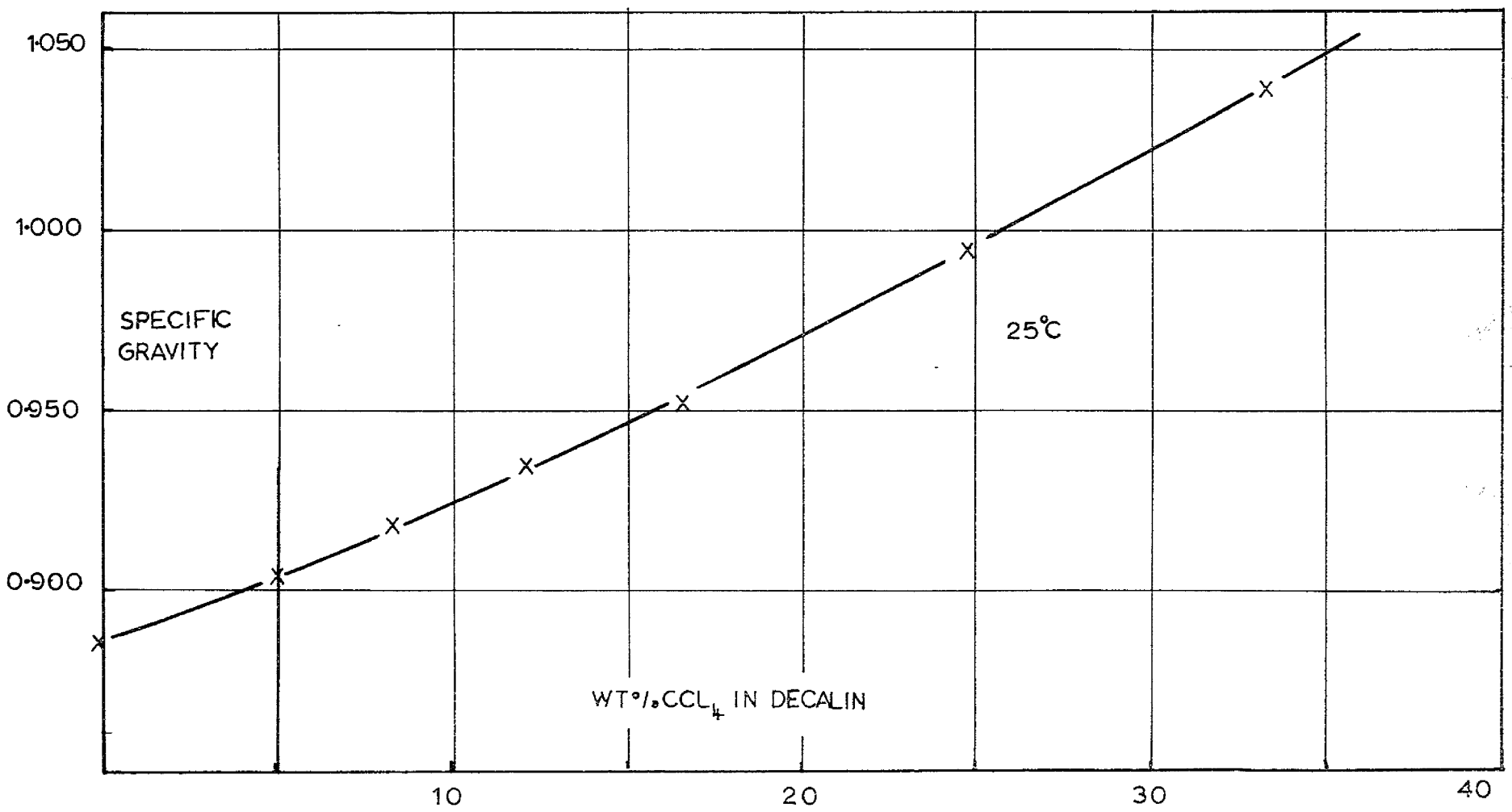
(b) Ethanol/water

wt. % C_2H_5OH in soln.	Measured S.G.	Predicted S.G.
5	0.9882	0.9837
10	0.9804	0.9712
15	0.9733	0.9588
20	0.9664	0.9369
40	0.9315	0.8992

Table 3.6.

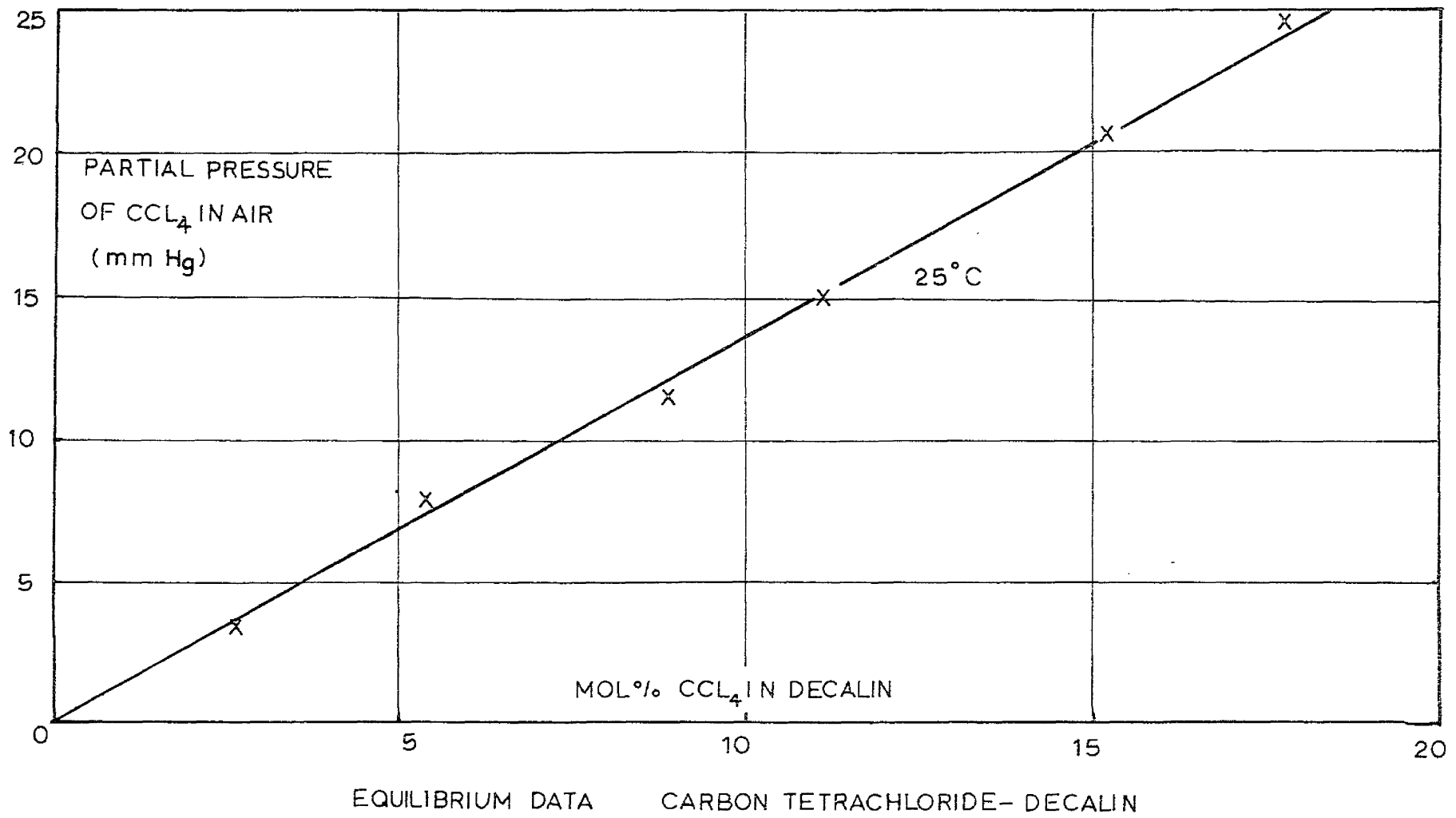
SYSTEM PROPERTIES: - HEATS OF MIXING, CARBON TETRACHLORIDE/DECALIN

Test No.	Mass Decalin gm	Mass CCl_4 gm	T Decalin °C	T CCl_4 °C	T mix. °C	$H_{Th.}$ Cal	$H_{Act.}$ Cal	% Heat lost	% wt CCl_4 in solution
1	120.1	11.2	19.2	19.0	19.1	919.6	915.8	0.41	8.5
2	70.9	14.5	22.5	22.1	22.3	671.1	665.7	0.80	17.0
3	112.7	23.5	18.8	18.3	18.6	890.0	883.4	0.74	17.2
4	113.8	29.8	23.2	22.8	22.8	1136	1124	1.06	20.8
5	114.7	34.6	24.8	24.4	24.3	1251	1228	1.84	23.2
6	113.2	41.9	22.0	21.3	21.4	1125	1099	2.36	27.0
7	116.1	60.6	22.6	22.2	22.0	1269	1239	2.36	34.3
8	111.5	74.3	22.5	22.0	21.8	1279	1247	2.50	40.0
9	119.9	98.2	19.1	18.8	18.5	1239	1206	2.67	45.0
10	115.0	184.0	25.3	25.0	24.6	2026	1974	2.56	61.5
11	73.0	207.0	18.6	18.2	17.9	1268	1236	2.53	74.7



SPECIFIC GRAVITY OF CARBON TETRACHLORIDE-DECALIN SOLUTIONS

FIG. 3.1.



EQUILIBRIUM DATA CARBON TETRACHLORIDE– DECALIN

FIG. 3.2.

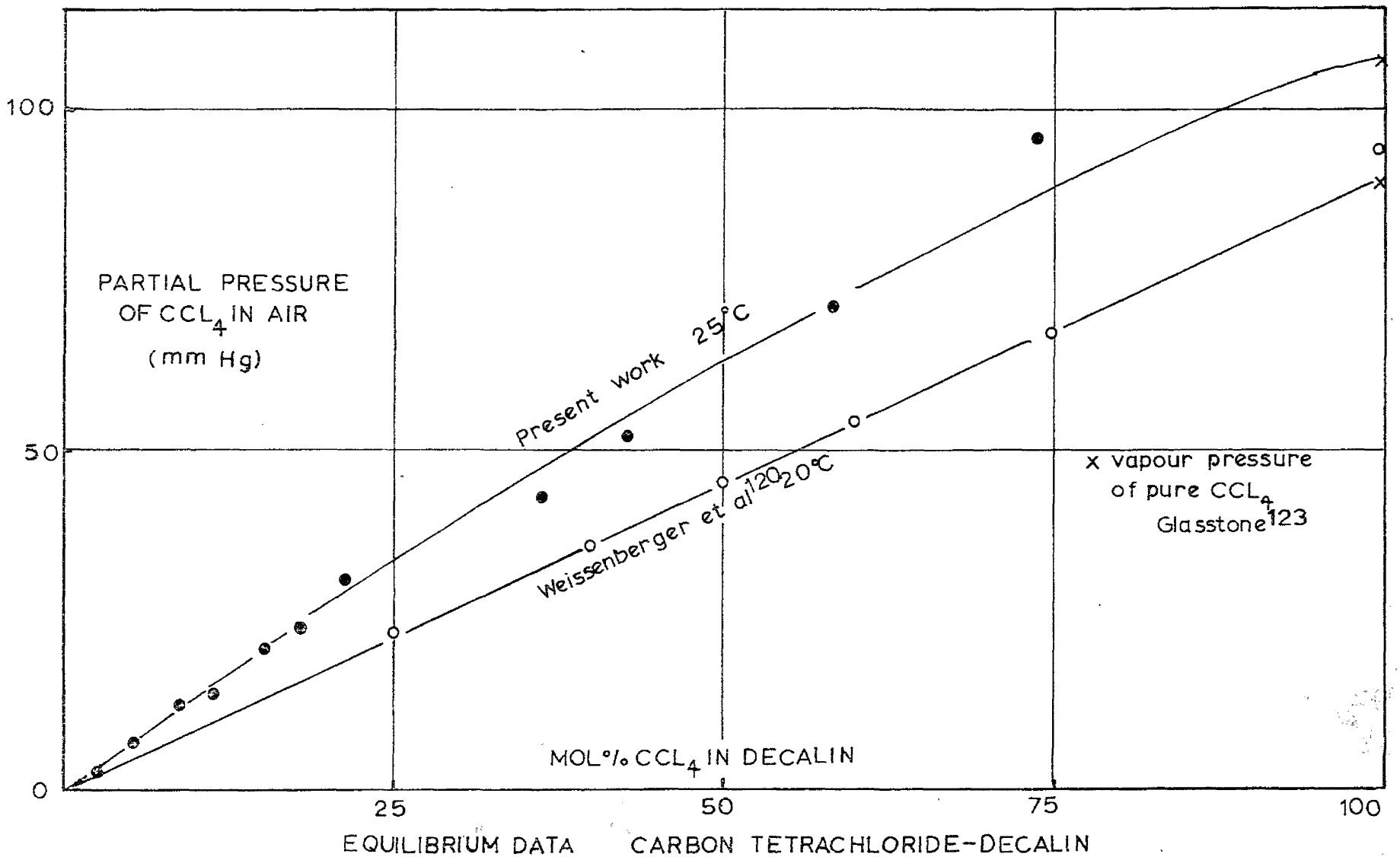
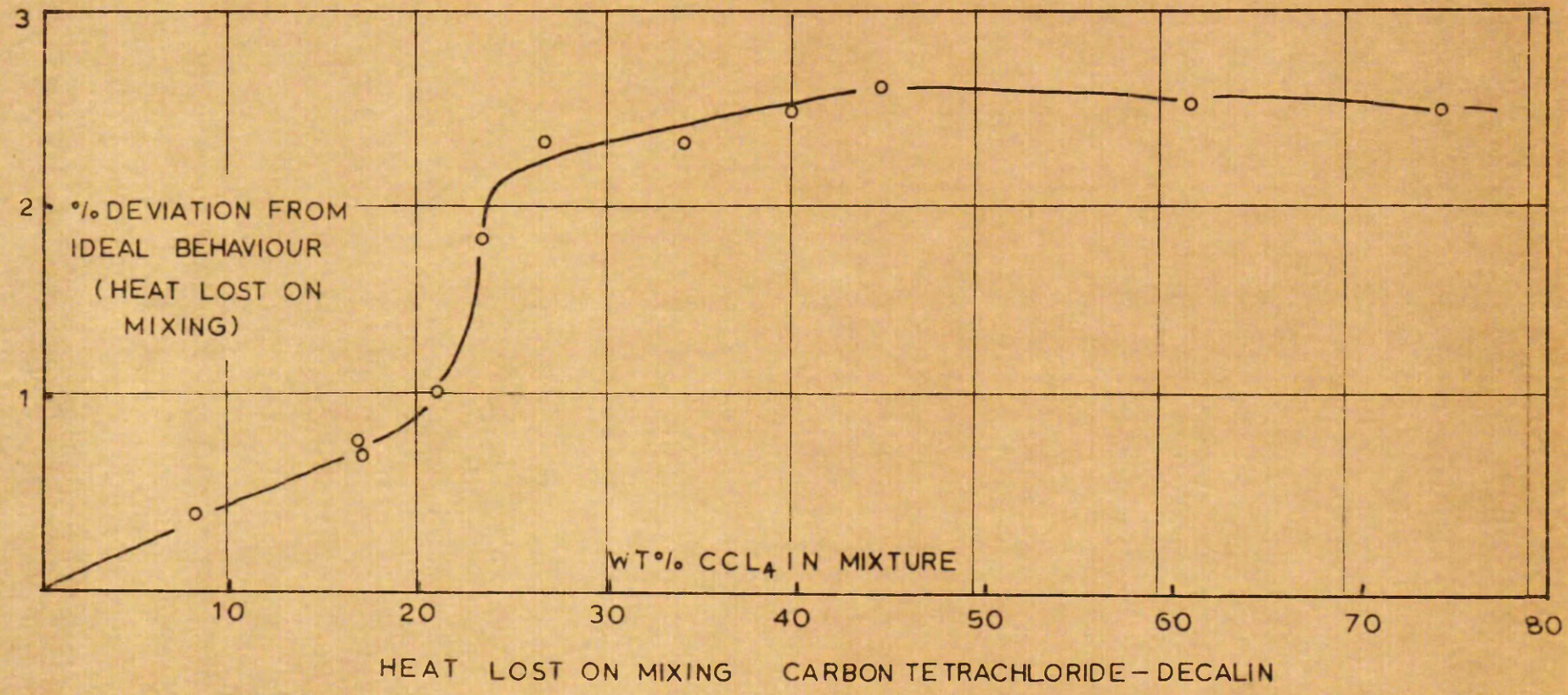

100
50
0
PARTIAL PRESSURE
OF CCL_4 IN AIR
(mm Hg)
Present work 25°C
Weissenberger et al[120] 20°C
x vapour pressure
of pure CCL_4
Glasstone[123]
MOL% CCL_4 IN DECALIN
25
50
75
100
EQUILIBRIUM DATA CARBON TETRACHLORIDE-DECALIN

FIG. 3.3.



HEAT LOST ON MIXING CARBON TETRACHLORIDE – DECALIN

FIG. 34.

4. EXPERIMENTAL TECHNIQUES FOR HYDRAULIC MEASUREMENTS

4.1. APPARATUS

The hydraulic studies were carried out using the same apparatus as was used in the mass transfer studies.

4.1.1. Froth heights (Z_f)

The froth heights were measured visually, using a cathetometer. To enable the sharpest possible image to be obtained, a strip of black paper was attached to a glass column wall on the opposite side from the cathetometer. In the case of the decalin and carbon tetrachloride froth height measurements, a vertical slit was cut in the black paper and a 60 watt lamp was placed behind. The cathetometer was then focussed on this illuminated slit. For the water froth height measurements, a slightly different procedure was adopted. A red dye (Azo Rodine 2 6) which was chosen for its zero effect on the surface tension of water[109] was added, and illumination of the coloured froth was ~~done~~ arranged from above using a 60 watt lamp. The cathetometer was focussed on the centre of the froth.

At low gas rates the froth was fairly stable and the cathetometer could be arranged such that the horizontal cross wire would lie along the top of the image of the froth. At higher gas rates, however, the froth was much more active, and the cathetometer was adjusted in such a way that the line defining the interface between the froth and the gas appeared to oscillate above and below the horizontal cross wire. The cathetometer was so arranged that same areas of background appeared above and below the cross wire,

This latter procedure was fairly easy to carry out on the air/water system but less easy on the air/decalin and air/carbon tetrachloride systems due to the less apparent contrast.

The method used was considered superior to the usual

method of ~~visually~~ visually determining the froth height by comparison with a graduated strip attached to the transparent column section above the plate. The froth heights could be measured to 0.1 in. in the case of air/water systems and 0.2 in. in the other two systems. One reason for the superiority of this method is that the image viewed through a telescope is two-dimensional and so is easier to compare against a scale.

4.1.2. Clear liquid heights (Z_c)

These were measured by attaching one end of an inclined glass tube to a tapping below the plate and the other end to the air space about 2 ft above the plate. The clear liquid height was then obtained by multiplying the length of liquid in the tube by the sine of the angle of inclination.

4.1.3. Plate pressure drop (ΔP)

The pressure drops were measured by means of a simple U-tube manometer attached to points above and below the plate. The manometer contained water for the air/carbon tetrachloride and air/decalin runs and water/carbon tetrachloride for the air/water runs.

4.1.4. Procedure

Before each run, the cathetometer was focussed on the base of the plate to give a zero point for the froth height readings. The apparatus was then started up and readings were taken of froth height, clear liquid height and plate pressure drop for a series of air rates at various different liquid rates. The froth height was taken as the average of three readings.

4.2. RESULTS

The experimental results are given in Table 4.1, 4.2, 4.3 and are represented graphically on as Figs. 4.1 to 4.12. The hold up, froth density and gas residence

time were calculated from the following formulae.

$$H_G = \frac{Z_f - Z_c}{Z_f} \qquad \text{4.1.}$$

$$\phi_f = \frac{Z_c}{Z_f} \varrho_L \qquad \text{4.2.}$$

$$t_G = \frac{Z_f - Z_c}{12 V_s} \qquad \text{4.3.}$$

4.2.1. Froth heights

Air/Water. The froth height versus gas rate curves differ from those obtained by Crozier[98] Gerster[33] and others[30,84] in that they rise to a maximum, fall, then rise once more. They also differ in that they cross over at high gas rates viz. at V_s = 4.0 ft/sec as was expected from visual observations. At low gas rates (below V_s = 1.8 ft/sec) the froth is a stable cellular foam composed of large bubbles, the height being proportional to liquid rate. As the gas rate increases, these bubbles can be seen to break down and a froth is formed whose mobility increases with gas rate. The process of bubble rupture results in a fall in froth height until the process is completed. Then as the mobility of the froth increases, the froth height increases.

Air/carbon tetrachloride. The froth height versus air rate curves show a more typical pattern, the froth height increasing regularly with both gas rate and liquid rate.

Air/decalin. For the air/decalin system, the froth height versus gas rate curve is more complicated and is similar to the air/water results in that the froth height tends to fall with gas rate at higher liquid rates and rises at lower liquid rates. At a liquid rate of 3000 lb/ft^2 hr, an interesting transition is shown between the two trends.

4.2.2. Clear liquid heights

These all fall with gas rate and rise with liquid rate. The effect of liquid rate is more pronounced at the lower gas rates.

4.2.3. Plate pressure drops

It was found from these tests that the pressure drops always rise with gas rate, and at lower gas rates rise with liquid rate, but at higher gas rates are independent of liquid rate.

4.2.4. Gas hold up

Air/water. For the air/water system, the gas-liquid hold up rises sharply with gas rate to a value of approx. 0.5 at Vs = 1.65 ft/sec and remains constant until Vs = 3.0 ft/sec. It then rises again with gas rate. The effect of liquid rate is difficult to determine but seems to be fairly small.

Air/carbon tetrachloride. For the air/carbon tetrachloride system, the effect of gas rate is the same, i.e. to increase the hold up. The hold up values are much higher than for the air/water system, around 0.75. The 'flat' portion of the air/water curve is also evident. Liquid rate appears to have very little effect.

Air/decalin. The air/decalin system also shows the same relationships between hold up and gas rate. The liquid rate once again appears to have no effect except for the possibly erroneous values at L = 110 gal/ft^2 hr. The average hold up value again is higher than that of water i.e. 0.88.

4.2.5. Froth specific gravity

Air/water. The specific gravity falls with gas rate. There is no appreciable effect of liquid rate. The results are correlated fairly well by Crozier's [98] correlation. (Fig.4.9)

$$- \ln \phi_f = 0.715F + 0.45 \qquad \text{——————(4.4)}$$

Air/carbon tetrachloride. The specific gravity falls with gas rate and is fairly independent of liquid rate. The results are correlated by a line parallel to Crozier's correlation but somewhat below it.

Air/decalin. The specific gravity once more falls with gas rate with a slight liquid rate effect. The values are much lower than could be correlated by Crozier's equation.

4.2.6. Gas residence times

Air/water. The gas residence times show the same relationship with gas rate as the froth heights i.e. they rise to a maximum and then fall to a minimum and begin to rise again. The effect of liquid rate is to increase the gas residence time also the greater the liquid rate, the greater the gas rate at which the minimum gas residence time occurs.

Air/carbon tetrachloride. The gas residence time falls with gas rate and increases with liquid rate although the effect is small.

Air/decalin. The gas residence time falls with gas rate similar to the air/carbon tetrachloride values but the effect of the liquid rate is much more pronounced.

Table 4.1.

Air/water system Hydraulic test results

Run No.	V_s ft/sec.	F	L_v gal/hr ft^2	ΔP in H_2O	Z_f in	Z_c in	H_G	ϕ_f lb/ft^3	t_G sec
1	1.16	0.32	90	1.5	2.05	1.44	0.30	0.70	0.0440
2	1.65	0.46	"	2.0	2.19	1.23	0.44	0.56	0.0485
3	2.33	0.65	"	2.5	2.13	1.16	0.46	0.54	0.0348
4	3.46	0.96	"	4.1	2.51	1.09	0.57	0.43	0.0341
5	1.28	0.35	150	1.7	2.15	1.66	0.23	0.77	0.0320
6	1.65	0.46	"	2.0	2.37	1.26	0.47	0.53	0.0558
7	2.15	0.59	"	2.5	2.45	1.20	0.51	0.49	0.0484
8	2.95	0.68	"	3.4	2.46	1.16	0.53	0.47	0.0366
9	3.46	0.96	"	4.2	2.51	1.16	0.54	0.46	0.0324
10	4.30	1.19	"	5.2	3.37	0.85	0.75	0.25	0.0467
11	1.17	0.32	300	1.8	2.15	1.81	0.16	0.84	0.0242
12	1.65	0.46	"	2.2	2.91	1.44	0.51	0.49	0.0740
13	2.28	0.63	"	2.3	2.77	1.30	0.53	0.47	0.0535
14	3.00	0.83	"	3.3	2.58	1.16	0.55	0.45	0.0394
15	3.80	1.05	"	4.7	2.86	0.72	0.75	0.25	0.0469
16	4.87	1.35	"	6.2	4.12	0.92	0.88	0.22	0.0546
17	1.04	0.30	450	1.9	2.55	1.81	0.29	0.71	0.0596
18	1.73	0.48	"	2.4	3.50	1.61	0.54	0.46	0.0910
19	2.34	0.65	"	2.9	3.15	1.47	0.54	0.46	0.0577
20	3.09	0.86	"	3.7	2.87	1.23	0.57	0.43	0.0433
21	4.14	1.15	"	5.2	3.02	1.03	0.66	0.34	0.0401
22	4.71	1.31	"	6.0	3.64	1.10	0.70	0.30	0.0450

Table 4.2.

Air/carbon tetrachloride system Hydraulic test results

Run No.	V_s ft/sec.	F	L_v gal/hr ft^2	ΔP in H_2O	Z_f in	Z_c in	H_G	ρ_f lb/ft^3	t_G sec
1	1.40	0.39	0	1.7	2.1	0.6	0.71	0.39	0.089
2	1.99	0.55	"	2.5	2.2	0.5	0.77	0.36	0.071
3	2.34	0.65	"	3.2	2.2	0.5	0.77	0.36	0.061
4	2.70	0.76	"	3.9	2.3	0.5	0.78	0.35	0.056
5	1.34	0.37	190	1.9	2.2	0.7	0.68	0.51	0.093
6	1.90	0.52	"	2.5	2.3	0.6	0.77	0.41	0.075
7	2.48	0.69	"	3.4	2.4	0.6	0.75	0.40	0.060
8	3.02	0.85	"	4.3	2.6	0.5	0.81	0.30	0.058
9	1.30	0.36	310	2.2	2.3	0.8	0.65	0.55	0.096
10	1.95	0.54	"	2.7	2.5	0.7	0.72	0.45	0.077
11	2.70	0.76	"	4.0	2.7	0.6	0.78	0.35	0.065
12	3.22	0.91	"	5.1	2.8	0.5	0.82	0.28	0.060

Table 4.3.

Air/decalin system Hydraulic test results

Run No.	V_s ft/sec.	F	L_w gal/hr ft^2	ΔP in H_2O	Z_f in	Z_c in	H_G	ϕ_f lb/ft^3	t_G sec
1	1.33	0.37	110	1.2	2.1	0.5	0.76	0.21	0.100
2	1.80	0.50	"	1.7	2.1	0.3	0.86	0.13	0.083
3	2.32	0.64	"	2.5	2.2	0.3	0.86	0.12	0.068
4	2.78	0.77	"	3.2	2.4	0.2	0.92	0.07	0.066
5	3.03	0.83	"	3.6	2.4	0.2	0.92	0.07	0.060
6	1.56	0.43	330	1.8	3.3	0.8	0.76	0.21	0.133
7	2.14	0.59	"	2.5	3.2	0.5	0.84	0.14	0.105
8	2.52	0.69	"	3.0	2.6	0.3	0.88	0.10	0.076
9	3.21	0.88	"	3.8	2.7	0.2	0.93	0.07	0.065
10	3.57	0.98	"	4.7	2.9	0.2	0.93	0.06	0.063
11	1.59	0.44	560	2.3	4.5	1.0	0.78	0.20	0.183
12	2.06	0.57	"	2.8	4.4	0.9	0.79	0.18	0.142
13	2.52	0.69	"	3.3	4.3	0.8	0.81	0.17	0.116
14	3.06	0.84	"	3.7	4.0	0.6	0.85	0.13	0.092
15	3.42	0.94	"	4.5	3.5	0.4	0.88	0.10	0.075

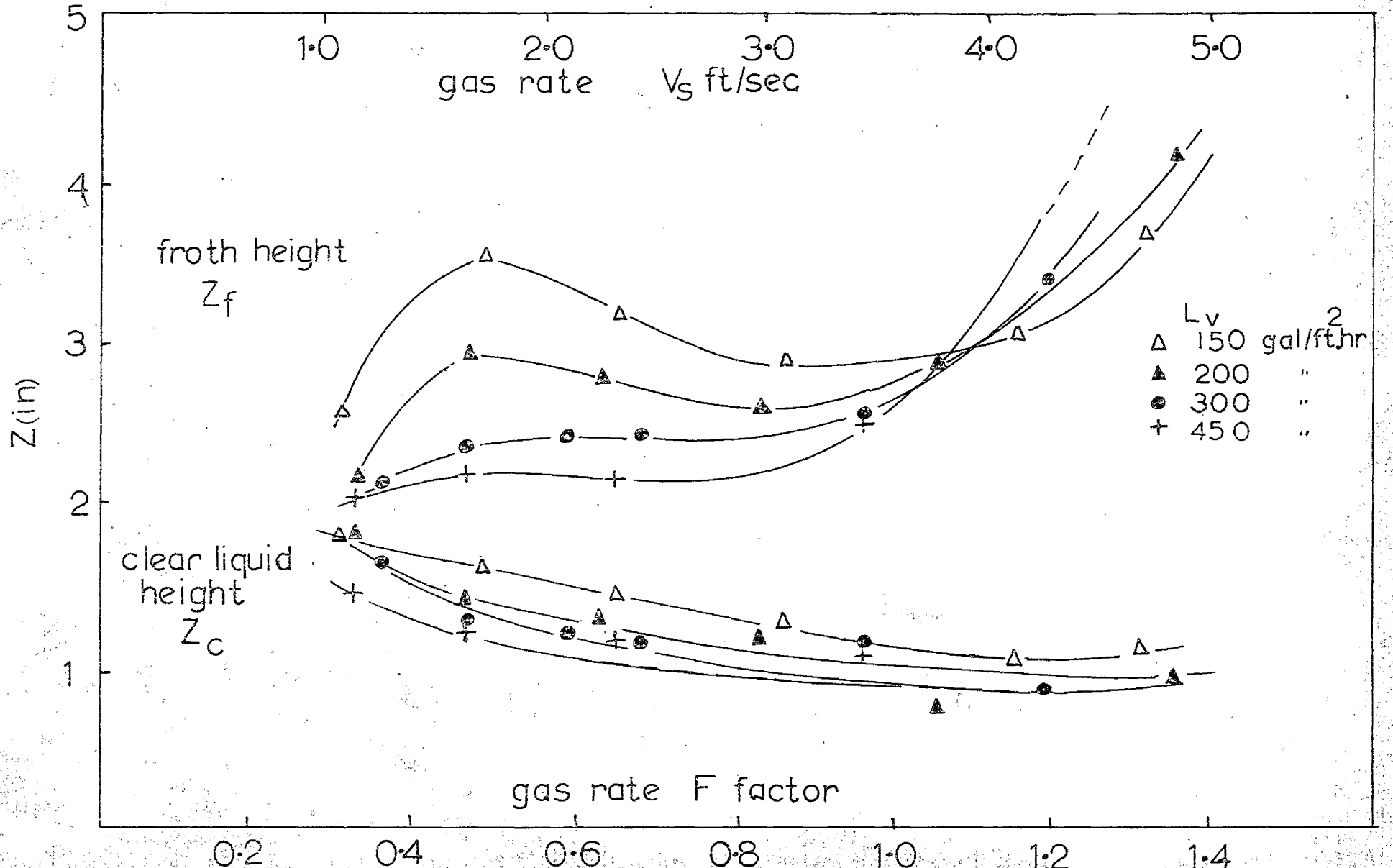
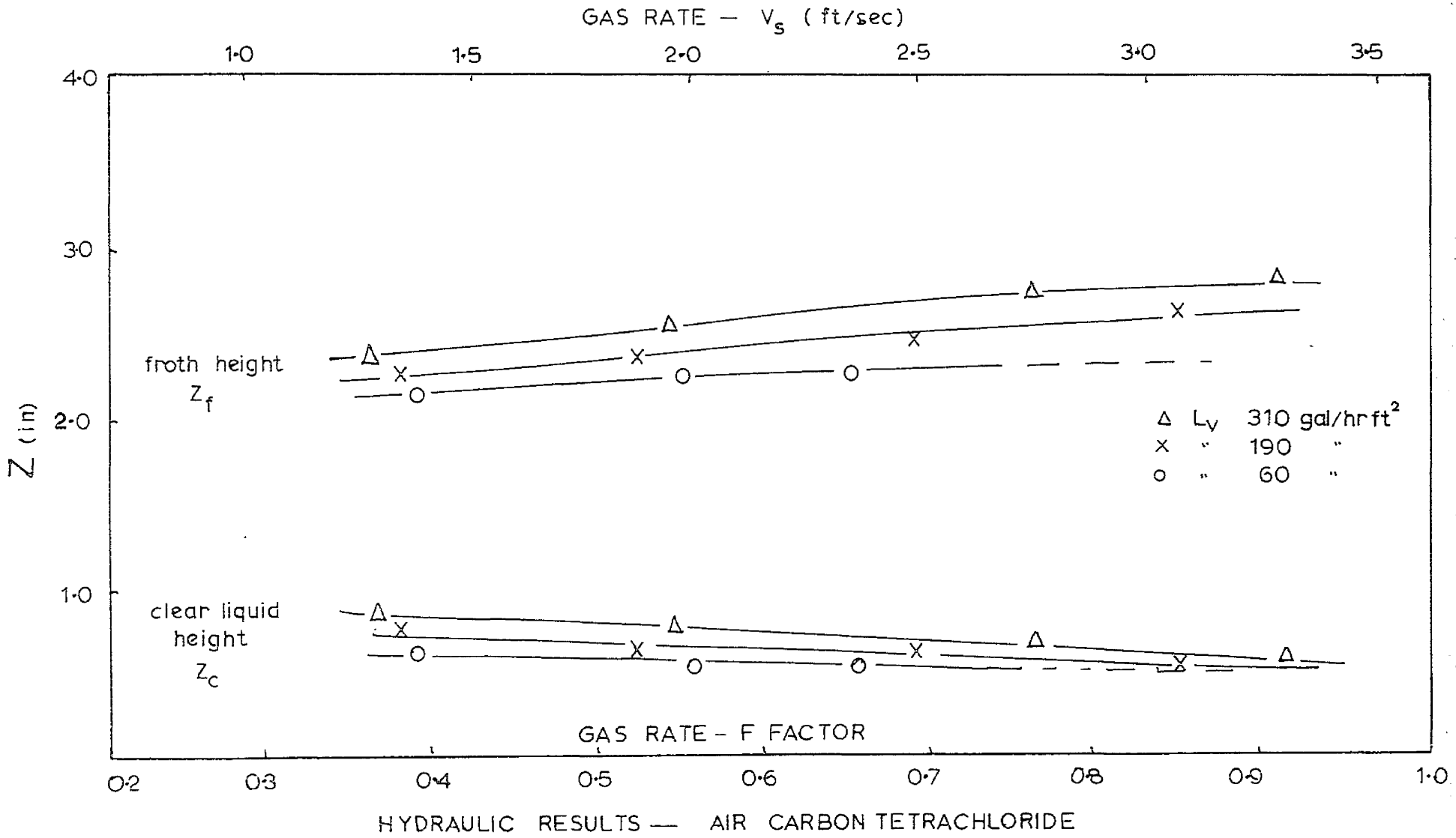


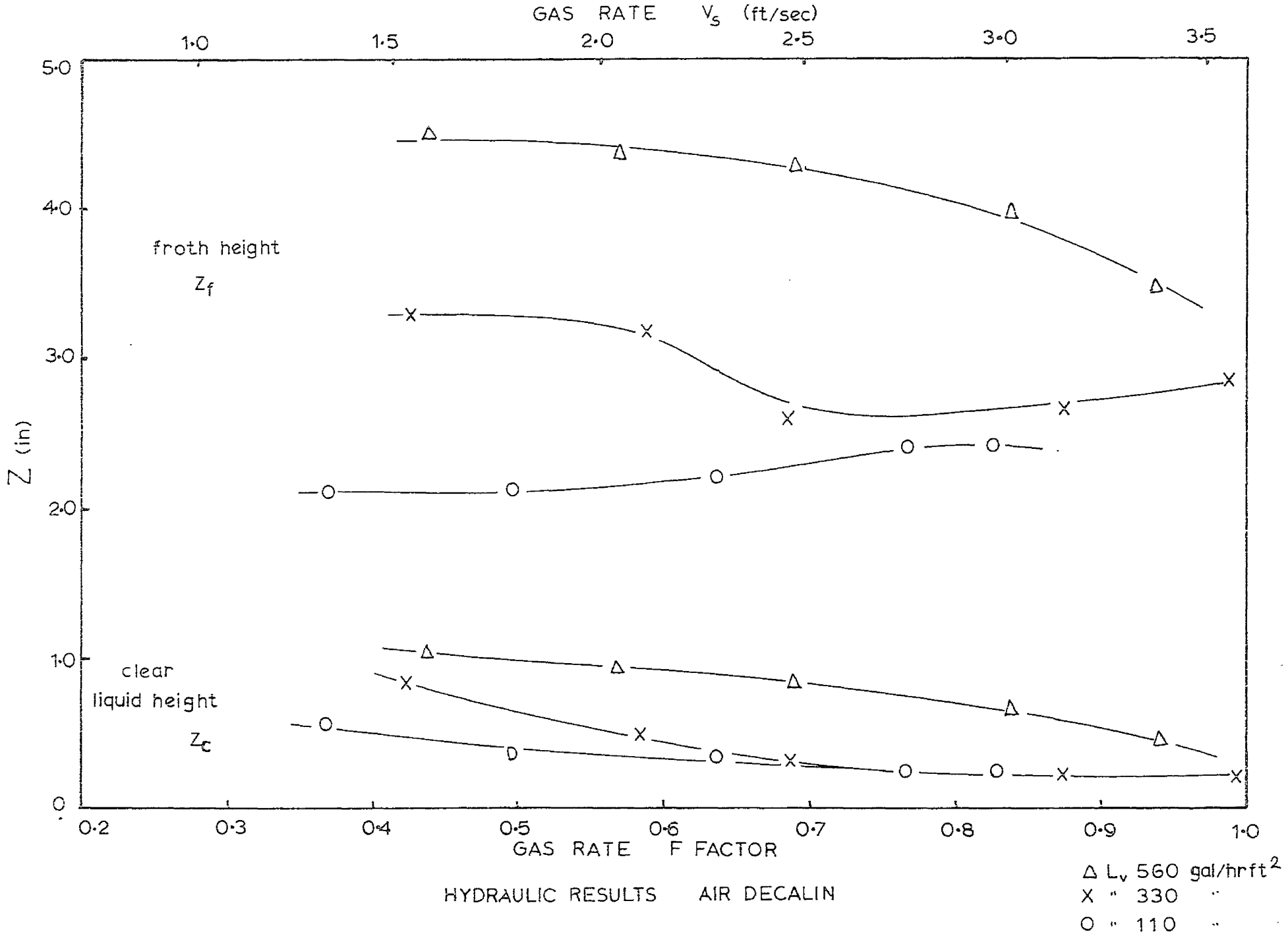
FIG.4.1.

hydraulic results air water system



HYDRAULIC RESULTS — AIR CARBON TETRACHLORIDE

FIG. 4.2.



HYDRAULIC RESULTS AIR DECALIN

FIG. 4.3.

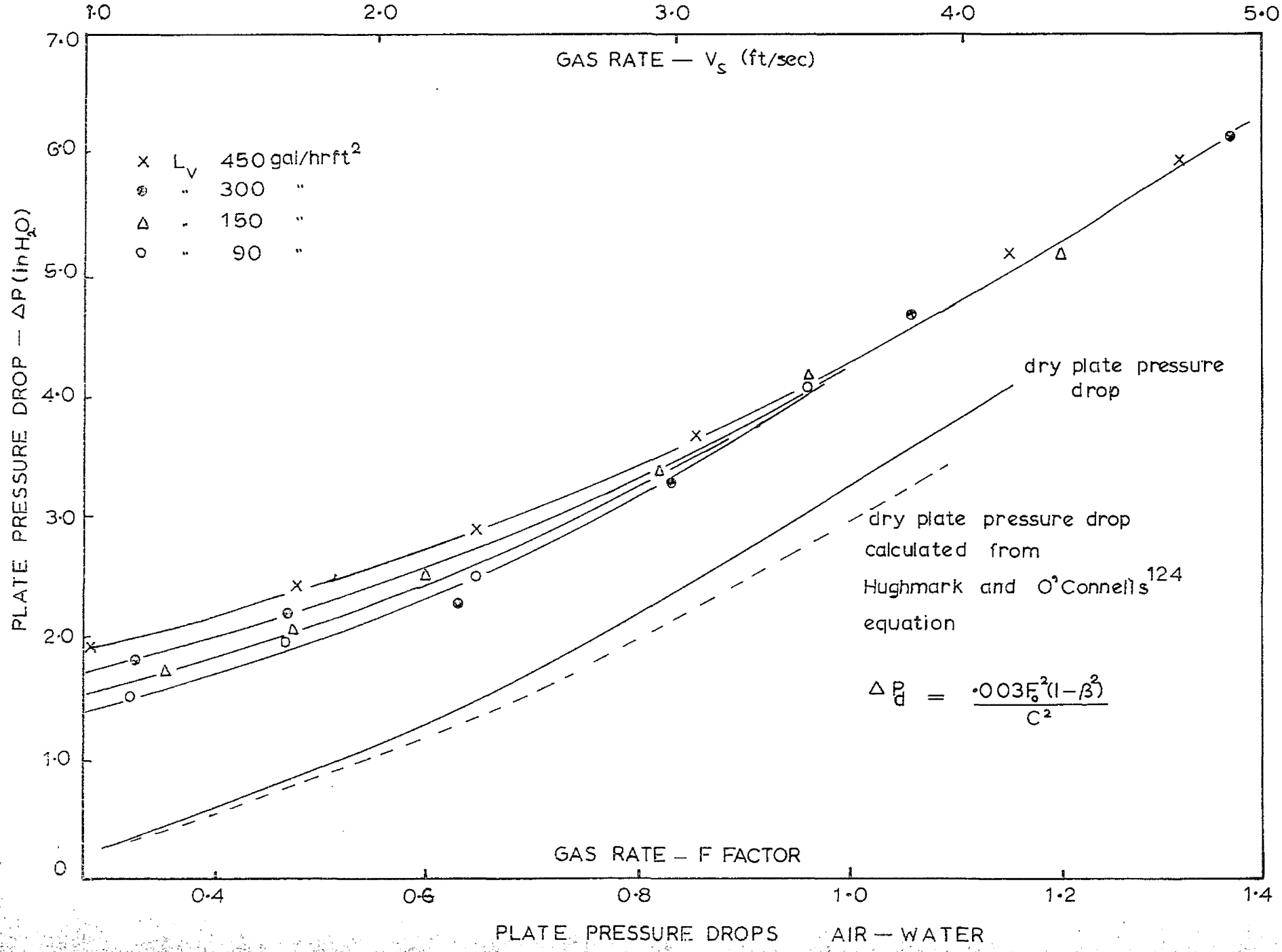


PLATE PRESSURE DROPS AIR — WATER

FIG. 44

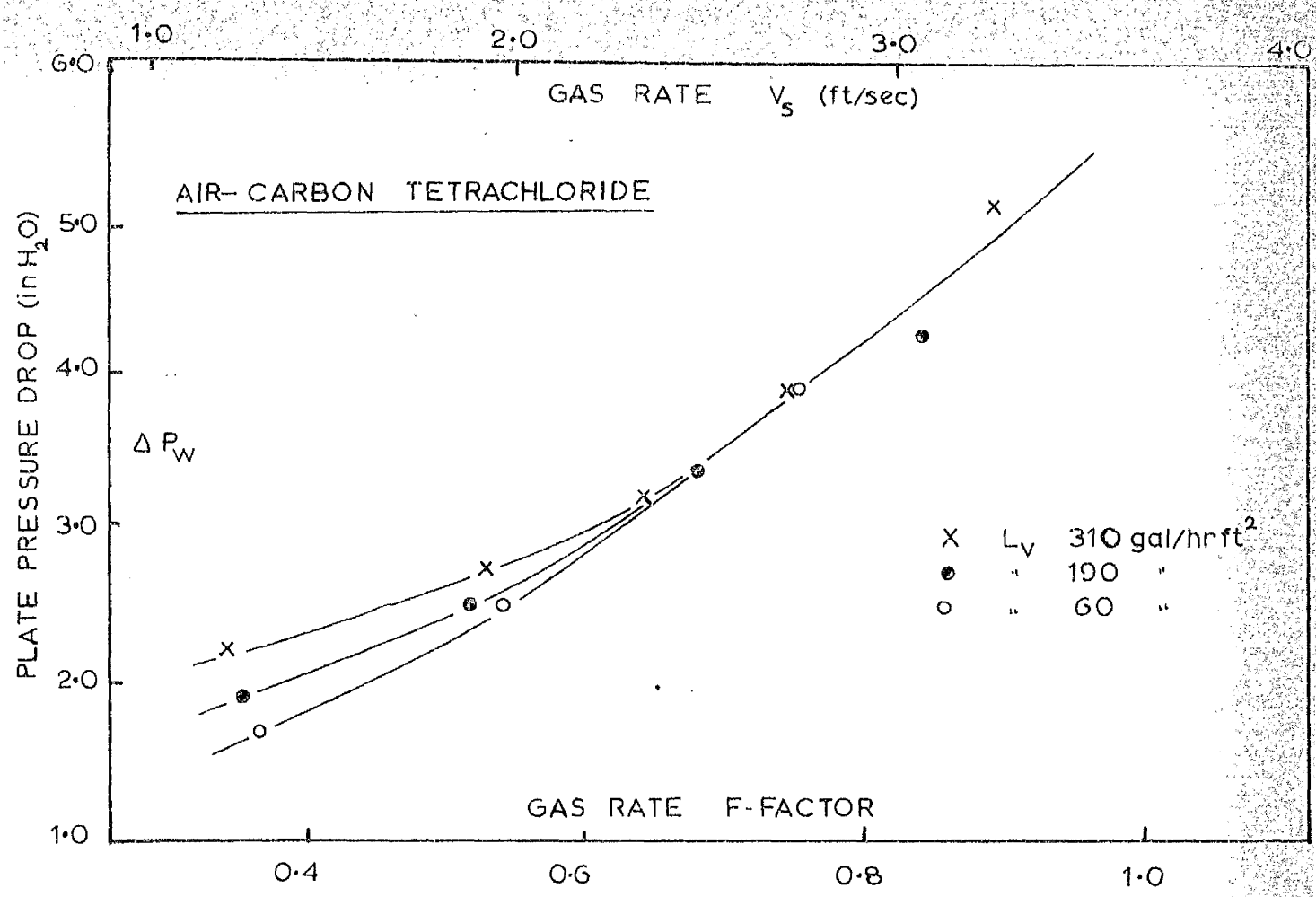

GAS RATE V_s (ft/sec)
AIR– CARBON TETRACHLORIDE
PLATE PRESSURE DROP (in H_2O)
ΔP_W
X L_V 310 gal/hr ft^2
● " 190 "
○ " 60 "
GAS RATE F-FACTOR

FIG. 4.5.

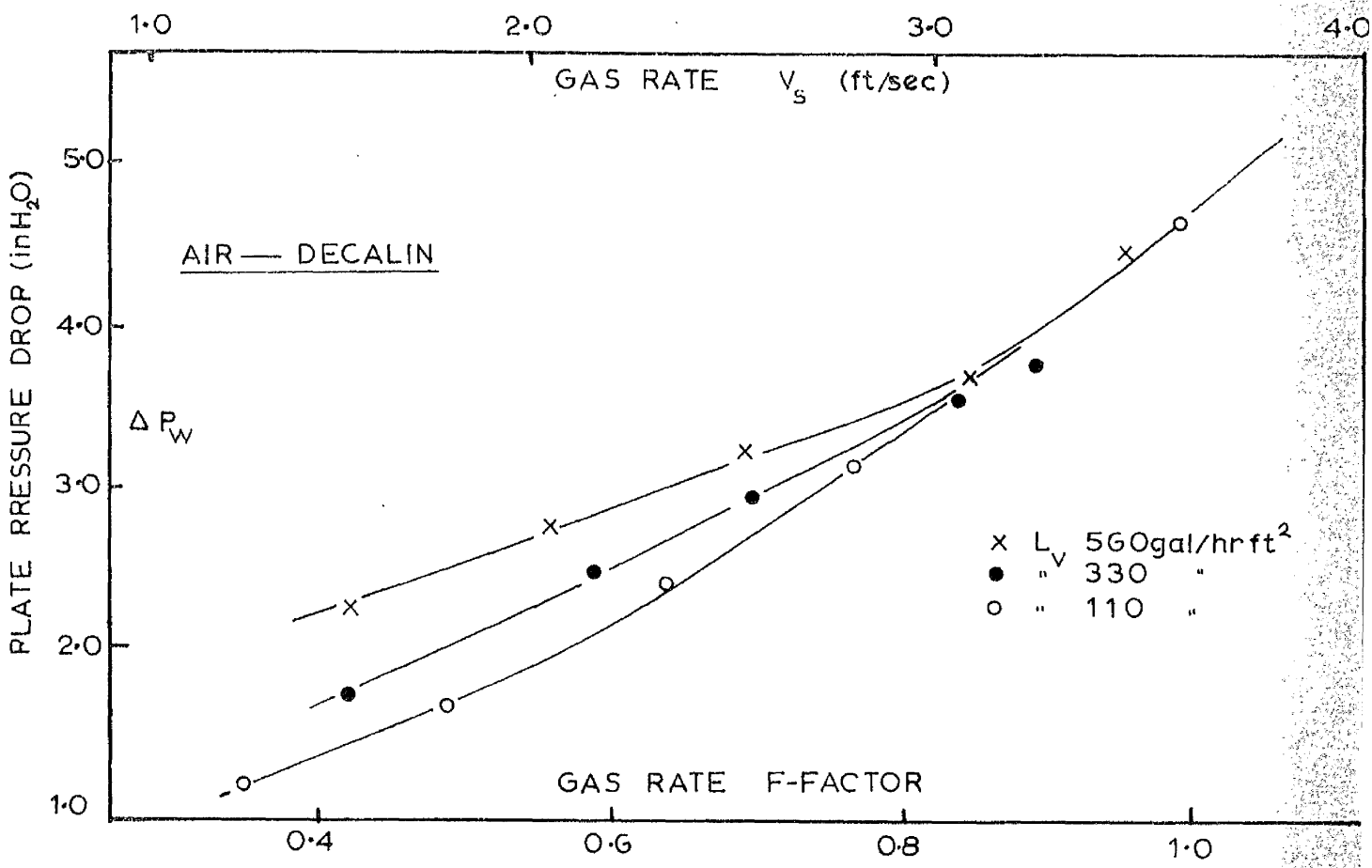

GAS RATE V_s (ft/sec)
AIR — DECALIN
PLATE RRESSURE DROP (in H_2O)
ΔP_W
X L_V 560 gal/hr ft^2
● " 330 "
○ " 110 "
GAS RATE F-FACTOR

FIG. 4.6.

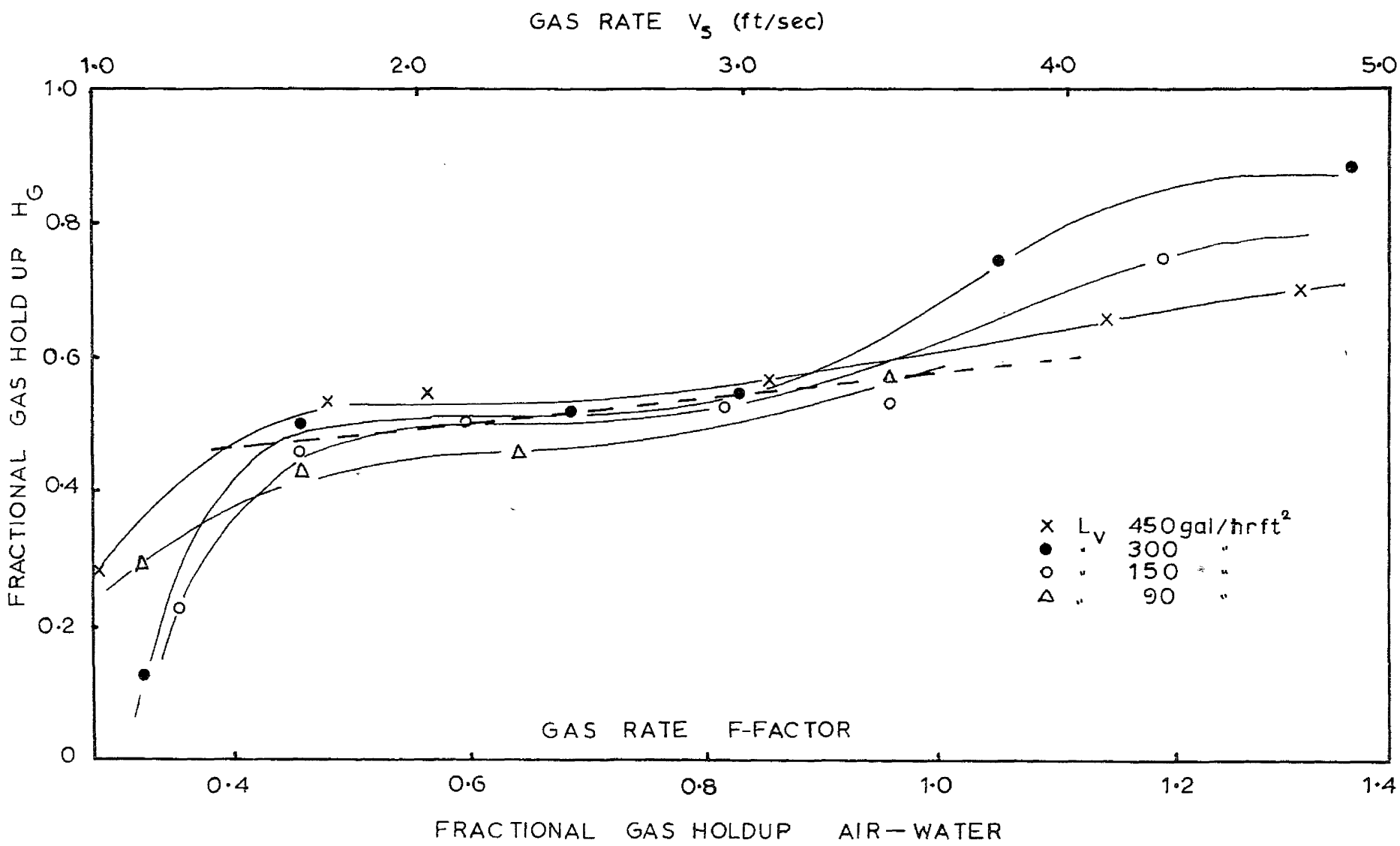

GAS RATE V_S (ft/sec)
1·0
2·0
3·0
4·0
5·0
FRACTIONAL GAS HOLD UP H_G
1·0
0·8
0·6
0·4
0·2
0
× L_V 450 gal/hr ft²
● " 300 "
○ " 150 "
△ " 90 "
GAS RATE F-FACTOR
0·4
0·6
0·8
1·0
1·2
1·4
FRACTIONAL GAS HOLDUP AIR—WATER

FIG. 4.7.

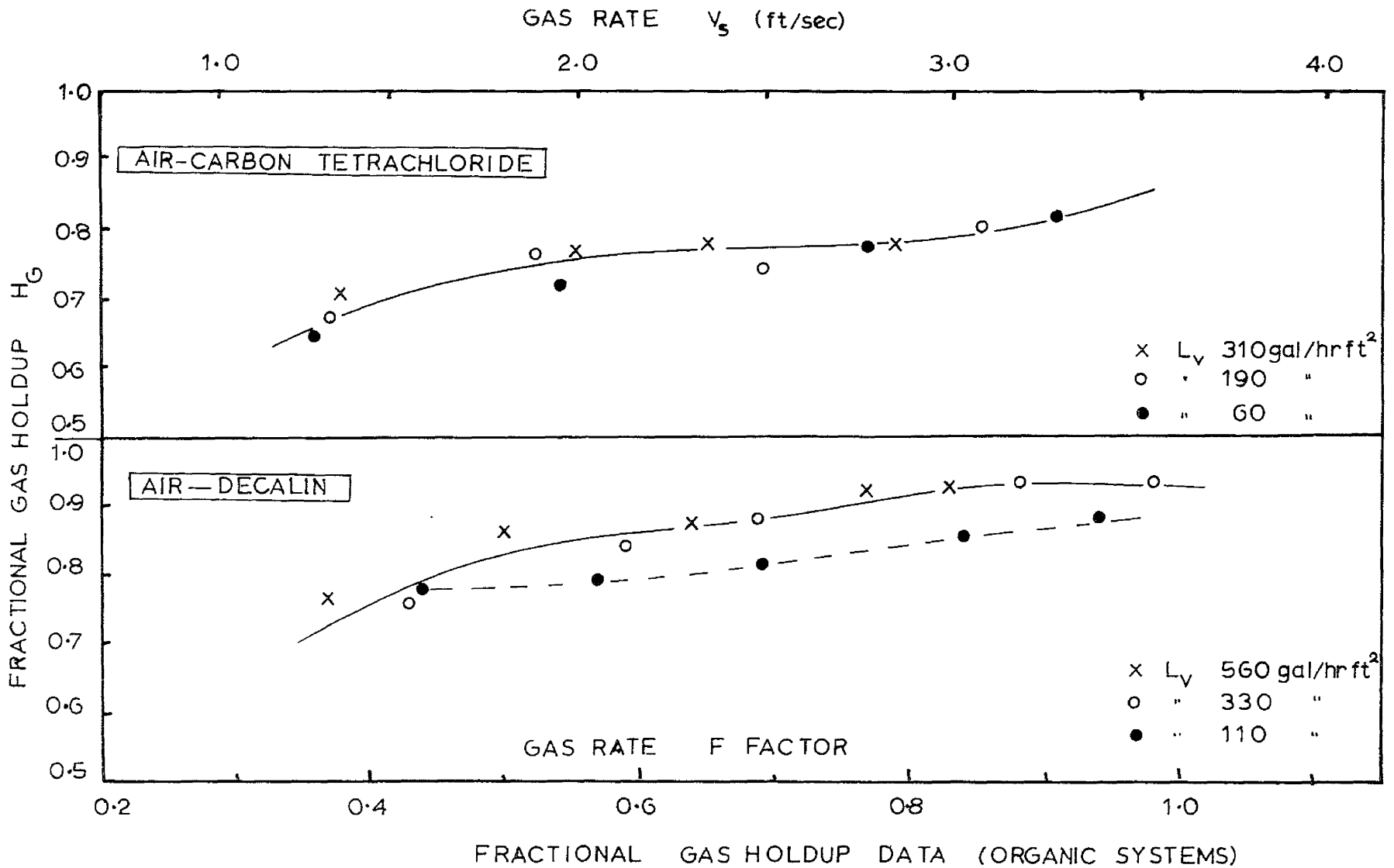
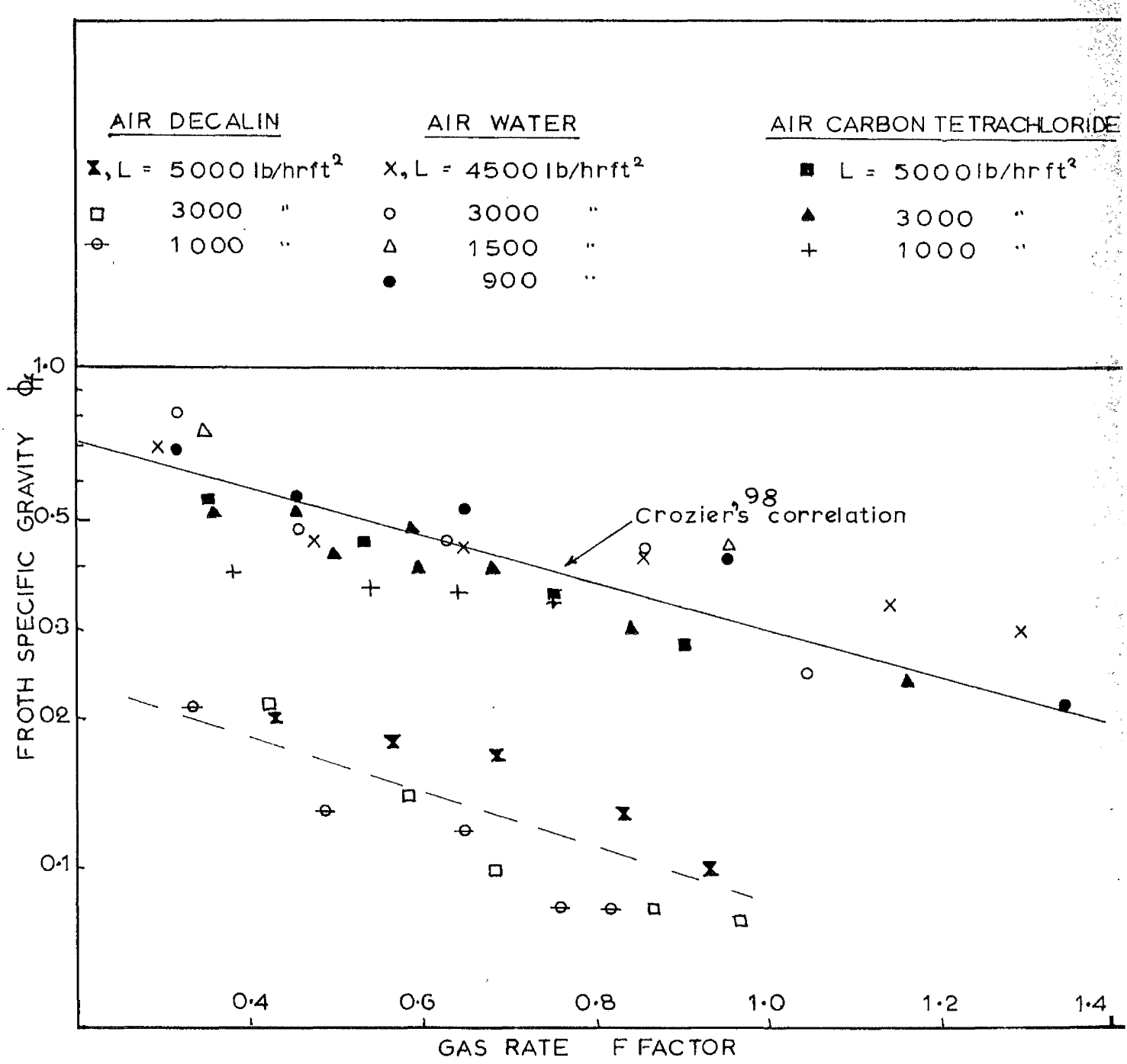
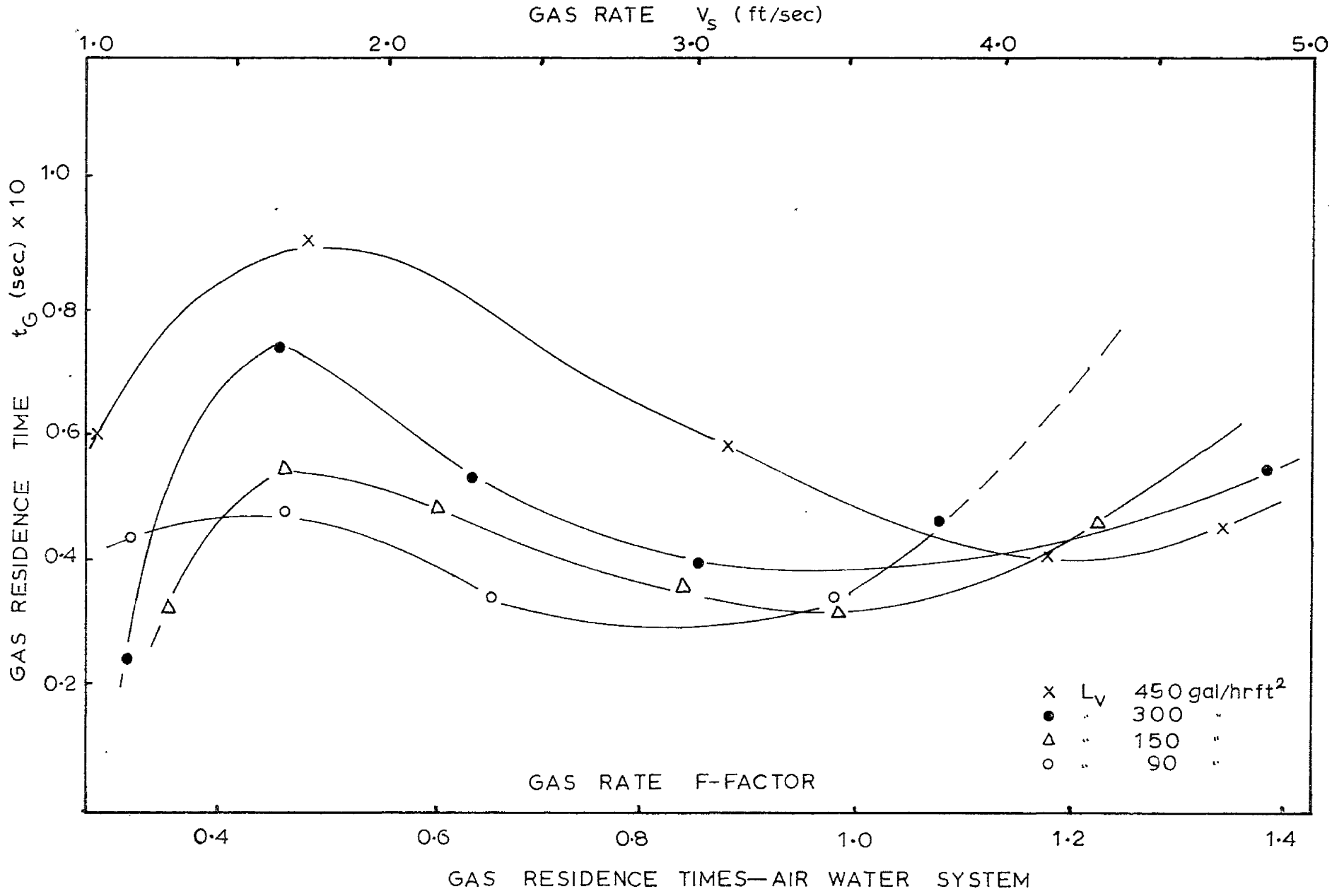

GAS RATE V_s (ft/sec)
1·0
2·0
3·0
4·0
AIR-CARBON TETRACHLORIDE
× L_V 310 gal/hr ft²
o " 190 "
● " 60 "
AIR—DECALIN
× L_V 560 gal/hr ft²
o " 330 "
● " 110 "
FRACTIONAL GAS HOLDUP H_G
1·0
0·9
0·8
0·7
0·6
0·5
GAS RATE F FACTOR
0·2
0·4
0·6
0·8
1·0
FRACTIONAL GAS HOLDUP DATA (ORGANIC SYSTEMS)

FIG. 4.8.



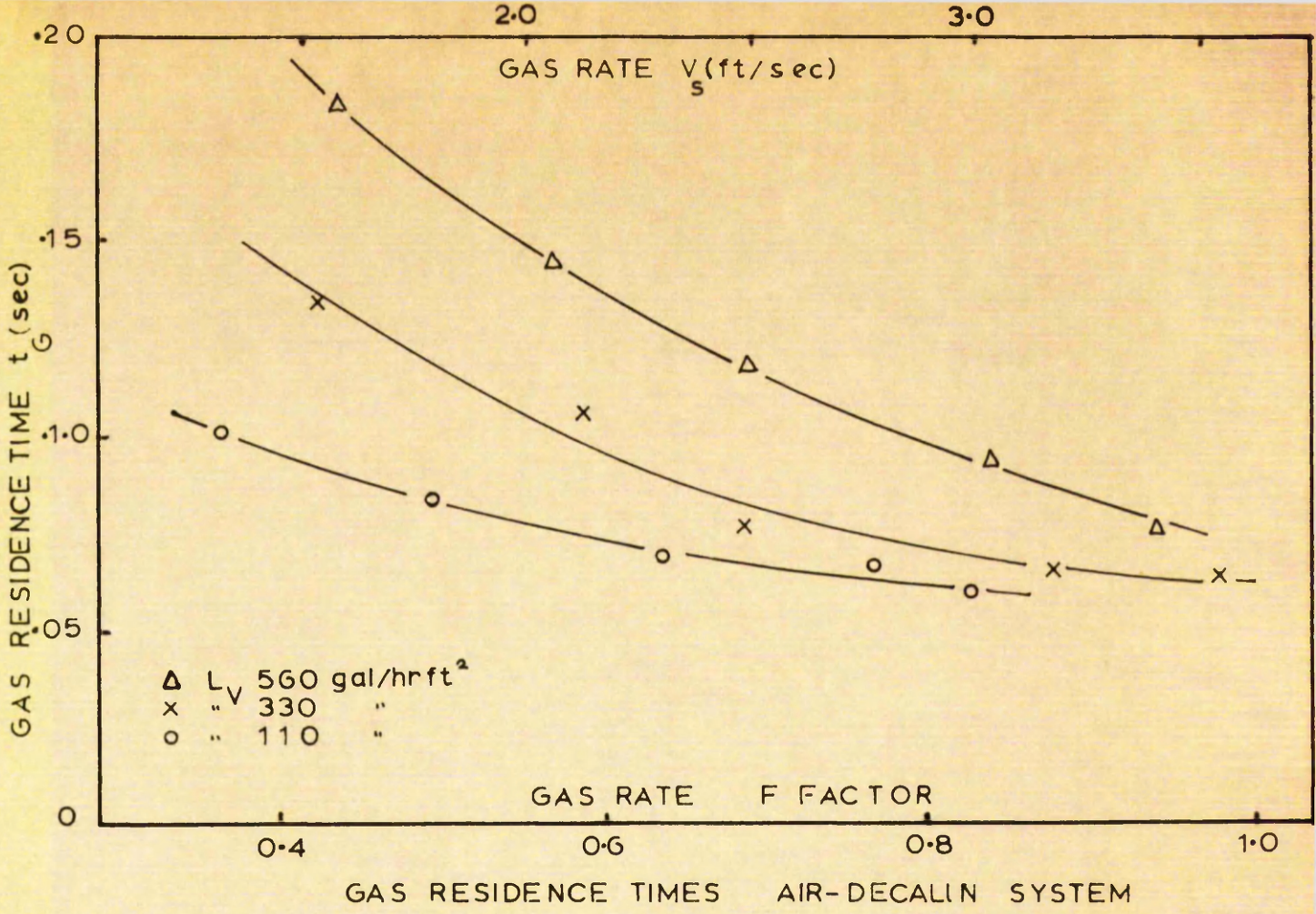
EFFECT OF GAS RATE ON SPECIFIC GRAVITY OF FROTH

FIG. 4.9.



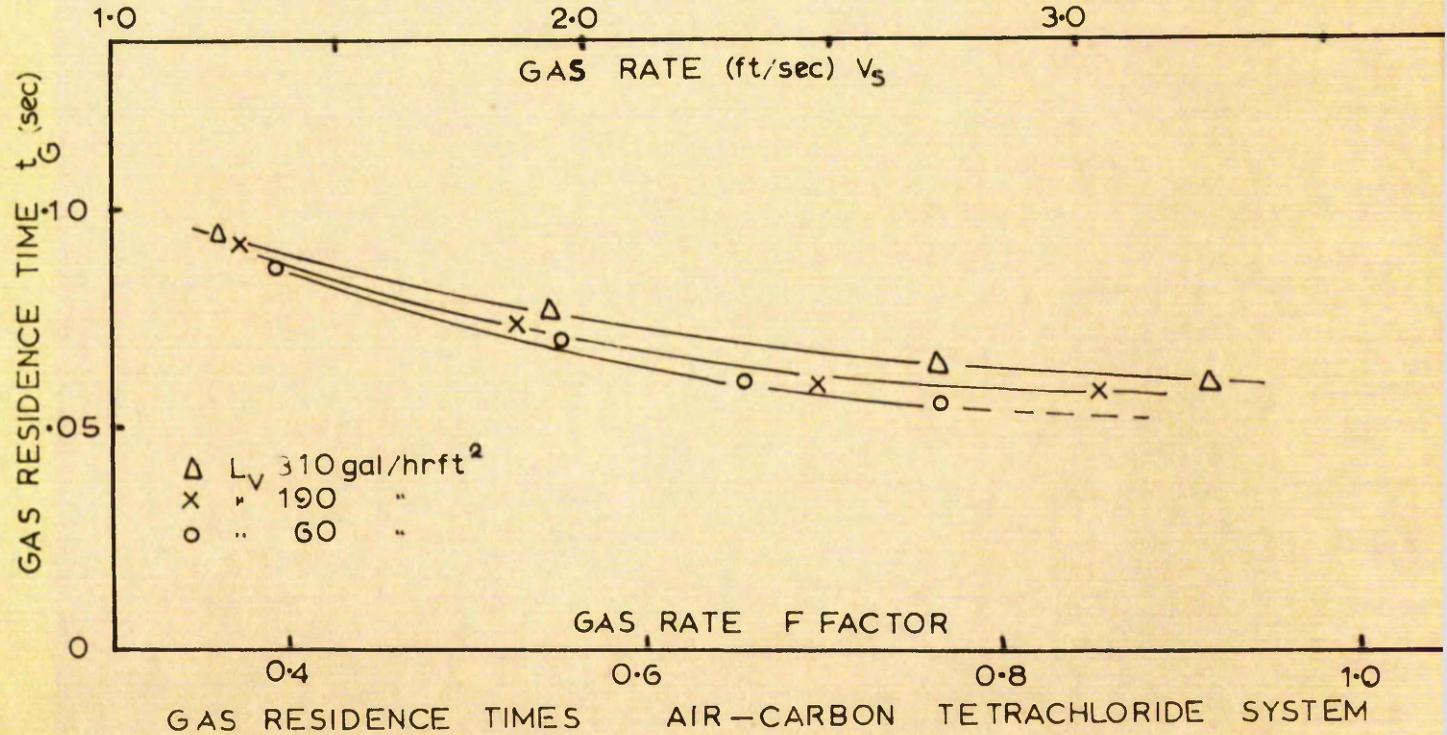
GAS RESIDENCE TIMES—AIR WATER SYSTEM

FIG. 4.10.



GAS RESIDENCE TIMES AIR-DECALIN SYSTEM

FIG. 4.11.



GAS RESIDENCE TIMES AIR—CARBON TETRACHLORIDE SYSTEM

FIG. 4.12.

5. MASS TRANSFER STUDIES

5.1. AIR/WATER SYSTEM

5.1.1. Apparatus

The vapour-liquid contacting device was the 9 in sieve plate, used in the absorption experiments and described fully in Appendix E. This was fitted in a 6 ft high glass column. Air was supplied by a centrifugal fan which could provide velocities up to 3.6 ft/sec through the column, and this was drawn from the laboratory through three thermostatically controlled heaters rated at 1, 1.5 and 2 kW. Liquid was delivered to the plate by a small centrifugal pump and was returned to a 3 gallon sump tank, which was connected to the pump suction. The tank was heated by a thermostatically controlled 700 W heater, which was also fitted with a rheostat to alter the wattage. The apparatus used is shown on Plates 1 and 2.

The air flow was measured by an orifice plate fitted between the column and a calming section upstream from the fan. The pressure drop across the plate was measured by a two-liquid manometer which was approximately four times as sensitive as an equivalent water manometer.

Liquid flow was measured by a Fischer & Porter flowmeter with interchangeable tubes and floats.

Temperatures were measured at the air inlet to the column and at the inlet and outlet weirs on the plate with thermometers reading to 0.1 deg C.

The inlet humidity was measured by a suction psychrometer as described in Appendix F giving an accuracy of within 1%.

The mass of water in the sump was measured by an inclined manometer to 0.1 lb.

The dye concentration was measured to within 0.1% by a Cambridge Unicam 1500 absorptiometer.

5.1.2. Experimental programme

Preliminary experiments showed that the effect of gas rate on efficiency was somewhat complex and that the effect of liquid rate on efficiency was linear. It was thought that the gas rate-efficiency curves would be more accurately obtained by cross plotting data from liquid rate-efficiency plots at five different gas rates as, the relationship in the latter case being linear, fewer experimental values need be obtained than those necessary to define a complex curve.

The liquid rate was varied from the minimum to the maximum operating conditions of the plate i.e. from 70 to 800 gal/hr ft^2. The air rates were varied from 1.49 to 4.54 ft/sec, the velocity being based on the bubbling area of each plate.

5.1.3. Experimental procedure

As the apparatus was run at an inlet air temperature of 60°C to give a high rate of evaporation of water, it was necessary to calculate the inlet air wet-bulb temperature, as it was not easy to measure it directly with sufficient accuracy. The laboratory air humidity was measured by the psychrometer and prepared charts enabled the wet bulb temperature corresponding to a dry-bulb temperature of 60°C to be arrived at quickly.

Once this value was known the air fan was switched on and the flow set approximately to a prearranged value. The thermostatically controlled heater or heaters appropriate to the air flow was switched on and set to 60°C. The water circulation was started and the flow set at a predetermined value. The water heater was switched on and the thermostatic control set to the value of the wet-bulb temperature of the air entering the column. Once the system was at the working temperatures, the voltage (and hence power) to the water heater was reduced and

the apparatus was allowed to run for ten minutes to ensure that equilibrium adiabatic conditions were achieved.

About 1 gm of dye was added to the water, and after three minutes to allow for complete dispersion the run was started.

Readings were taken at equal time intervals, the duration of the interval depending on the length of run which was decided previously. The following sets of readings were recorded during each run:-

Wet and dry-bulb temperatures of the ambient air.
Sump liquid level.
Air flow manometer reading.
Water flow rate.
Inlet and outlet temperatures of the liquid on the plate.

Samples of the water leaving the plate were also taken after each set of readings.

The wet-bulb temperature of the air entering the column was computed from the prepared charts after each set of readings and the thermostatic control of the water was adjusted to the new value, if necessary. It was generally possible to analyse the samples for dye concentration immediately after taking.

After the requisite number of readings and samples had been taken, i.e. after the volume in the sump tank had diminished by approximately 30%, the heaters and liquid and air pumps were switched off and the water was allowed to drain back into the sump tank. The contents of the sump tank were drained into a stainless steel bucket, and weighed.

The sump tank scale readings were plotted against time and the mean line used in preference to actual readings to give the volume of water lost during the run. This procedure obviated any errors arising from taking only two readings, at the beginning and end of a run.

The dye concentration in the samples was also plotted against time. As concentration is proportional to optical density at the low concentrations used, the concentration may be expressed as optical density since the calculations do not necessitate knowledge of absolute concentration.

An objection to the previous workers'[30,106] analysis of the problem was that they assumed the rate of concentration of solute to be linear with time and ~~only~~ took samples only at the beginning and end of each run. This is not valid as the rate of change of concentration is inversely proportional to the square of the ~~rate of change of the~~ volume of the solution, (see Appendix B) hence the graph of concentration against time has an exponential relationship. Consequently the average value for the concentration of the dye during a run should be taken from the curve, and not, as the previous workers had assumed, on the arithmetic mean of the initial and final concentrations.

5.1.4. Calculation of results

Calculation is complicated by the fact that some dye is lost continuously in the form of entrained droplets of solution from the system. It is assumed that the dye lost is at the average concentration this being justifiable because the concentrations are below 0.01%. A mass balance then gives:-

$$W_e C_A = W_1 C_1 - W_2 C_2$$

$$\therefore W_e = \frac{W_1 C_1 - W_2 C_2}{C_A}$$

mass of water due to loss by humidification only,

$$= W_h = W_1 - W_2 - W_e$$

Where C_1 = initial concentration of dye
C_2 = final concentration of dye
C_A = average concentration of dye
W_1 = initial mass of water
W_2 = final mass of water
W_e = mass of water lost by entrainment

In this experiment only W_2 is measured and the mass M of water lost by all methods from the system,

$$W_e = \frac{(W_2 + M)\, C_1 - W_2 C_2}{C_A} \qquad C_A = \frac{\int_{t_1}^{t_2} C\, dt}{t_m}$$

$$= \frac{MC_1}{C_A} - \frac{W_2(C_2 - C_1)}{C_A}$$

C in optical density units

t_m is mean time over run

and $W_h = M - W_e$

Then if t is time of run in hours, G_a is flow of air in lb/hr. then Δ h, the increased humidity of the outlet air in grain/lb is given by $\Delta h = \frac{W_h \times 7{,}000}{G_a \times t}$

and Murphree gas film efficiency is

$$E_{MV} = \frac{\Delta h}{h_e - h_i}$$

h_i is inlet humidity, grain/lb

h_e is equilibrium humidity, grain/lb

The value of the equilibrium humidity is taken as the humidity of air at a wet-bulb temperature equivalent to that of the mean of the inlet water temperature on the plate and the calculated wet-bulb temperature of the inlet air. These two temperatures and the outlet water temperature were usually within 0.1 deg C of each other.

Specimen Calculation

Run 11, data from Table 5.2.

Mass of water at end of run = 18.4 lb (weighed)

(corrected for weight of samples) = 18.7 lb

Scale reading at beginning and end of run = 54.2 and 26.4

(from mean line through 9 points)

$\therefore$ M = (54.2 - 26.4) 0.321 (0.321 is calibration factor

= 8.91 for sump tank)

C_A is obtained by measuring area under the curve of optical density against time with a planimeter, and dividing the area by the mean time. C_1 and C_2 are also taken from the graph.

$$\therefore W_e = 8.91 \times \frac{0.266}{0.309} - 18.7 \times \frac{0.361 - 0.266}{0.309}$$

$$= 7.66 - 5.75$$

$$= 1.91 \text{ lb}$$

$$W_h = 8.91 - 1.91 = 7.00 \text{ lb}$$

$$\Delta h = \frac{7.00 \times 7,000}{270 \times 2.0} = 90.8 \text{ grain/lb}$$

$$h_e = 173.2 \text{ grain/lb}$$

$$E_{MV} = \frac{90.8}{173.2 - 58.0} = \frac{90.8}{115.2} = 77.8\%$$

$V_S = 3.34$ ft/sec. $\qquad L_V = 200$ gal/ft^{2}hr

$F = .86$

5.1.5. Results

The results are listed in Tables 5.1, 5.2. The effect of gas rate and liquid rate on plate efficiency, E_{MV} is shown on Figs. 5.1 and 5.2 and on number of transfer units, N_{OG} on Figs. 5.3. and 5.4.

5.2. AIR/CARBON TETRACHLORIDE SYSTEM

5.2.1. Apparatus

The equipment used was an integral part of the gas absorption apparatus. The plate used was the same plate as in the air-water tests and was identical to the one used in the absorption experiments, and was installed in the humidification column of the absorption apparatus. The results reported were obtained on the modified apparatus (Section 5.3.2.). Air was drawn into the column from the laboratory and met a downcoming stream of pure carbon tetrachloride on the plate, The air/carbon tetrachloride mixture passed via a wire mesh type demister to the absorption tower. The unevaporated carbon tetrachloride was recycled to a storage tank. The apparatus is more fully described in section 5.3.

5.2.2. Experimental programme

As many tests were carried out simultaneously with the absorption tests, the plate could not be operated independently. Information derived from simultaneous experiments was supplemented by individual humidification runs to give a comprehensive study of the effect of gas rate on efficiency at three liquid rates. The range of gas velocities was from 1.40 to 3.40 ft/sec, based on the bubbling area; the liquid rates were 1300, 3000 and 5000 lb/hr ft^2 of plate cross sectional area.

5.2.3. Experimental procedure

Before the start of a humidification (or absorption) run, the gas analysis unit was switched on and the meter purged by drawing through a sample of air from the laboratory by means of a water ejector powered by a small centrifugal pump. The automatic temperature recorder was also switched on to allow the electronic components to come to their working temperature. When

the analyser was completely purged and warmed up, the air blower was started and the flow set to a mean value. The pumps delivering decalin to the absorption plate and stripping tower were started and the flow rates adjusted to convenient values. These values were not critical unless an absorption run was being done simultaneously and were not measured but were of the order of 30 and 100 gal/min respectively. The carbon tetrachloride pump was switched on and the flow rate was adjusted to a pre-designated value. The two-way manifold on the gas analyser was switched over to allow a sample of air/carbon tetrachloride mixture to flow through the analyser under its own pressure. The water aspirator was switched off, and the flow through the meter was adjusted by means of the needle valve to the correct value as indicated by the float gauge provided on the instrument.

The air flow was then adjusted to approximately the desired value. It was not possible to set the air flow to a pre-determined value as the flow could only be obtained from an involved calculation because the orifice plate meter was originally intended to measure the flow to the absorption column. This meant that the parameter for measurement of gas and liquid rate effects on mass transfer had to be liquid rate and no gas rate parameter studies were undertaken.

The thermostatically controlled heating tapes were then switched on with the automatic temperature recorder drive. The temperatures were scrutinised carefully and when they and the value of the carbon tetrachloride concentration on the indicator were steady, usually after a period of 5-10 minutes, depending on ambient temperature, the run was started.

Readings were taken every three minutes for nine minutes of the air manometer, column pressure manometer, and carbon tetrachloride liquid Rotameter. The value of the carbon tetrachloride concentration was also noted. Between actual readings a watch was kept on the concentration, the flow rate

through the analyser, and the various temperatures, to ensure equilibrium conditions were always maintained. After the nine minute run period, the heating tapes were switched off and the carbon tetrachloride pump stopped. After a few minutes delay to clear the system of carbon tetrachloride vapour, the decalin and then the air pump was switched off. The ancillary equipment e.g. analysis unit, were then switched off.

The atmospheric pressure was read on a standard Fortin barometer.

5.2.4. Calculation of results

The recorded data were scanned and runs were rejected if variations in temperatures were more than 4 deg F. The readings were then averaged prior to calculations. The orifice meter measured the flow of gas entering the absorption column and from the concentration of carbon tetrachloride in the gas, as measured by the gas analyser, the flow of air entering the absorption column could be calculated. As this had to be equal to the flow of air entering the humidification column, the superficial velocity V_S and the F factor could be calculated for the humidification system.

The number of transfer units Ng was calculated by comparison of the enthalpies of the gas above and below the plate with the enthalpies of gas at the temperatures of carbon tetrachloride entering and leaving the plate. The method used was developed for use with air/water systems and a modified enthalpy was used. The method of Carey and Williamson[110] was used to evaluate the integral. Humidities and other properties of air/ carbon tetrachloride mixture were taken from achart published in Chemical and Metallurgical Engineering[114] reproduced here as Fig. 5.11.

Plate efficiencies were calculated by the formula

$$N_{OG} = -\ln(1 - E_{MV})$$

Specimen calculation

Run 2

Air rate

The flow of air entering the absorption column is calculated using the method in the specimen calculation in section 5.3 on gas absorption. Run 2 of the air/carbon tetrachloride experiments was done simultaneously with run 1 of the gas absorption experiments, hence flow of air entering absorption column

= 289 lb/hr ft^2 of column area

Flow of air entering humidification column

= 289 lb/hr ft^2 of column area

humidification column pressure = 76.1 cm Hg

inlet air temperature = 62°F

∴ density of air entering = .071 lb/ft^3

∴ velocity of air entering humidification column

$$= \frac{289}{.071 \times 3600} = 1.13 \text{ ft/sec.}$$

superficial velocity, V_s = 1.13 x 1.26

i.e. velocity based on bubbling area = 1.42 ft/sec.

Number of transfer units

N_{OG} is calculated from the formula

$$N_{OG} = \int \frac{di\, G}{i_L - i_G}$$

The enthalpies, i. are given by the equation,

$$i = C_S r\, T + \lambda_o H$$

for air/carbon tetrachloride

$C_S r$ = 0.44 - Treybal page 169

λ_o = 90.4 Btu/lb Fig. 5.11

The value of the integral is calculated as follows:-

	Above plate (1)	Below plate (2)	Average
Temperature of carbont tetrachloride ^{o}F	63	49	56
i_L Btu/lb	84.7	58.7	69.7
i_G Btu/lb	39.2	16.0	27.6
Δi Btu/lb	45.5	42.7	42.1

$$\frac{\Delta i\ (av)}{\Delta i\ (1)} = 0.93 \qquad \frac{\Delta i\ (av)}{\Delta i\ (2)} = 0.99$$

value of factor, f, from Carey-Williamson chart

$$= 1.01$$

$$N_{OG} = \frac{39.2 - 16.0}{42.1 \times 0.99} = \frac{0.58}{}$$

5.2.5. Results

These are given in tabular form in Table 5.3. The effect of gas rate on mass transfer is shown on Fig. 5.5 as F factor against N_{OG}, the number of transfer units and on Fig.5.6 as superficial velocity, V_s, against E_{MV}, the plate efficiency.

5.3. GAS ABSORPTION SYSTEM

5.3.1. Apparatus:- original design

The apparatus as originally built had three towers, the humidification, absorption and steam stripping towers, and was designed to operate continuously. The towers were built of copper sections 9 in diameter, 9 in high, with brass flanges, with the exception of three glass sections installed to enable visual measurements to be made where necessary. The absorption and humidification towers contained six, and the steam stripping tower eight, sections. The purpose of the humidification tower was to provide a mixture of air and carbon tetrachloride vapour. One sieve plate was used to allow study of its performance, and gave a mixture of about 4-6% by volume of carbon tetrachloride in air. There were three continuous circuits in the original design, the vapour, decalin and carbon tetrachloride circuits.

Gas circuit. The stripped air/carbon tetrachloride mixture leaving the absorption tower (about 2% concentration of carbon tetrachloride by volume) was pumped by a lobe-blower to the humidification tower through 4 in diameter copper piping. On the sieve plate in the tower the rising gas came into contect with liquid carbon tetrachloride flowing across the plate, and the gas left the plate enriched in carbon tetrachloride, the concentration being 4-6% by volume. Before leaving the top of the column, entrained droplets of carbon tetrachloride were removed by a 'Knitmesh' de-mister and the gas vapour mixture passed through a 4 in diameter pipe to the bottom of the absorption tower. An orifice meter was inserted in the 4 in diameter line to measure the gas flow. The carbon tetrachloride enriched air then rose through the absorption column contacting a stream of decalin on the perforated plate which was sited between the second and third sections (numbering from the bottom) both of

glass. A sheet of perforated zinc was installed between the first and second sections in an attempt to smooth out fluctuations in the gas flow. The air, now stripped to a concentration of about 2% carbon tetrachloride by volume, left the tower via a demister identical to that installed in the humidification tower, and was drawn once more through the blower. The gas space above the plate in the tower was three sections high and it was intended that this space would permit the entrained droplets to disengage naturally rather than impinge upon other surfaces whereupon additional mass transfer might take place. Gas sampling devices, see Fig. 5.13, were installed immediately below the plate and as far above the plate as was possible. These devices were designed to take a uniform sample across the column and to permit disengagement of any entrained or weeping droplets using the principle of the cyclone separator. The analytical technique is described in detail in Appendix D. Two heating tapes, 1 and 2 kW respectively were wound round the length of pipe from the top of the humidification tower to the bottom of the absorption tower. The 1 kW tape was fitted with thermostatic controls, so that once the vapour had been heated up to the required working temperature by the combination of tapes, the larger could be switched off and the temperature could be held accurately to the value required.

Thermocouples were inserted in the vapour line, above and below the humidification plate, in the line leaving the humidification tower, and above and below the absorption plate. These thermocouples were connected to a Honeywell 24-point temperature recorder which recorded a temperature every two seconds.

Decalin circuit. Decalin was drawn from a 50 gallon storage tank and pumped by a centrifugal pump to the top of the absorption column. From there the decalin flowed down a 3/4 in diameter

tube to the perforated plate behind the inlet weir. There was a clearance of 1/4 in between the tube and the plate. After traversing the plate and contacting the rising gas the carbon tetrachloride enriched decalin flowed from beyond the exit weirs down twin 1 in diameter flexible downcomers. After a vertical distance of one foot to allow for disengagement, the downcomers were joined by a 'Y'-piece to a single 1 in diameter copper tube which ran down the centre of the column and was brazed to the bottom section. Exterior to the bottom section a glass 3/4 in diameter tube joined to the bottom section by flanges led the decalin via a 'U' seal to another 50 gallon storage tank.

From there the 'rich' decalin was pumped by a similar pump to the top of the steam stripping column which contained six plates each with a single bubble-cap. In the column the decalin was contacted with low pressure steam, 2-3 lb/in^2 to strip the decalin of carbon tetrachloride. From the bottom of the column a mixture of stripped decalin and water from the condensed steam flowed via a 'U' seal to a tun dish, providing a constant head for an Alfa-Laval disc-type bowl centrifuge, which had a capacity of 50 gallons per hour. This machine separated the water, which was sent to drain, and the decalin, which was pumped by a gear pump via an Alfa-Laval plate cooler to the original storage tank to complete the cycle.

The line from the pure or 'lean' decalin storage tank to the top of the absorption tower was wrapped in a 500 W and 750 W heating tape, the 500 W tape being thermostatically controlled. Thermocouples recorded the temperature of decalin in the absorption tower at the entrance and exit weirs, entering the steam stripping tower, and entering and leaving the plate cooler. The temperature of the lean decalin leaving the centrifuge was also indicated on a Rototherm dial thermometer.

Carbon tetrachloride circuit. Carbon tetrachloride was stored in a 20 gallon tank and was delivered from there to the top of the humidification tower by a vane pump of the type used in petrol pumps. After humidifying the gas stream the remaining carbon tetrachloride was returned to the storage tank via a 'U' seal. The flow of carbon tetrachloride was controlled by a gate valve, (the pump having a built in by-pass system) and was measured by a Rotameter. A thermostatically controlled 500 W heating tape was wound round the line to the humidification tower to adjust the liquid temperatures to the desired value. Thermocouples measured the temperature of carbon tetrachloride entering the humidification tower, in the entrance and exit weirs and returning to the storage tank.

The mixture of carbon tetrachloride vapour and steam from the top of the steam stripping tower was condensed in a tube and shell condenser, and the condensate was passed to a glass gravity separator. The water was led to drain and the carbon tetrachloride was returned to the storage tank.

Difficulties occurring in original design. A few preliminary runs showed that the carbon tetrachloride collected in the phase separator contained unacceptable quantities of decalin, about 30% by weight usually. This could not, of course, be returned to the carbon tetrachloride storage tank and had to be collected in an additional storage tank. This immediately negated the concept of continuous operation, as the length of run was governed by the amount of pure carbon tetrachloride available and introduced another lengthy process of recovery. Another even more disturbing feature was that the carbon tetrachloride appeared to hydrolyse in the steam stripping tower. Samples of water from the tower were found to contain considerable quantities of chloride ion. This resulted in corrosion of the column walls and plates and the

products of corrosion were carried to the centrifuge where they were deposited on the centrifuge discs. These deposits seriously reduced the capacity of the centrifuge which was at best too small, and the output of stripped decalin could not match the rate at which lean decalin was used in the absorption tower; once again the length of run depended on the quantities of material originally available. Eventually the fresh carbon tetrachloride picked up moisture from the air and itself became a corroding agent and the results of corrosion repeatedly blocked the very fine filter in the carbon tetrachloride pump, thus delivery of a constant volume of fluid to the humidification tower could not be maintained in many runs. Furthermore, the flowmeters were of the design in which the float travels up and down a central steel wire, which tended to corrode, causing the float to stick frequently and rendering impossible attempts at maintaining steady flow conditions.

Attempts were made to cut down the contamination of carbon tetrachloride by decalin in the phase separator by varying the flow rates of steam and rich decalin to the steam stripping tower, but although improvements were made it was impossible to cut down the concentration of decalin to an acceptable value, and this defect of the system had just to be accepted.

The contaminated carbon tetrachloride was fractionated batchwise under vacuum in a 6 in diameter 12 ft high packed column. The fractionation was stopped when the concentration of carbon tetrachloride in the kettle was about 5-10% and this residue was returned to the rich decalin tank for steam stripping.

The corrosion problem was tackled initially by regular, vigorous cleaning before and after each run and a programme of 20 runs was carried out under the above conditions. It was found that, although steady conditions of concentration, temperature etc. were achieved initially, as soon as the decalin was delivered

to the absorption tower the concentration of carbon tetrachloride in air began to fall in a non-linear manner, and unfortunately supplies of material were not sufficient to permit running the apparatus until the concentration had come to a steady value. It was also found that the time lag of the gas analysis unit was too long to permit changeover from gas samples above and below the plate and consequently it was decided to analyse the gas stream below the plate only.

During the calculations appropriate to each run, it was necessary to calculate by mass balance the concentration of carbon tetrachloride in the vapour leaving the absorption plate, ~~by mass balance~~, and to assume that this value was the same as that of the vapour entering the humidification plate, and also it had to be assumed that the concentration of carbon tetrachloride in vapour entering the absorption plate as measured by the analysis unit, was the same as that leaving the humidification plate.

While these assumptions would be valid in an ideal system, it was felt that they were a source of error, especially in view of the differences in pressure throughout the system, and the fact that the measured concentration of carbon tetrachloride in the gas continued to fall in spite of every effort to seal off leaks. Because of the rather wide scatter of the results from this series of runs it was decided to redesign the apparatus and abandon the ideal arrangement of continuous operation.

5.3.2. Modified apparatus

Although the contamination of carbon tetrachloride by decalin in the recovery process ~~by decalin~~ and the corrosion due to dissociation of carbon tetrachloride were a nuisance, these problems were solved or were accepted, and they resulted only in a lengthy recovery process or tedious cleaning processes. They did not

affect the accuracy of the runs (other than by imposing a limit on the length of each run) but decreased, very considerably, the number which could be done in a given time.

The main source of error in the experiments which were carried out was felt to be the presence of unstable conditions in the gas circuit due to wide pressure differences and consequent leakages, and that these errors could be minimised by arranging the apparatus to run on an open air circuit. This involved the blower drawing in air from the laboratory and blowing in to the humidification tower which thus became under slight positive pressure. The air and carbon tetrachloride mixture then passed to the absorption tower where absorption of the carbon tetrachloride took place, also under pressure. The vapour leaving the absorption tower contained about 2% carbon tetrachloride and this was led to an additional tower 5 ft high by 9 in diameter packed with ½ in saddles. The decalin, on leaving the absorption tower, passed to the rich decalin tank and a valving arrangement allowed the rich oil pump to pass this decalin to the top of the packed tower to strip the remaining carbon tetrachloride from the rising vapour. The decalin coming from the foot of the stripping column was held in an additional pair of storage tanks or recycled if necessary. The stripped air was led by flexible ducting and passed out of the windows of the laboratory.

These modifications ensured that the vapour was always under pressure. This fact eliminated, among other things, the need to use suction to draw gas samples through the analysis unit.

Furthermore, it could safely be assumed that the concentration of carbon tetrachloride in the air going to the humidification tower was zero, which removed one of the assumptions already mentioned. Previously, when the apparatus was shut down

or during runs at low vapour velocities, decalin wept through the perforations on the plate and collected in the bottom of the column. Although provision was made for draining off this liquid, it was not possible to remove decalin collecting on the gas sampling device as the vapour velocities were too low to permit effective performance as a cyclone separator and it was thought that additional mass transfer might take place thereupon, giving a false reading on the analysis meter. Accordingly the sampling point was moved to a point on the vapour line just prior to entry to the column, and the sampling device was replaced by a simple perforated tube.

The corrosion problem arising from the presence of chloride ions in the steam stripping tower was eliminated by delivering a constant flow of concentrated sodium carbonate solution which completely eliminated corrosion and products of corrosion. This meant that the centrifugal separator worked always at maximum output and did not have to be cleaned as regularly as before. Also the filter in the centrifuge inlet was removed and replaced by a new design using glass wool. The corrosion due to the carbon tetrachloride itself in circuit could not be removed but its effects were minimised by removing the filter from the pump and replacing it with a filter in the storage tank, by lining the tank with thick polythene sheeting and by replacing the flowmeter by another in which the float did no travel on a central wire.

These improvements, while not giving the performance hoped for in the original design, gave much better results as the inlet carbon tetrachloride concentration reading remained steady and the number of runs in a given time could be increased because of fewer shut downs for maintenance.

A general view of the apparatus is shown on Plate 3.

5.3.3. Operation - modified apparatus

Each run was preceded by a warming up period to allow the gas analysis unit and the temperature recorder to attain their working temperatures. The air blower and heating tapes were switched on and the air flow adjusted approximately to a predetermined value.

When the air leaving the plate was at its working temperature of 25°C the decalin pump to the absorption tower was switched on along with its controlled heating tapes. When it was at the working temperature, 25°C, in the inlet weir, the carbon tetrachloride pump and associated heating tapes were switched on together with the decalin to the stripping column. The liquid flow rates were adjusted to the predetermined values and the plant was allowed to reach equilibrium.

When stable conditions had been held for five minutes the run proper was started, each run taking twelve minutes or more if the flow rates were low enough to permit longer running.

Readings were taken every four minutes as follows:

1. The column pressures in humidification and absorption towers.
2. The gas flow manometer reading, and the flow rates of decalin and carbon tetrachloride.
3. During the run temperatures were taken automatically ~~during the run~~ of:-
   (a) inlet and outlet gas at absorption plate
   (b) inlet and outlet decalin at absorption plate
   (c) inlet and outlet gas at humidification plate
   (d) inlet and outlet carbon tetrachloride at humidification plate
   (e) ambient air, gas leaving humidification tower, decalin entering absorption tower, carbon tetrachloride entering humidification tower.
4. Concentration of carbon tetrachloride in air from analysis unit. Samples were taken of inlet and outlet decalin from

the absorption plate at 0, 4 and 12 minutes after commencement. Atmospheric pressure was taken before every run.

At high temperatures, i.e. in the steam stripping tower, decalin dissolves small amounts of water and on cooling in the plate cooler this water comes out of solution as a very fine stable emulsion. Invariably, the decalin used in the absorption process contained some water in this form, and the samples collected were shaken up with anhydrous sodium carbonate and allowed to stand overnight to remove this water.

The procedure was repeated for different gas rates and liquid rates.

Recovery process. The inlet steam valve to the steam stripping tower was opened, and the cooling water to the overhead condenser was turned on. Once the tower was suitably warmed up, rich decalin was introduced at the top. Also, a solution of concentrated sodium carbonate was made up and placed in an aspirator bottle above the tower from which it flowed under gravity to the top of the tower.

The primed centrifuge was started up, and the mixture of decalin and water, emerging from the bottom of the steam stripping column was fed to it, via a tun dish, to ensure that the machine operated under a constant head.

The operating temperature of the centrifuge was approximately 70°C. The flow of rich decalin to the tower was about 45 gal/hr. The centrifuge discharged the water to drain and by means of a gear pump the stripped decalin was returned to the appropriate storage tank via the Alfa-Laval plate cooler. The mixture of condensed steam and impure carbon tetrachloride appearing in the phase settler, separated under gravity and the aqueous layer passed to drain. The impure carbon tetrachloride layer was collected in enamelled pails and was stored in a large

stainless steel tank until sufficient was collected to provide a charge for the packed distillation column. This was operated batchwise and the mixture of carbon tetrachloride and decalin was pumped by a Mono pump into the kettle and steam was supplied at 20 lb/in^2 initially. The column was run under about 20 in Hg of vacuum and the carbon tetrachloride was distilled over to give a product of acceptable purity (99%). The steam pressure was raised as the kettle temperature rose, but it was impossible to raise the temperature to the boiling point of decalin, approximately 190°C, and so the distillation was stopped with a mixture of 80% decalin and 20% carbon tetrachloride in the kettle. This mixture was drained and returned to the rich decalin storage tank for further steam stripping.

5.3.4. Experimental programme

The intended programme had to be curtailed because of the time-wasting difficulties encountered in developing the apparatus. The effect of gas rate on Murphree gas film efficiency was studied at different liquid rates. The gas rate varied from 1.42 to 2.94 ft/sec. through the bubbling area. The liquid rates were 1000, 3000 and 5000 lb/ft^2hr.

5.3.5. Calculation of results

On the completion of each run, the samples of decalin were analysed for their carbon tetrachloride content. After drying, the specific gravity of each sample was measured using density bottles in a constant temperature bath set at 25°C. The concentration of carbon tetrachloride present was then read from a previously constructed calibration graph (see Fig. 3.1). The density could be measured to the third decimal place and the concentration read with an accuracy of 1.0%. With a knowledge of the flow of decalin to the plate, and the inlet

and outlet concentrations of carbon tetrachloride, the mass of carbon tetrachloride absorbed from the vapour could be calculated.

The concentration of carbon tetrachloride in the inlet air read directly from the analysis unit indicator was in percent by volume (mol %) and this was converted to percent by weight. This also was calculated to 1.0%. The mass of gas flowing was calculated by reading the density from a chart of gas density against concentration for various pressures and inserting the values so obtained in the equation

$$G = 734 \times \rho_G^{1/2} \times h_w^{1/2}$$

where h_w is the pressure drop across the orifice in inches of water.

From the gas mass flow and the inlet concentration, the mass of carbon tetrachloride and dry air in the inlet gas could be calculated, and from the mass of carbon tetrachloride absorbed by the oil, the mass of carbon tetrachloride leaving the plate could be calculated. The mass of dry air entering the plate is the same as that leaving, and hence the concentration of carbon tetrachloride in the outlet vapour could be calculated.

The concentration of carbon tetrachloride in the decalin leaving the plate was converted to mol % and the corresponding partial pressure of carbon tetrachloride was read off from the equilibrium curve. Fig. 3.2. Dividing this figure by the column pressure gave the vapour concentration in the outlet gas if the mass transfer process had reached equilibrium.

The Murphree plate efficiency was then calculated as follows:-

$$E_{MV} = \frac{\text{Concn.}CCl_4 \text{ in inlet vapour} - \text{Concn. in outlet vapour}}{\text{Concn.}CCl_4 \text{ in inlet vapour} - \text{Concn. in outlet vapour in equilibrium with outlet oil}}$$

The superficial vapour velocity was calculated from the mass flow and density of gas and the active area of the plate.

Specimen Calculation

Run 1.

Average specific gravity of decalin entering plate = 0.893

" " " " " leaving plate = 0.910

∴ Concentration of carbon tetrachloride in inlet decalin stream = 1.60 wt. %

Concentration of carbon tetrachloride in outlet decalin stream = 6.12 wt. %

Flow of decalin to plate = 1000 lb/ft^{2}hr.

∴ Mass carbon tetrachloride in inlet stream = 16.0 lb/ft^{3}hr.

" " " " outlet " = $984 \times \frac{6.12}{93.88}$

= 64.2 lb/ft^{2}hr.

mass carbon tetrachloride transferred from gas stream = 64.2 - 16.0

= 48.2 lb/ft^{2}hr

Average concentration of carbon tetrachloride in inlet gas stream = 4.65 mol %

Pressure at orifice = 759.1 mm Hg Temperature = 64°F

Density at orifice = 0.0911 lb/ft^3

Air manometer reading = 2.7 in water

Gas flow = $734 \times (2.7)^{1/2} \times (0.0911)^{1/2}$

= 364 lb/ft^{2}hr

4.65 vol % = 20.60 wt %

mass CCl_4 in inlet gas stream = 20.60 x 364

= 75.0 lb/ft^{2}hr

mass CCl_4 in outlet gas stream = 75.0 - 48.2
= 26.8 lb/ft^{2}hr

mass of outlet gas stream = 364 - 48
= 316 lb/ft^{2}hr

Concn.of CCl_4 in outlet gas stream = $\frac{26.8}{316}$
= 8.48 wt %
= 1.71 mol %

Concn. of CCl_4 in outlet decalin stream = 6.12 wt %
= 5.61 mol %

partial pressure of CCl_4 in equilibrium with this concentration from Fig. 3.2. = 7.2 mm Hg

Column pressure = 761.1 mm Hg

Equilibrium outlet gas concentration = $\frac{7.2}{761.1}$
= 0.94 mol %

$$\therefore E_{MV}\% = \frac{(4.65 - 1.71) \times 100}{4.65 - 0.94} = 79.3\%$$

$$V_S = \frac{364 \times 1.26}{3{,}600 \times 0.0901} = 1.42 \text{ ft/sec through bubbling area}$$

where 1.26 is ratio of column cross sectional area to bubbling area

$$F = 1.42 \times (0.0901)^{1/2} = 0.43$$

$$N_{OG} = -2.3 \ln (1 - E_{MV})$$
$$= \underline{1.57}$$

5.3.6. Results

The results are given in Table 5.4 and are expressed graphically in Figs. 5.7, 5.8, 5.9, and 5.10.

TABLE 5.1

MASS TRANSFER RESULTS:- AIR/WATER SYSTEM

Run No.	L_v gal/ft^{2}hr	V_s ft/sec	F	E_{MV} %	N_{OG}
1	300	4.54	1.17	89.5	2.24
2	450	"	"	86.7	2.01
3	550	"	"	85.1	1.90
4	600	"	"	86.0	1.96
5	700	"	"	83.5	1.79
6	150	3.78	0.97	88.9	2.19
7	300	"	"	86.8	2.03
8	450	"	"	83.4	1.79
9	600	"	"	83.5	1.79
10	700	"	"	82.6	1.74
11	200	3.34	0.86	77.8	1.52
12	300	"	"	78.8	1.55
13	450	"	"	82.7	1.75
14	600	"	"	86.4	1.99
15	750	"	"	91.4	2.40
16	70	2.40	0.62	80.5	1.63
17	140	"	"	81.6	1.69
18	280	"	"	82.7	1.75
19	280	"	"	83.8	1.81
20	420	"	"	85.8	1.95
21	450	"	"	86.1	1.99
22	540	"	"	84.1	1.83
23	680	"	"	89.2	2.21
24	800	"	"	90.0	2.28
25	200	1.49	0.39	84.7	1.86
26	450	"	"	88.7	2.16
27	700	"	"	91.4	2.40

TABLE 5.2.

RECORDED RESULTS FOR RUN 11 USED IN SPECIMEN CALCULATIONS

Time min	T_w	T_d	Sc	h_m	R	T_1	T_2	S	O.D	T_m	h_i
0	13.70	18.12	54.2	4.10	29.4	28.30	27.89	1	.266	28.12	56.8
15	13.87	18.30	50.8	4.08	29.4	28.10	27.76	2	.274	28.17	57.5
30	14.01	18.43	47.4	4.12	29.4	28.31	27.91	3	.282	28.22	58.2
45	14.09	18.40	44.1	4.18	29.4	28.12	27.90	4	.293	28.27	58.9
60	14.14	28.50	40.6	4.03	29.4	28.23	27.89	5	.306	28.27	58.9
78	13.92	18.30	37.1	4.02	29.4	28.24	27.91	6	.316	28.20	57.9
90	14.03	18.18	34.4	4.14	29.4	28.27	27.92	7	.329	28.28	59.0
105	13.90	18.39	29.3	4.16	29.4	28.29	27.93	8	.343	28.17	57.5
120	13.80	18.13	25.9	4.18	29.4	28.13	27.81	9	.361	28.17	57.5
Average				4.11	29.4	28.23				28.21	58.0

T_w = wet-bulb temperature of inlet air before heaters (^oC)

T_d = dry-bulb temperature of inlet air before heaters (^oC)

Sc = scale reading on sump tank (in)

h_m = pressure drop recorded on air manometer (in)

T_1 = temperature of liquid entering plate (^oC)

T_2 = temperature of liquid leaving plate (^oC)

S = number of sample

O.D = optical density of sample

T_m = calculated wet bulb temperature at 60^oC (^oC)

h_i = inlet humidity calculated from T_w and T_d (grain/lb)

TABLE 5.3

MASS TRANSFER RESULTS:- AIR/CARBON TETRACHLORIDE SYSTEM

Run No.	L lb/ft^{2}hr	L_V gal/ft^{2}hr	V_S ft/sec	F	E_{MV} %	N_{OG}
1	1300	82	1.41	0.38	42	0.53
2	"	"	1.42	0.38	42	0.54
3	"	"	1.77	0.48	37	0.45
4	"	"	1.94	0.53	34	0.40
5	"	"	2.13	0.57	36	0.43
6	"	"	2.17	0.58	35	0.41
7	"	"	2.50	0.67	36	0.43
8	"	"	2.64	0.70	37	0.45
9	"	"	2.96	0.79	35	0.41
10	"	"	2.98	0.80	36	0.43
11	"	"	2.98	0.80	33	0.38
12	3000	190	1.43	0.38	50	0.70
13	"	"	1.87	0.51	44	0.57
14	"	"	2.33	0.63	44	0.57
15	"	"	3.22	0.88	41	0.52
16	5000	310	1.43	0.38	60	0.93
17	"	"	1.87	0.51	54	0.78
18	"	"	2.40	0.65	53	0.76
19	"	"	2.98	0.81	50	0.68
20	"	"	3.38	0.92	47	0.62

TABLE 5.4

MASS TRANSFER RESULTS:- ABSORPTION SYSTEM

Run No.	L lb/ft^{2}hr	L_v gal/ft^{2}hr	V_s ft/sec	F	E_{MV} %	N_{OG}
1	1000	110	1.42	0.43	79.3	1.57
2	"	"	1.40	0.42	77.9	1.51
3	"	"	1.79	0.53	73.7	1.35
4	"	"	2.02	0.61	72.7	1.31
5	2000	220	1.42	0.43	78.5	1.54
6	"	"	2.10	0.62	73.5	1.34
7	"	"	2.89	0.87	71.9	1.28
8	"	"	2.92	0.87	72.4	1.30
9	3000	330	1.42	0.42	80.4	1.63
10	"	"	2.11	0.63	80.9	1.65
11	"	"	2.86	0.86	79.8	1.60
12	4000	450	2.94	0.89	80.3	1.63
13	5000	560	1.45	0.43	88.2	2.13
14	"	"	2.12	0.63	88.9	2.19
15	"	"	2.91	0.86	88.1	2.12

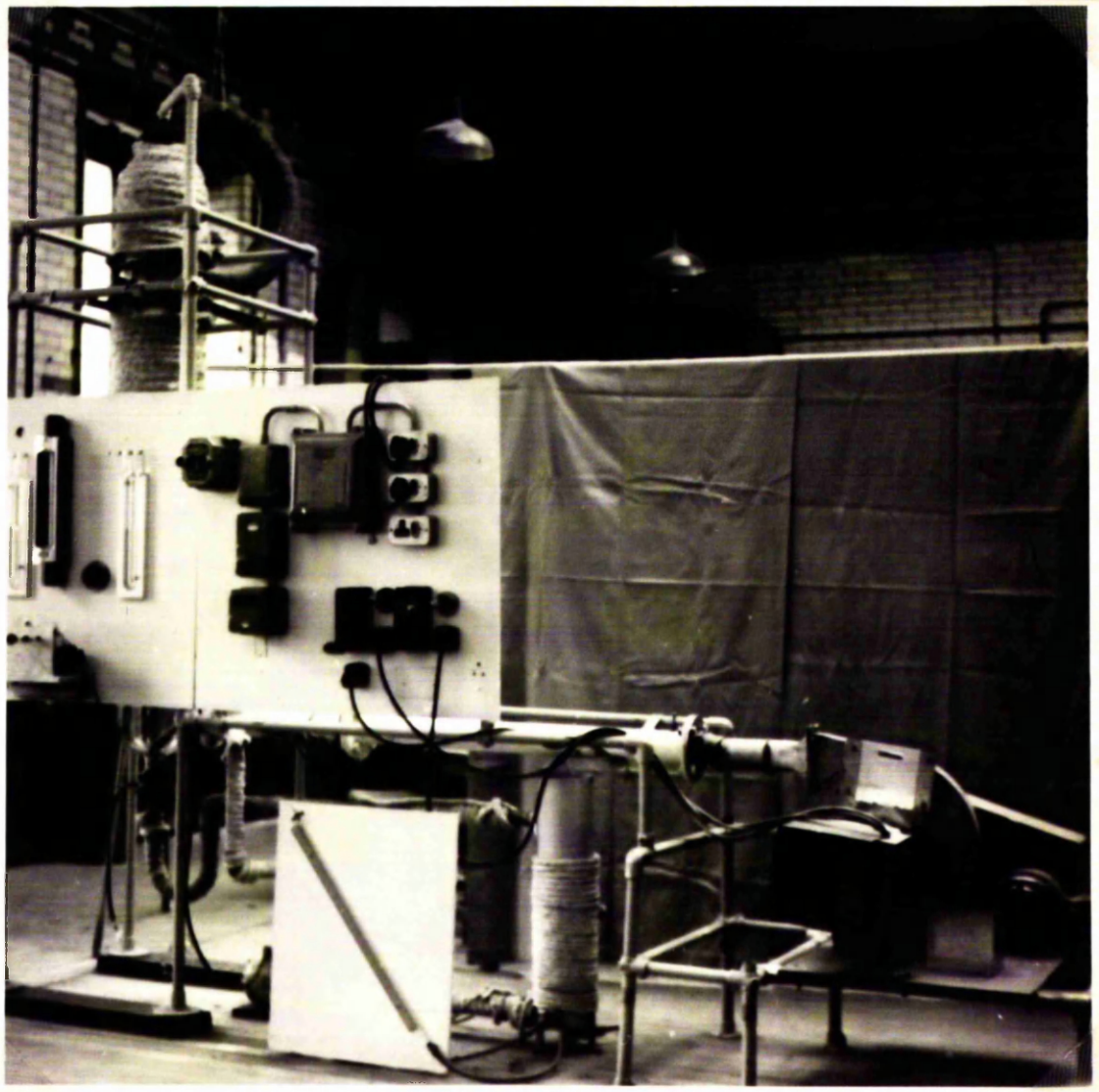


PLATE 1

Apparatus used in air/water experiments

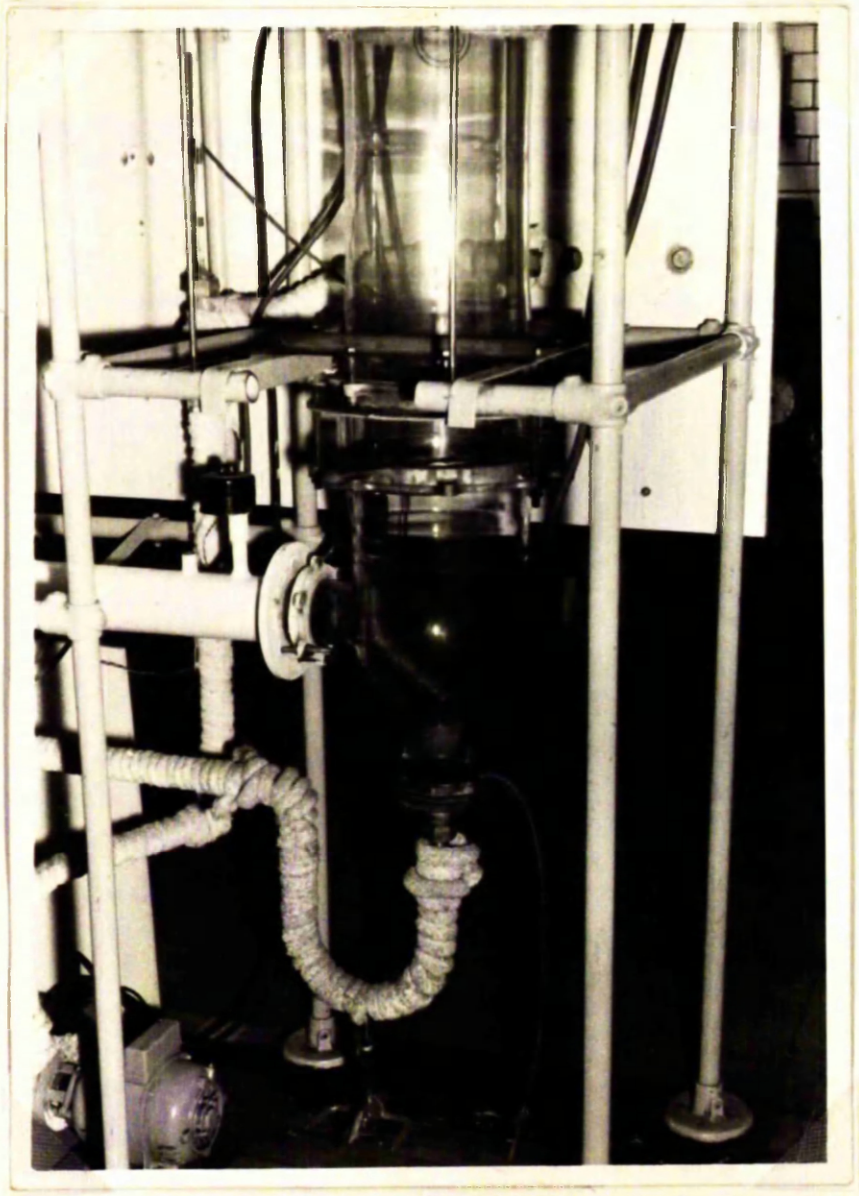


PLATE 2

Detail of apparatus used in air/water experiments.

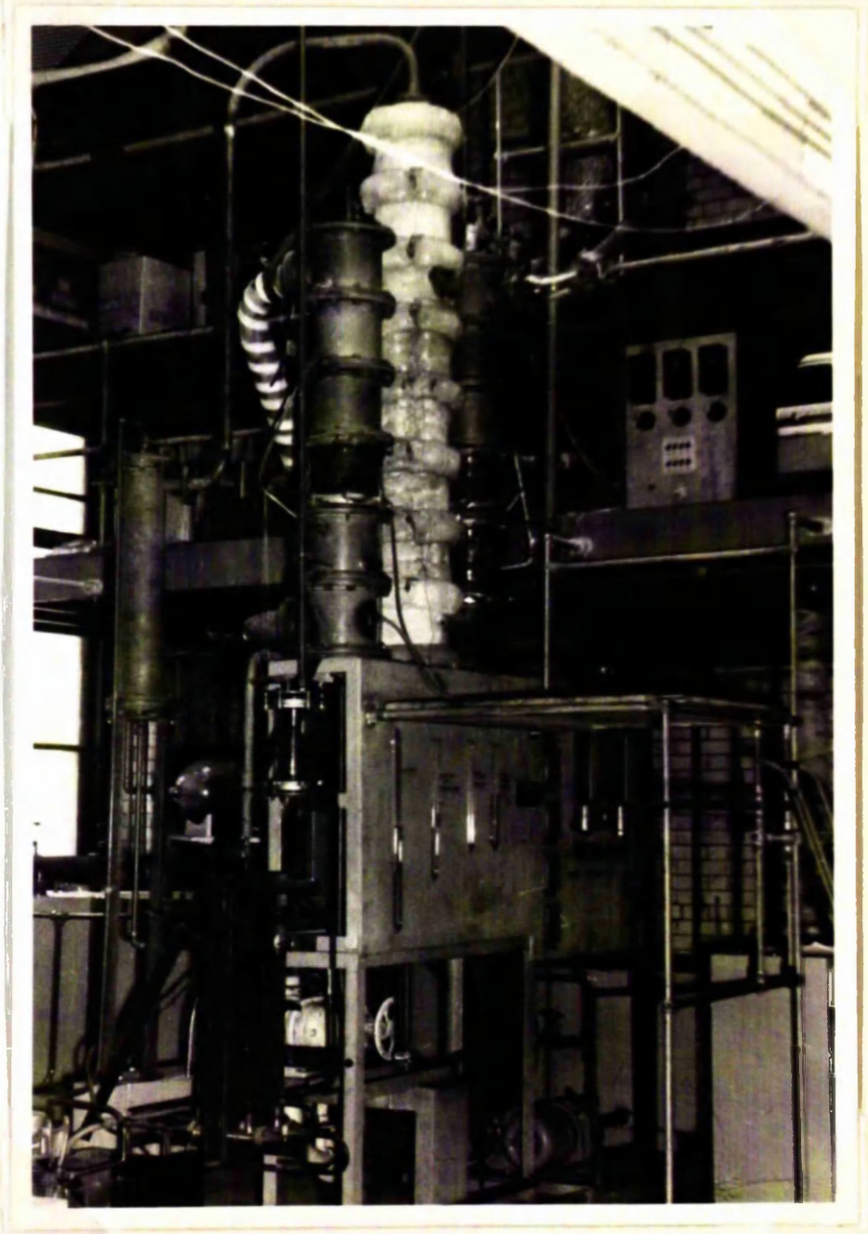


PLATE 3

Apparatus used in gas absorption and air/carbon tetrachloride experiments.

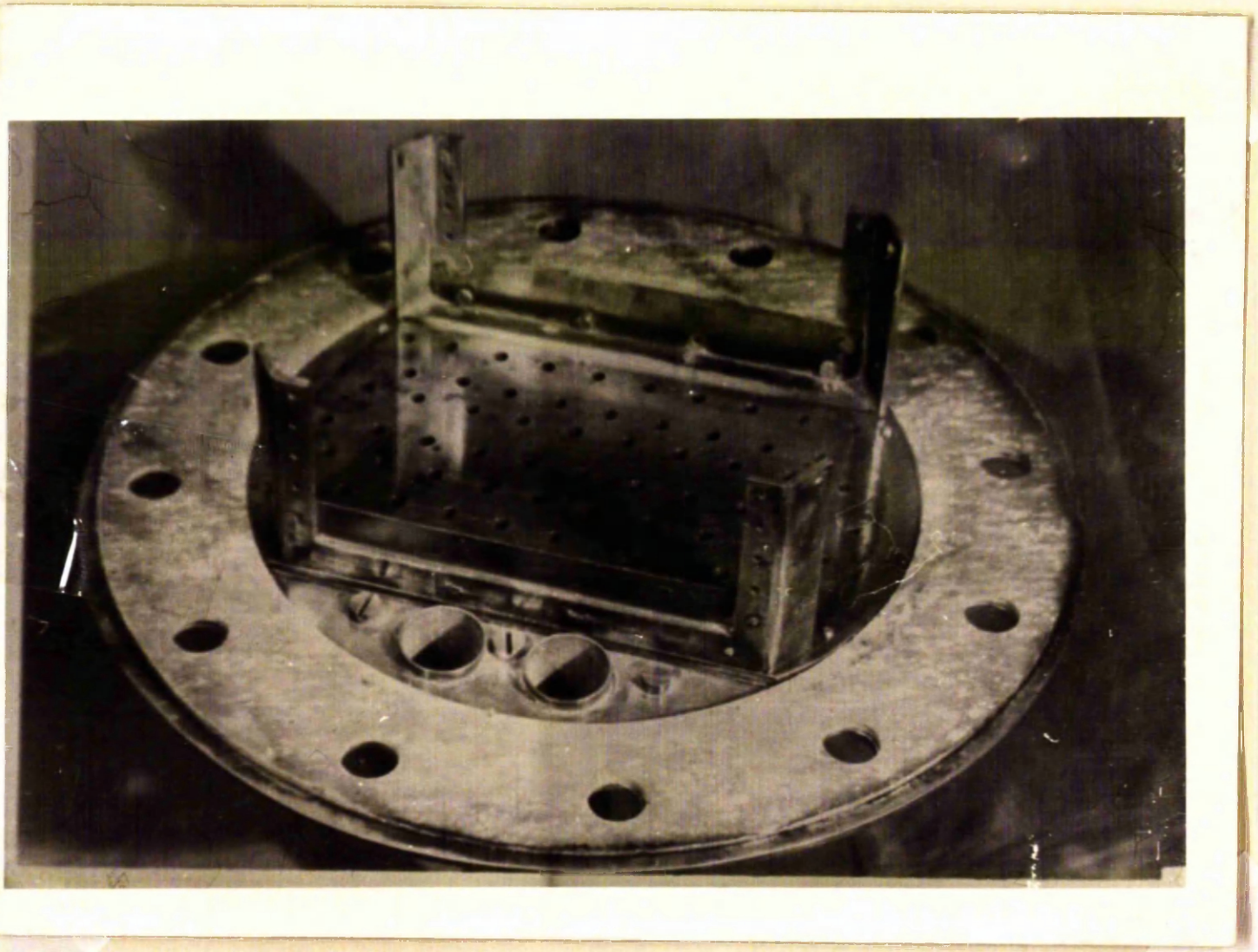
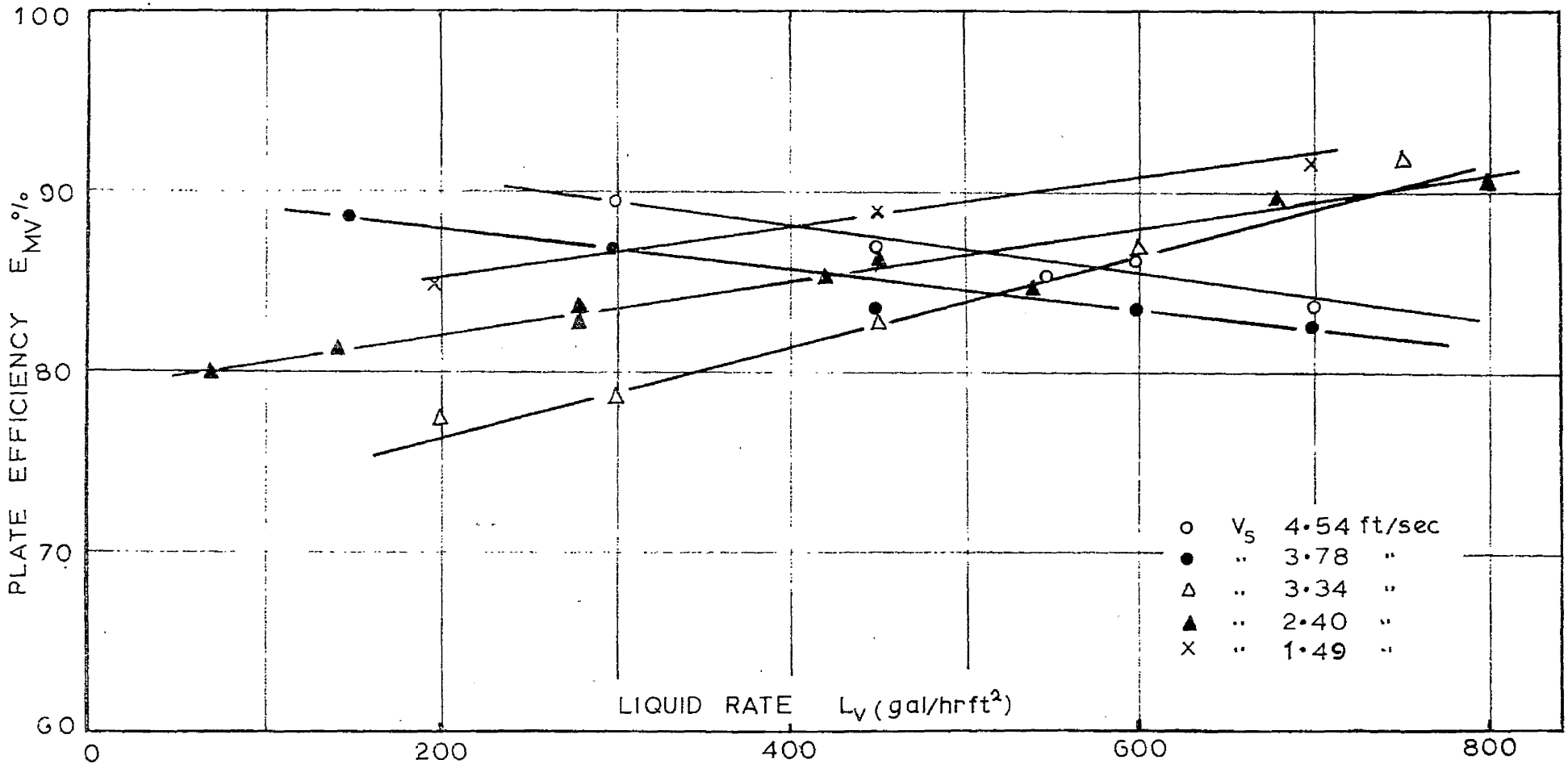


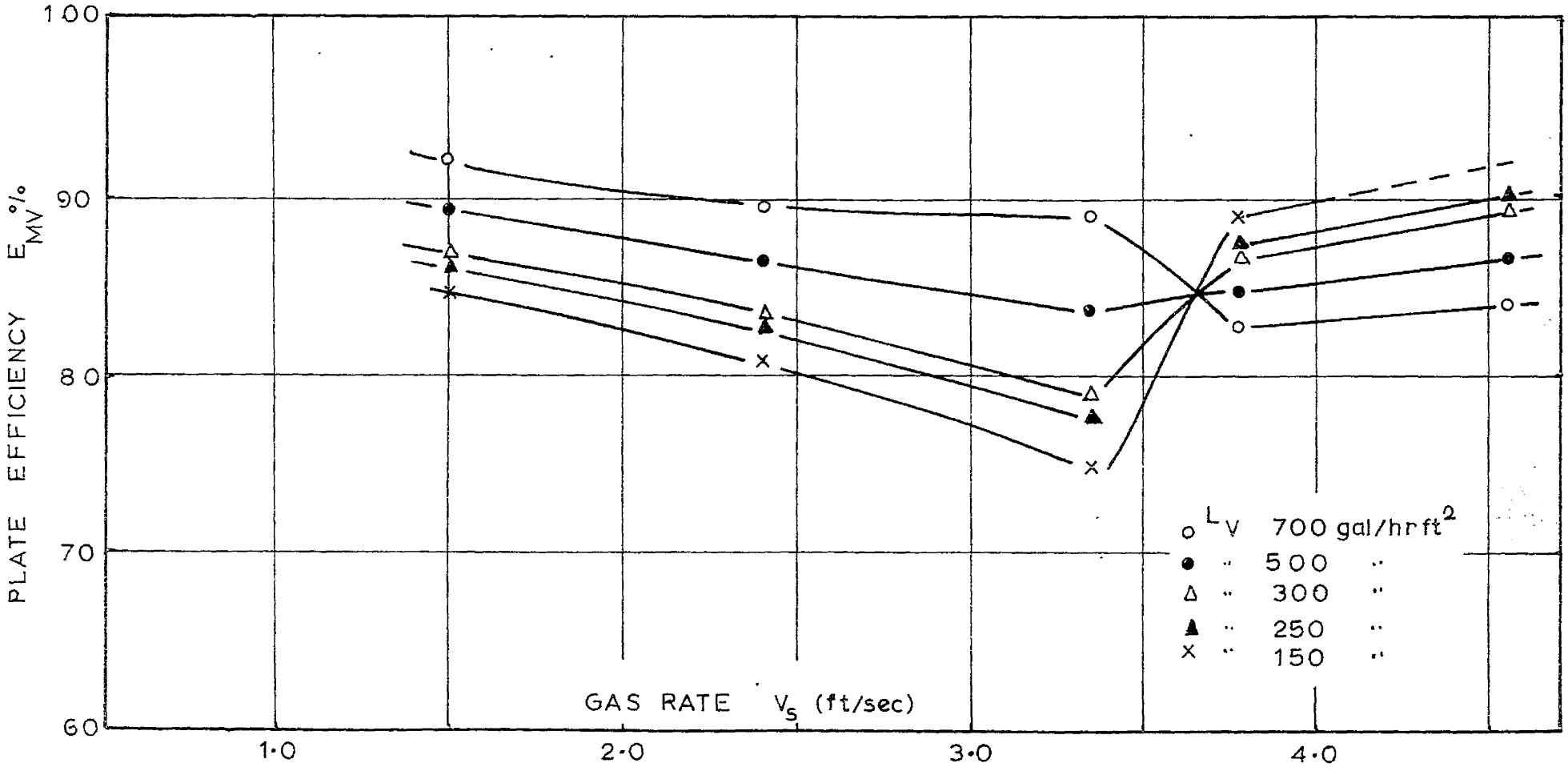
PLATE 4

9 in diameter sieve plate used in mass transfer and hydraulic experiments.



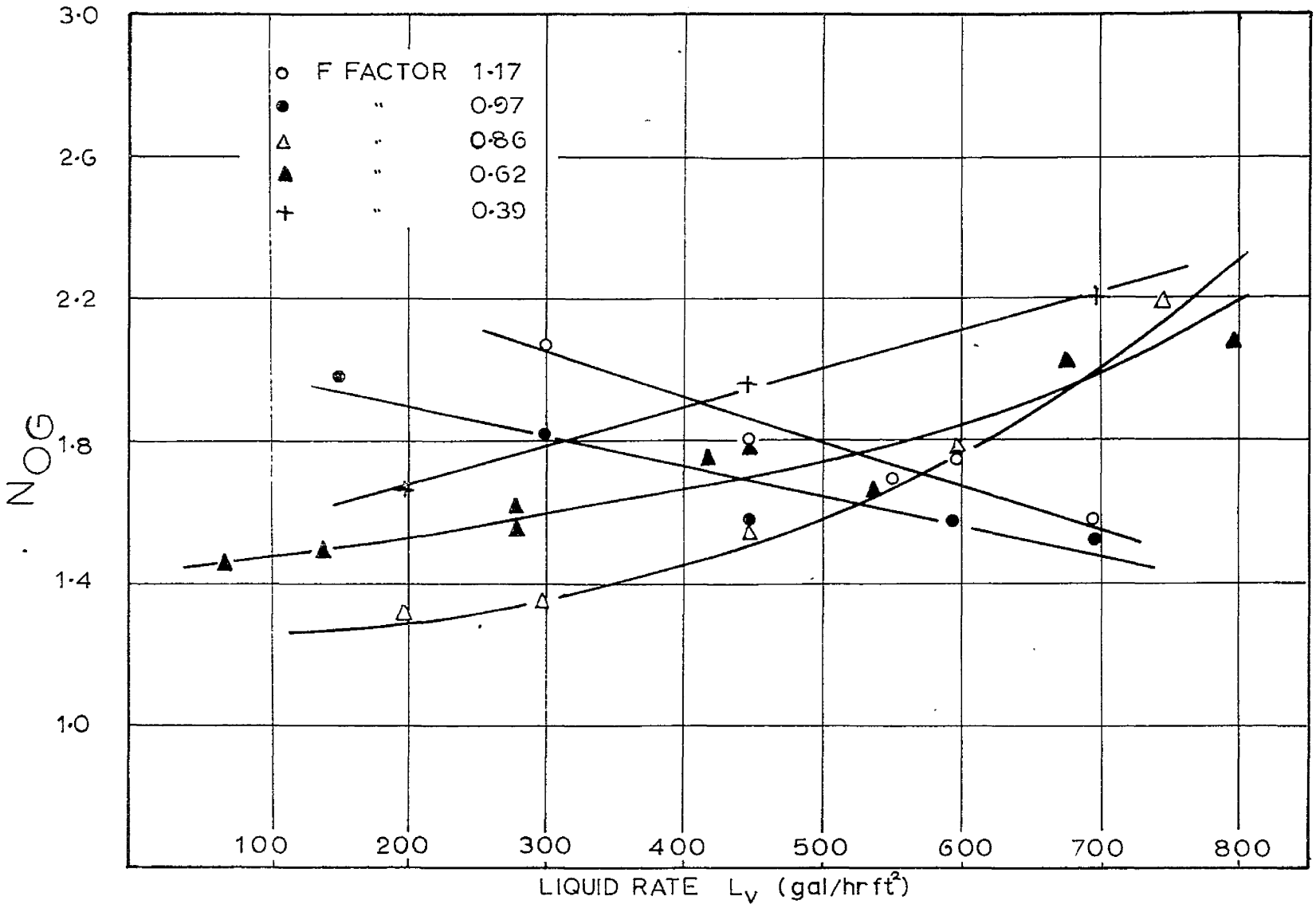
EFFECT OF LIQUID RATE ON PLATE EFFICIENCY E_{MV}
(AIR WATER SYSTEM)

FIG. 5.1.



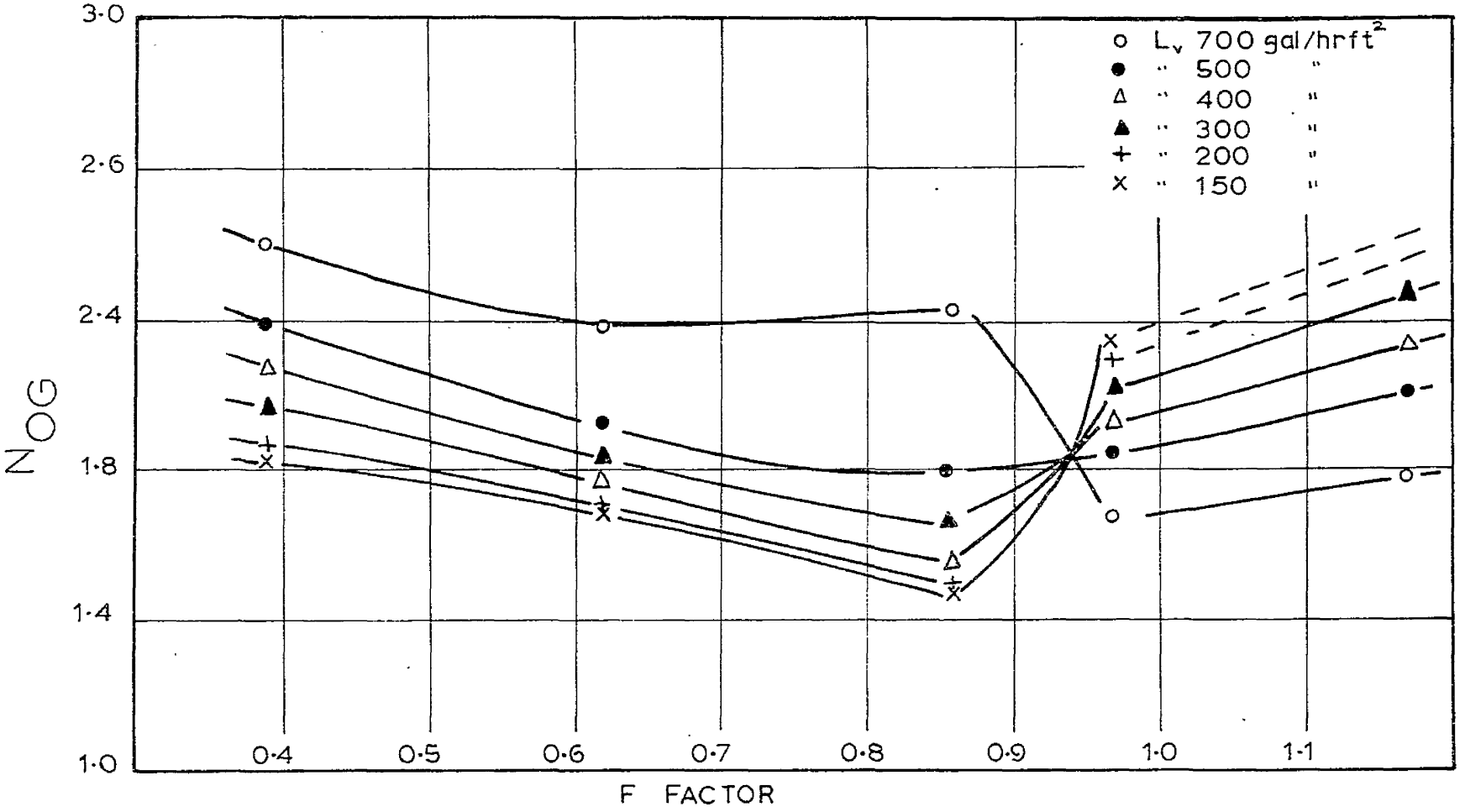
EFFECT OF GAS RATE ON PLATE EFFICIENCY E_{MV}
(AIR WATER SYSTEM)

FIG. 5.2.



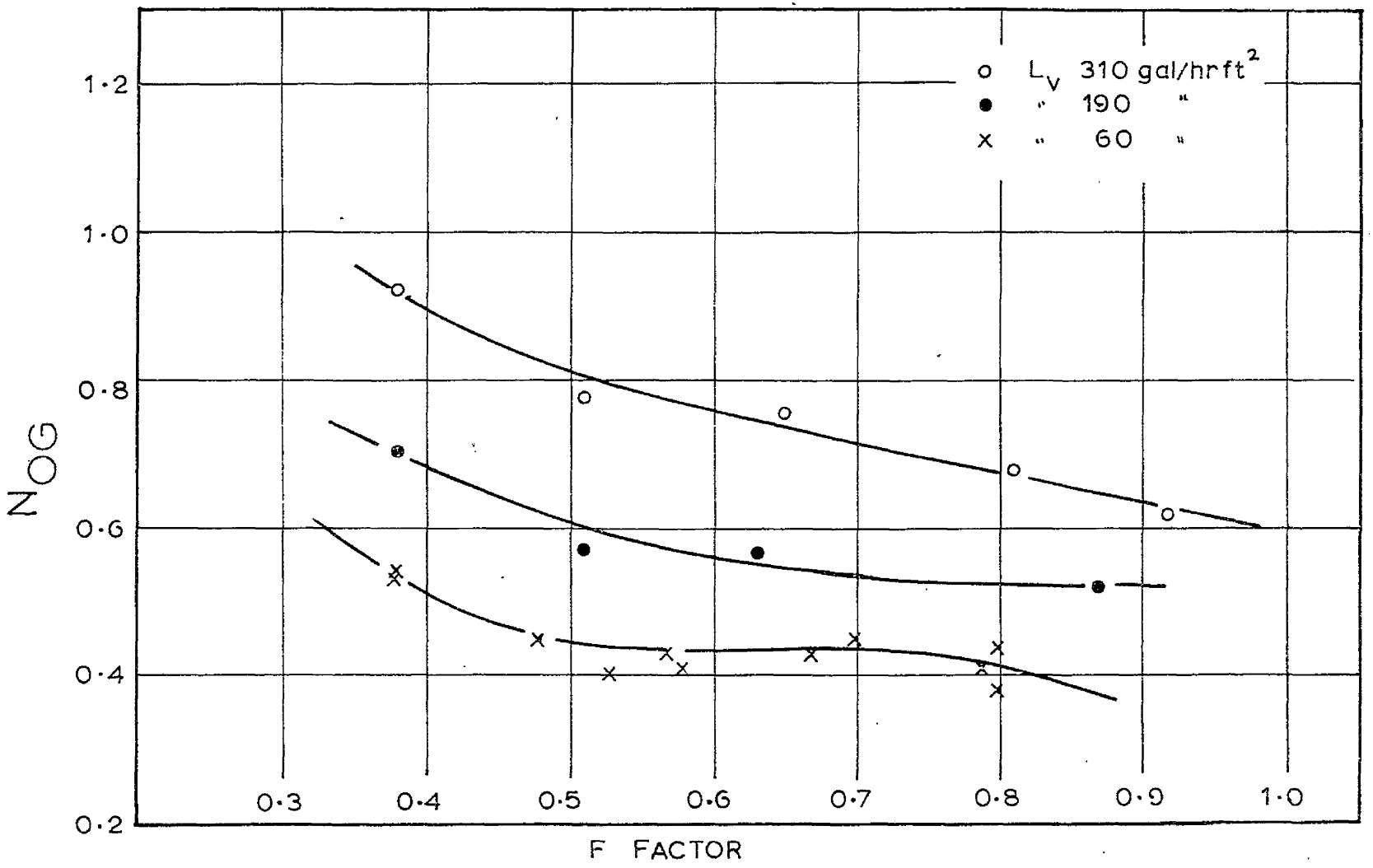
EFFECT OF LIQUID RATE ON No. OF TRANSFER UNITS, N_{OG}.
(AIR—WATER)

FIG. 5.3.



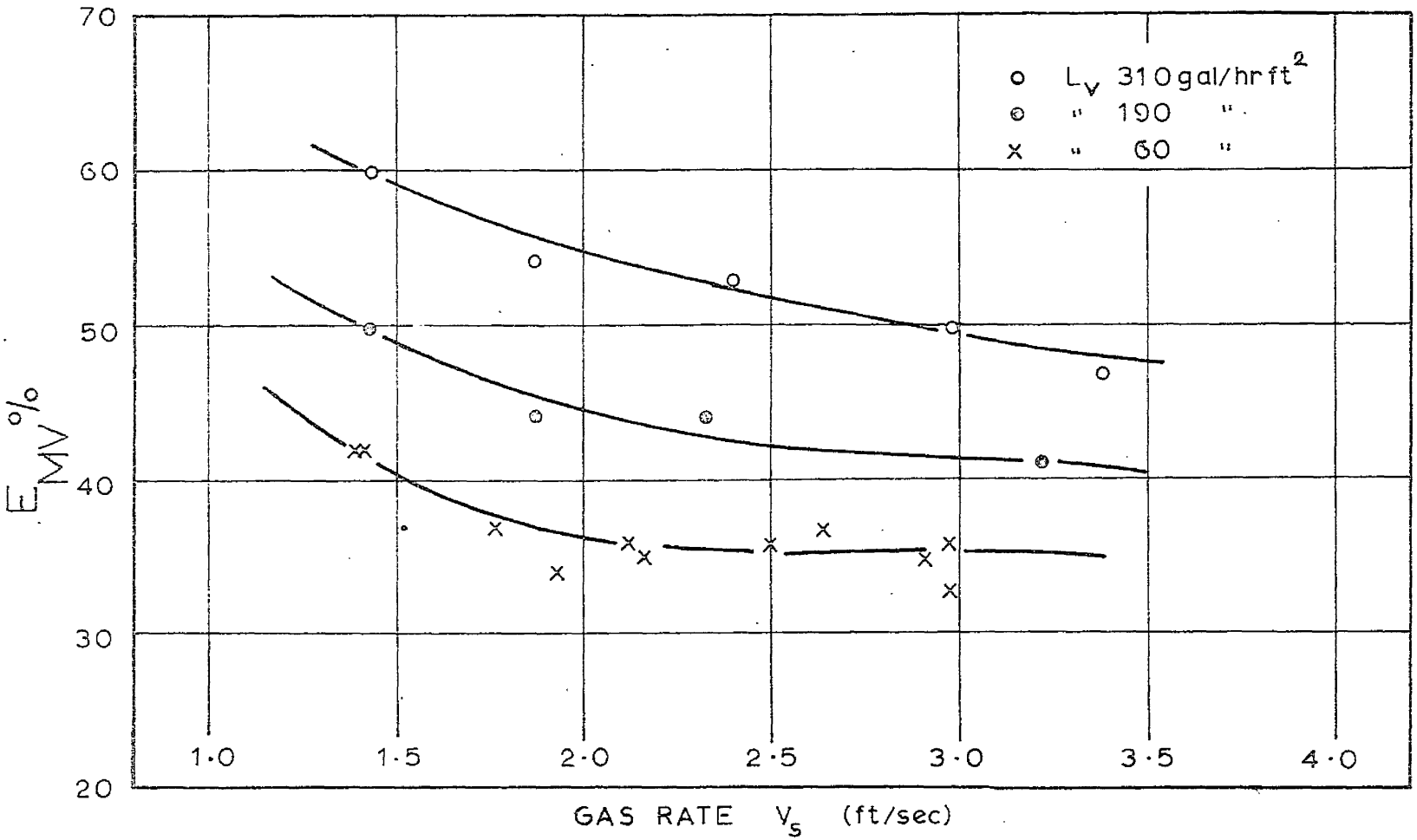
EFFECT OF GAS RATE (F FACTOR) ON No. OF TRANSFER UNITS N_{OG} (AIR–WATER)

FIG. 5.4.



EFFECT OF AIR RATE (F FACTOR) ON No. OF TRANSFER UNITS N_{OG}
(AIR–CARBON TETRACHLORIDE)

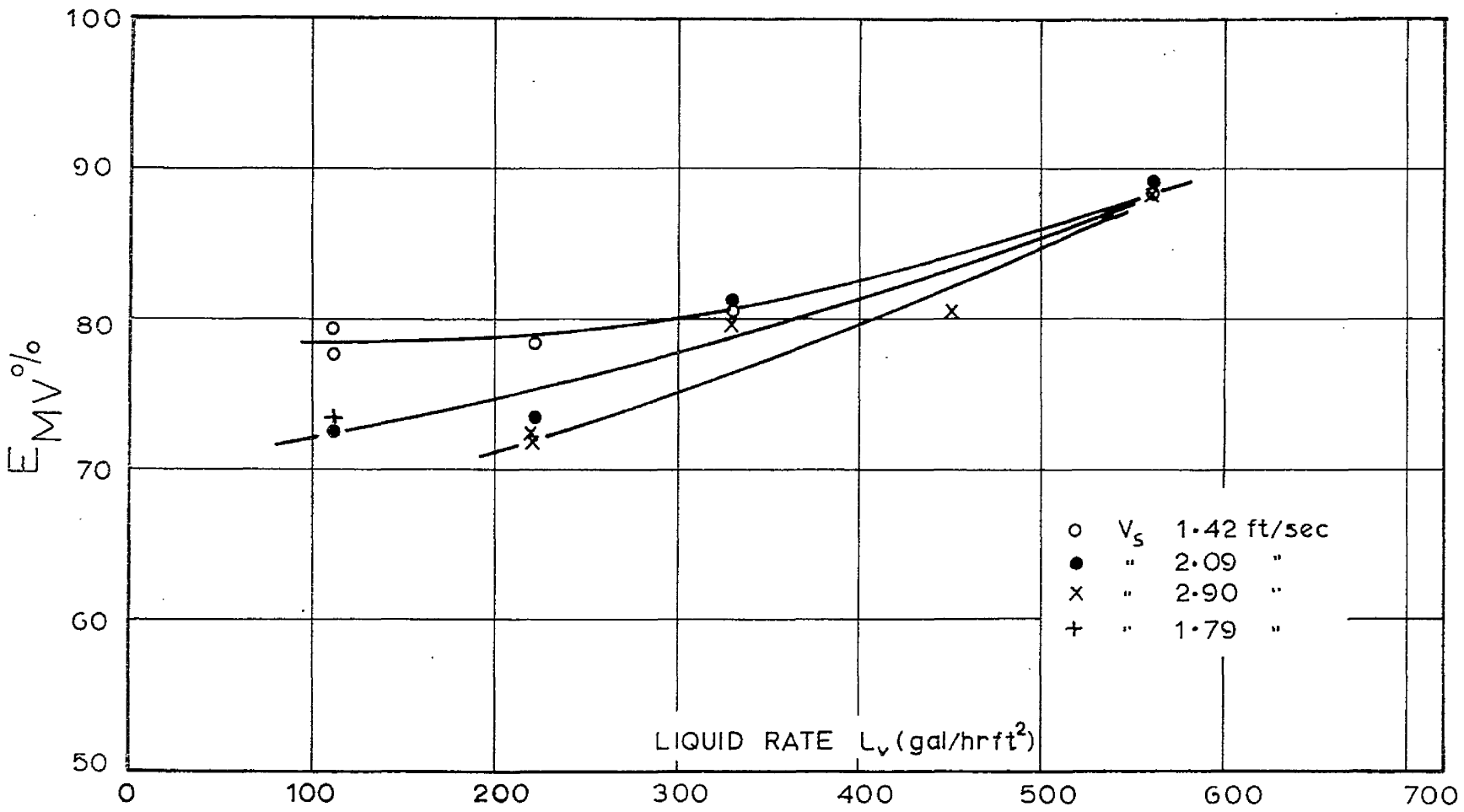
FIG. 5.5.



EFFECT OF GAS RATE (V_s) ON PLATE EFFICIENCY, E_{MV}

(AIR — CARBON TETRACHLORIDE)

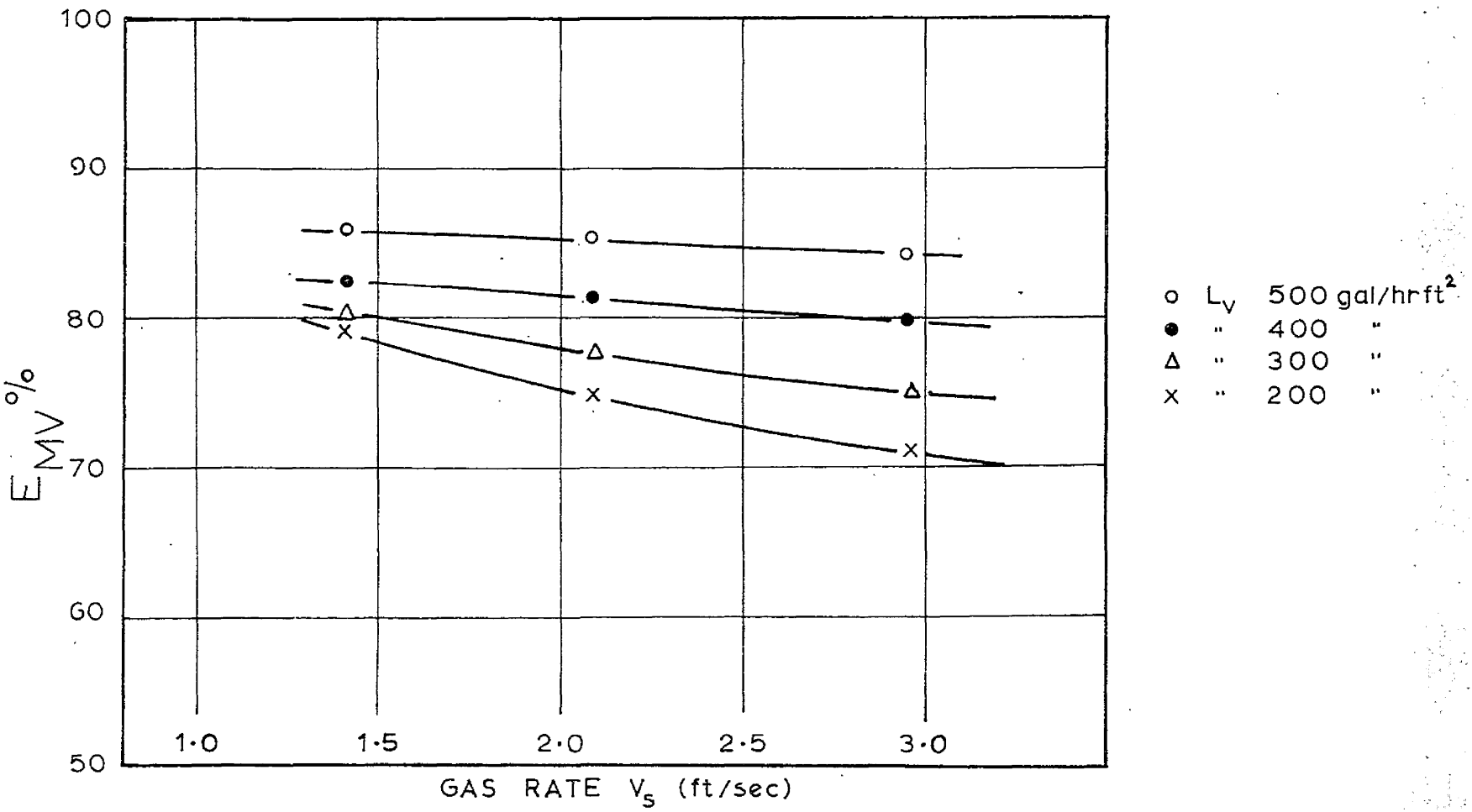
FIG. 5.6.



EFFECT OF LIQUID RATE ON PLATE EFFICIENCY, E_{MV}

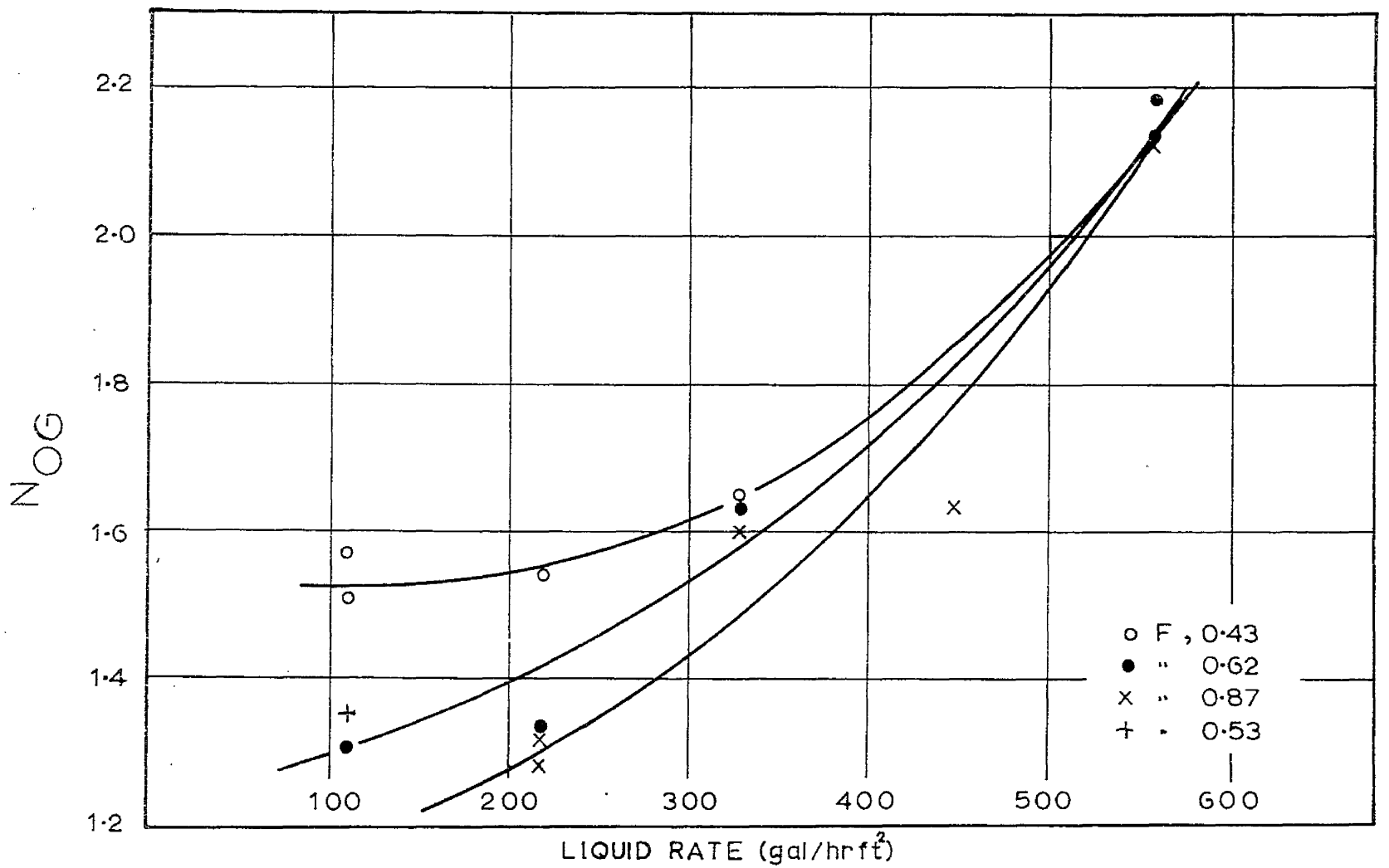
(GAS ABSORPTION SYSTEM)

FIG. 5.7.



EFFECT OF GAS RATE ON PLATE EFFICIENCY E_{MV}
(GAS ABSORPTION SYSTEM)

FIG. 5.8.



EFFECT OF LIQUID RATE ON No. OF TRANSFER UNITS N_{OG}

(GAS ABSORPTION SYSTEM)

FIG. 5.9

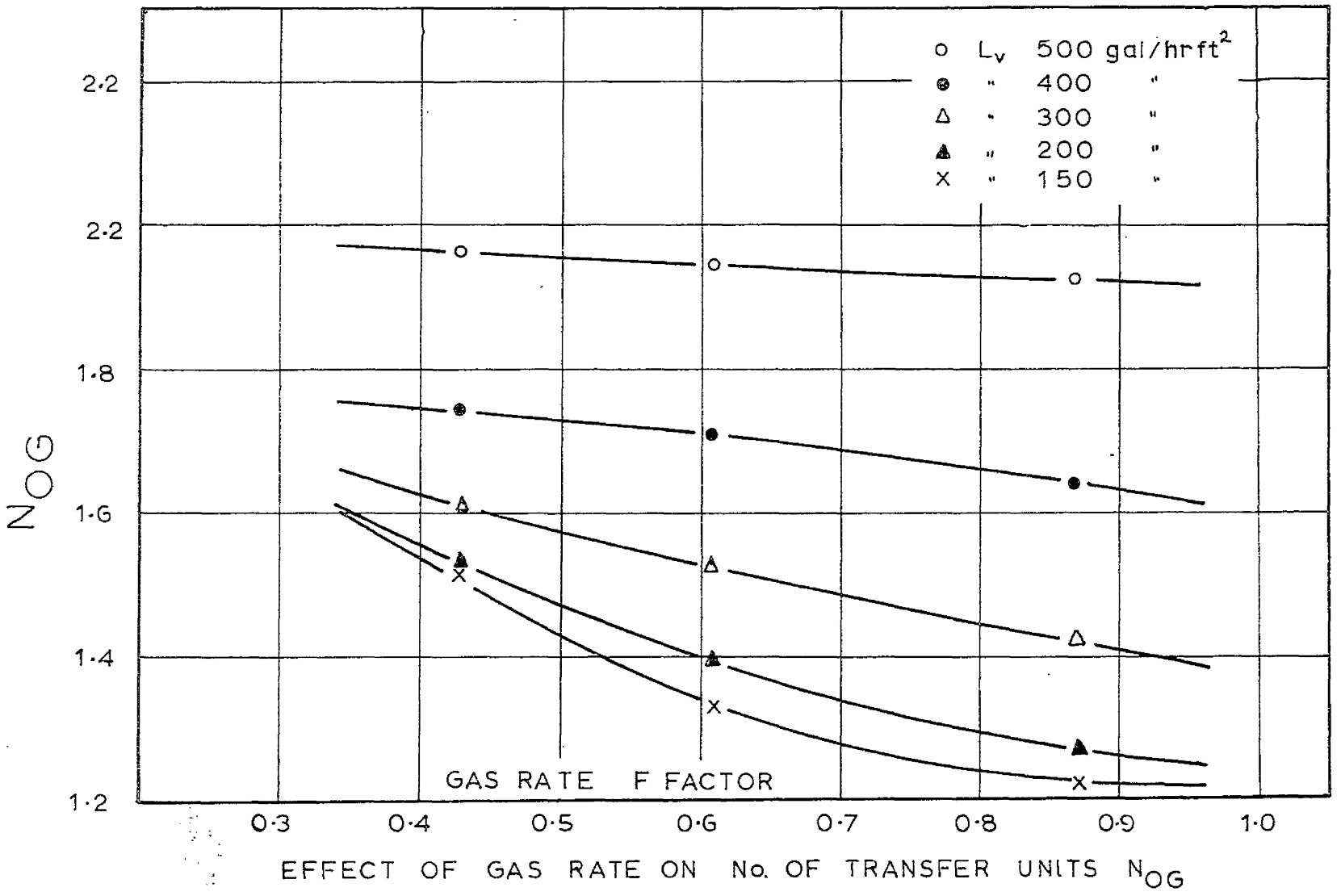

o L_v 500 gal/hr ft^2
● " 400 "
Δ " 300 "
▲ " 200 "
X " 150 "
N_{OG}
2·2
2·2
1·8
1·6
1·4
1·2
GAS RATE F FACTOR
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0
EFFECT OF GAS RATE ON No. OF TRANSFER UNITS N_{OG}

FIG. 5.10.

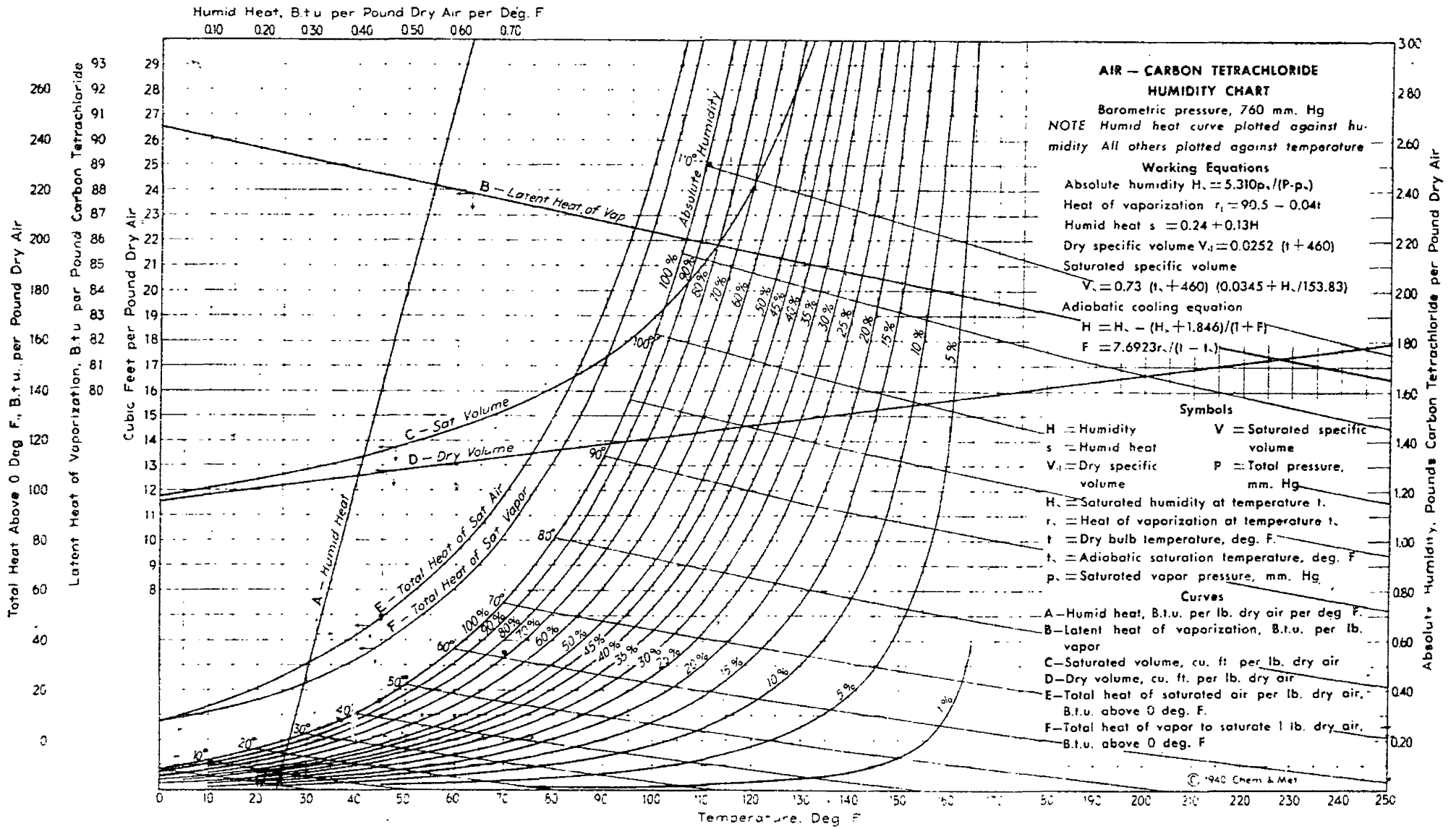
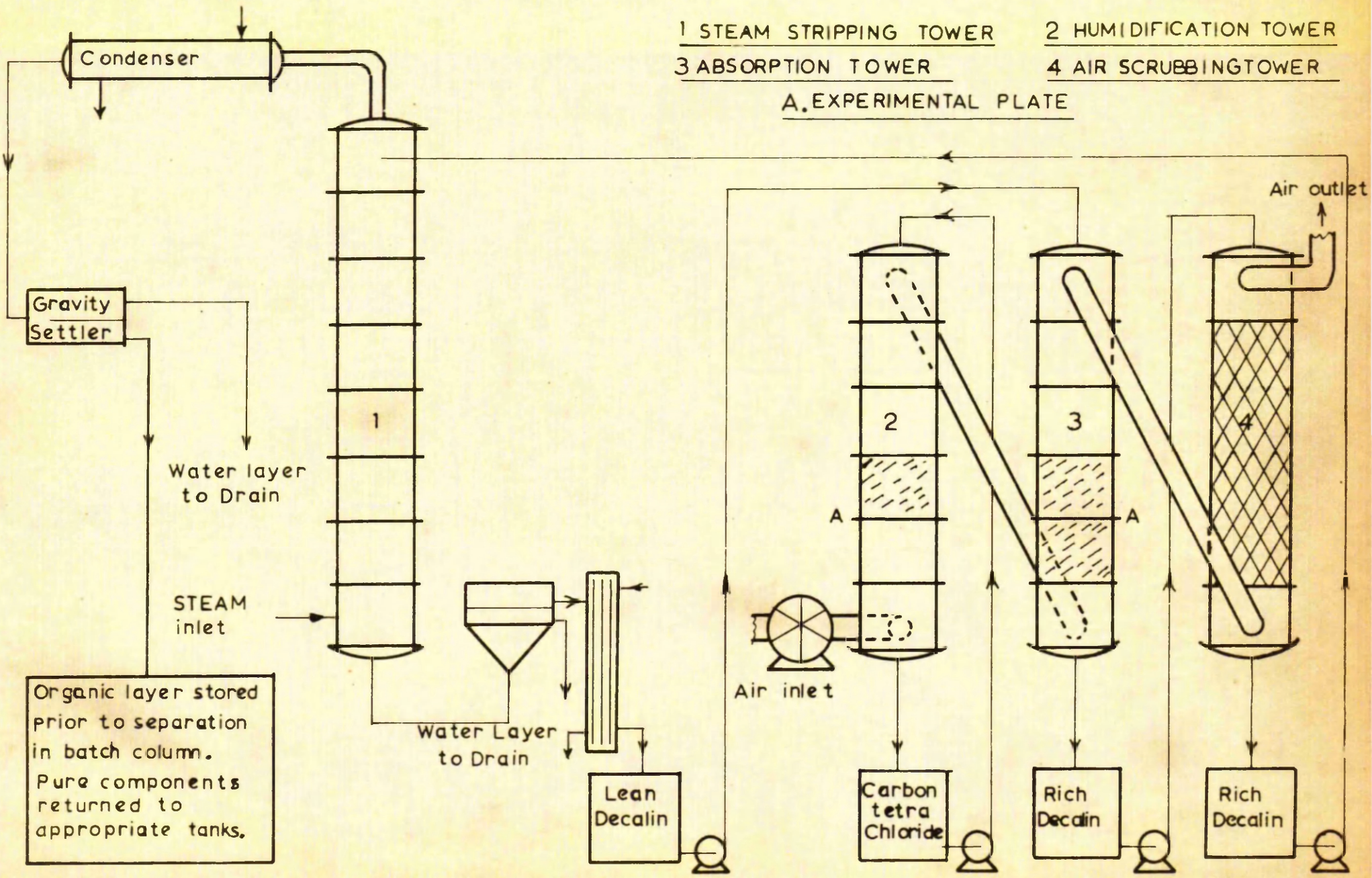

Humid Heat, B.t.u per Pound Dry Air per Deg. F
0.10 0.20 0.30 0.40 0.50 0.60 0.70
Total Heat Above 0 Deg F., B.t.u. per Pound Dry Air
Latent Heat of Vaporization, B.t.u per Pound Carbon Tetrachloride
Cubic Feet per Pound Dry Air
Absolute Humidity, Pounds Carbon Tetrachloride per Pound Dry Air
Temperature, Deg F
A – Humid Heat
B – Latent Heat of Vap
C – Sat Volume
D – Dry Volume
E – Total Heat of Sat Air
F – Total Heat of Sat Vapor
Absolute Humidity
AIR — CARBON TETRACHLORIDE
HUMIDITY CHART
Barometric pressure, 760 mm. Hg
NOTE Humid heat curve plotted against humidity All others plotted against temperature
Working Equations
Absolute humidity $H_s = 5.310p_s/(P-p_s)$
Heat of vaporization $r_t = 99.5 - 0.04t$
Humid heat $s = 0.24 + 0.13H$
Dry specific volume $V_d = 0.0252\ (t + 460)$
Saturated specific volume
$V_s = 0.73\ (t_s + 460)\ (0.0345 + H_s/153.83)$
Adiabatic cooling equation
$H = H_s - (H_s + 1.846)/(1 + F)$
$F = 7.6923r_s/(t - t_s)$
Symbols
H = Humidity
s = Humid heat
V_d = Dry specific volume
V = Saturated specific volume
P = Total pressure, mm. Hg
H_s = Saturated humidity at temperature t.
r_s = Heat of vaporization at temperature t_s
t = Dry bulb temperature, deg. F.
t_s = Adiabatic saturation temperature, deg. F
p_s = Saturated vapor pressure, mm. Hg
Curves
A—Humid heat, B.t.u. per lb. dry air per deg F.
B—Latent heat of vaporization, B.t.u. per lb. vapor
C—Saturated volume, cu. ft per lb. dry air
D—Dry volume, cu. ft. per lb. dry air
E—Total heat of saturated air per lb. dry air, B.t.u. above 0 deg. F.
F—Total heat of vapor to saturate 1 lb. dry air, B.t.u. above 0 deg. F
© 1940 Chem & Met

FIG. 5.11.



APPARATUS USED FOR ABSORPTION AND HUMIDIFICATION

FIG. 5.12

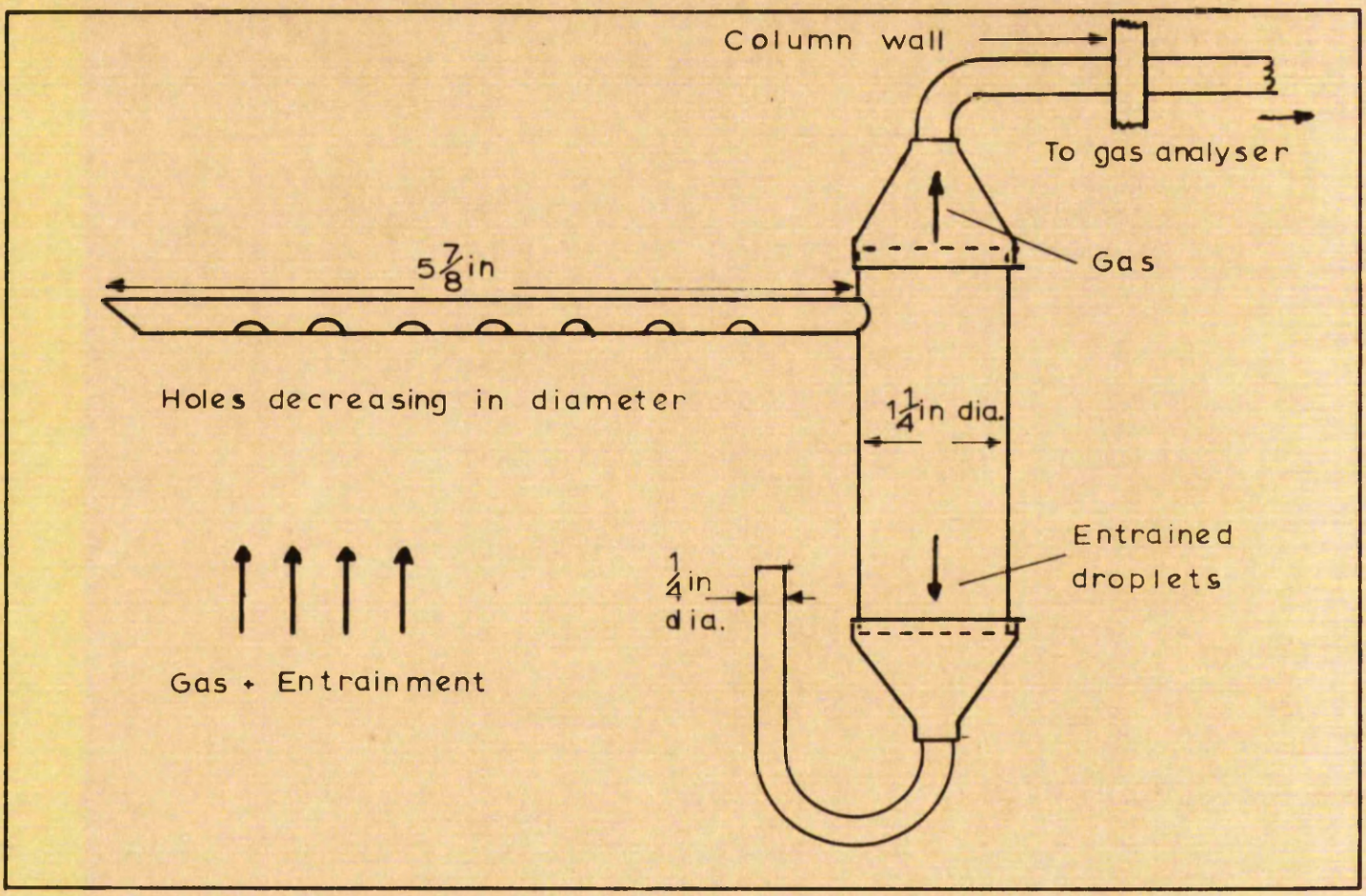


FIG. 5.13.

GAS SAMPLING DEVICE

6. DISCUSSION OF RESULTS

6.1 HYDRAULIC STUDIES

6.1.1 Air/water

While the clear liquid height and plate pressure drops obey the same relationship with air and liquid rates as has been found by other investigators, the dependence of the froth height on air rate differs markedly from that previously observed. The rise and fall of the curve with its corresponding effect on the gas residence time is thought to be explained partly by the theory proposed by Calderbank and Rennie[101] and the following mechanism is proposed.

As the air rate increases at low air rates, i.e. up to $F = 0.5$, bubbles are formed at the orifices at constant frequency, the size of the bubble increasing with air rate. The volume of the bubbles increases until the arrangement of closest packing of spheres is reached. Further increase in gas rate, above $F = 0.5$, causes this structure to break down and smaller bubbles are formed, causing the froth height to decrease. At the same time, however, the increasing gas rate is accommodated by an increasing velocity of rise of the bubbles, an effect which tends to increase the froth height. The net result of these two opposing processes is to decrease the froth height slowly. As can be expected, the effect of the second process would be less at the higher liquid rates and so the slope of the froth height versus air rate curves is greater at the higher liquid rates. A value of air rate will be reached for each liquid rate at which the second process predominates and the froth height begins to rise again e.g. at $F = 0.7$ for $L_v = 90$ gal/hr ft^2 and $F = 1.0$ at $L_v = 450$ gal/hr ft^2. It seems reasonable to expect that at the larger liquid rates, the initially greater gas hold up would delay the appearance of this minimum on the curves of froth height and gas residence time against air rate. The rate at which the curves rise again will also depend on the liquid rate,

as one could expect that the rising velocity of the bubbles, which is increasing with air rate, will increase faster at the lower liquid rates because there is less hydrostatic head to oppose their upward motion. This will explain the difference in slope of the curves above F = 1.0 and the fact that there is a cross-over point at this value where the froth heights and gas residence times are approximately independent of liquid rate. One could expect, incidentally, an efficiency at this F factor which is also independent of liquid rate.

The above theory is supported by the variation of the fractional gas hold up with air rate. Up to F = 0.5 approximately, the hold up increases fairly rapidly until a value of H_G = 0.5 approximately which corresponds with a closest packing of spheres volume of 0.52. The hold up remains fairly constant at this value in harmony with the concept of the two opposing processes of bubble rupture and increase in velocity of rise. At F = 1 the gas hold up fraction starts to rise again corresponding with the effect of the increase in velocity of rise gaining the ascendency on the overall process. Jetting and spouting will also increase the gas hold up fraction. Visual observations confirmed three regimes:

(a) A bulky cellular foam at low air rates, corresponding to the bubbles approaching the close packing arrangement.

(b) An actively moving froth above F = 0.5 composed of smaller bubbles, corresponding to the increase in velocity of rise with air rate.

(c) At air rates above F = 1.0, the plate at low liquid rates no longer had any liquid seal and at high liquid rates, oscillations were observed.

The oscillations noted in (c) could be due to the

processes observed by West et al[26] where the gas velocity caused bubbles larger than the distance between two orificies to be formed with the consequent non-synchronised bubbling of all the orificies. The effect of air rate on the specific gravity of the foam, $\emptyset_f$, was similar to that noticed by Crozier[98] and the data are correlated fairly well by his equation: (see Fig. 4.9)

$$\ln \frac{1}{\emptyset_f} = 0.715F + 0.45$$

A slight liquid rate effect was noted but not sufficient to warrant amendment of the equation.

6.1.2 Air/carbon tetrachloride

The effects of air and liquid rates on the froth height, clear liquid height and plate pressure drop are those usually described in the literature. The gradual increase in froth height may mean that the closest packing arrangement has already been passed and that the increasing froth height is due to the bubbles formed at the orifice being of constant size but increasing in velocity of rise with air rate. This may be borne out by the fractional gas hold up values which are all above the 0.52 value. The hold up is increasing with air rate but fairly slowly. The values of the froth specific gravity are somewhat below the line of Crozier's correlation but the deviation is less than that of some of the data from which the correlation was obtained. In an attempt to explain the discrepancy between measured and calculated mass transfer efficiencies, Ellis and Rose[37] also suggested that air/carbon tetrachloride froths were less dense than air/water froths. The main source of error is in the measurement of clear liquid height which could only be measured to 0.1 in, which can give rise to a percentage error of 20% at the lower values.

The gas residence times fall with air rate, indicating that a similar fall in efficiency is to be expected. Only at higher air rates does liquid rate have a noticeable effect on the gas residence time.

6.1.3 Air/decalin

While the effect of air and liquid rates on clear liquid height and plate pressure drop is usual, the effect of liquid rate on the froth height is much more marked than in the air/water and air/ carbon tetrachloride tests, especially at the lower air rates. The fact that at L_v = 560 gal/hr ft^2, froth height decreases with air rate and that at L_v = 110 gal/hr ft^2, the froth height increases, may be due to the competition of the two processes of bubble rupture and increase of velocity rise, the liquid rate determining the ascendency of each process. The curves show a resemblance to the air/water curves between F = 0.6 and 1.0, allowing for the exaggerated liquid rate effect. The hold up fraction values, H_G, seem to support this theory as they are above the close packing figure of 0.52. The curve is essentially the same shape as the air/carbon tetrachloride system with the exception that the L_v = 330 gal/hr ft^2, values do not fall on a mean line. The specific gravity of the froth is far lower than would be expected and comes nowhere near the Crozier correlation.

The gas residence times decrease with air rate but depend upon liquid rates at the lower air rates, predicting similar relationships with plate efficiency, gas rate and liquid rate.

6.1.4 Gas hold up results

The values of the fractional gas hold up, H_G, shown on Figs. 4.7 and 4.8, all show a slight increase with F factor and little or no effect of liquid rate. The difference in magnitude

of values of H_G at the same F factor for different systems was presumed to be due to the variation in physical properties, and it was found that the results for the three systems could be correlated by a single equation,

$$H_G = 0.25\,F - 0.0087\,\sigma\,\rho_L + 0.55 \qquad \text{(6.1)}$$

where σ is the surface tension of the liquid,(dyne/cm)and ρ_L is the density of the liquid,(gm/cm^3) This correlation shown on Fig. 6.1 is correct to 5% within the range F = 0.4 to F = 0.9. Beyond this range the accuracy is less, depending on the system considered.

The variation of froth character with system properties is not as would be expected from consideration of the work done in bubble dynamics, but as has already been mentioned, most of the work reviewed in Section 1.8 is not representative of conditions existing on a sieve plate operating under normal conditions. It is interesting to compare this equation with the work of Mersmann [125] who studied the operation of a sieve plate with regard to the conditions which allowed all the holes to function. He concluded that all holes function after a certain minimum throughput was exceeded and that this throughput depended on hole size and number and on interfacial tension and fluid density. The results were confirmed by many observations on large scale equipment.

One factor which is not often considered in studying the structure of foams and froths on bubble-plates is the stability of the foam leaving the plate and descending the downcomer. The time taken for the liquid to disengage from the vapour in the downcomer will have an effect on the foam height. It was noticed in the course of the work that extremely stable foams formed by detergents did not disengage at all in the downcomer and the column above the plate became completely choked.

It is possible that the system properties do not affect directly the structure of the froth, but do so indirectly due to their effect on the stability of the froth disengagement time in the downcomer. Danckwerts et al.[40] discussed the stability of froths in terms of the drainage of liquid from the spaces between the bubbles, and concluded that viscosity would have a direct effect on the stability. Although no viscosity effect was found here, it is possible that other physical properties affect stability in the same manner.

The variation in gas hold up caused by the system properties will affect the other variables e.g. froth height and gas residence time, and explains the differences at the same operating conditions for different systems. It was not possible to obtain equations to correlate froth height and gas residence time with any acceptable accuracy.

It can be concluded that the premise that equal gas and liquid rates on identical plates for different systems, will result in equal gas residence times, does not hold for the systems studied in this work.

6.2 MASS TRANSFER STUDIES

6.2.1 Air/water system

The effect of liquid and gas rates on plate efficiency E_{MV} (Fig. 5.1 and 5.2) seems to be more complicated than has been found by other workers. Ellis and Moyade[30] found that plate efficiency increased with liquid rate and decreased with gas rate in a regular manner. Garner and Freshwater[106], on studies on a 5 ft diameter bubble-cap tray, found that the curves of plate efficiency against gas and liquid rate passed through a maximum value for E_{MV}, but once again in a regular manner. Mackay[84] found that relationships similar to those of

Ellis and Moyade applied to a Kuhni plate. Rush and Stirba[35] concluded that liquid rate had no effect on E_{MV} for gas-phase controlled systems on sieve plates, and that increases in gas rate tended to decrease the value of E_{MV} only slightly. The gas-phase controlled system used by Gerster et al.at the University of Delaware[33] for bubble cap and sieve plates, showed a slight increase in E_{MV} with liquid rate and a decrease with vapour rate. The trend of the results of this investigation agree with the conclusions of Ellis and Moyade, Mackay and Gerster et al.at vapour rates below 3.3 ft/sec.

The results from the present work were compared with those of Ellis and Moyade whose comprehensive results on a 4¼in diameter plate enabled comparisons to be made at the same free area(5%) and the same weir height (1 in) as the present work. The comparison is shown on Fig. 6.3 for an F factor of 0.49. Agreement is excellent over the complete range of liquid rates. A comparison is also made with the data of Ellis and Rose[37] at an F factor of 0.72. The plate used by the latter workers was again 4¼ in diameter with a 1 in weir but with a free area of 8%. Agreement is good at the lower liquid rates. Since plate efficiency for a gas-film controlled system does not depend on the degree of mixing, it can be considered to be independent of plate diameter provided that the overwhelming proportion of mass transfer takes place on the plate itself and mass transfer on the walls of the column is a very small proportion of the total mass transfer.

The complex effect of gas and liquid rates on E_{MV} found here, is in agreement with that expected from observations made in the studies of the hydraulic behaviour on the plate. Consideration of Fig. 4.10 shows substantially the same effects of gas and liquid rates on the gas residence time t_G. The critical transition value of gas rate is not so pronounced as

in the case of the plate efficiency but is still within the range 3 to 4 ft/sec. The effect of liquid rate is very similar in each case. It was not possible to measure the air flow accurately at low air rates and no mass transfer work was done below V_s = 1.4 and the maximum value of E_{MV} at low air rates predicted from Fig. 4.1 cannot be demonstrated.

The mass transfer efficiency, expressed as the number of transfer units N_{OG} is compared with gas and liquid rates on Fig. 5.4. Values of N_{OG} from this graph are plotted against the corresponding values of t_G on Fig. 6.2. The values used are shown on Table 6.1. It can be seen that with the exception of five points, a linear relationship between gas residence time and transfer units is well defined for all values of gas and liquid rates, indicating that gas residence time is a primary influence in mass transfer. The five irregular points all occur at gas rates above 3.3 ft/sec and it would seem that mass transfer takes place additional to that resulting from contact of gas and liquid on the plate. It was thought that this additional mass transfer would very likely be due to additional transfer on the walls of the column caused by the greater entrainment at the higher velocities. The following mechanism is proposed to explain the effects of gas and liquid rates on mass transfer over the whole range of values studied.

1. As air rate increases at low air rates, bubbles are formed at constant frequency and volume of bubbles increases.

2. The volume of the bubbles increases to reach arrangement of close packing of spheres at a gas hold up of about 52%.

3. Further increases in gas rate cause the structure to break down slowly, and smaller bubbles are formed with a consequent decrease in the height of the froth. The gas hold up will, however, remain the same, as raising the gas velocity

only increases the rising velocity of the bubbles. This effect tends to increase the height of the foam.

4. Eventually the rate at which the bubbles decrease in size falls off and the increasing rising velocity of the bubbles causes the foam to expand once more and the gas hold up increases. This gives a minimum value of the gas residence time which, from Fig. 4.10 depends on liquid rate. This means that at a specific value of V_s (say 3.3 ft/sec) the gas residence time plot still falls for high liquid rates while it rises for low liquid rates and consequently the efficiency versus gas rate curves will cross over.

5. A further complicating factor is that around 3.5 ft/sec the gas velocity disrupts the orderly system and the orifices bubble non-uniformly as reported by West et al[26]. Bubbles larger than the distance between orifices are formed and unstable conditions make their appearance such as jetting and spouting and oscillation of the froth on the plate. In the case of low liquid rates, however, the seal is not high enough to permit oscillation and the instability manifests itself in high entrainment.

At high liquid rate, the entrainment is not so obvious but the oscillations and spouting cause a decrease in interfacial area (although not necessarily gas hold up) and the already falling curve of E_{MV} against gas rate falls more steeply.

The entrained water deposits itself on the column walls and since there is no plate above, the column functions as a wetted-wall column for about 3-4 ft above the plate. This is an area of high mass transfer and as the volume of water on the walls is an appreciable portion of the hold up on the plate (calculated to be about 25% at lowest liquid

rate) the overall effect is to increase further the plate efficiency at low liquid rates. Above 3.8 ft/sec at all liquid rates, entrainment is severe and the wetted-wall mass transfer is important. The effect of increasing gas rate after this point is to increase the surface area slowly and all the efficiency curves begin to rise again. Above V_s = 3.8 ft/sec the air velocity is too great for stable operations at the lowest liquid rates and the plate ceases to carry any liquid.

6.2.2 Air/carbon tetrachloride system

The effect of gas and liquid rate on plate efficiency, (Fig. 5.6)seems more typical than in the case of the air/water system, but the range of gas rates is smaller and the effect of gas rate is much the same for both systems within the range of V_s from 1.4 to 3.4 ft/sec. The effect of liquid rate is more noticeable for the air/carbon tetrachloride system. The effects of both gas and liquid rates are broadly the same as those found by other workers studying gas-phase-controlled systems as described in Section 6.2.1.

Quigley et al.[66] studied formation of froths of air in carbon tetrachloride but gave no mass transfer data. Westkaemper and White[126] gave mass transfer results but not from mass transfer on a sieve plate. The only reported results which seem to be comparable with the present work are those of Ellis and Rose.[37] The comparison is made on Fig. 6.4 and it can be seen that the present results are substantiallyare self-consistent so it would than were expected. The results are self-consistent so it would because of seem that the reason for the low values is either ~~due to~~ because of the different methods (i.e. whether the driving force is taken as enthalpy difference or partial pressure difference) used for calculating the results, or the different experimental procedures.

It is not possible to compare the results that would be obtained by each method of calculation for the air/carbon tetrachloride system, but Garner and Freshwater[106] have compared the results obtained by both methods for the air/water system and found that each method gave results of approximately the same magnitude. It has not been possible to test the validity of the assumption that "modified" enthalpies can be used.

The major difference between the two experimental procedures is that while the experiments of Ellis and Rose took place under adiabatic conditions, the present work did not and the temperature differences across the plate were considerable. The average temperature drop at runs of 82, 190 and 310 gal/hr ft^2 were 17.5, 11 and 7 deg F respectively. This means that the temperature of the liquid film at the phase boundary must be extremely low and consequently the partial pressure of carbon tetrachloride at the interface will be very low. The phase boundary temperature will be far lower than the average of the inlet and outlet liquid temperatures over the plate, and as this value was used in the calculation of results, this could explain the low values of E_{MV}. It is also possible that the extremely cold boundary film prevents molecular diffusion within the bulk of the liquid. Danckwerts et al.[40] discuss the effects of "thermal distillation" on plate efficiency and point out that where the temperature of the boundary film is much higher than the bulk of liquid, increased efficiency may result from flashing of superheated liquid during the process of surface renewal. Perhaps the effect of the boundary film temperature being much lower than that of the bulk liquid ~~has an effect~~ is detrimental to plate efficiency due to serious inhibition of the rate of surface renewal caused by low rates of molecular diffusion. The fact that the average temperature difference across the plate depends on liquid rate may explain why the effect of liquid rate on plate efficiency is greater in this work than in that of

Ellis and Rose and is greater than that found in the air/water studies.

The fall in plate efficiency with gas rate as predicted from the gas residence times from Fig. 4.11 is as expected. The effect of liquid rate is greater than would be expected. The effect of gas residence time on mass transfer is shown on Fig. 6.5 where mass transfer is expressed in terms of the number of transfer units, N_{OG} obtained from Fig. 5.5. The values used are shown in Table 6.2. The points fall into three groups and the best line through each group and the origin is drawn. The slope of each line depends upon the liquid rate which follows from the fact that liquid rate has a considerable effect on N_{OG} but little effect on t_G. Fig. 6.5 illustrates fairly well the importance of the gas residence time as a fundamental influence on mass transfer.

6.2.3 Gas absorption system

The scatter of the results is greater than for the air/water and air/carbon tetrachloride systems. The effect of gas rate on efficiency is the same as that in the other two systems over the range of gas rates common to all three. The effect of liquid rate is similar in all three systems over the common range and the absorption results show the same trend as the air/water system results at liquid rates above those used in the air/carbon tetrachloride experiments i.e. gas rate has progressively less effect on efficiency as liquid rate increases. The magnitude of the effects of liquid rate is different for each system. The effects of liquid and gas rate, are, as before, approximately similar to those found by other workers studying gas film controlled systems.

The variation of plate efficiency with gas and liquid

rates considered separately is as predicted by the gas residence time studies, but the combined effect is the opposite of that expected, i.e. at low liquid rates, gas rate has a minimum effect on gas residence time, but has a maximum effect on plate efficiency.

The effect of gas residence time on number of transfer units is shown on Fig. 6.6. The values used are in Table 6.3. As expected, due to the above-mentioned conflict, it is not possible to correlate any of the points by a line drawn from the origin. Some of the points can be correlated by a line through $N_{OG} = 0.8$, but it is not possible to demonstrate clearly a linear relationship between N_{OG} and t_G.

6.3 COMPARISON OF MASS TRANSFER RESULTS

6.3.1. Air/carbon tetrachloride system

The efficiencies of the air/carbon tetrachloride system were calculated from the measured efficiencies of the air/water system using the method developed by Gerster et al. as discussed in Section 1.6. The plate efficiencies E_{MV} were converted to the number of transfer units N_{OG} by the equation:-

$$N_{OG} = \ln (1 - E_{MV})$$

As both systems are completely gas-film controlled, the number of transfer units for the air/carbon tetrachloride system N_{OG}'' is obtained by multiplying the number of transfer units of the air/water system N_{OG}' by the ratio of the corresponding Schmidt numbers as in the following equation:-

$$N_{OG}'' = N_{OG}' \left(\frac{Sc'}{Sc''}\right)^{1/2}$$

The values of Sc' and Sc'' are obtained from Sections 3.1.1 and 3.1.2.

Thus for any given F factor and liquid rate, the value of N_{OG} for the air/carbon tetrachloride system can be calculated and hence E_{MV} the plate efficiency.

Calculated values for air/carbon tetrachloride plate efficiencies are compared with experimental values in Table 6.4 and Fig. 6.7. It can clearly be seen that the predicted values for E_{MV} fall substantially below the measured values. As can be seen from Table 6.4, this is not due to the difference in gas residence times, as in all cases the value of t_G is higher for the air/carbon tetrachloride system at identical conditions of gas and liquid flow. The discrepancy is most likely to be due to the low experimental mass transfer results for the air/carbon tetrachloride system as discussed in Section 6.2.

It is possible that the method of prediction is wrong, and to explore this suggestion further, the data of Ellis and Rose were used. These authors find that their E_{MV} values for the air/carbon tetrachloride system calculated from their air/water results were substantially lower than their experimental values and suggested that this is due to the lower froth density of the air/carbon tetrachloride mixtures. It was noted in Section 6.1 that the air/water results of Ellis and Rose agreed closely with the present work at the lower liquid rates. It is reasonable to assume that this is due to similar structures of the air/water froths and it was also assumed that at the same liquid rates the structures of the air/carbon tetrachloride froths would also be identical. This assumption was necessary as Ellis and Rose do not give any information on froth structure. For an F factor of 0.72 and L_V = 200 and 300 gal/hr ft^2, the present air/water results were used to calculate corresponding values for the number of transfer units for the air/carbon tetrachloride system as in

Table 6.5. The present work, Figs. 4.9 and 4.10, was used to obtain values for the gas residence time for both systems at F = 0.72 and L_v = 200 and 300 gal/hr ft^2. The value of the number of transfer units was then corrected by multiplying by the ratio of the gas residence times. The linear connection between N_{OG} and t_G has already been established Figs. 6.2 and 6.5. This gives a corrected value for N_{OG} for the air/carbon tetrachloride system and, on converting this to the corresponding value of E_{MV}, good agreement is reached with the experimental values of E_{MV} obtained by Ellis and Rose.

This comparison gives support to the suggestion that the method of calculation is correct and that the mass transfer results for the air/carbon tetrachloride system found in this work are artificially low.

6.3.2 Gas absorption system

As the gas absorption system is not a humidification system it is possible that there is also a resistance to mass transfer from a film on the liquid side of the phase boundary. If this is the case, then Equation 1.17 applies. However, in this system studied here, the value of m was found to be so low (m = 0.0018) that the effects of any liquid film can be ignored and the system treated as gas phase controlled only. This also means that the effects of liquid mixing can be neglected.

Accordingly values for E_{MV} were calculated from the air/water results in the same manner as in 6.3.1 and were compared with the values determined experimentally. The comparison is shown on Table 6.6 and on Fig. 6.8 for liquid rates L_v = 200 and 400 gal/hr ft^2. As can be seen, the calculated values are considerably below the experimental values. This can be explained by examination of the gas residence times given in the

last two columns of Table 6.6. The gas residence times for the air/water system are all substantially lower than those for the gas absorption system at identical gas and liquid rates.

The results were corrected for this difference, as in the previous section, by multiplying the value of the number of transfer units for the absorption system, N_{OG}''', calculated from the air/water system results, by the ratio of the gas residence times. The comparison between the values of the plate efficiency for the absorption system E_{MV}''' calculated in this manner, and the experimental values are shown in Table 6.7 and for values of L_T = 200 and 400 gal/hr ft^2 on Fig. 6.9. The agreement is much better especially at the higher liquid rates. The difference between experimental and calculated values at the lower liquid rate is possibly due to the discrepancy between the experimentally determined values of gas residence time and number of transfer units as discussed in Section 6.2.3. However, it is safe to assume that the difference between the experimental and calculated values in Table 6.6. can be attributed, at least partly, to the divergence of gas residence times at identical gas and liquid rates.

It is also possible that corrections should be made for differences in interfacial areas at identical gas and liquid rates.

As the experimental values for the air/carbon tetrachloride system seemed to be artificially low, it was considered pointless to calculate gas absorption efficiencies from this source but the data of Ellis and Rose were used instead. The comparison of calculated and measured values is shown on Table 6.7 and, as can be seen, the agreement is good, probably because of similarity of the gas residence times. (The gas residence times for the air/carbon tetrachloride systems are taken from the present work as in Section 6.3.1).

TABLE 6.1

Air/water system

Gas residence time t_G and corresponding numbers of transfer units, N_{OG}

F	0.4		0.6		0.8		1.0		1.15	
L_v	t_G	N_{OG}	t_G	N_{OG}	t_G	N_{OG}	t_G	N_{OG}	t_G	N_{OG}
150	.054	1.82	.046	1.69	.035	1.52	.037	2.17	-	-
300	.072	1.79	.054	1.79	.040	1.58	.042	2.06	.050	2.24
450	.086	2.15	.080	1.90	.058	1.75	.043	2.01	.041	2.18

TABLE 6.2

Air/carbon tetrachloride system

Gas residence time t_G and corresponding number of transfer units N_{OG}

F	0.4		0.6		0.8		0.9	
L_v	t_G	N_{OG}	t_G	N_{OG}	t_G	N_{OG}	t_G	N_{OG}
82	.086	0.51	.064	0.42	.055	0.41	-	-
190	.088	0.68	.068	0.55	.058	0.52	.058	0.52
310	.090	0.90	.072	0.77	.064	0.68	.062	0.64

TABLE 6.3

Absorption system

Gas residence time, t_G and corresponding number of transfer units, N_{OG}

F	0.4		0.6		0.8		0.9	
L_v	t_G	N_{OG}	t_G	N_{OG}	t_G	N_{OG}	t_G	N_{OG}
110	.095	1.56	.078	1.31	.060	1.22	-	-
340	.142	1.58	.095	1.47	.073	1.38	.065	1.34
560	.200	2.24	.135	2.24	.095	2.24	.082	2.24

TABLE 6.4

F	L_v	N_{OG}'	$\frac{(Sc')^{1/2}}{(Sc'')^{1/2}}$	N_{OG}'' calc.	N_{OG}'' exp.	E_{MV}'' calc.	E_{MV}'' exp.	t_G'	t_G''
0.6	300	1.97	.56	1.10	.88	66	59	.07	.09
0.6	"	1.79		1.00	.74	63	52	.06	.07
0.8	"	1.58		.88	.66	59	49	.04	.06
0.4	200	1.86		1.04	.70	64	51	.06	.09
0.6	"	1.73		.97	.57	62	44	.05	.07
0.8	"	1.54		.86	.54	58	42	.04	.06

TABLE 6.5

F	L_v	N_{OG}'	t_G'	t_G''	N_{OG}'' calc.	N_{OG}'' corr.	E_{MV} corr.	E_{MV} exp.*
.72	200	1.62	.042	.060	.91	1.27	72	69
.72	300	1.60	.046	.065	.94	1.32	73	73

* Data from Ellis and Rose[37]

( )' = air/water system, ( )'' = air/carbon tetrachloride system.

TABLE 6.6

F	L_v	N_{OG}'	$\frac{(Sc')^{1/2}}{(Sc''')^{1/2}}$	N_{OG}''' calc.	N_{OG}''' exp.	E_{MV}''' calc.	E_{MV}''' exp.	t_G'	t_G'''
0.45	150	1.80	0.62	1.12	1.50	67	78	0.055	0.096
0.60	"	1.69	"	1.05	1.36	65	74	0.049	0.082
0.80	"	1.52	"	0.94	1.26	61	71	0.037	0.064
0.45	200	1.84	"	1.14	1.53	68	73	0.062	0.102
0.60	"	1.73	"	1.07	1.43	65	76	0.051	0.085
0.80	"	1.54	"	0.96	1.33	61	73	0.038	0.065
0.45	300	1.93	"	1.20	1.58	69	79	0.074	0.107
0.60	"	1.79	"	1.11	1.51	67	78	0.056	0.090
0.80	"	1.58	"	0.98	1.43	62	76	0.041	0.070
0.45	400	2.01	"	1.25	1.71	71	82	0.085	0.142
0.60	"	1.86	"	2.15	1.68	68	81	0.075	0.104
0.80	"	1.68	"	1.04	1.60	64	80	0.055	0.080

$( )'$ = air/water system, $( )'''$ = gas absorption system.

TABLE 6.7

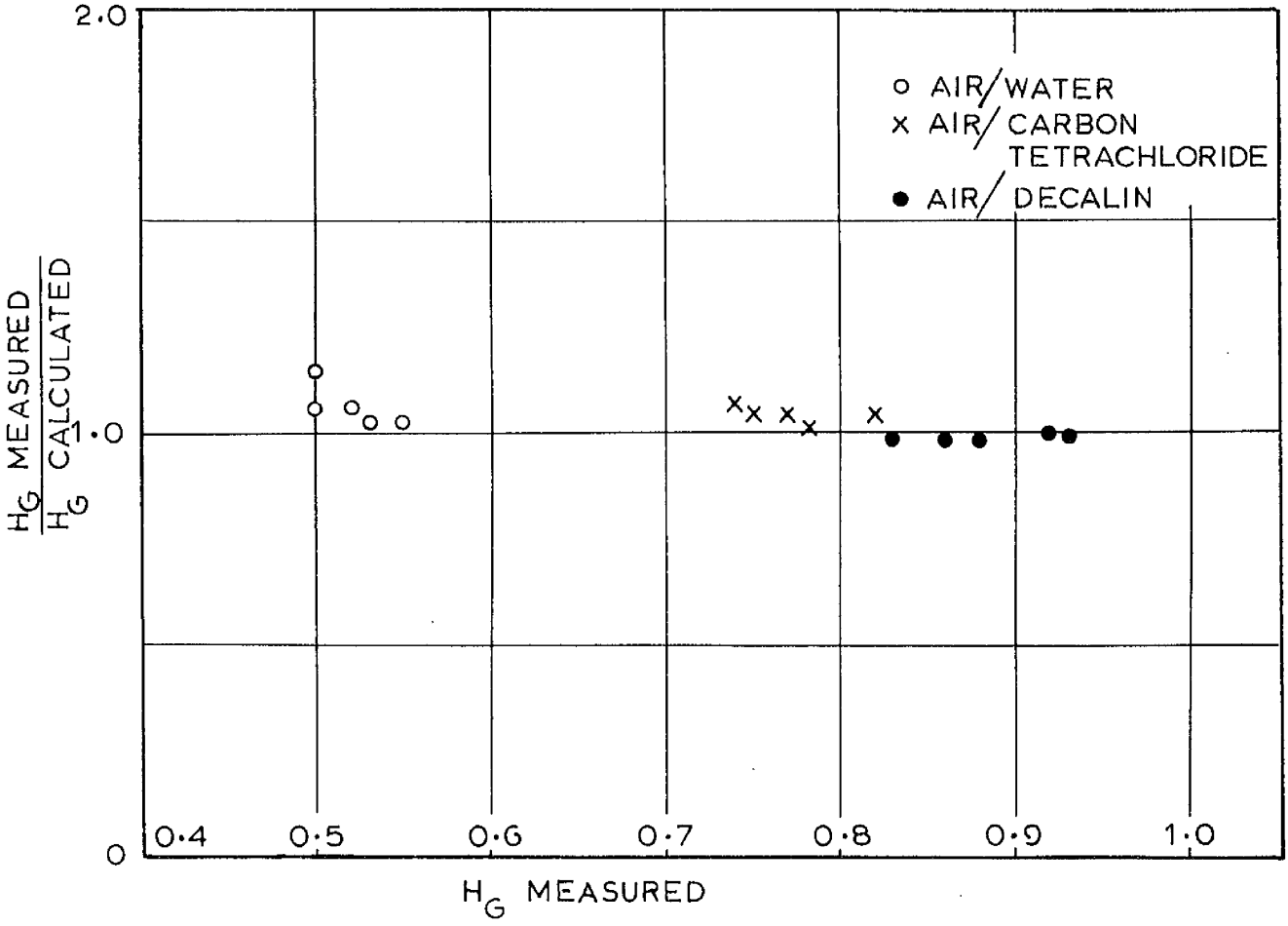
F	L_v	N_{OG}'	t_G'	t_G'''	N_{OG}''' calc.	N_{OG}''' corr.	E_{MV}''' corr.	E_{MV}''' exp.
0.45	150	1.80	0.055	0.096	1.12	1.95	86	78
0.60	"	1.69	0.049	0.082	1.05	1.75	83	74
0.80	"	1.52	0.037	0.064	1.94	1.63	80	71
0.45	200	1.84	0.062	0.102	1.14	1.87	85	79
0.60	"	1.73	0.051	0.085	1.07	1.78	83	76
0.80	"	1.54	0.038	0.065	0.96	1.64	80	73
0.45	300	1.93	0.074	0.107	1.20	1.73	82	79
0.60	"	1.79	0.056	0.090	1.11	1.79	83	78
0.80	"	1.58	0.041	0.070	0.98	1.67	81	76
0.45	400	2.01	0.085	0.142	1.25	2.08	88	82
0.60	"	1.86	0.075	0.104	1.15	1.59	80	81
0.80	"	1.68	0.055	0.080	1.04	1.51	78	80

$( )'$ = air/water system, $( )'''$ = gas absorption system

TABLE 6.8.

F	L_v	N_{OG}'' *	t_G''	t_G'''	$\frac{(Sc'')^{1/2}}{(Sc''')^{1/2}}$	N_{OG}''' calc.	N_{OG}''' exp.	E_{MV}''' calc.	E_{MV}''' exp.
0.72	200	1.19	0.61	0.60	1.11	1.32	1.37	73	74
0.72	300	1.43	0.64	0.68		1.59	1.46	80	77

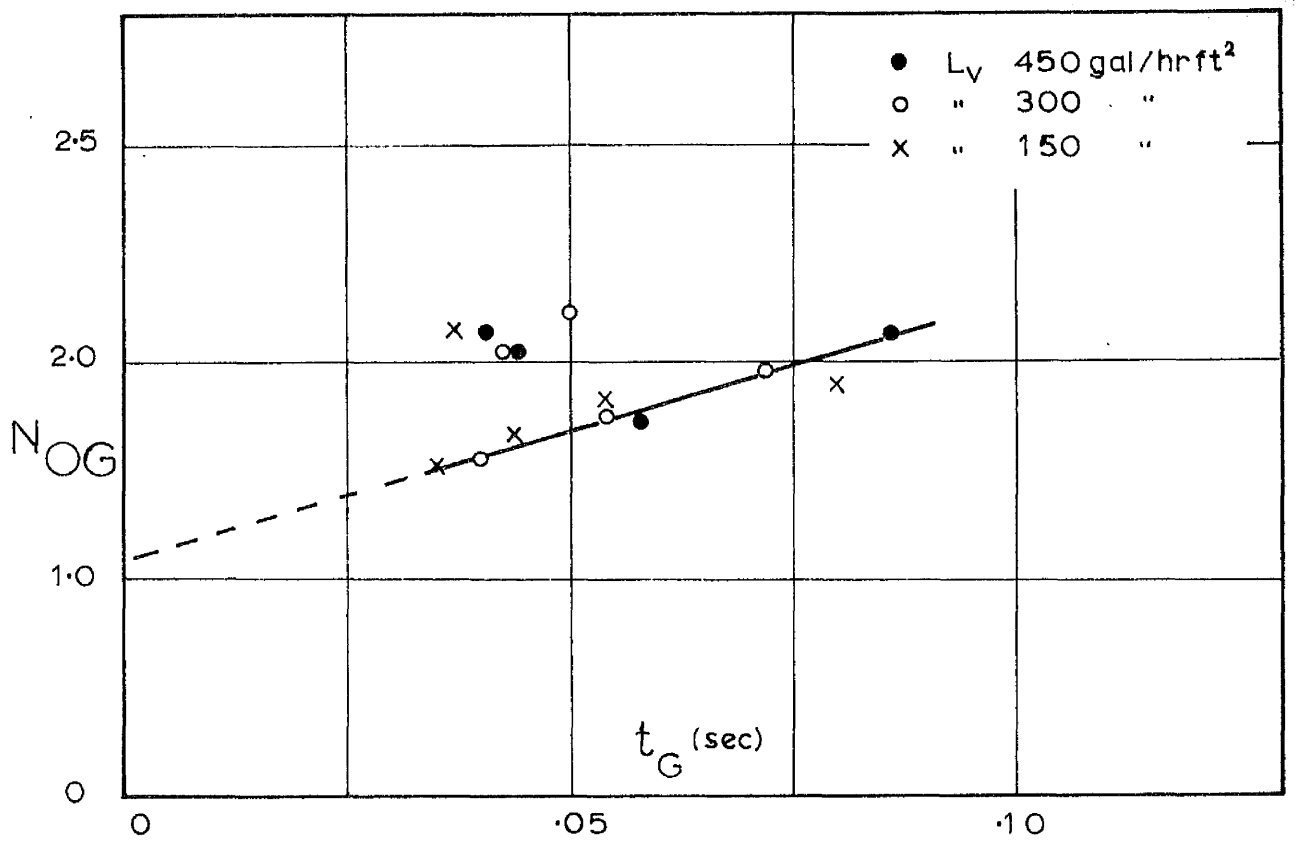
* Data from Ellis and Rose 37.



COMPARISON OF MEASURED VALUES OF FRACTIONAL GAS HOLDUP H_G WITH VALUES PREDICTED FROM EQUATION 6.1.

$$H_G = \cdot 25F - \cdot 0087\gamma\dot{e}_L + \cdot 55$$

FIG. 6.1.



EFFECT OF GAS RESIDENCE TIME t_G ON No. OF TRANSFER UNITS N_{OG} (AIR WATER SYSTEM)

FIG. 6.2.

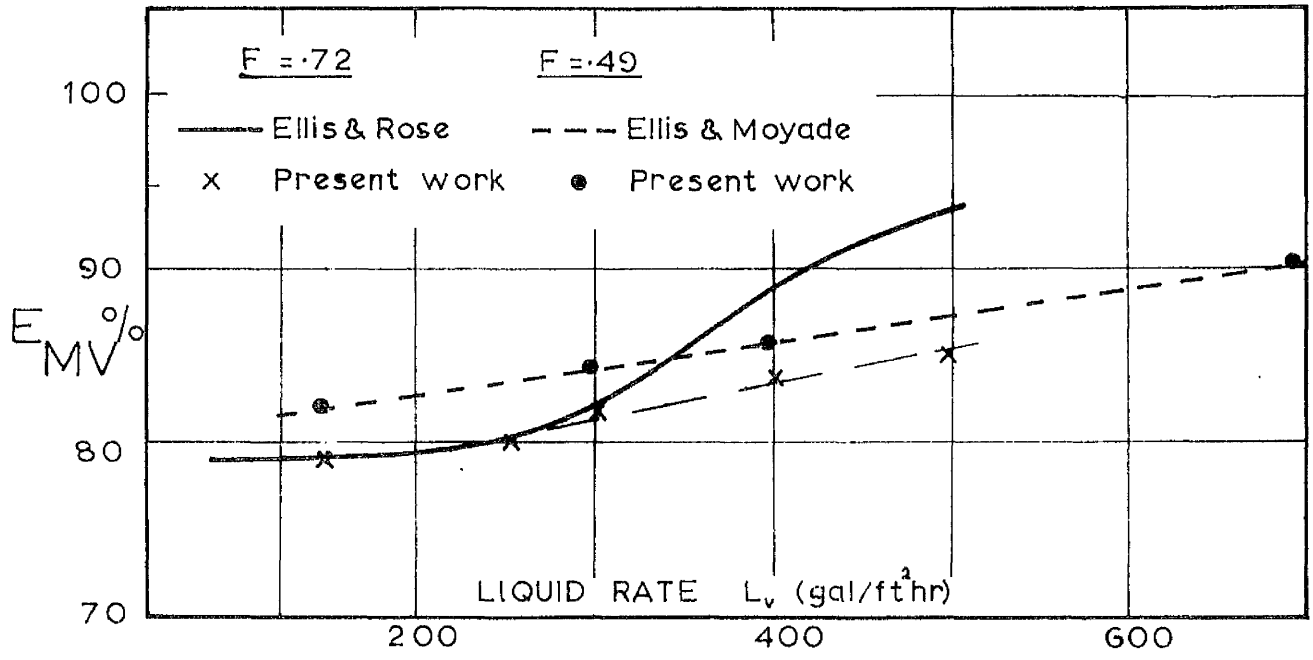


PLATE EFFICIENCY COMPARISONS (AIR WATER SYSTEM)

FIG. 6.3.

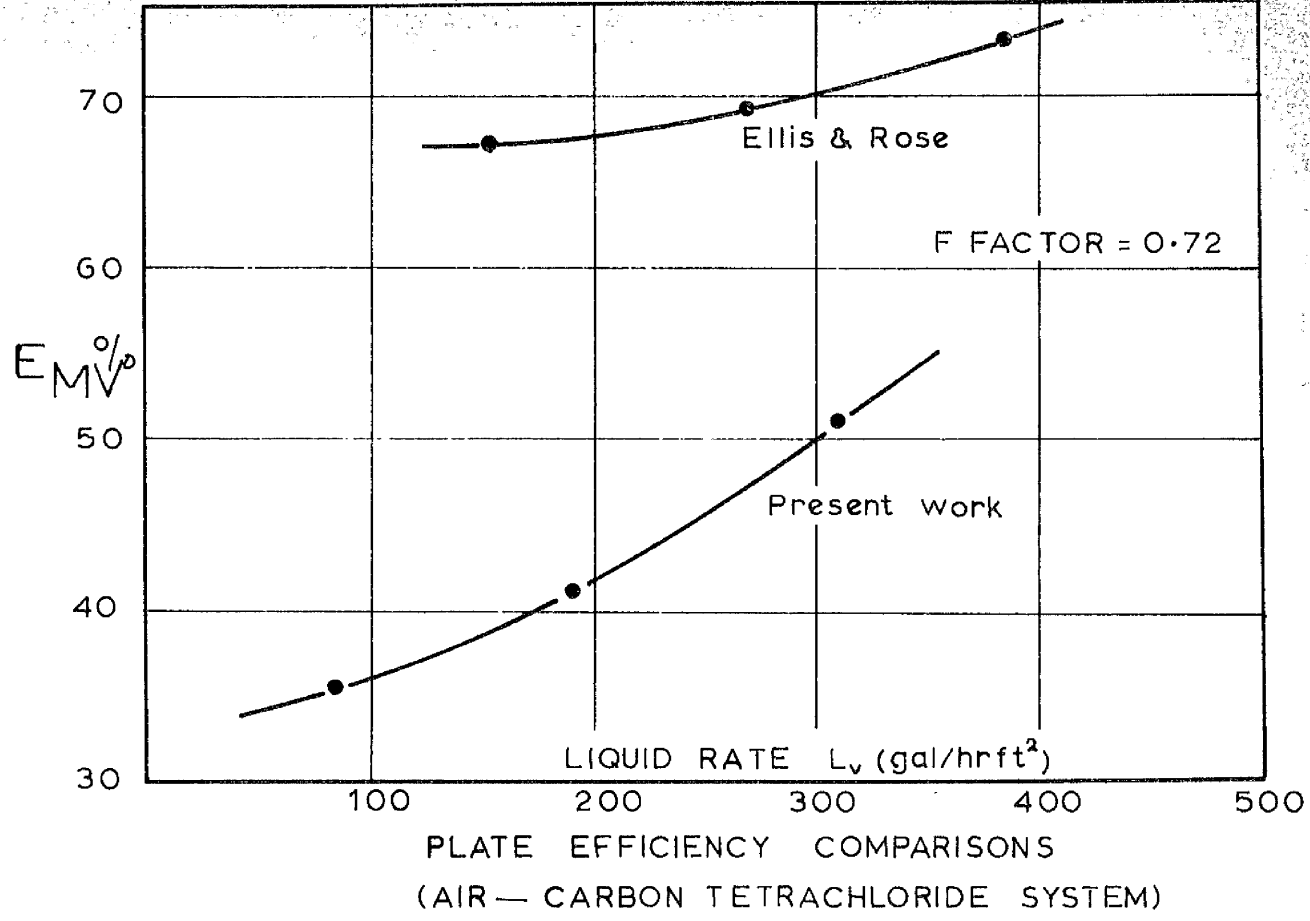
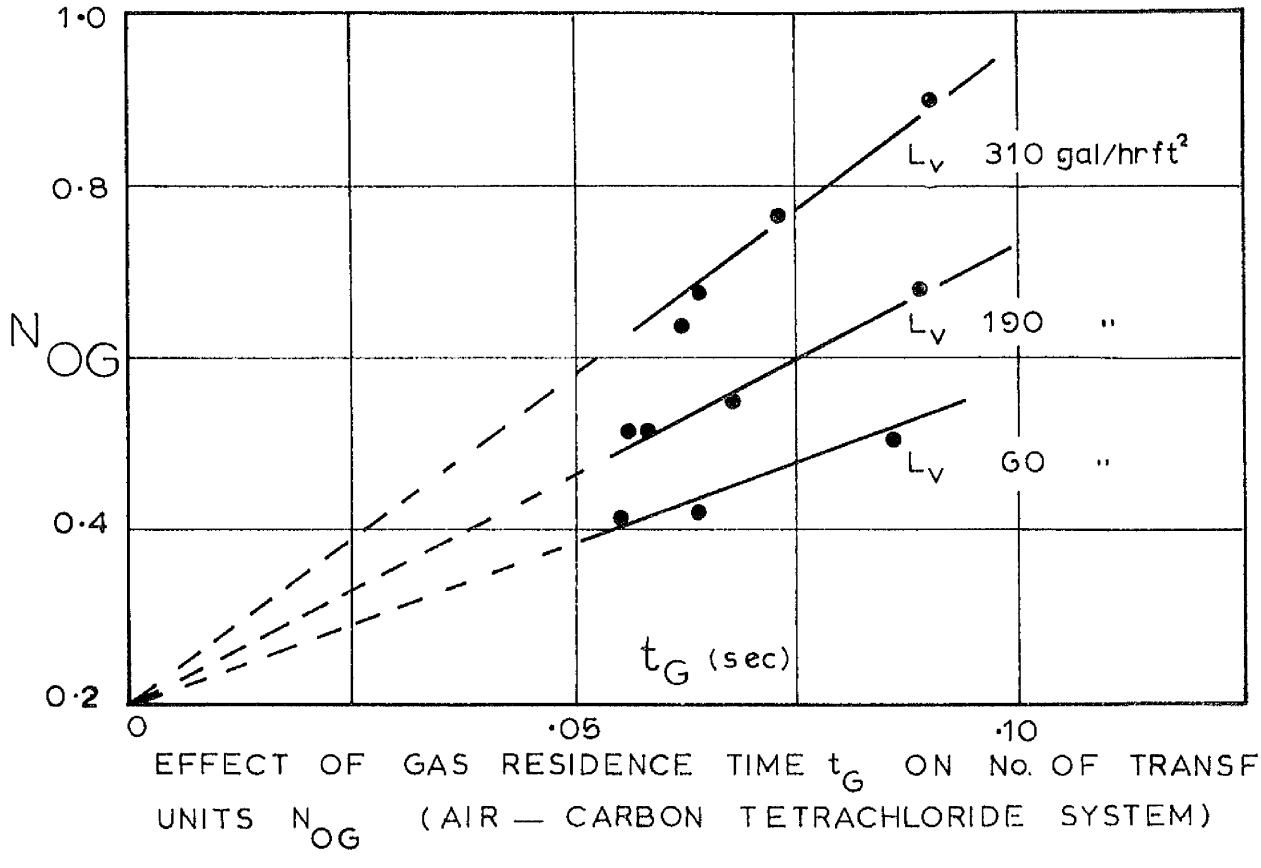


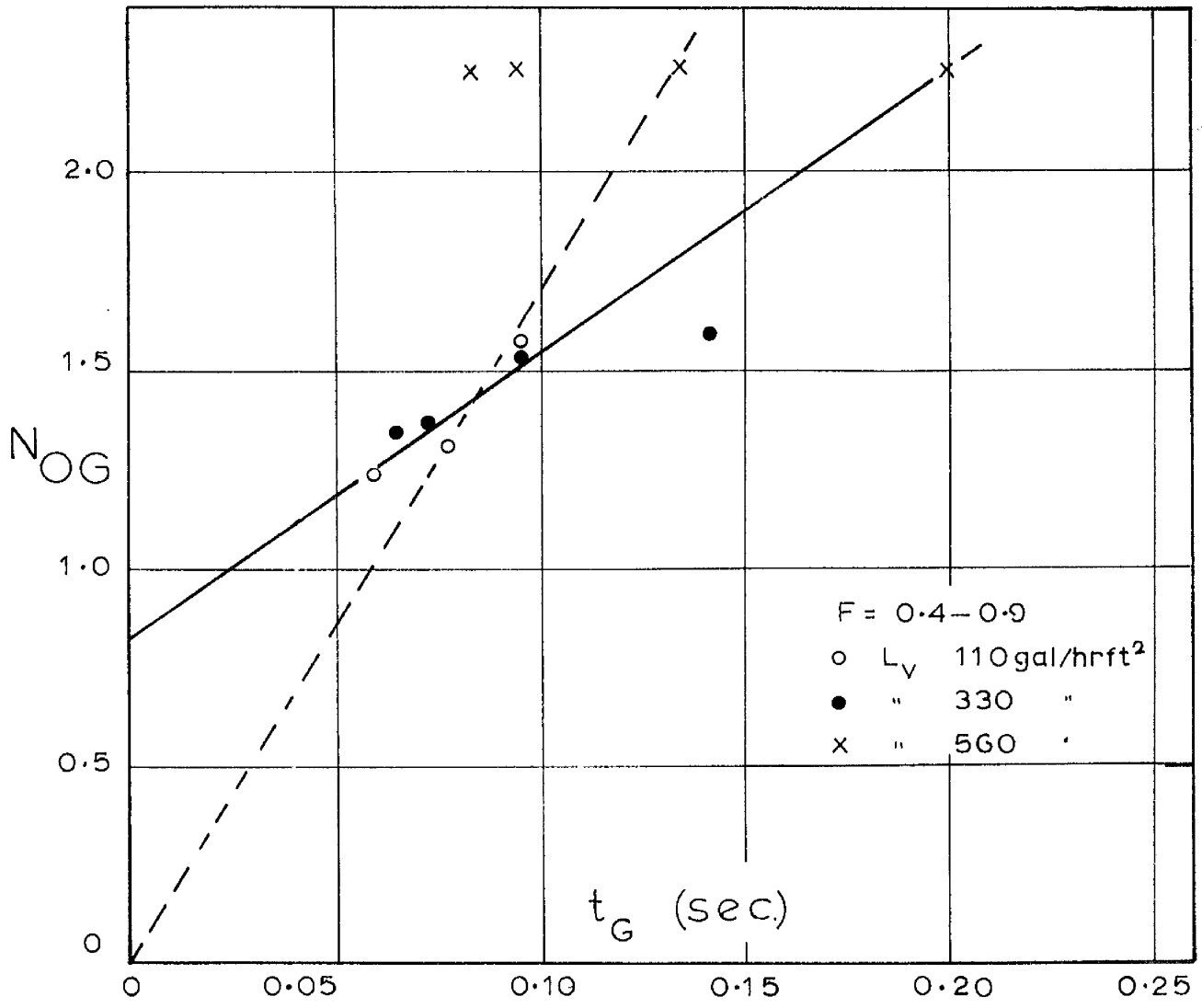
PLATE EFFICIENCY COMPARISONS
(AIR — CARBON TETRACHLORIDE SYSTEM)

FIG. 6.4.



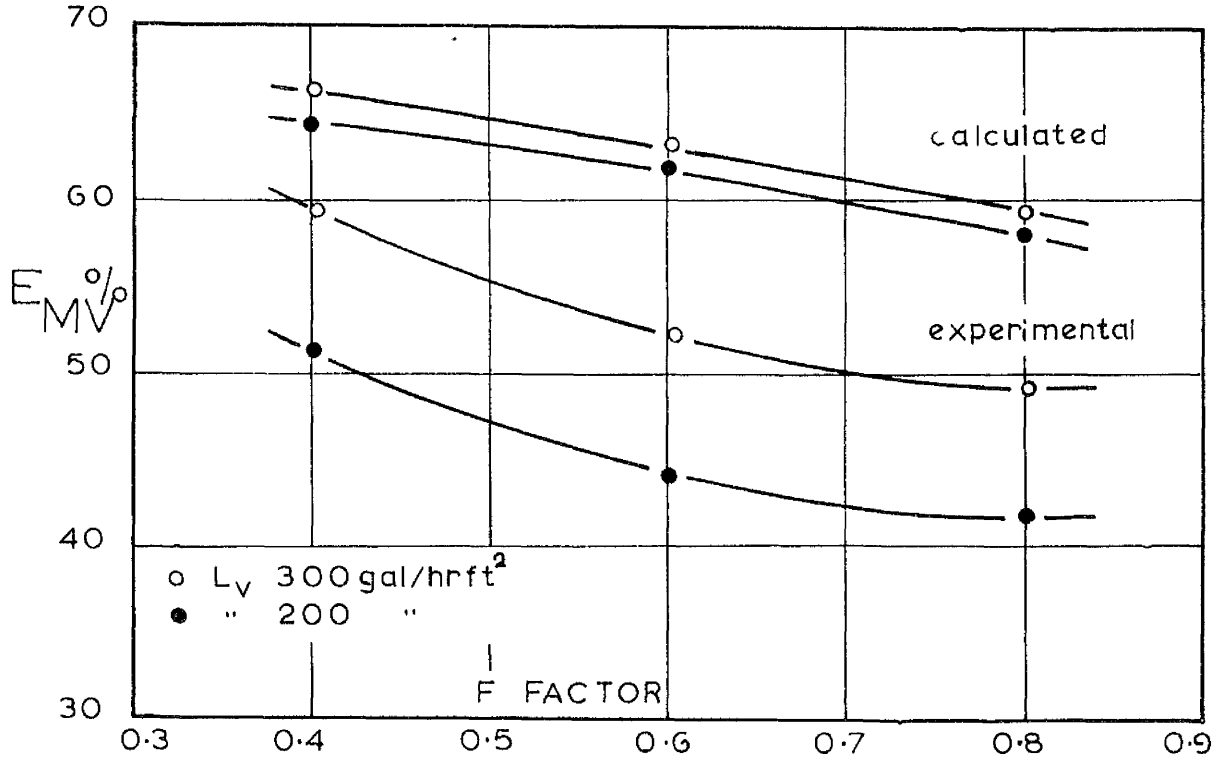
EFFECT OF GAS RESIDENCE TIME t_G ON No. OF TRANSFER UNITS N_{OG} (AIR — CARBON TETRACHLORIDE SYSTEM)

FIG. 6.5



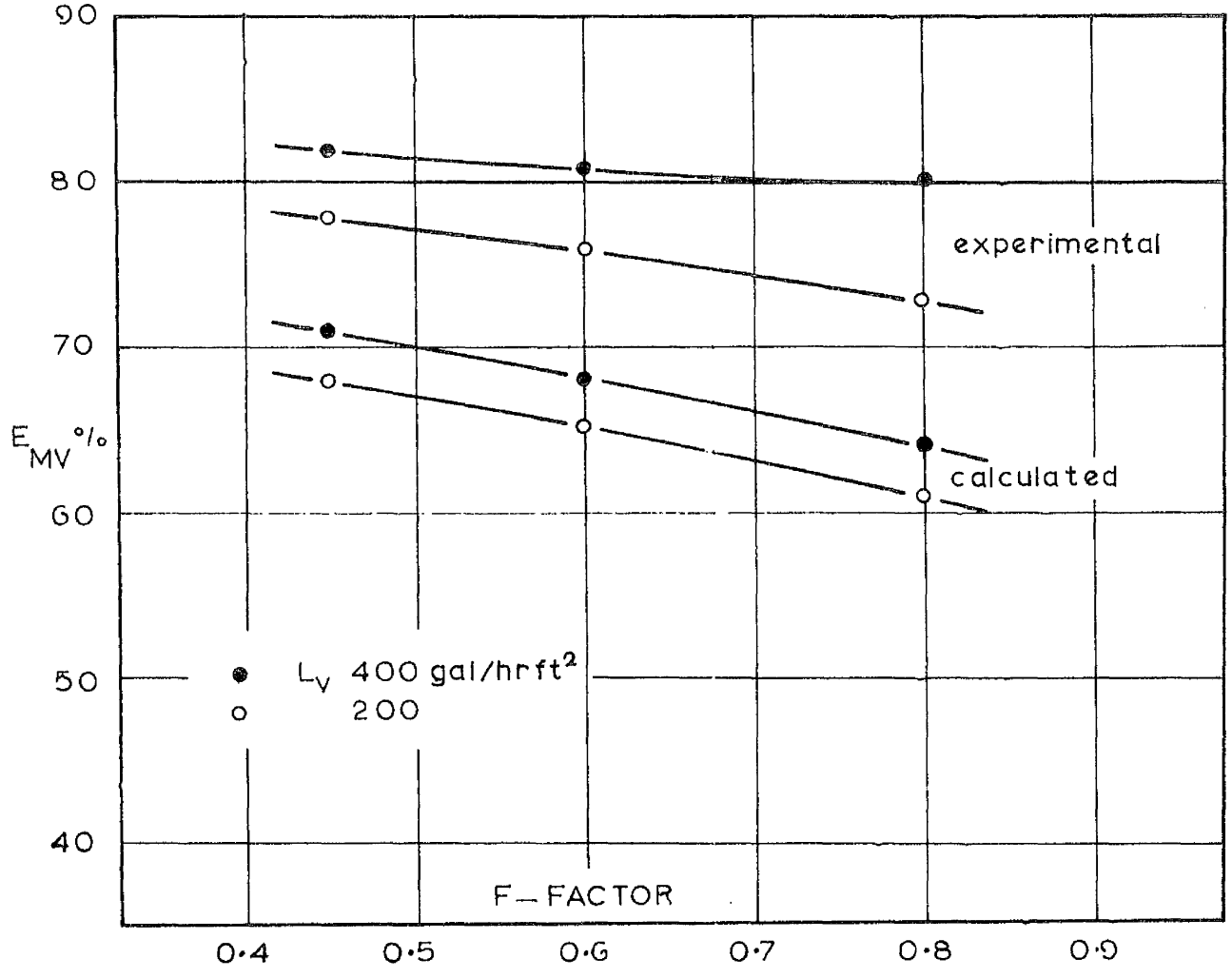
EFFECT OF GAS RESIDENCE TIME t_G on No. OF TRANSFER UNITS N_{OG} (ABSORPTION SYSTEM)

FIG. 6.6.



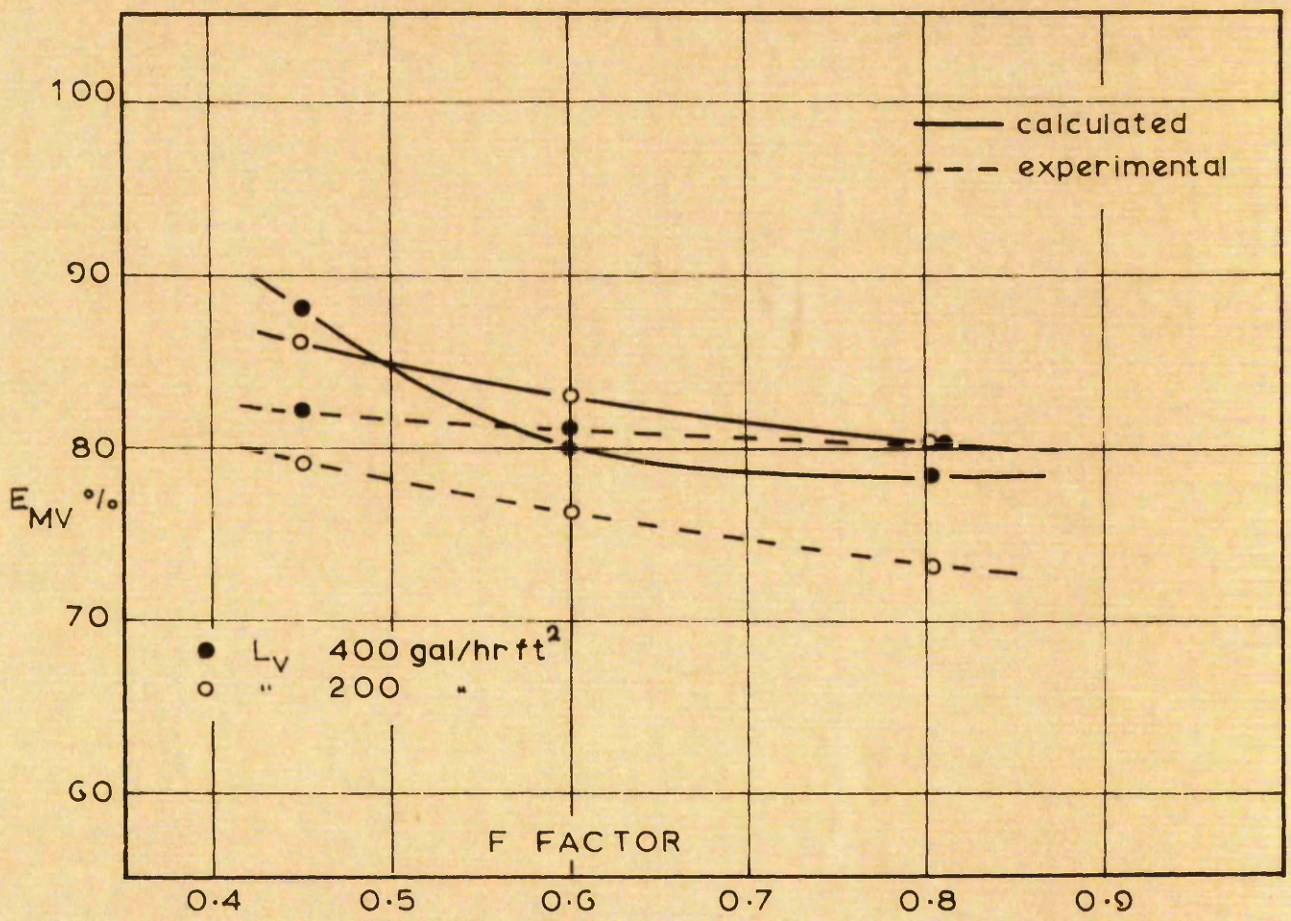
CALCULATED AND EXPERIMENTAL VALUES OF PLATE EFFICIENCY E_{MV} (AIR CARBON TETRACHLORIDE SYSTEM)

FIG. 6.7.



CALCULATED AND EXPERIMENTAL VALUES OF PLATE EFFICIENCY E_{MV} (GAS ABSORPTION SYSTEM)

FIG. 6.8.



EXPERIMENTAL VALUES OF PLATE EFFICIENCY, E_{MV}, AND CALCULATED VALUES, CORRECTED FOR DIFFERENCES IN GAS RESIDENCE TIMES. (GAS ABSORPTION SYSTEM)

FIG. 6.9.

7. CONCLUSIONS

1. Studies of the hydraulic behaviour of the air/water, air/carbon tetrachloride, air/decalin and air/carbon tetrachloride/decalin gas absorption systems on the 9 in diameter sieve plate used in this work indicated that the structure of the froths of these systems were not dependent solely on the gas and liquid rates. It is suggested that differences in physical properties of the three systems have an effect on froth structure and hence on the area and time available for mass transfer. An equation is presented ~~correlating~~ expressing the fractional gas hold up in terms of surface tension and liquid density as well as gas and liquid rates. It was not possible to obtain a correlation for gas residence time or interfacial area.

2. The effects of gas and liquid rate on mass transfer of the three systems were found to be the same in general as those reported in the literature. Where direct comparisons were possible it was found that the air/water mass transfer results agreed in magnitude with those of other workers whereas the air/carbon tetrachloride results were much lower. It was concluded that the method used to calculate the air/carbon tetrachloride results was in error due to the very large temperature difference across the plate.

3. The three systems were found to be solely gas-phase controlled and comparisons were made of the experimental values for plate efficiency E_{MV} with the values calculated by the Gerster method. Considerable disagreement was found and it was concluded that this was due to differences in gas residence times for the three systems. When corrections

were made for this, agreement was good or significantly better.

4. When efficiency predictions of the gas absorption system by the Gerster method from both aqueous and organic sources were made and when identical gas residence times were considered, or suitable corrections made, agreement was found to be satisfactory in both instances.

5. It was concluded that, in using the Gerster method to predict plate efficiencies, it is not always correct to base the prediction on similar gas and liquid rates and that more experimental data are necessary on the effects of system properties on the structure of froths on sieve plates operating under normal conditions. It is possible that the influence of system properties could be a direct result of their effect on froth structure and consequently interfacial area for mass transfer or an indirect result of their effect on the stability of froth and hence on the capacity of the downcomers which will govern the volume of froth on the plate and consequently the gas residence time.

APPENDIX A

Measurement of concentration change in dilute aqueous solution.

In an attempt to improve the Garner and Freshwater method[106] for plate efficiency measurement which depends on a change in concentration of an aqueous solution, four systems were studied. The first was the measurement of concentration change by the change in electrical conductivity of a solution. Electrical conductivity can be measured very accurately for very dilute solutions and at first sight was a very convenient method. However it necessitated large supplies of distilled water, or large quantities of solute to nullify the effect of the change in conductivity of tap water, both of which considerations were not practicable.

The second choice was the use of flame photometetry to measure minute quantities of sodium. The flame photometer can measure to 3 ppm of sodium in water but this material was not suitable again due to the unavailability of large quantities of distilled water and due to interference from sodium in tap water. Lithium was then considered as there would be no interference from tap water or other sources. The accuracy is about 4 ppm and an exploratory run was tried using lithium chloride. The results were fairly satisfactory but the accuracy was not as good as was expected and the apparatus had to be carefully calibrated as the relationship between scale reading and concentration is non-linear.

The third method considered was the concentration of a very dilute solution of a radioactive substance. The accuracy of measurement is extremely high, and measurement is done automatically. This idea had to be rejected on the grounds of cost

and because some of the radioactive material would be entrained into the laboratory atmosphere with consequent danger to health.

The fourth and final method considered was the use of a dye solution and measurement of the concentration changes with an absorptiometer. This method seemed ideal at first as, only small quantities need be used, and analysis is simple fast and accurate, however some difficulty was experienced in selecting a suitable dye. The most important criterion is that the dye does not affect the properties of water and with this in view a short-chain acid dye Azo Rhodine 2g was chosen. This dye was used for the hydraulic studies for the air/water system, but in the first mass transfer runs, the concentration rate fell at a much greater rate than was expected and it was realised that the dye was adsorbing on the metal and rubber surfaces in the apparatus. The apparatus was cleaned and repainted and rubber parts were replaced with copper. A search for another dye was conducted and several were rejected on the grounds of either their effect on the properties of water or their adsorbing tendencies. Eventually a disperse dye was selected and found to be satisfactory. Dyes of this class are actually insoluble and form an extremely fine dispersion of which the concentration or optical density can be measured by an absorptiometer in the same manner as a normal dye solution. The name of the dye chosen and found satisfactory was Duranol Brilliant Yellow.

APPENDIX B

Rate of concentration of a solution.

If the concentration of a solute in a solvent is

$$c = \frac{q}{Q}$$ where q is the mass of solute and Q is the volume of solution,

the rate of concentration is

$$\frac{dc}{dt} = \frac{d\,\frac{q}{Q}}{dt}$$

$$= \frac{-q\,\frac{dQ}{dt}}{Q^2}$$

If the rate of change of volume of solution is constant, as in a humidification process running under steady state conditions

$$\frac{dQ}{dt} = B$$

$$\therefore \quad \frac{dc}{dt} = \frac{-qB}{Q^2}$$ as q also is constant,

then the rate of concentration of solute is inversely proportional to the square of the volume.

APPENDIX C

Calculation of viscosity of carbon tetrachloride and carbon tetrachloride/air mixtures.

The viscosity of carbon tetrachloride vapour was calculated from the equation of Hirschfelder, Bird and Spotz[117].

$$\mu \times 10^5 = \frac{266.93\ (MT)^{1/2}}{\sigma^2} \quad \left(\frac{V}{W(2)}\right)$$

where μ is viscosity, cP, M molecular weight, T temperature ^{o}K, σ molecular diameter, $\frac{V}{W(2)}$ is a function of the collision integral obtained graphically. The equation was solved using nomographs published by Bromley and Wilke[122]. Values of the viscosity were obtained for 15, 20, 25°C which was the range of operating temperatures.

Viscosities of the mixtures were calculated by the equation on p. 16, 17 of Norman[3].

$$\mu_{AB} = \frac{\mu_A}{1 + \frac{Y_B}{Y_A} K_{AB}} + \frac{\mu_B}{1 + \frac{Y_A}{Y_B} K_{BA}}$$

$$\text{where } K_{AB} = \frac{\left[1 + \left(\frac{\mu_A}{\mu_B}\right)^{1/2} \left(\frac{M_B}{M_A}\right)^{1/4}\right]^2}{\frac{4}{\sqrt{2}} \left[1 + \frac{M_A}{M_B}\right]^{1/2}}$$

$$\text{and } K_{BA} = \frac{\left[1 + \left(\frac{\mu_B}{\mu_A}\right)^{1/2} \left(\frac{M_A}{M_B}\right)^{1/4}\right]^2}{\frac{4}{\sqrt{2}} \left[1 + \frac{M_B}{M_A}\right]^{1/2}}$$

where μ_{AB} is viscosity of mixture, Y_A and Y_B molecular fractions, μ_A and μ_B, viscosities and M_A and M_B molecular weights of the pure components.

APPENDIX D

Gas analysis unit.

The underlying principle of this analyser is that the thermal conductivity of a gas mixture is proportional to the concentration. When current is supplied to a wire enclosed in a gas filled chamber, the temperature rises to an equilibrium value at which the rate of energy supplied by the current is equal to the rate of energy lost by the wire in the form of heat. The heat will be lost in four ways, by conduction and radiation, gas convection and gas conduction. Provided the first three effects can be minimised or held constant, the value of the equilibrium temperature of the wire will depend on the thermal conductivity of the gas. Thermal conductivities of gases vary fairly widely e.g. the value for hydrogen is seven times and that for carbon tetrachloride about a quarter the value of air. Consequently, if a second gas is introduced to the chamber, the value of the equilibrium temperature will alter, due to the change in thermal conductivity, by an amount depending on the concentration of the second gas. So, if the equilibrium temperature for a gas mixture can be measured and compared with the equilibrium temperature of a component, the difference will be a measure of the concentration.

Since the resistance of a wire is proportional to the temperature, measurement of the former may be used to determine the latter, especially in this case, where the current used for heating may also be used for resistance measurement.

Resistance is easily measured by the Wheatstone bridge and this is the arrangement employed in this instrument.

The comparison device or katharometer comprises four

identical platinum wires enclosed in separate cells in a solid block, each of which is the arm of a Wheatstone bridge. In this case, three of the cells are fitted with air and sealed, and the gas sample for analysis is introduced to the fourth. If the gas sample is also air, the bridge will be perfectly balanced and the galvanometer deflection will be zero. If the sample introduced contains carbon tetrachloride, the difference in conductivity will throw the bridge out of balance and the value of the galvanometer deflection will depend on the concentration of the carbon tetrachloride. The galvanometer can be calibrated by introducing samples of known concentration. In this case the galvanometer was calibrated by the manufacturers to read directly in volume per cent.

Description of apparatus.

Originally, it was intended to analyse the gas stream above and below the plate in the absorption column and for this purpose two ¼in diam.copper pipe lines lead the gas from the sampling points to a two way manifold mounted on the same back plate as the katharometer itself. Immediately after the manifold, flow was controlled by a needle valve and the gas then passed through an absorption chamber containing calcium chloride to remove water vapour before entering the katharometer. The gas stream, on leaving the katharometer passed through a glass float gauge and the flow was adjusted by the needle valve to the recommended value as designed by a mark on the gauge. The gas could then be returned to the column but as such a tiny flow was involved, it was vented to the atmosphere. The galvanometer was a standard Cambridge indicator fitted with a selector switch for either of two scales, 0-10% and 0-20% by volume, to allow for the

difference in range of concentration of the two samples. The galvanometer was connected to the katharometer by compensating leads.

The absorption system was used in two arrangements, with the air in open or closed cycle. With the system in closed circuit, the column was under suction and the gas samples had to be drawn through the analyser by a water jet ejecter operated by a small pump. This aspirator was also used to purge the unit by drawing air in from the laboratory. When the absorption system was on open circuit, the sample of gas was able to flow through the analyser under the pressure of the column.

As there is a danger of the carbon tetrachloride condensing in the lines of the equipment, the analyser was installed inside a box with a Perspex door. The box was heated by an electric light bulb and a small air blower circulated the air which was kept at about 30°C when the instrument was in use. The sample lines were heated by a small 50 watt heating tape controlled by a Sunvic controller.

Operation.

One disadvantage of this instrument is that there is an operational time lag as the temperature of the wire in the cell changes. This meant that as the runs were necessarily short, it was not possible to use both sampling points. The sampling point above the plate was fitted with a de-entraining device, Fig. 5.13, embodying the cyclone separator principle. However the rate of flow of the gas to the analyser was not sufficient for successful operation and as the entrained droplets tended to form a film, with consequent additional mass transfer, it

was decided to use the lower sampling point. As this in turn was liable to interference from liquid weeping from the plate above, the sampling point was moved to the line just before entrance to the column. Before the start of each run, the light bulb and air circulator in the air bath were switched on. The aspirator arrangement was switched on also to draw air through the meter. This was essential as carbon tetrachloride tends to build up on the calcium chloride in the absorption chamber and the flow through the cell is so small that it was thought stagnant pockets would exist unless purged. About ten minutes was necessary to allow the air bath to come to working temperature and for the reading on the galvanometer to fall to zero. Occasionally, the galvanometer was re-zeroed by an adjustment fitted to the Wheatstone bridge for that purpose.

During the run, provided the preliminary procedure was carried out, the performance of the meter was highly satisfactory, giving a continuous, easily read reading. As the values of the gas concentration were usually in the range 0-7%, only the 0-10% scale on the galvanometer was used. Attempts were made to check the readings by passing saturated carbon tetrachloride/air mixtures at various temperatures through the meter but the error in this method was too high to provide a check on the galvanometer reading.

Comments.

Analysis is always a problem in mass transfer research, and while in this case the claims of the manufacturers were not quite met, the instrument employed gave a highly satisfactory method of continuously reading the concentration of gas entering the absorption column. The instrument could be read accurately

to the first decimal place and the second estimated with a high degree of confidence. This gave an accuracy of better than 1% for a full scale deflection of the lower scale range (0-10%). Its main disadvantage was in the time lag which prevented analysis at two different points.

The applicability of this type of instrument to other mass transfer research systems must be considerable. Conversion scales can be obtained to enable the meter to be used for different mixtures.

APPENDIX E

Description of the sieve plate.

The two sieve plates used were identical, being fabricated from 1/8 in brass plate. The overall diameter of each plate was 14 in and the internal diameter 9 in. A drawing of the plate is shown (Fig. E.1). Each plate had 69 3/16 in diameter holes on a 3/4 in triangular pitch which gives a free area of 5%. Twin 1 in diameter downcomers were fitted to each plate. The inlet and outlet weir heights were both 1 in. The plate was designed to have a variable weir height by fitting inserts, but only the 1 in insert was used. One of the plates used is shown on Plate 4.

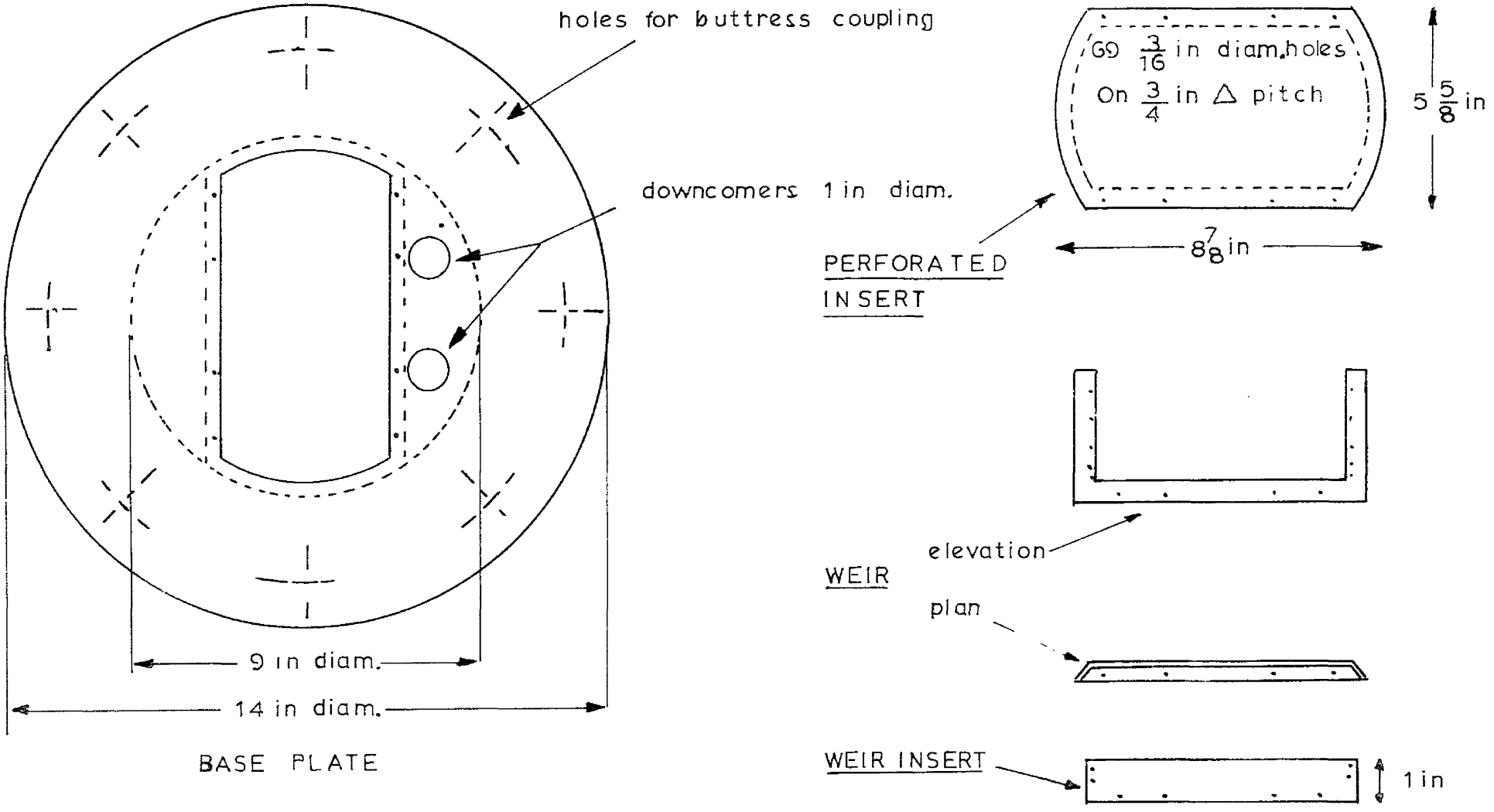


FIG. E1 CONSTRUCTION OF SIEVE PLATE

APPENDIX F

Suction psychrometer

A sketch of the psychrometer is shown on Fig. F.1. Air is drawn down a ¾ in diameter glass tube fitted with two thermometers, by a small centrifugal air blower. The thermometer nearest the fan is connected to a water reservoir by a cotton wick to ensure that the surface of the thermometer bulb is always wet. The thermometers read to and were correct to 1 deg C.

This arrangement ensures that the psychrometer operates above the minimum gas velocity of 15 ft/sec recommended by Treybal[44], while the fan being upstream of the thermometers presents any errors due to the heating effect of the fan.

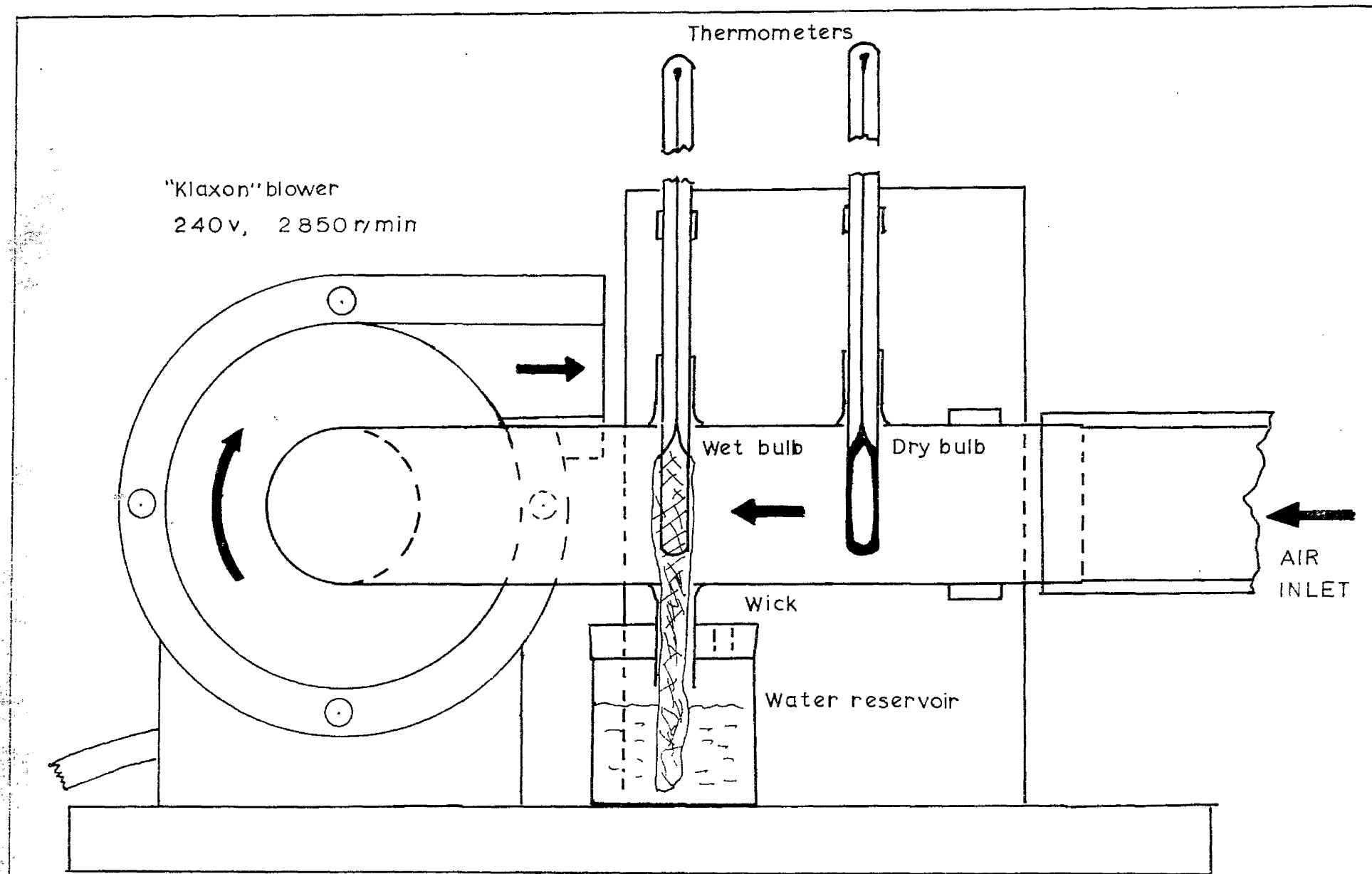


FIG F1. WET AND DRY BULB SUCTION PSYCHROMETER

SYMBOLS USED

A_G	Function of diffusive properties of gas phase (sec^{-1}).
A_L	Function of diffusive properties of liquid phase (sec^{-1}).
a	Area available for mass transfer (ft^2).
$\bar{a}$	Area available for mass transfer (ft^2/ft).
C	Orifice coefficient.
C_1	Initial concentration, units of optical density.
C_2	Final concentration, units of optical density.
C_A	Average concentration, units of optical density.
C_S	Humid heat, (Btu/lb).
D	Diffusion coefficient (appropriate units).
D_{AB}	Diffusion coefficient of A through B (ft^2/hr)
D_B	Diameter of bubble (ft).
D_E	Eddy diffusion coefficient (ft^2/sec).
D_G	Diffusion coefficient in gas phase (cm^2/sec).
D_L	Diffusion coefficient in liquid phase (cm^2/sec).
D_O	Diameter of orifice (ft).
E	Overall column efficiency.
E_{dif}	Diffusional plate efficiency.
E_{MV}	Murphree gas phase plate efficiency.
E_{ML}	Murphree liquid phase plate efficiency.
E_{OG}	Murphree gas phase point efficiency.
E_{OL}	Murphree liquid phase point efficiency.
F	F factor = $V_S \rho_G^{0.5}$.
F_O	F factor through orifice = $V_O \rho_G^{0.5}$.
G	Mass flow of gas based on cross sectional area of column ($lb/hr\ ft^2$).
G_a	Mass flow of air (lb/hr).
G_M	Molal flow of gas (lb mol/hr).
H	Absolute humidity (lb/lb).
H_G	Gas hold up as fraction of total hold up on plate.
h_e	Humidity of air at equilibrium conditions (grain/lb).

h_i Humidity of air at inlet (grain/lb).

h_w Pressure drop across orifice (in H_2O)

i_G Enthalpy of gas phase (Btu/lb).

i_L Enthalpy of gas phase at temperature of liquid (Btu/lb).

K_{OG} Overall gas phase mass transfer coefficient (ft/hr).

K_{OL} Overall liquid phase mass transfer coefficient (ft/hr).

k_G Gas film mass transfer coefficient (ft/hr).

k_L Liquid film mass transfer coefficient (ft/hr).

L Mass flow of liquid, based on cross-sectional area of column (lb/hr ft^2).

L_M Molal flow of liquid (lb mol/hr).

L_V Volume flow of liquid, based on cross-sectional area of column (gal/hr ft^2).

$\frac{L}{V}$ Reflux ratio, dimensionless.

M Total mass of water lost from system (lb).

m Gradient of equilibrium curve.

$\bar{m}$ Henry's law constant.

N_A Mass transfer rate of diffusing component A (lb mol/hr ft^2).

N_G Number of transfer units in gas film.

N_L Number of transfer units in liquid film.

N_{OG} Overall number of gas phase transfer units at a point
(or)
Number of gas phase transfer units over plate for gas phase controlled system.

N_{OL} Overall number of liquid phase transfer units at a point.

n Number of mixing pools.

P Total pressure of system (mm Hg).

P^* Total pressure of system (atm).

P_e = Peclet number, dimensionless = $\frac{Z_L U_L}{D_E}$

Q_G Volume flow of gas (ft^3/hr).

Re_O Reynolds no. through orifice.

r Psychrometric ratio.

S Rate of surface renewal (sec^{-1}).

Sc Schmidt number, dimensionless = $\frac{\mu}{\rho D}$

T	Temperature.
T_K	Absolute temperature (^oK).
t_1	Initial time (hr).
t_2	Final time (hr).
t_m	Mean time (hr).
t_e	Time of exposure of element of liquid at phase boundary. (hr).
t_G	Gas residence time (sec).
t_L	Liquid residence time (sec).
U_L	Mean liquid velocity across plate (ft/sec).
V	Volume (ft^3).
V_g	Gas velocity through column (cm/sec).
V_O	Gas velocity through orifice (ft/sec).
V_S	Superficial gas velocity, velocity through bubbling area (ft/sec).
W_1	Initial mass of water (lb).
W_2	Final mass of water (lb).
W_e	Mass of water lost by entrainment (lb).
W_h	Mass of water lost by humidification (lb).
x	Concentration of diffusing component in bulk of liquid phase (lb mol/ft^3).
x_i	Concentration of diffusing component at phase boundary (lb mol/ft^3).
x_n	Composition of liquid leaving plate n (lb mol/ft^3).
x_{n+1}	Composition of liquid leaving plate n+1 (lb mol/ft^3).
x^*_n	Composition of liquid in equilibrium with gas leaving plate n (lb mol/ft^3).
y	Concentration of diffusing component in bulk of gas phase (lb mol/ft^3).
y_i	Concentration of diffusing component at phase boundary (lb mol/ft^3).
y_n	Composition of gas leaving plate n (lb mol/ft^3).
y_{n-1}	Composition of gas leaving plate n-1 (lb mol/ft^3).
y^*	Composition of transferring component in gas phase in equilibrium with liquid on the plate (lb mol/ft^3).

y^*_n Composition of gas leaving plate n, in equilibrium with liquid leaving plate (lb mol/ft^3).

Z Thickness of laminar film between two phases (ft).

Z_c Clear liquid height (in).

Z_f Froth height (in).

Z_L Distance travelled by liquid (ft).

Z_w Weir height (in).

GREEK SYMBOLS

α	Relative volatility.
β	Free area, fraction of column cross section.
γ	Surface tension (dyne/cm).
η	Kinematic viscosity (ft^2/hr).
λ	Dimensionless number $= m \frac{G_M}{L_M}$
λ_o	Latent heat of vapourisation at 0^oF (Btu/lb).
μ	Viscosity.
μ_G	Viscosity of gas phase (cP).
μ_L	Viscosity of liquid phase (cP).
ϱ	Density.
ϱ_f	Density of foam (lb/ft^3).
ϱ_G	Density of gas phase (lb/ft^3).
ϱ_L	Density of liquid phase (lb/ft^3).
$\dot{\varrho}_G\ \dot{\varrho}_L$	Density of gas or liquid phase (gm/cm^3).
ϕ_f	Specific gravity of froth.
Δh	Change in humidity of air, (grain/lb).
Δi	Change in enthalpy (Btu/lb).
ΔP	Plate pressure drop (in H_2O).
ΔP_D	Dry plate pressure drop (in H_2O).

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