CHAPTER I

LITERATURE SURVEY
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The undefined complexity of an actual industrial process of solute extraction or absorption by or from millions of tiny droplets moving in a highly mobile field cannot be represented by exact mathematical equations. Simplifications necessary to set up a model upon which a mathematical analysis may be based are numerous and in certain respects unrealistic. The most popular simplification is the assumption of a single drop (or bubble) moving through a stationary fluid; the velocity of this fluid particle and the rate of mass transfer are thus taken to be independent of the disturbing influence of the presence of other fluid particles, of the motion of the continuous medium, or of the so-called wall-effect. Such a simplification greatly facilitates theoretical as well as experimental studies of mechanisms of drop motion and mass transfer, yielding mathematical expressions or empirical results which, along with appropriate correction factors, can be used for the design of industrial equipment.

In general, the life of a drop in a spray column passes through three distinct stages: stage of formation at entry to the column, stage of travel through the continuous phase, and the stage of coalescence at the terminal end of the column—though, following Rose and Kintner117, the second stage may be further divided into a sub-stage during which the drop velocity
increases from zero to a maximum value, and a sub-stage during which the drop travels at this maximum terminal velocity. In the following literature survey, the main emphasis is on investigations relating to the formation stage.

1. Prediction of drop size

The primary object of dispersing one phase into another is to create a large interfacial area available for mass transfer. Also of importance is the comparatively high rate of mass transfer per unit of interfacial area during the formation stage. As new area is formed, the two different concentrations in the dispersed and continuous phases are, in terms of distance, momentarily extremely close to each other. The concentration gradient which depends upon this distance is then of a very high order. [The stretching of surface during oscillation of a drop produces similar results.]

Enormous interfacial area may be created by sub-division into micron-size droplets, but efficient recovery of two separate phases is a matter of equal importance. In addition, in the second stage, the mass transfer rate per unit area is appreciably more for larger drops because of increased internal circulation. There is thus an optimum size below which dispersion into droplets becomes economically undesirable.

An excellent review of methods for formation of drops, and for prediction of drop size from a consideration of nozzle
size, formation time, volumetric flow rates and physical characteristics of systems has been given by Chand^{24}. For such calculations the equation given by Hayworth and Treybal^{72} appears to give the best results, though Chand^{24} suggests the replacement of the last term in the original equation (written for C.G.S. units):

\[ V + 0.000411 \frac{q u^2}{\Delta Q} = 0.0021 \frac{dN}{\Delta Q} + 0.01069 \left[ \frac{dN}{\Delta Q} \right]^{1.5} + 0.01069 \left[ \frac{dN}{\Delta Q} \right]^{1.5} \]

by

\[ 0.05013 \left[ \frac{dN}{\Delta Q} \right]^{1.5} \]

to obtain a better accord between predicted and observed values. For high orifice velocities, the semi-theoretical equation of Christiansen and Hixson^{26} is likely to be more applicable.

Siemes^{126} has pointed out that simultaneous mass transfer with drop formation is likely to influence drop size. The exact nature of this influence is as yet uncertain. None of these equations has, therefore, been used in the present work, and drop size values listed in various tables are those experimentally observed.

2. **Shape of forming drops**

It is usual to assume pendant drops as being spherical in shape in order to facilitate calculation of an average area during formation. During the early period of formation, the
portion of the sphere covered by the orifice is large. During the latter period, the combination of elongation, necking down and abandonment of a portion behind the neck causes deviations of some magnitude. In spite of these shortcomings, the spherical model has been found to be adequate, as the net error in calculation on this score is often much less than that due to other simplifying assumptions. It is also desirable that the area-volume relationship should be simple enough to permit mathematical manipulation for calculation of instantaneous interfacial area. However, some methods for calculating areas and volumes of non-spherical drops and bubbles are available.

The shape of a drop forming slowly at a submerged orifice is the basis for the hanging drop (pendant drop) method for determining interfacial tension. The equation for the shape shown in Fig. 1-1, according to Fordham, who extended the earlier calculations of Bashforth and Adams, is:

\[ \frac{1}{\xi} + \sum \frac{\varphi}{x} = \frac{1}{b} + \frac{b^2 g (\Delta \varphi) z}{\sigma b} \]

in which \( \varphi \) and \( x/\sin \varphi \) are the two principal radii of curvature at \( \xi, \Delta \varphi \) is the difference in the density of the dispersed and continuous phases, and \( \sigma \) is the interfacial tension between the two phases. This equation does not lend itself to easy mathematical manipulation.

Poutanen and Johnson have shown that the equation of a littus:

\[ r^2 \varphi = 1 \]
resembles the true shape of a gas bubble forming at a submerged nozzle. They have generalised the geometry of the littus by using:

\[ r^2 \theta = 1 \]

to describe such a shape even more accurately. This method of calculation of area involves a shape factor similar to that of Andreas et al. with a series of auxiliary graphs. Area becomes, for the model depicted in Fig. 1-2:

\[ A = \int_{\theta_1}^{\theta} \frac{\sin \theta}{\theta^{2/n}} \left[ 1 + \frac{1}{n \theta \tan \theta} \right] \, d\theta \]

and the volume is:

\[ V = -\pi \int_{\theta_1}^{\theta} \frac{\sin^2 \theta}{\theta^{2/n}} \left[ 1 + \frac{1}{n \theta \tan \theta} \right] \, d\theta \]

Using a digital computer, they have established a series of tables of A and V for various values of \( \theta \) and \( n \). The method is likely to be applicable to liquid drops after some modifications, and may aid in more exact calculation of mass transfer area during formation.

Halligan and Burkhart have derived a series of equations for the profile of a growing droplet analogous to those obtained by the Laplace pressure balance method for static drops. The effect of added circulation inside the drops has been taken into account by a parameter \( f \). Though cumbersome to use, these equations predict with a fair degree of accuracy the actual shape of a drop at a submerged nozzle.

A review of some other important work on this subject has been given by Brodkey.
3. Experimental work on extraction during formation

The current literature of chemical engineering contains a large number of theoretical and experimental investigation reports on mass transfer and analogous heat transfer studies of drops and bubbles in spray, wetted-wall, packed, pulsating and a variety of other types of columns. A representative selection of work relating to spray columns is listed on pp. 14 - 22; in this list, an asterisk mark indicates that the work cited is particularly relevant to the present study of mass transfer during drop or bubble formation.

Experimental technique has a significant bearing on assessment of observed data; it is hence necessary to examine critically various direct and indirect methods used by different investigators. Indirect methods have involved mainly extrapolation procedures, either to zero column height or to zero formation time: experimental data points, however, show a considerable degree of scattering in the region beyond which extrapolation is required. Direct methods are more accurate, but some of these not only require a more sophisticated technique but also need some additional assumptions to be made regarding the mechanism of mass transfer.

Some of the work on mass transfer has been based on consideration of formation, travel and coalescence stages as a single composite whole, due to the difficulty of determining separately the extraction achieved during these three stages.
REPORTED EXPERIMENTAL INVESTIGATIONS ON EXTRACTION IN SPRAY TOWERS

Part I: Drops in liquids

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<th>Investigators</th>
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<td>Angelo and Lightfoot(^3)</td>
<td>Water - Isopar H -(i) Benzyl alcohol,</td>
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<td></td>
<td>(ii) (\alpha) -Methylbenzyl alcohol, (iii)</td>
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<tr>
<td></td>
<td>Acetophenone</td>
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<tr>
<td>Appel and Elgin(^5)</td>
<td>Toluene - Benzoic acid -Water</td>
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<tr>
<td>Ayen and Westwater(^7)</td>
<td>Glycerol -(i) Acetone (ii) iso-</td>
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<td></td>
<td>Amyl alcohol</td>
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<tr>
<td>Bergelin, Lockhart and Brown(^12)</td>
<td>Tetrachloroethylene -iso-Propanol-</td>
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<td></td>
<td>Water</td>
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<td>Besdel and Brounshtein(^13)</td>
<td>Benzene -Acetic acid-Water</td>
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<td>Boys-Christensen and Terjesen(^16)</td>
<td>Water-Carbon tetrachloride-</td>
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<td>(i) o-Nitrophenol, (ii) Iodine</td>
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<tr>
<td>Calburn and Welsh(^28)</td>
<td>iso-Butanol-Water</td>
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<tr>
<td>x Coulson and Skinner(^31)</td>
<td>Water-Benzene-(i) Benzoic acid,</td>
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<td></td>
<td>(ii) Propionic acid</td>
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<td>Crittendon and Hixsen(^32)</td>
<td>Water-Hydrogen chloride-Pentanols</td>
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<td>Elgin and Browning(^39)</td>
<td>iso-Propyl ether- Acetic acid-Water</td>
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<td>x Farmer(^41)</td>
<td>Water-Acetic acid-(i) Polar solvents,</td>
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<td>(ii) Carbon tetrachloride</td>
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<tr>
<td>Fleming and Johnson(^42)</td>
<td>Methyl iso-butyl ketone-Acetic acid-Water</td>
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<thead>
<tr>
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<tr>
<td>Poord</td>
<td>Water- (i) Benzyl alcohol, (ii) Furfural, (iii) Ethyl acetate, (iv) iso-Butanol</td>
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<tr>
<td>Fujinawa, Maruyama and Nakaike</td>
<td>Water-Acetic acid -(i) Cyclohexane, (ii) Benzene, (iii) iso-Propyl ether, Toluene</td>
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<td>Garner and co-workers</td>
<td>Water-(i) Furfural, (ii) Aniline, Water - Benzene-(i) Acetone, (ii) Propionic acid</td>
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<td>Garner, Poord and Tayebeh</td>
<td>Water-(i) Furfural, (ii) iso-Butanol, (iii) Ethyl acetate</td>
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<td>Garner and Hale</td>
<td>Toluene-Diethylamine-Water</td>
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<tr>
<td>Garner and Skelland</td>
<td>Water-Butanol, Nitrobenzene-Acetic acid- Water, Nitrobenzene-Propionic acid -Water</td>
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<tr>
<td>Geankoplis and Hixson</td>
<td>iso-Propyl ether-Ferric chloride- Aqueous hydrochloric acid</td>
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<td>Geankoplis, Wells and Hawk</td>
<td>Toluene-Acetic acid- Water</td>
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Part I: Drops in liquids (contd.)

<table>
<thead>
<tr>
<th>Investigators</th>
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<td>Galperin and Assmus⁵⁷</td>
<td>o-Xylene-Acetic acid-Water</td>
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<tr>
<td>Giers and Hougen⁵⁸</td>
<td>Diethyl ether- Adipic acid-Water</td>
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<tr>
<td>Handles and Baron⁶⁷</td>
<td>Water-Acetic acid-(i) Methyl iso-butyl ketone, (ii) Ondina-17 oil, (iii) Ondina + kerosene, Water-Benzene-(i) Acetic acid, (ii) Benzoic acid, (iii) Phenol, (iv) Salicylic acid</td>
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<tr>
<td>Haselden and Thorogood⁶⁸</td>
<td>Water-(i) Ethyl acetate,(ii) Cylohexanol, (iii) n-Butanol</td>
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<tr>
<td>Heertjes and deNie⁷³</td>
<td>Benzene-Acetic acid-Water</td>
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<tr>
<td>Heertjes, Helve and Talsma⁷⁴</td>
<td>iso-Butanol-Water</td>
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<tr>
<td>Johnson, Hamielec, Ward and Golding⁸¹,⁸²</td>
<td>iso-Butanol-Water</td>
</tr>
<tr>
<td>Johnson, Minard, Huang, Hansuld and McNamara⁸³</td>
<td>Water-Ethylene dichloride-(i) Acetic acid, (ii) Propionic acid</td>
</tr>
<tr>
<td>Johnson and Bliss⁸⁴</td>
<td>Methyl iso-butyl ketone-Water-(i) Acetic acid, (ii) Propionic acid, Benzene-Acetic acid-Water</td>
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<tr>
<td>Kreager and Geankoplis⁹³</td>
<td>Methyl iso-butyl ketone-Propionic acid-Water</td>
</tr>
<tr>
<td>Investigators</td>
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<tr>
<td>Kylander and Garvin</td>
<td>Capryl alcohol - Aq. hydrochloric acid - (i) Cobalt chloride, (ii) + Nickel chloride</td>
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<td>Laddha and Smith</td>
<td>Water - (i) iso-Butyraldehyde, (ii) 3-Pentanol</td>
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<td>Licht and Conway</td>
<td>Water - Acetic acid - (i) iso-Propyl ether, (ii) Ethyl acetate, (iii) Methyl iso-butyl ketone</td>
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<td>Licht and Pansing</td>
<td>Water - Acetic acid - (i) Methyl iso-Butyl ketone, (ii) Carbon tetrachloride + oil, (iii) Perchloroethylene</td>
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<td>Marsh and Heideger</td>
<td>Water - Methyl carbitol-Benzene + carbon tetrachloride</td>
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<td>Meissner, Stokes, Hunter, and Morrow</td>
<td>Methyl ethyl ketone - Water - Aqueous calcium chloride</td>
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<td>Nandi and Viswanathan</td>
<td>Water - Acetic acid - Nitrobenzene</td>
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<td>Popeovich, Jervis and Trass</td>
<td>Water - Sodium iodide - iso-Butanol</td>
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<td>Row, Koffolt and Withrow</td>
<td>Water - Benzoic acid - Toluene</td>
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<tr>
<td>Sawistowski and Goltz</td>
<td>Water - Benzene - (i) Acetic acid, (ii) Monochloroacetic acid, (iii) Acetone</td>
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### Part I: Drops in Liquids (contd.)

<table>
<thead>
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<td>Shastri*2^</td>
<td>Water-Propionic Acid—(i) Trichloroethane (ii) Tetrachloroethane (iii) Tetrachloroethylene</td>
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<tr>
<td>Sherwood, Evans and Longcor*24</td>
<td>Water-Acetic acid—(i) Benzene, (ii) Methyl iso-butyl ketone</td>
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<td>Sivaraman*27</td>
<td>Water-Acetone-Kerosene</td>
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<td>Skelland and Wellek*29</td>
<td>Water—(i) Ethyl acetate, (ii) Ethyl acetoacetate, (iii) Glycol diacetate, (iv) Glyceryl triacetate</td>
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<td>Smirnov and Lileva*30</td>
<td>Water—Benzene—(i) Acetic acid, (ii) Propionic acid, (iii) Butyric acid</td>
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<td>Smith and Beckmann*31</td>
<td>Water—Methyl iso-butyl carbinol</td>
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<td>Tayeban*32</td>
<td>Water—(i) Diol, (ii) Benzyl alcohol</td>
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<td>Thorsen and Terjesen*34</td>
<td>Water—o-Nitrophenol—(i) Carbon tetrachloride, (ii) Methylene bromide</td>
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<tr>
<td>Ueyama and Kida*35</td>
<td>Ethanol-Benzene, Water—(i) Benzyl alcohol, (ii) Butanol</td>
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<td>Investigators</td>
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<tr>
<td>Vogt and Geankoplis$^{139}$</td>
<td>Water - Methyl iso-butyl ketone, (i) Formic acid, (ii) Propionic acid</td>
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<tr>
<td>Ward and Quinn$^{140}$</td>
<td>Water - (i) Benzene (ii) Toluene</td>
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<tr>
<td>West, Herrman, Chong and Thomas$^{141}$</td>
<td>Water - Acetic acid - Benzene</td>
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<tr>
<td>West, Robinson, Morgen-thaler, Beck and McGregor$^{142}$</td>
<td>Water - Acetic acid - Benzene</td>
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<tr>
<td>Zilaznak$^{149}$</td>
<td>Water - Acetic acid - (i) Benzol, (ii) Ethyl acetate, (iii) Carbon tetrachloride, Water - Propionic acid - Benzol</td>
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**Part II : Bubbles in liquids**

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<tbody>
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<td>Adeney and Becker$^{1}$</td>
<td>Water - (i) Oxygen (ii) Nitrogen (iii) Air</td>
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<tr>
<td>Calderbank and Lochiel$^{21}$</td>
<td>Water - Carbon dioxide</td>
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<tr>
<td>Calderbank, Moo-Young and Biddy$^{22}$</td>
<td>Water - Carbon dioxide</td>
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<thead>
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<tr>
<td>x Calderbank and Patra</td>
<td>Water - (i) Carbon dioxide, (ii) Sulphur dioxide (iii) Acetylene</td>
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<tr>
<td>Coppock and Meikeljohn</td>
<td>Water - Oxygen</td>
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<tr>
<td>Datta, Napier and Newitt</td>
<td>Water - Carbon dioxide</td>
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<tr>
<td>Deindoerfer and Humphrey</td>
<td>Water - Carbon dioxide</td>
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<tr>
<td>Eckenfelder and Barnhart</td>
<td>Water - Air</td>
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<tr>
<td>Guyer and Pfister</td>
<td>Water - Carbon dioxide</td>
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<tr>
<td>Hammerton and Garner</td>
<td>Water - (i) Methane, (ii) Ethylene,</td>
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<td>(iii) Carbon dioxide, (iv) Oxygen,</td>
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<td></td>
<td>(v) Hydrogen</td>
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<td>Ippen and Carver</td>
<td>Water - Air</td>
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<td>Kishinevskii and Mochalova</td>
<td>Carbon dioxide - (i) Monoethanolamine,</td>
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<td></td>
<td>(ii) Sodium hydroxide solution</td>
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<td></td>
<td>(iii) Sodium carbonate solution</td>
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<tr>
<td>Ledig and Weaver</td>
<td>Carbon dioxide - (i) Water (ii) Sodium hydroxide solution (iii) Potassium hydroxide solution, Ammonia - (i) Water, (ii) Ammonium hydroxide solution</td>
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Part II : Bubbles in liquids (concl.)

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<td>Haze and Himmelblau</td>
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<td>Pasveer</td>
<td>Water - Air</td>
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<td>Redfield and Houghten</td>
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<td>Dextrose solution</td>
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<td>Siddique</td>
<td>Water - Ethylene, Sodium carbonatesolution - Sulphur dioxide</td>
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<tr>
<td>Tereshkevitch</td>
<td>Water - (i) Air, (ii) Oxygen</td>
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<tr>
<td>Zdonik</td>
<td>Water - (i) Air, (ii) Nitrogen</td>
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Part III : Drops in gases

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<th>Baker</th>
<th>Water - Ammonia</th>
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<tr>
<td>Constan and Calvert</td>
<td>Sulphur dioxide - (i) Glycerine</td>
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<td>(ii) Water (iii) Propylene glycol</td>
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<td></td>
<td>(iv) Ethylene glycol</td>
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<tr>
<td>Dixon and Russell</td>
<td>Water - Carbon dioxide</td>
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<tr>
<td>Groothuis and Kramer</td>
<td>Sulphur dioxide - (i) Organic solvents, (ii) Water</td>
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<td>Guyer, Tobler and Farmer</td>
<td>Water - Carbon dioxide</td>
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Part III: Drops in gases (concl.)

<table>
<thead>
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<th>Investigators</th>
<th>Systems</th>
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<tr>
<td>Haslam, Ryan and Weber</td>
<td>Water – Sulphur dioxide</td>
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<tr>
<td>Hatta, Ueda and Baba</td>
<td>Water – (i) Ammonia, (ii) Carbon dioxide</td>
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<tr>
<td>Hixson and Scott</td>
<td>Water – (i) Ammonia, (ii) Sulphur dioxide, Oil – Air + Benzene</td>
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<td>Johnstone and Williams</td>
<td>Sodium hydroxide solution – (i) Carbon dioxide, (ii) Hydrogen chloride, (iii) Sulphur dioxide, Sodium hydroxide + Sodium peroxide—Hydrogen sulphide, Sulphuric acid—Ammonia</td>
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<td>Kowalke, Hougen and Watson</td>
<td>Water – Ammonia</td>
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<tr>
<td>Shablin</td>
<td>Water – (i) Ammonia, (ii) Carbon dioxide</td>
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<tr>
<td>Whitman, Long and Wang</td>
<td>Water – (i) Ammonia, (ii) Carbon dioxide</td>
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<tr>
<td>Yano and Kawai</td>
<td>Water – Carbon dioxide</td>
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</table>
Work of this nature has been included in the above listing, but is excluded from the later critical evaluation.

In addition, experimental work on mass transfer in spray columns has also been reported by Atwood, Kishinevskii and Korneinik, Kroepelin, Neumann and Proett, Michels, Pang Sheng Li and Reed.

The work which has been mainly or partly directed towards experimental determination of extraction during the formation stage may, on the basis of the experimental approach adopted, be classified in the following categories:

(a) Extrapolation to zero formation time
(b) Extrapolation to zero column height
(c) Formation - collapse technique
(d) Measurement of pressure or volume change
(e) Measurement of amount of extraction in short columns

(a) **Extrapolation to zero formation time**

The experimental method of Whitman, Long and Wang, who studied the extent of absorption of ammonia and carbon dioxide by water drops, consisted in forming drops of the dispersed phase (water) at a capillary tip placed in an absorption chamber filled with the gas to be absorbed (ammonia or carbon dioxide), allowing these drops to fall through the entire length of the chamber, collecting them under a
layer of kerosene, and analysing them to determine the amount of gas absorbed (Fig. 1-3).

After falling through the absorption chamber (C), the drops passed through the kerosene layer in receiver(e) at the bottom of the chamber. The level of this layer was maintained constant by a mercury levelling device(f) and, when an amount of water sufficient to fill the discharge tube (F) became available, a sample was withdrawn through tube (g) for analysis. Tube (h) was used for introducing kerosene into the receiver.

By manipulation of a stopcock the drop formation time was varied, and results for various formation periods thus obtained were plotted. Extrapolation to zero formation time was then assumed to provide an indication of the amount of extraction occurring subsequent to the completion of the formation stage. On the basis of these experiments, Whitman et al. 146 concluded that the amount of carbon dioxide absorbed per unit drop volume was a linear function of the time of formation, and hence linear extrapolation to zero formation time was permissible. Results with the ammonia-water system indicated a linear correlation between the mass transfer coefficient and the time of formation.

Similar methods were used by Hatta, Ueda and Baba 71 for ammonia-water system, and by Hatta and Baba 70 for carbon dioxide-water system with essentially similar conclusions.

With some differences in detail, the same experimental
approach has been applied to binary liquid-liquid systems by
Johnson, Hamielec, Ward and Golding in their study of waterethyl acetate, water-butanol and water-cyclohexanol systems.
Zilaznak has similarly investigated extraction in some ternary liquid-liquid systems, the systems being water-acetic acid-benzol, water-propionic acid-benzol, water-acetic acid-ethyl acetate, and water-acetic acid-carbon tetrachloride.

An important implicit assumption in this extrapolation method is that absorption or extraction during free fall and coalescence is not considered to be a function of concentration in the dispersed phase at the end of the formation stage. This assumption cannot be true, since a higher concentration in the drop at the end of this stage (when mass transfer is occurring from the continuous phase) means a smaller driving force for diffusion and hence less absorption or extraction during free fall and coalescence. Except in the reported results of Licht and Conway, the fraction extracted during formation has invariably been found to be markedly dependent on formation time, and is of a considerable magnitude when the equilibrium distribution ratio is favourable. West, Robinson, Morgenthaler, Beck and McGregor, for instance, reported 14-20 percent extraction during formation in benzene-acetic acid-water system. In the present work, up to 90 percent of solute present in the dispersed phase has been extracted during the formation stage. It is obvious that in such cases, linear extrapolation to zero formation time is unlikely to provide results which are
sufficiently accurate for testing theoretical correlations.

(b) **Extrapolation to zero column height**

Sherwood, Evans and Longcor\textsuperscript{124} used a different extrapolation procedure for estimation of extraction during formation. Acetic acid was extracted from drops of benzene and methyl iso-butyl ketone in a glass column; in the lower part of this column, drops were formed at the tip of a stainless steel hypodermic needle or a fire-polished glass tube. The organic phase was withdrawn at the upper end through a cone-shaped receiver. The column height was varied in different experiments by adjusting the position of the nozzle tip. Values of fraction unextracted, for constant formation time, were extrapolated to zero column height in order to estimate the fraction that remained unextracted at the end of the formation stage. Experimental results indicated that the relationship between column height and the logarithmic value of unextracted fraction was linear, and the amount of equilibrium achieved during formation was dependent both on drop size and formation time.

West, Robinson, Morgenthaler, Beek and McGregor\textsuperscript{142} used a similar method, but obtained results which differed considerably from those of Sherwood et al., though differences in equipment or procedure were not significant enough to explain variations of such magnitude, the possibility of contamination by surface-active agents having affected the earlier data could
not be ruled out. An attempt was made by West et al. to interpret their data on the basis of the unsteady-state equation of Higbie\textsuperscript{75}, with the incorporation of an empirical correction factor, the latter being assumed to be a function of system characteristics.

In investigations by Skelland\textsuperscript{128} on transfer of acetic acid and propionic acid from nitrobenzene drops to water, by Peerd\textsuperscript{43} on transfer from furfural drops and benzyl alcohol drops to water, and from water drops to isobutanol and to ethyl acetate, by Tayeban\textsuperscript{132} on transfer from diol drops and benzyl alcohol drops to water, and from water drops to diol, and by Hale\textsuperscript{63} on transfer of diethylamine from toluene drops to water, the same extrapolation procedure was used to calculate the amount of extraction during formation.

Though this procedure is preferable to that of extrapolation to zero formation time, erratic behaviour of drops during uncontrolled coalescence renders it subject to a considerable degree of error. It is also doubtful, as pointed out by Licht and Pansing\textsuperscript{102}, whether a plot of logarithmic value of fraction unextracted against column height can be reasonably assumed to be a straight line all the way back to zero column height.

Licht and Pansing, and Licht and Conway\textsuperscript{101} earlier, isolated the coalescence effect by using two columns (Fig.1-4). One of these was of the type previously used for determination of total extraction in all three stages. In the second column,
Licht and Conway
drops were formed at a nozzle tip and travelled through the continuous phase, as in the first column, but were allowed to coalesce in a lower section of the column separated from the main section by means of an open stopcock. After the requisite amount of the dispersed phase had passed through the column, the stopcock was closed and the ensuing calculations were based on the column length between the nozzle tip and the stopcock. Data from the second column were then extrapolated to zero column height to find the magnitude of extraction during formation.

Licht and Conway studied extraction of acetic acid from water drops by iso-propyl ether, methyl iso-butyl ketone and ethyl acetate, and concluded that, with this extrapolation procedure, the fraction extracted during formation was practically independent of formation time.

Licht and Pansing, however, found that this fraction was dependent on formation time as well as drop size; the systems investigated were water-acetic acid-perchloroethylene, water-acetic acid-methyl iso-butyl ketone, and water-acetic acid-carbon tetrachloride + oil. Earlier results reported by Farmer\textsuperscript{41} and by Katz\textsuperscript{87}, and later results reported by Yano and Kawai\textsuperscript{147} and by Ueyama and Kida\textsuperscript{135}, also corroborate conclusions showing the fractional equilibrium achieved to be a function of time.

The apparent conflict of conclusions arises partly from
uncertain effects during the coalescence stage when this stage is not eliminated from calculations, and partly from the use of systems with high dispersed phase/continuous phase distribution coefficients. These high distribution coefficients imply a reduction in the absolute amounts of solute that can get transferred even on complete achievement of equilibrium; in addition, it is possible to show theoretically that a higher distribution coefficient also results in a reduction in the rate at which this equilibrium is achieved. The experimental error with such coefficients becomes considerable in comparison with the extent of extraction achieved, data points become badly scattered in the vicinity of zero column height, and any estimate of fraction extracted is necessarily inexact.

(c) **Formation-collapse technique**

In a novel technique developed by Coulson and Skinner, and later adapted with some modifications by Popovich, Jervis and Trass, by Calderbank and Patra, and by Sawistowskl and Goltz, fluid spheres are allowed to form at the end of a nozzle tip, and before they are large enough to get detached from the nozzle, are forced to collapse back into the capillary tubing leading to the nozzle. The extraction thus occurs during two twin stages of formation and collapse.

In Coulson and Skinner's apparatus for slow formation of drops (Fig. 1-5), the dispersed phase flowed from a small
Fig. 1-5

Apparatus for study of extraction into forming drops

Coulson and Skinner
reservoir through a needle valve to form a drop at the end of a glass jet fixed to the bottom of the column holding the continuous phase. A side tube was fixed just below the jet so that the flow of the liquid was cut off on turning a two-way stopcock and the liquid was forced out of the system by the hydrostatic head of the continuous phase. The cycle was repeated until a liquid sample sufficient for analysis had been collected.

For shorter times of formation, an automatic apparatus (Fig. 1-6) was used. The head of the liquid forming the continuous phase in the column was balanced by an equivalent head at the inlet and outlet pipes. A slight reduction in pressure at the top of the column resulted in drop formation, while a slight increase had the reverse effect. Two ball valves regulated the ingress from the inlet tube and the withdrawal into a measuring burette. By alternate fluctuations in pressure and by means of a variable throw eccentric, drops of different sizes could be formed and withdrawn.

The systems investigated comprised water-propionic acid-benzene, and water-benzoic acid-benzene, with benzene as the dispersed phase in either case. Mass transfer coefficients were calculated by taking the average time of exposure to be 60 per cent of the total time of formation and collapse. The coefficients thus calculated were found to be independent of drop size, but were observed to decrease with increasing time.
Apparatus for study of rapidly forming drops

Coulson and Skinner
of formation.

An assumption in this type of procedure is that the mechanism of mass transfer during collapsing of fluid spheres is the same as that during their formation, and that identical equations can be taken to apply in both cases. Popovich, Jervis and Trass\textsuperscript{113} attempted to prove this assumption experimentally. Their experimental set-up (Fig. 1-7) for the study of diffusion of sodium iodide from water droplets into a continuous medium of iso-butanol consisted of a graduated microlitre syringe connected, through a lever, to two variable speed motors, by means of which the position of the piston of the syringe could be altered to form and withdraw drops at uniform rates. In order to facilitate analysis, an I-radio tracer was used, and all experiments were conducted inside a radiochemical glove box. The results of these experiments indicated that the above assumption might be broadly correct, but because of a considerable scattering of data points (presumably due to experimental errors) it is not possible to draw any firm conclusions from these experiments.

The formation-collapse technique was also used by Calderbank and Patra\textsuperscript{23} for measurement of absorption of carbon dioxide, acetylene and sulphur dioxide by water during bubble growth and withdrawal. A metal bellows, containing the gas to be absorbed, was placed in a chamber in which pressure was varied sinusoidally to a desired amplitude with a predetermined
FIG. 1-7

EXPERIMENTAL MASS TRANSFER APPARATUS.

Popovich et al.
frequency. The motion of the bellows resulted in the formation and collapse of bubbles from a glass capillary tube submerged in water. The quantity of gas absorbed was measured by a micrometre screw adjustment on another bellows connected to the first one by means of a U-tube; the amount of adjustment required to maintain constant pressure indicated the amount of gas absorbed. The control of the entire operation was facilitated by use of an optical arrangement to display a magnified image of the bubble on a screen: the maximum size of the bubble was continuously adjusted to a set datum by a screw drive adjustment.

Through a use of this technique, Calderbank and Patra concluded that a correlation of experimental results was possible if the area of the bubble in the mass-transfer equation was empirically taken as:

\[ A = A_f \left[ 1 - \left( \frac{t}{t_f} \right)^n \right] \]

where \( n = 1.86 \pm 0.06 \) for diameter from 0.5 to 1.0 cm. and \( A_f = \) maximum area of the drop obtained after \( t_f \) sec. at the end of the formation stage.

They also observed low rates of solute transfer for upward pointing capillaries, due presumably to the phenomenon of solute downflow, and concluded that the formation stage did not exhibit an enhanced solute transfer rate, especially when the resistance to mass transfer lay primarily in the continuous phase.
Using the formation-collapse procedure, Sawistowski and Goltz\textsuperscript{120} studied mass transfer rates of acetic acid, acetone and monochloroacetic acid, and derived an equation for extraction in liquid-liquid systems, similar to one derived by Heertjes \textit{et al.}\textsuperscript{79} for drops in gases.

(d) **Measurement of pressure or volume change**

Groothuis and Kramers (loc. cit.) studied the absorption of sulphur dioxide by drops of water and some organic solvents by recording the change in volume or pressure that occurred as a result of absorption. In their apparatus for direct measurement of absorption during formation (Fig. 1-8), drops were formed at the end of a thick-walled glass capillary at a constant rate by displacing the liquid with mercury. Mercury itself was displaced by a plunger pushed by a mechanical drive. The flow rate of the liquid could be independently adjusted by controlling the plunger velocity, and the volume of the drop could be calculated by observing the amount of displacement of mercury caused by the movement of the plunger. For times of formation less than five seconds, the amount of sulphur dioxide gas absorbed was determined by measuring the change of volume at constant temperature; this change was estimated from a photographic recording of the movement of a drop of acetone in a calibrated glass capillary. For slower rates of formation, the absorption vessel was connected to a manometer filled with acetone. Changes in pressure caused by absorption and indicated by this manometer were utilized to calculate the amount of gas taken up by the
Apparatus used for formation times longer than 5 seconds

Groothuis and Kramers
dispersed phase. The results of experiments were correlated through an equation derived by assuming that the process of drop formation was essentially one of addition of fresh elements to the drop surface.

Dixon and Russell\textsuperscript{37}, who had earlier investigated the absorption of carbon dioxide by water drops, used a method for measurement of change of carbon dioxide pressure as an index of the amount of absorption. They explained their results on the basis of a so-called degree of turbulence, defined as the reciprocal of the radius of the nozzle tip.

In a variation of this type of technique, Calderbank and Patra\textsuperscript{23} determined the absorption rate during bubble formation in a liquid phase by continuous photographic recording of bubble volumes throughout the growth period.

(e) Measurement of amount of extraction in short columns

This experimental approach is based on the assumption that, provided the time taken by a drop or bubble for free fall or rise is negligible in comparison to the time of formation, the entire absorption or extraction may be assumed to be occurring during the formation stage alone. This principle was employed by Heertjes and deNier\textsuperscript{73} in their investigations on iso-butanol-water system. The experimental set-up (Fig. 1-9) consisted of a short spray column with one capillary at one end and a small surface of coalescence at the other in order
Fig. 1-9

Sketch of the apparatus

Sketch of the valve.

Heertjes and deNIE
to keep mass transfer during drop rise and at the interface of the coalescence as small as possible. The design of apparatus permitted independent variability of drop size as well as formation time. Drop size was controlled by means of a photoelectric device which was actuated when the top of the forming drop intercepted a narrow light beam, and which in its turn actuated a relay to close a valve. After its release, the drop travelled through a distance of 1 cm. through the continuous phase and coalesced at a liquid-liquid interface adjusted at this height. A predetermined rest-time was designed to elapse between release of a drop and start of formation of the next drop; this necessitated taking into consideration an extra rest-time stage during which diffusion occurred from the residual drop at the capillary tip.

Some of the advantages offered by this sophisticated technique were offset by inclusion of this rest-time stage and the stage of uncontrolled coalescence in the experimental procedure, and the results obtained by Heertjes and deNie can consequently be properly analysed only if the extraction during these two stages can be considered negligible or capable of being theoretically determined. A correlation of results has been attempted by Heertjes and deNie on the basis of surface-renewal and surface-stretch models.

A short column for direct measurement of extraction
during formation was also used by Vir\textsuperscript{136}, but in this case the coalescence stage was eliminated by taking the drops out of the column before these coalesced. There was no rest-time stage. Results obtained during the present investigations show that this method gives fairly satisfactory results.