Chapter 1 A

SURVEY OF EXPERIMENTAL WORK REPORTED IN LITERATURE

Hydrodynamic background
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HYDRODYNAMIC BACKGROUND

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 simplifications 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 factor, can be used for the design of industrial equipment.

Three significant characteristics—drop size, drop shape and drop velocity—affect the extent of mass transfer in any particular system. Empirical methods have been developed to predict these as well as the effect of surface active agents,
particularly as it affects internal circulation. These constitute
the preliminary considerations reviewed in this chapter. The
review is not comprehensive; its purpose is to present briefly
the more important work in the subsidiary fields. The equations
presented here are not used in later computational work, since
direct experimental measurements (e.g., of drop size) are easily
made and provide more realistic values.

4.1-1 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 phase 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 micro-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 frequently
more for larger drops because of increased internal circulation.
There is thus an optimum size below which dispersion into drop-
lets becomes economically undesirable. The design of a spray
tower requires a knowledge of drop sizes consistent with the
properties of the liquids used and the design and size of the dispersing nozzles.

Markins and Brown (117) in 1919 made a simplified calculation for the volume of a drop detaching from a nozzle at a negligible small flow rate by equating buoyancy and interfacial tension forces and correcting the volume for the fraction of the liquid which remained attached to the nozzle after drop break-off. Hayworth and Treybal (125) and Null and Johnson (222) have attempted to develop equations for drop size as a function of interfacial tension, viscosity of continuous phase, nozzle diameter and flow rate of the dispersed phase through the nozzle. The Hayworth-Treybal equation is:

\[ V + 0.000411 \, \frac{\rho_d u^2}{\Delta \rho} = 0.0021 \, \frac{\sigma \, d_n}{\Delta \rho} + 0.01069 \]

\[ \frac{\sigma 1.1205 \, u \, 0.5475 \, u \, 0.2335}{\Delta \rho^{1.5}} \]

This equation is semi-empirical in nature and is based on a force balance made by expressing the various contributing forces acting on the drop as fractions of the total drop volume.

Null and Johnson have given a graphical correlation in terms of the two groups:

\[ \frac{g^2 \Delta \rho}{8 \sigma} \quad \text{and} \quad \frac{g \, u^2 \rho_d}{d_n \cdot g \cdot \Delta \rho} \]

and have claimed a prediction accuracy of 10 to 30 percent.

Hayworth and Treybal's correlation includes the effect of the
continuous phase viscosity; according to Mull and Johnson, this effect is not important.

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 (42). For such calculations the equation (1-1) given by Hayworth and Treybal (125) appears to give the best results, though Chand suggests the replacement of the last term in the original equation (written for C.G.S. units):

\[ V + 0.000411 V^{2/3} \frac{\Delta \rho^2}{\Delta \rho} = 0.0021 \frac{\sigma \Delta \rho}{\Delta \rho} + 0.01069 \]

\[ d_{n} = 1.1205 \frac{u \mu}{\rho \Delta \rho} + 0.2445 \]

\[ d_{n} = 0.9460 \frac{u \mu}{\rho \Delta \rho} + 0.2790 \]

by

\[ 0.05013 \frac{u \mu}{\rho \Delta \rho} \]

in order to obtain a better accord between predicted and observed values. For high orifice velocities, the semi-theoretical equation of Christiansen and Hixson (46) is likely to be more applicable. Narayan, Basu and Roy (218) have proposed the empirical equation:

\[ \frac{d}{d_n} = 6.203 \frac{\Delta \rho}{\rho} 0.096 \]

\[ Re = 0.056, We = 0.222, Fr = 0.272 \]

However, this equation fails to predict the correct drop diameter in case of high d/d_n ratios, small nozzle diameters and high
continuous phase viscosities.

Recent studies recognize two different stages during formation of a drop. During the first stage, drop formation occurs upto a volume at which releasing and adhering forces are in equilibrium. When this equilibrium is attained, drop release takes place. Rao, Kumar and Kuloor (237) have derived two different relations for these two stages. The mechanism of separation described by them is, however, not entirely consistent with experimental observation. The influence of interfacial tension has been derived by them, as by Hayworth and Treybal, from experiments with surface active agents. Ryan (249) also has produced an empirical equation.

Heertjes et al. (127) have presented correlations for the prediction of volume for drops formed at non-wetted capillaries in liquid-liquid systems. The analysis again is based on a two-stage drop formation process.

Another approach, based on the bubble formation model of Kurana and Kumar (178) has been presented by Kumar (177) and is found to be reasonably applicable to formation of drops as well as bubbles from single submerged nozzles. This model treats both the phenomena jointly as the formation of a dispersed phase entity resulting from injection, the size depending upon operating parameters and physical properties.

Scheele and Meister (254) have given a model for drop formation based on a force-balance and have reported that their experimental data were in accord with this model. Their theoretical treatment of the process of drop growth during release
neglects some important phenomena such as kinetic and interfacial tension forces. The prediction of the partition of the drop between releasing drop and rest drop is based on the Harkins and Brown factor. This is open to objection because the factor was determined for static conditions, that is, at infinitely slow drop formation.

Drop size studies have also been made by Skelland and Raval (269) by forming non-Newtonian pseudo-plastic drops in a continuous toluene phase and chlorobenzene drops in a non-Newtonian continuous phase. The investigation is confined to power law fluids, and expressions are developed for long and short nozzles in terms of a two stage drop formation process. Variables like nozzle size, formation time and rheological properties of eight different fluids have been studied by them.

Izard (152) has described a method which is different from other correlations in that the shapes of drops forming at the nozzle are calculated from the properties of the system by means of a pressure balance made across the drop interface. Force balances of the buoyancy, momentum, viscous drag and interfacial tension are then made at horizontal sections throughout the drop. If the net forces in the direction of growth at some horizontal section are positive, the growing drop is assumed to pinch off and break away at the section. There is reportedly a close agreement between the predicted and experimental drop volumes under widely varying physical properties of interfacial tension, viscosity and density.

Siemes (262) has pointed out that simultaneous mass transfer with drop formation is likely to influence drop size.
The exact nature of this influence is yet uncertain.

14-2  Drop shape during formation and travel

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 nonspherical 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 (77) who extended the earlier calculations of Bashforth and Adams (14), is:

\[ \frac{1}{\rho} + \frac{\sin \theta}{x} = \frac{2}{b} + \frac{x^2 (\Delta \rho) z}{\sigma \cdot b^2} \]

in which \( \rho \) and \( x/\sin \theta \) are the two principal radii of curvature at \( (x, z) \), \( b \) is the radius of curvature at \( 0 \), \( \Delta \rho \) is the difference in the density of the dispersed and continuous phases, and \( \sigma \) is the interfacial tension between the two phases. This equation
\[ \frac{1}{p} - \frac{\sin \phi}{x} = \frac{z}{b} + \frac{g (\Delta p) z}{\sigma} \]

**FIG. I-I: THEORETICAL DROP SHAPE**
does not lend itself to easy mathematical manipulation.

A less exact method of finding drop volume and shape by
direct observation has been given by Null and Johnson (222).

Poutanen and Johnson (231) have reported that the equation
of a littus:

\[ r^2 \theta = 1 \]

resembles the true shape of a gas bubble forming at a submerged
nozzle. They have generalised the geometry of the littus by using

\[ r^3 \theta = 1 \]

to describe such a shape even more accurately. This method of
calculation of area involves a shape factor similar to that of
Andraas et al. (2). Area becomes, for the model depicted in Fig.1.2

\[ A = \pi \int_{0}^{\theta_1} \sin \theta \left( 1 + \frac{1}{n \theta^2} \right)^{\frac{1}{2}} d\theta \]

and the volume is:

\[ V = \pi \int_{0}^{\theta_1} \sin^2 \theta \left( 1 + \frac{1}{n \theta \tan \theta} \right) d\theta \]

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 (114) have derived a series of
equations for the profile of a growing droplet analogous to those
FIG. 1-2: VARIOUS DROP SHAPES FOR EQUATION $r^n \theta = 1$

- $r^2 \theta = 1$
- $r^4 \theta = 1$
- $r^6 \theta = 1$
obtained by the Laplace pressure balance method for static drops. The effect of added circulation inside the drop has been taken into account. Though cumbersome to use, these equations predict with a fair degree of accuracy the actual shape of drop at a submerged nozzle.

The shape of a drop or bubble as it moves through the continuous phase is seldom spherical. It may be ellipsoidal or with a flattened front with a tail at the rear end. In general, the material of the drop or bubble is arranged in a shape commensurate with the net hydrodynamic, capillary and gravitational forces acting on it. In addition, there may be an oscillation in shape of a fluid sphere between oblate and prolate forms.

Garner and Skelland (96) have reported that, in their studies on extraction from single drops, oscillations in drop shape from oblate to prolate spheroidal helped to increase the mass transfer rate to even double of the expected values.

Ladyzhenskii (181) has carried out a mathematical analysis of capillary, hydrodynamic and gravitational forces affecting the shape of a rising bubble in a stationary medium, and has come to the conclusion that the effect of the first two of these forces is negligible. For bubbles of air (0.15 to 4 cc.) rising in water his experimental data over a wide range of Reynolds number conform to the following equations:

\[ V = \sum_{i=1}^{i=n} z_i \pi_i P_i^2 \]

and

\[ L = \sum_{i=1}^{i=n} (\Delta z_i^2 + \Delta P_i^2)^{\frac{1}{2}} \]
where \( z \) is the distance from the upper curvature to any \( \phi \) horizontal plane passing through the spheroid, \( V \) is the volume of the bubble, \( L \) its meridional length, and \( p \) the radius of the plane.

A review of some other important work on this subject has been given by Brodkey (29).

1A–3. Drop terminal velocity

The velocity of a liquid drop which is moving freely through another liquid in the gravitational field can be obtained conveniently by equating it to the velocity of an equivalent sphere, i.e., a sphere of the same volume and density as the drop. Stokes (276) studied the movement of solid spheres in fluid and found that the resistance to motion could be represented by

\[
F_D = 6\pi \mu r v
\]

provided the sphere is moving in an infinite medium of high viscosity with internal forces small as compared to viscous forces. Lamb (182) equated buoyant force with drag force (resistance to motion) acting on a fluid sphere and obtained the equation:

\[
v = \frac{2gr^2 \Delta \rho}{9 \mu_c}
\]

Bond (20) and Bond and Newton (21) have shown that for small drop radii, the rate of descent of a drop is very close to the value given by Stokes' law for solid spheres. After a certain critical drop radius defined by

\[
v = \frac{c}{g \Delta \rho}
\]
the rate of descent deviates from Stokes law. Later, Hadamard (112) and Rybczynski (250) have independently studied the motion of spheres of one fluid in another. The Navier-Stokes equation is solved with the assumption that the velocity and the stress are continuous across the interface. In creeping flow region, Hadamard has derived the following equation:

$$V = \frac{2}{9} g r^2 \frac{\Delta \rho}{\mu_c} \left( \frac{3 \mu_c + 3 \mu_d}{2 \mu_c + 3 \mu_d} \right)$$

In case of a gas bubble rising through a liquid phase, $\rho_c \gg \rho_d$ and $\mu_c \gg \mu_d$, and the velocity is:

$$V = \frac{1}{2} g r^2 \frac{\rho_c}{\mu_c}$$

This is 50 percent higher than that predicted by Stokes law.

Hadamard and Rybczynski have also concluded that the variation in velocity and the resistance to motion is to some extent due to internal circulation within the fluid sphere. A gradual transition from stagnancy to full circulation is predicted by Boussinesq (22). In considering a so-called dynamic surface tension, he has introduced the concept of superficial viscosity having an average value of $\zeta$ across the interface. According to him Hadamard's constant should not have equalled.

$$\frac{3 \mu_c + 3 \mu_d}{2 \mu_c + 3 \mu_d} \quad \text{but} \quad \frac{\zeta + \gamma (3 \mu_c + 3 \mu_d)}{\zeta + \gamma (2 \mu_c + 3 \mu_d)}$$

Since there is no method available for calculation of $\zeta$, this correlation is of little practical use.

Klee and Treybal (168) have reported rise velocities of drops through water. They have correlated their results using
dimensional analysis for the two regions below and above the peak velocities. The correlation is reported by them to permit easy computation of drop velocities and to show good agreement with results obtained by them and previous workers.

Hu and Kintner (141) have studied the fall of drops of ten different organic liquids through a stationary water phase and given expressions based on the Weber group, a physical property group, the Reynolds number and the drag coefficient as correlating moduli. The curve between $C_D \cdot \text{We}^{0.15}$ and $\text{Re}/\text{P}^{0.15} = 22$. This point seems to predict the peak velocity and its related quantities. Through visual and photographic studies Johnson and Braida (156) have observed that peak velocity occurs at a drop diameter where oscillation is noted to start.

The form of the two Hu-Kintner equations is as below:

$$C_D \cdot \text{We}^{0.15} = 1 + 1.333 \cdot (\text{Re}/\text{P}^{0.15})^{1.275}, \text{Re}/\text{P}^{0.15} \leq 22$$

$$C_D \cdot \text{We}^{0.15} = 0.033 + 0.045 \cdot (\text{Re}/\text{P}^{0.15})^{2.37}, \text{Re}/\text{P}^{0.15} > 22$$

Siddique (261) has applied these equations to the motion of air bubbles in water and has found that the exponent 0.15 for $P$ is unsuitable for describing his experimental results. He has suggested that 0.21 would be a better value.

Licht and Narasimhamurty (194) have conducted a similar study. A comparison with Hu and Kintner's work indicates that Licht and Narasimhamurty have found higher fall velocities, the difference amounting to roughly 10 percent. This may be attributed to a difference either in methods of timing employed or in the physical properties of the liquids used. The ratio of the drag
coefficient of a liquid drop to that of a rigid sphere of the same volume and density and same fall velocity does not show a satisfactory correlation in this work. Hughes and Gilliland (145) also have given a correlation in terms of a terminal velocity group, a surface tension group and a specific gravity group, but the agreement between observed and calculated volumes is not very satisfactory. They have assumed that the density and viscosity ratios are unimportant. This is reasonably true for liquid drops falling through gases but not through liquids. They have also published a review of drop motion in which a description of the effect of acceleration distortion, circulation and oscillation on the time-distance-velocity relationships has been included.

Johnson and Braida (156) have reported velocity data for organic liquid drops falling in water and aqueous glycerol solutions. According to them, the left hand side of the Hu-Kintner equations should be modified to

$$c_D^{0.85} \rho_p^{0.15}/(\frac{\mu_g}{\mu_d})^{0.14}$$

to account for the viscosities of continuous and dispersed phases.

The equations proposed so far are applicable for low Reynolds numbers and most of them are empirical. At large Reynolds numbers, a theoretical analysis becomes complicated because of non-linear differential equations of motion. For this region Chao (43) has been the first to give the problem an adequate treatment. His analysis is based upon the principles of Prandtl's boundary layer theory with the assumption that the deviations from irrotational flow are confined to adjacent this layers on both sides of the interface. In the vicinity of the interface the
radial gradient of the tangential velocity must have an opposite sign to that given by potential solution. This is necessary condition for the transfer of momentum.

The result of the analysis is given by Winnikow and Chao (315) in the form of a drag coefficient for drops with complete internal circulation and negligible flow separation

$$C_D = \frac{16}{Re} \left[ 1 + \frac{0.814}{Re^2} \right] \left( \frac{2.3 \mu_d/\mu_w}{1 + \left( \frac{\rho_d/\rho_w}{(\rho_d/\rho_w)^{1/3}} \right)^2} \right)$$

This equation differs from Chao's original equation which omitted curvature terms in the boundary conditions. It has been shown that for air bubbles rising in some organic solvents the agreement with theoretical equation is satisfactory.

Terjesen et al. (280) have determined the terminal velocities of drops of organic liquids falling through water uncontaminated with surface-active materials. The presence of these reduces drop circulation and in turn drop velocity. It is found that the velocities obtained from non-oscillating drops exceed those reported in literature. The results are, however, well below theoretical values for liquid drops based upon Chao's model with fully developed internal circulation.

When drop diameter is plotted against drop velocity, the curve generally passes through a maximum or peak value. Around this value drop oscillation starts and any further increase in drop diameter leads to a decrease in terminal velocity of the oscillating drop. Hu and Kintner (141) have given an empirical expression for obtaining the peak velocity. Terjesen et al. (280) have found the terminal velocity of oscillating drop to be
proportional to the inverse square root of the drop diameter in high interfacial-tension system in the equation:

\[ v = \frac{6.8}{1.65 - \frac{\sigma}{\rho_d}} \sqrt{\frac{\sigma}{3\rho_d + 2\rho_c}} \sqrt{d} \]

The onset of oscillating motion is attributed to the instability in the stream pattern around the drop. Magarvey and Bishop (202) have postulated that unsymmetric and unstable wake behind the drop creates a pulsating pressure distribution over the surface of the drop and this constitutes the driving mechanism for the quasi-state of oscillatory motion. This point of view seems to agree with that of oscillatory motion. This point of view seems to agree with that of Schreuder and Kintner (255), who state that a necessary condition for oscillation is the presence of a vortex trail and this is the driving force for oscillations.

### 1A-4 Surface active agents

The effect of surface active agents on the rate of mass transfer was reported in 1939 by Johnstone (162) who found that addition of even a small amount of Tergitol decreased the extraction of acetic acid by water from ether considerably. An instance of an opposite nature was provided by Chu, Taylor, and Levy (48) who observed that the rate of extraction in a packed column increased linearly with decrease in interfacial tension by addition of small amounts of a highly surface active agent, presumably because of the ability of the packing to break up the dispersed phase into smaller drops at low interfacial tension. Farmer (74) obtained increased rates of extraction of acetic acid from carbon-tetrachloride drops by water by addition of Tergitol, the increase
being ascribed wholly to reduction in drop size. West, Robinson, Morgenthaler, Beck and McGregor (307) suggested that discrepancies between their results on extraction of acetic acid from benzene and that of Sherwood, Evans and Longcor (259) could be explained by the presence of traces of plasticizer extracted from Tygon tubing in the benzene feedline.

How trace qualities of surface active agents affect the rate of mass transfer is a question yet to be answered. The explanations advanced so far suggesting their possible functions can be classified either as barrier type of theories or as hydrodynamic type of theories. The former are based on the assumption that surface active molecules adsorbed at a liquid-liquid interface form a kind of barrier which interferes with passage of diffusing solute molecules, whereas the latter assume that the adsorbed molecules are some how capable of modifying the hydrodynamic conditions in the vicinity of interface.

Hutchinson (147) has reported that resistance to mass transfer in the presence of a surface active agent is highly specific. Favouring the barrier theory, he has suggested that the action is not mechanical but involves forces of a physical or chemical nature. The extraction of acetic acid from benzene drops by water has been studied by West, Herrman, Chong and Thomas (306) by adding various alcohols to the benzene phase and it has been suggested that the effect produced is that of an interfacial barrier.

Lewis (190) has suggested that only rigid films are capable of reducing the rate of mass transfer. Under the experimental conditions prevailing in his transfer cell, Lewis considered
transfer of turbulence across an interface to be an important mechanism in mass transfer, and ascribed the reduction in transfer of turbulence to the presence of adsorbed surface active molecules. Lindland and Terjesen (196) have pointed out that, in water–carbon tetrachloride with iodine or o-nitrophenol as solute, the resistance to mass transfer is mainly located in the continuous phase outside the drops. In such a case, internal circulation cannot directly assist in the mass transfer, but it might help indirectly by altering the hydrodynamic conditions outside the drop.

The nature of the hydrodynamic effect on mass transfer, particularly when internal circulation occurs in a moving drop, is not yet fully understood. Garner and Skelland (93) have shown that surface active agents can stop internal circulation and thereby reduce both the rate of fall of the drop and the rate of mass transfer. Garner and Hafe (88) have reported that, in extracting diethylamine from toluene by drops of water in the presence of Teappol, their technique of visual observation failed to reveal any internal circulation irrespective of the presence or absence of a surface active agent. The retardation of mass transfer was presumably due to a barrier effect.

One of the objects of the work by Boye-Christensen and Terjesen (26) was to probe this hypothesis. Their finding is that a retardation occurs in the rate of drop movement in the presence of surface active agents, and they have suggested that this can be taken as an indication of their effect on the internal circulation and thus be compared with their effect on the rate of mass transfer. In a study of effect of hexadecanoyl sulphate and sodium undecanoyl sulphate on extraction of o-nitrophenol and
iodine from aqueous solutions by single drops of carbon tetrachloride, they have found that high rates of mass transfer in pure systems are not caused by internal circulation in liquid drops. With a weak surface active agent, the limiting reduction in the rate of fall of the drops can be obtained with much lower concentrations of the agent than is necessary to give the corresponding limiting reduction in the rate of mass transfer. If the reduction in the rate of fall is taken as an indication of inhibition and final elimination of internal circulation, then internal circulation and mass transfer need to be considered as independent phenomena. A comparison with solid spheres shows that surface active agents can make the rates of mass transfer and terminal velocities equal to those for solid bodies and internal circulation, oscillation and the zig-zag path are completely eliminated. The high rates of mass transfer obtained in the absence of surface active agents are not applicable on the basis of oscillation or internal circulation alone, and the explanation must be sought in the micro structure of the flow pattern.

Sigwart and Nassenstein (264) have investigated the conditions existing at the phase boundaries in the case of mass transfer in liquid-liquid systems by schlieren optics using various solutes. They have found that many systems exhibit eruptive conditions in the interface, due probably to the presence of surface active agents. Annular vortices are observed to be formed due to the rupture of the liquid film surrounding a drop as it emerges through a capillary.

Recently Huang and Kintner (142) have studied the effect of such agents on mass transfer inside drops. In the model
suggested by them, the surfactant accumulating in the rear of the drop acts as a barrier to hinder the passage of diffusing molecules and partly reduces mass transfer. For a complete explanation, both types of theories—barrier and hydrodynamic—are recommended by them.

1A-5 Drop circulation, wake formation and associated phenomena

Any drop or bubble moving in a viscous fluid tends to circulate due to the shear stress applied at its interface by the ambient fluid. Circulation increases with the diameter of the drop and with the velocity ratio \( \frac{\mu_s}{\mu_d} \) of the two fluids. The mobile nature of the interface reduces the viscous fraction and increases the drop velocity. Thus transfer rate for circulating drops is higher than for rigid drops. For a rigid sphere, the external Sherwood number varies as \( Sc^{1/3} \), while for a circulating drop it varies as \( Sc^{1/2} \). Thus circulation increases the transfer coefficient by a factor of \( Sc^{1/6} \).

According to the classical theories of Hadamard (112) and Rybczynski (250), circulation sets in whenever a drop moves in a viscous fluid. Figure (1-3) shows Hadamard streamlines compared with the experimental lines obtained by Spelles (273). A gradual transition from stagnancy to full circulation is postulated by Boussinesq (22), but some experimental observations have shown that circulation starts only above a certain value of Reynolds number; this transitional Reynolds number depends on the viscosity ratio and interfacial tension between the two fluids, and decreases with increase in the continuous phase viscosity (95).

Garner and Skelland (95) have suggested an equation for the transitional Reynolds number determining the onset of
FIG. 1-3: COMPARISON OF THEORETICAL AND EXPERIMENTAL CIRCULATION PATTERN

HADAMARD [112]  

SPELLES [273]
circulation, but this equation is not very accurate since circulation is highly dependent on fluid purity and on the presence of surface active agents (26,88,106). The lower the interfacial tension, the lower the transitional Reynolds number, and higher is the overall transfer coefficient. For a drop with high surface tension, small amount of impurities are sufficient to produce an appreciable surface tension gradient at the interface, thereby retarding circulation. Bond and Newton (21) have carried out a dimensional analysis of the problem of drop circulation and proposed the following criterion for predicting the transition from stagnancy to circulation:

\[
\frac{d^2 \Delta \rho}{4 \cdot \sigma} < 1 : \text{Stagnant sphere}
\]

\[
\frac{d^2 \Delta \rho}{4 \cdot \sigma} > 1 : \text{Circulating sphere}
\]

Interfacial tension \(\sigma\) is held as an important factor in the situation. This inference is drawn from experimental data in laminar flow when the drop diameter is small. However, this criterion is rather inadequate since circulation is known to be strongly affected by small changes in surface tension caused by surface active agents. The experimental results of Bond and Newton are explained by Savic (251) on the assumption that a relatively incompressible surface layer exists around the drop surface. The layer may result either from molecules of surface active agents absorbed on the interface or from orientated molecules of the substance composing the continuous phase.

It is now generally agreed that the absorbed film of a surface active agent which sets up tangential forces on the drop surface reduces or arrests circulation. The motion of the drop interface causes a concentration gradient of the surface active
agent, resulting in an interfacial tension gradient. Thus retardation of circulation is associated with surface tension gradients along with the interface rather than with a simple reduction in surface tension. For a given system, the effect of a surface tension gradient increases with decreasing drop diameter, and below a certain size circulation is reduced or arrested with the transfer coefficients approaching the rigid drop model values.

According to Savic (251) a rigid cap may be formed on the rear portion of the drop, confining circulation to the front portion. There are two possible reasons. Firstly, the velocity near the rear stagnant part is small. Secondly, the surface active material is accumulated in the part near the point of separation of flow. The theory proposed by Frumkin and Levich (81) differs from that of Savic in assuming that molecules of surface agent which are swept towards the rear diffuse back into the drop. The early work of Boussinesq (22) is also pertinent to this problem. He allowed for the effect of surface viscosity on the terminal velocity and circulation patterns of fluid drops.

The dependence of circulation on the difference in interfacial tension has been experimentally verified quantitatively. Levich (189) and Schechter and Farley (253) have attempted to obtain a quantitative expression by assuming slow motion of the drop in the external phase, so that the inertia terms in the equation of motion can be neglected, and a criterion for the critical drop diameter (at which circulation ceases) can be developed. Mathur (205) has shown that the critical diameter is proportional to square root of the ratio between interfacial
resistance and the difference in the densities of the two phases, and is independent of the viscosity of either phase.

The lack of rigidity at the liquid-liquid interface makes the drop liable to be deformed and to attain a quasi-steady state of oscillatory motion. According to Terjesen et al. (26) the onset of oscillatory motion is due to an instability in the stream pattern around the drop. According to Garner (99) oscillations reduce the external resistance to mass transfer. Magarvey and Bishop (202) have suggested that oscillations make the wake behind the drop unsymmetrical and unstable, and this results in discharging wake interior into the outer stream. Thus the turbulence at the rear of the drop increases the rate of mass transfer. Oscillations usually set in at Reynolds number between 150 to 200; for correlating mass transfer coefficient, a higher exponent than 3 then becomes necessary.

Evidence presented by Boys-Christensen and Terjesen (26) indicates that high rates of mass transfer obtained with pure systems may not be wholly due to internal circulation in the fluid drops. This conclusion may be contrasted with that of Garner (99) who postulates that internal circulation reduces the boundary layer thickness. Terjesen et al. (26) have pointed out that internal circulation does lead to a thinning of boundary layer but it appears that this effect is insufficient to account for the great difference between the rates of mass transfer for drops and solid spheres. From experimental results, continuous phase film coefficients are found to satisfy the same correlation irrespective of whether the drop circulates or not. The probable explanation is that in the correlation the difference between the
circulating and non-circulating drops is fully accounted for by the higher Reynolds numbers by virtue of greater velocities of fall. Thus higher rates of mass transfer obtained for circulating drops may be attributed to hydrodynamic causes such as wake formation and boundary layer separation, rather than internal circulation.

Garner (99) has studied the effect of wake behaviour and boundary layer separation on the rate of mass transfer. The volume of wake formed behind the drop is found to depend upon the angle of boundary layer separation. Conkie and Savic (51) have suggested that the angle of separation should be 108° for circulating spherical drops and the same value is obtained for rigid spheres, but Garner's observations show that for Reynolds numbers about 500 the angle of separation for circulating fluid spheres is 140°, and for rigid spheres nearly 105°. In the case of fully circulating drops, the separation point should shift to the rear stagnant point and no separation of the boundary layer should occur. The transfer coefficient should then approach the value predicted by the potential flow theory. Levich (189) has observed an angle of separation of 2° for a drop falling through an uncontaminated gas at a Reynolds number of 300.

An interesting point regarding the decrease of mass transfer coefficient of fluid spheres with time has been noted by Deindoerfer and Humphary (63). Their experiments show that transfer coefficients of one to two second old oxygen bubbles rising in water are in agreement with those obtained from the Higbie generation theory, but the coefficients of 6 second old bubbles are close to those predicted by the rigid sphere theories. High rates
of mass transfer have also been measured by Garner and Lane (92) during the first few seconds after drop detachment from the nozzle. Initial high rates are attributed to high circulation velocity and oscillations arising in breaking away of the drop from the nozzle. No oscillations of the drop are observed upon separation from the forming nozzle by Marsh and Heideger (203), but high transfer rates are obtained for the period immediately following formation. The probable reason for initial high transfer rates can be the intensive circulation caused by the dispersed phase fluid as it enters the drop. Thus a decrease in the transfer coefficient may be correlated with rapid decay of circulation; after a short period the drop will be either stagnant or slowly circulating depending on the relative phase velocity, interfacial tension, viscosity and drop diameter.

Hammerton and Garner (115) have reported that the rate of mass transfer does not vary between 1 and 5 seconds after a drop or bubble release. Baird and Davidson (9) also have found no dependence of transfer coefficients on age until a diameter of 2.5 cm is exceeded. Calderbank and Lochiel (37) have confirmed that the rate of transfer does not vary as bubble ages from roughly one to six seconds after release at least over a diameter range of 0.5 - 2.65 cm. This may be contrasted with the results of Deindoerfer and Humphrey (63) obtained with bubbles smaller than 0.5 cm. However, later work has shown a decrease of about 45 percent of mass transfer coefficient between 0.5 - 1.0 second age limit, and this is in agreement with the studies of Marsh and Heideger (203).

It has been noticed that with smaller bubbles the transfer
coefficient is fairly independent of time. For larger bubbles the coefficient is found to decrease with rising time. Calderbank and Lochiel (37) have suggested that unsteady state value of the transfer coefficient can probably be attributed to unsteady state concentration profiles, wake transfer and surface phenomena. If it takes a considerable time for steady concentration profiles to become established outside the interface, unsteady state terms will contribute to the transfer rate and their magnitude will be an inverse of bubble age. Theoretical analysis indicate that for fully circulating fluid sphere the steady state should become established as soon as the sphere travels through a distance equal to its diameter. Since complete circulation establishes at \( Re > 100 \), the time-dependent transfer rate cannot be explained as entirely due to gradual build up of concentration profiles.

A rising bubble carries behind it a turbulent wake, and for \( Re < 160 \) the wake is steady and moves as a unit with the bubble. The initial rate of transfer of solute into the wake is high. As solute accumulates in the wake, the concentration driving force is reduced and the transfer rate decreases. The transfer process is, therefore, time-dependent, and steady state is established when the rate of transfer from the rear of the bubble (or drop) to the wake equals that from the wake to the bulk of continuous phase. Baird and Davidson (9) suggest that low rate of saturation of the turbulent wake under the spherical cap bubble, where mass transfer is by eddy diffusion rather than by convection, is the determining factor. They find no significant effect of time on transfer coefficient for bubbles below 2.5 cm diameter, and postulate that circulation and renewal of wake allow a steady state
to be set up behind the smaller bubble.

Leonard and Houghton (188) are of the view that mass transfer induces electrokinetic potential at the interface and this leads to formation of a thin layer of stagnant liquid around the surface of the bubble. They further assume that the volume of film remains constant during rise, so that its thickness increases as the bubble dissolves. Hence the transfer rate decays because of increase in film thickness. It is probable that transfer reduction on aging may be associated with the presence of trace impurities in the bulk phase. The amount of contamination on the interface varies with time through diffusion of material towards bubble. The increase in the surfactant impurities progressively reduces the internal circulation and results in a decrease in the transfer coefficient.
Chapter 1 B

SURVEY OF EXPERIMENTAL WORK REPORTED IN LITERATURE

Mass transfer to and from spheres
The current literature on chemical engineering contains a large number of experimental investigation reports on mass transfer studies on drops or bubbles in wetted wall, packed, spray, pulsating and a variety of other types of columns. Since the mechanism of heat transfer is in many ways analogous to that of mass transfer, many research reports on heat transfer have a great deal of relevance to various aspects of mass transfer processes. In addition, results obtained in liquid-gas, liquid-solid and gas-solid systems are often a pointer to the behaviour of liquid-liquid systems. To present an exhaustive survey of all such studies is almost an impossible task; however, a brief study of work on mass transfer on single drops, single bubbles and single solid particles is necessary in the present context. A summary of reported investigations appears in Table B-1, B-2, B-3, B-4 in the Appendix. Some of the more widely known studies are discussed in this chapter.

1B-1 Fluid-Solid Systems

The mechanisms of mass transfer in solid and fluid particles have certain differences, but many empirical equations for heat and mass transfer have common applicability. At low Reynolds numbers, the transfer behaviour is nearly the same. A summary of reported experimental work is given in Table B-1 in the Appendix.
McCune and Wilhelm (209) have measured transfer rate of 2-naphthol pellets and flakes into water stream with fairly large bed heights and at conditions sufficiently removed from saturation. The Reynolds number range is from 14 to 1765. Gaffney and Drew (83) have carried out a similar study in benzene-salicylic acid, n-butyl alcohol-succinic acid and acetone-succinic acid systems using pelleted particles. The Reynolds number range is 1 to 800. Hobson and Thodos (135) have passed a water stream through beds of celite spheres soaked in saturated solutions of water-isobutyl alcohol and water-methylethyl ketone, and calculated transfer rates at zero time. Evans and Gerald (73) have used beds of granules of benzoic acid at low Reynolds numbers. Dryden, Strang and Withrow (65) have given experimental data for transfer from solid pellets in packed beds to water flowing at low velocities. Solids employed are 2-naphthol and benzoic acid. Mass transfer coefficients of benzoic acid spheres to water have been obtained by Williamson, Bazaire and Geankoplis (312). The data obtained are in the Reynolds number \( \text{Re} = \frac{d_p}{\mu} \) range of 0.08 to 120, and recommended equations for liquids are:

\[
J = 2.40 \text{Re}^{-0.66} \quad \text{Re} = 0.08 \text{ to } 125
\]

\[
J = 0.442 \text{Re}^{-0.31} \quad \text{Re} = 125 \text{ to } 5000
\]

where mass transfer factor \( J = \frac{k/\Delta}{(30)0.58} \). Resnick and White (239), McCune and Wilhelm (209), and Kettenring, Manderfield and Smith (165) have studied mass transfer between fluidized solid particles and flowing fluids.

Gamson, Thodos and Hugen (84), Wilke and Hugen (310), and Powell (232) have studied rate of evaporation of water from
spherical and cylindrical pellets into gas streams. Hougen and coworkers (84) have used shallow beds in which the possibility of large entrance and exit effects cannot be ruled out. The Reynolds number range in their experiments is 50 to 4000. Hurt (146), Remnick and White (239), Chu, Kalil and Wetteroth (47), and Bar-Ilan and Remnick (11) have vapourised naphthalene into air streams to measure the rate of evaporation. Particle diameters in these experiments range from 0.04 to 1.0 cm and Reynolds numbers vary from 0.8 to 2000.

Garner and Grafton (87) have used pressed pellets of benzoic acid and adipic acid mounted on the downstream side in a horizontal pipe, and a photographic technique for measurement of local and overall mass transfer rates in water. This technique requires a substantial dissolution of the particle, and results in deviation of shape from sphericity. Overall transfer rates are correlated by:

$$Sh = 44 + 0.48 Re^{3/2} Sc^{1/3}$$

where the limiting value of 44 is explained as caused by natural convection. That this explanation is not satisfactory is shown by the fact that Garner and Suckling (98) have used the same experimental set-up and measuring technique and, on the basis of additional data, correlated the new and old results by replacing 44 by 2 and 0.48 by 0.95. Garner and Keev (91), using a vertical pipe, have found a difference in rates depending upon the direction of flow. The work of Garner and coworkers is in the range of Re from 2 to 840, Sc from 788 to 1680 and for laminar flow of the solvent stream.
Work of similar nature has also been done in heat transfer 
(41,149,207, etc.). Kramers (170) has measured heat transfer rates 
from spheres to fluids in laminar flow and correlated his data 
with the equation:

\[ Sh = 2 + 1.3 \cdot Sc^{0.15} + 0.66 \cdot Re^{1/2} \cdot Sc^{0.31} \]

Powell (232) has studied the rate of evaporation of water 
from a single vertical cylinder exposed to an air stream perpendi-
cular to its axis. Frössling (80) has measured evaporation rates 
of naphthalene spheres into air and correlated his results with a 
semi-empirical equation:

\[ Sh = 2 + 0.552 \cdot Re^{1/2} \cdot Sc^{1/3} \]

Others, too, have correlated their data by expressions of the same 
form (108,139,232,236,288). The coefficients recommended range 
from 0.33 to 1.5, with exponent of the Reynolds number varying 
between 0.35 to 0.6. In some cases the limiting value of Sherwood 
number (=2) has been omitted; in others, velocities other than the 
approach velocity have been used. These experiments cover the 
range of Sc from 0.6 to 2.7 and Re upto 48000.

The solution rates of single benzoic acid spheres have been 
measured under natural and forced convection conditions by 
Steinberger and Treybal (275) in upward flowing streams of water 
and aqueous propylene glycol in laminar and turbulent flow. Sphere 
Reynolds numbers range from 10 to 16920, Schmidt numbers from 
987 to 69680, sphere/column diameter ratios from 0.123 to 0.497, 
and Grashoff numbers from 5130 to 125200. Based on the additivity 
of natural and forced convection a more general equation:

\[ Sh = Sh_0 + 0.347 \cdot Re^{0.62} \cdot Sc^{0.31} \]
has been proposed by Steinberger and Treymbal. This valid for heat and mass transfer data for single spheres immersed in bounded and free jet streams of gases and liquids for Reynolds numbers from 1 to 30,000 and Sc from 0.6 to 3000.

Linton and Sutherland (197) have measured the overall and local rates of dissolution of 3/8 inch diameter spheres of benzoic acid in uniform flow in a water tunnel at 490 < Re < 7580. The overall transfer is correlated by:

$$Sh = 0.582 \, Re^{1/2} \, Sc^{1/3}$$

The local transfer rates over the front half of the sphere are found to be in fair agreement with those from the theory of laminar boundary layer. The absolute local values at the front stagnation point are, however, low. This discrepancy is explained as due to a gradual transition from viscous flow to potential flow outside the boundary layer as Reynolds number increases. The relative transfer from the rear half of the sphere is observed to increase with Re.

A study of mass transfer from spheroids has been carried out by Skelland and Cornish (267). They have suspended oblate naphthalene spheroids in air streams and measured the rate of evaporation over a Reynolds number range of 130 to 6000 with major/minor axis ratios (eccentricities) varying from 1:1 to 1:3. The mass transfer coefficients are correlated empirically with Reynolds number. The importance of this study lies in approximating the shape of solids particles to that of liquid drops in many systems, and also taking into account the fact that in some systems internal conditions correspond very nearly to those of
stagnant non-oscillating spheroids.

13-2 Gas-Liquid Systems (Drops in Gases)

Appendix Table B-2 contains a summary of experimental reports on this subject.

In an early systematic study of absorption of carbon dioxide by water drops, Whitman, Long and Wang (308) used a small column of constant height. They varied the time of formation and by extrapolation to zero formation time found the amount of gas absorbed during free fall. Assuming this to be invariant, absorption during formation was calculated. The rate coefficients were found to be higher than those reported earlier for flat liquid surfaces or wetted-wall columns. In a corresponding study, Hatta, Veda and Baba (123) studied the absorption of ammonia in water drops. Since ammonia is highly soluble, the liquid film resistance is negligible in this case.

Later, Hixon and Scott (134) have attempted to isolate the wall effect from the absorption of drops by collecting liquid samples from the central core of the spray. They have measured rates of absorption of ammonia and sulphur dioxide by water, and benzene by straw oil, for several gases, liquid rates and tower heights.

Groothuis and Kramers (109) have made a continuous measurement of the amount of sulphur dioxide absorbed by drops of water and a number of hydrocarbons during the formation period, and have developed a theoretical model for dispersed phase resistance on the lines of the penetration theory. Free convection currents are found by them to increase the rate of absorption at long
formation times. At short times, a considerable increase in the rate is possibly due to mixing produced by the jet of the liquid leaving the capillary.

Dixon and Russel (64) have studied absorption of carbon dioxide by water drops and observed that during free fall the rate of absorption increases with the rate of drop formation. This is ascribed by them to differences in 'degree of turbulence' within drops, defined as a function of the reciprocal of the nozzle tip-radius.

Johnstone and Williams (163) have made experimental measurements to confirm theoretical calculations of Johnstone and Klein-schmidt (162). Shabalin (257) has investigated the absorption of ammonia and carbon dioxide in water and reached the conclusion that absorption of gases by small drops is analogous to the heating of a solid sphere in as much as it depends on diffusion in the immobile interior of the drop.

Rajan and Goren (234) have measured the amount of carbon dioxide gas absorbed by oil drops moving down a vertical wire. The variables studied are drop frequency, oil viscosity, wire size and column height. They postulate a model for mass transfer which assumes that the gas is absorbed by an almost stagnant liquid film between and covering the drops, that the film is subsequently mixed with a drop as it moves apart, and that the dissolved gas is carried from the column in the circulating loops of liquid within the drop.

18-3 Liquid-Gas Systems (Bubbles in Liquids)

Experimental work on bubbles in liquids, a summary of which appears in Table B-3 in the Appendix, has been more extensive than
the work on drops in gases.

The dissolution of single bubbles in free rise has been studied extensively in order to predict transfer coefficients for bubble swarms, particularly when the rate of solution is limited by diffusion in the continuous phase. Such liquid film-controlled processes are of particular importance in fermentation and sewage purification processes.

Mass transfer involving large single bubbles (0.8 to 4.2 cm in diameter) has been studied both theoretically and experimentally by Baird and Davidson (9) in the carbon dioxide-tap water system with a photographic continuous recording of bubble volumes. Experimental results have been found by them to be 50 percent greater than theoretically predicted values and the deviation is attributed by them to rippling at the bubble surface. However, as the introductory part of the present work points out, previous equations for predicting transfer rates have been rather unreliable and the deviation of experimental data from the equation used might have been due to this cause. On suppressing the rippling effect by adding n-hexanol, the values are reported by Baird and Davidson (9) to be approximately as predicted. The effect of a stagnant layer which partly covers the front surface of the bubble and makes diffusion less rapid has been noticed in an aqueous solution of Lissapol. However, it is not possible to assess the effect of contaminants which might have been present in tap water.

Motion picture techniques to record bubble history have also been used by Deindoerfer and Humphrey (63) and Mundkur (215) for the study of mass transfer for single carbon dioxide bubbles
(0.23 cm to 0.87 cm in diameter) in water. Their results show that the instantaneous mass transfer coefficient is time-dependent; this conclusion is found unacceptable by Calderbank and Lochiel (37) who attribute this effect to impurities present in the bulk phase.

Low (201) has reported data for absorption of single bubbles of oxygen (less than 0.5 cm diameter) in cumene in an absorption apparatus essentially similar to that used by Ledis and Weaver (186). Measured transfer rates have been compared by them with the theoretically predicted rates for absorption from spheres in potential flow and from rigid spheres. In the presence of cumene peroxide absorption rates are observed to be initially high but decay after about 15 seconds to a value expected for rigid spheres. These results are explained in terms of the accumulation of surfactant at the bubble surface.

Ishii and Johnson (151) have used a similar experimental set-up to study absorption of carbon dioxide to water and monoethanolamine solution. They have demonstrated the existence of the so-called wall effect. Barnett (12), who has studied bubble motion and mass transfer in non-Newtonian liquids, has explained that the rapidly decaying mass transfer rates obtained by Humphrey and Mundkur (215) are probably due to a mechanism triggered off by bubble release which causes wild oscillations. These oscillations produce an initially high transfer rate which rapidly decays to a low value when terminal velocity is established.

Ledig and Weaver (186) have used a dilatometeric technique of measuring the instantaneous volume of carbon dioxide bubbles in water in their study of mass transfer. Hammerton and Garner (115)
have used a modification of this technique. Their finding is that the liquid film coefficient for pure carbon dioxide bubbles is proportional to the square of the instantaneous bubble radius for diameters in range 0.6 - 1.1 cm. In this range, the velocity of rise is reported by them to be nearly independent of size. A comparative study of transfer from ethylene ethane, oxygen, hydrogen and carbon dioxide in water indicates that the approach suggested by Higbie (132) is valid for carbon dioxide bubbles (diameter 0.6 cm) and ethylene (diameter 0.3 cm). Timson and Dunn (284) have used the same approach in their study of absorption of air and oxygen in water and assumed perfectly circulating bubbles as a basis for predicting the rate of mass transfer.

Calderbank and Lochiel (37) have studied mass transfer from carbon dioxide bubbles (0.4 to 3.1 cm equivalent diameter) in water by a continuous measurement of the pressure change in an enclosed air space at the top of the column, caused by the change of liquid level when a bubble is released in the apparatus. The instantaneous mass transfer rates are found not to be time-dependent; these are relatively constant for bubbles of one to six seconds age. To the extent that drop shapes cannot be approximated by equations of oblate spheroids or spherical caps, experimental results tend to deviate from a set pattern.

Leonard and Houghton (188) have used a dilatometeric technique to study mass transfer rates of single bubbles in nitrous oxide-water and ethylene-water systems. Their results indicate that velocities of single bubbles are probably affected by mass transfer and radial motion and that the specific rate of absorption decreases with increasing distance from the bubble
release point. Absorption of nitrous oxide is reduced by the presence of inert gases inside the bubble and of surfactant hepateneoic acid in the aqueous phase, but these do not affect the velocity of rise. Their conclusion is that surface effects are significant in mass transfer from bubbles.

Laumont and Scott (183) have made an experimental study of liquid phase mass transfer from carbon dioxide bubbles travelling concurrently with water in a horizontal pipe. A model of the process based on a stream of spherical bubbles is developed and absorption is reported as a function of dimensionless groups. The rates of mass transfer are found to be much greater than may be expected with the same mean relative velocity in stationary liquids, presumably due to the action of the main stream turbulence which disrupts the boundary layer.

Redfield and Houghton (233) have used various compositions of dextrose and water to study mass transfer rates of single bubbles over a range of Reynolds numbers from 0.02 to 5000. In carbon dioxide-water system, the mass transfer coefficient is found to decrease with height of the column. Li, West, Vance and Moulton (192) have determined by chemical analysis liquid phase mass transfer coefficients for streams of bubbles of pure oxygen, 10 percent carbon dioxide in air, and 10 percent chlorine in air, all rising in water. They have measured bubble rates stroboscopically and rates of rise and bubble distortions photographically. The observed coefficients for oxygen and carbon dioxide are somewhat higher than those predicted by Higbie's equation. The experimental absorption coefficients of chlorine are in good agreement if simultaneous irreversible reaction with the transient water
film and a pseudo first order reaction are assumed.

Johnson, Basik and Hamielec (155) have found the absorption rates of carbon dioxide, ethylene and butane from single rising bubbles (0.4 - 2.0 cm equivalent diameter) in water. The technique is a modification of a method introduced by Ledig and Weaver (196). The results have been compared with theoretical equations for rate of gas solution at the frontal surface of the bubble based upon potential flow theory and Higbie theory. An equation correlating their own and other data in the Reynolds number range 500 to 20,000 has been obtained.

Calderbank, Johnson and Loudon (35) have modified the apparatus and data processing technique used by Lochiel and Calderbank (199). A constant volume technique is used for measuring the instantaneous rates of solution of rising gas bubbles in liquids; this simultaneously records the bubble shape, area and rising velocity at the time of measurement. The method has been used for carbon dioxide bubbles in water in two viscous Newtonian aqueous solutions of glycerol and in a non-Newtonian viscoelastic pseudo-plastic aqueous solution of polyethylene oxide. Results covering a wide range of bubble size (0.2 - 6.0 cm equivalent diameter) are reported.

Zieminski, Caron and Blackmore (323) have studied the effect of the presence of small quantities of mono and dicarboxylic acids and alcohols on the area and volume of air bubbles and the mass transfer coefficient of oxygen in water to show that the length of the carbon chain has a significant effect. Instantaneous mass transfer rates have been measured by Garbarini and Tien (85) from carbon dioxide bubbles rising through water using two different
methods. In the first method, two movie cameras are placed on a moving platform along perpendicular directions and are used to record the position and size change of the bubble. The second method measures the mass transfer rates by recording the pressure change in the free space at top of the bubble column, caused by a change in the bubble size. The coefficients determined by either method exhibit wide scattering; this is attributed to inaccurate surface area measurement.

13-4 Liquid-Liquid Systems

Investigations of liquid-liquid extraction from single drops (summarised in Table 13-4 in the Appendix) have the advantage that extraction can be carried out under known conditions of interfacial area and time of contact. The results are directly applicable to spray towers and perforated plate extractors, and can help to explain the mechanism of extraction in other types of equipment.

One of the first reported studies of this type is that of Sherwood, Evans and Longoor (259) who extracted acetic acid from drops of benzene and methyl-isobutyl ketone with water. The result indicated considerable agitation in the drop interior and showed that a large portion of extraction occurred during formation. The degree of extraction was many-fold greater than that predicted for rigid stagnant spheres.

West, Robinson, Morgenthaler, Beck and McGregor (307) have sought to interpret the data of Sherwood, Evans and Longoor on the basis of Higbie's unsteady state equation. In the usual equation, \( k = 1.13 \sqrt{D/\delta} \), they introduce a correction factor of 0.34
for benzene drops and 0.68 for methyl-isobutyl ketone drops. In
their own work on extraction of acetic acid from benzene drops
by water, they have obtained about 14 to 20 percent extraction
during formation. In the second stage, that of rise through the
continuous phase, extraction rates have been correlated empiri-
cally by equations of unsteady state diffusion in stagnant spheres.

Extraction during formation has been studied by Coulson and
Skinner (55) in a device which allows drops to form at the jet of
a nozzle and then collapse back. In their results, mass transfer
to a forming drop is almost independent of the formation time for
a range of ½ to 1 second. The overall transfer coefficient, based
on the average area exposed during formation, decreases with
increasing time of formation but is practically independent of
drop size. Smaller drops approach equilibrium more closely because
of the increased area of the interface per unit volume. The mass
transfer coefficient during the rise of a drop is found to increase
with drop size and decrease with increasing surface tension; in
addition, it is directly influenced by the relative velocity of
the drop.

Comparison of these results with those anticipated by
assuming that drops move as solid spheres, or alternatively that
their surface is renewed each time they move through one diameter,
suggests that the real conditions are somewhere between these two
extremes.

Licht and Conway (193) have used the linear extrapolation
technique to determine the rates of transfer during formation.
They find that the amount of extraction is independent of drop
size and formation time. These conclusions have been criticised
by Licht and Fensing (195) who have developed a theoretical model of solute transfer in various stages. They have studied, in particular, the extraction of acetic acid from three solvents, methyl isobutyl ketone, perchloroethylene and carbon tetrachloride oil in water, and find that magnitude of oscillations in falling drops is an important factor in rate of transfer.

Garner and Skelland (93) have investigated extraction of acetic acid from nitrobenzene drops and found that mass transfer during formation is a function of formation time and is adversely affected by drop size. The overall coefficient during free fall increases with drop size. Circulation is found to occur during this stage. The higher rate of mass transfer from larger bubbles is attributed to internal circulation and oscillation.

Garner and Hale (88) have studied the system toluene-diethylamine-water and found that the rate of transfer is dependent on the direction of the diffusion and on the nature of the dispersed and continuous phases. Presence of surface active agents reduces internal circulation within drops and also decreases the rate of mass transfer for noncirculating drops.

Lindland and Terjesen (196) have pointed out that in the system, water-carbon tetrachloride with iodine or o-nitrophenol as solute, the resistance to mass transfer is mainly located in the continuous phase. Internal circulation is observed to alter the hydrodynamic conditions outside the drop, thus assisting in mass transfer. The work of Boys-Christensen and Tejesen (26), to which a reference has already been made, shows that the high rates of mass transfer obtained with pure systems are not to be
explained solely in terms of internal circulation.

Garner, Poord and Tayeban (86) have obtained data for water in isobutyl alcohol, furfural in water, water in ethyl acetate, and benzyl alcohol in water. Thorsen and Tarjasen (283) have published data on four systems with high interfacial tension. Data from these two investigations have been fitted with equations of the form:

$$Sh = a + b \text{Re}^c \text{Sc}^d$$

Griffith (106) has presented equations for several liquid-liquid systems. Experimental data for isobutyl alcohol drops in water, ethyl acetate drops in water, and water drops in isobutyl alcohol are fitted with the equation:

$$Sh = 2 + 1.13 \text{Re}^{1/3} \text{Sc}^{1/3} K_v$$

where $K_v$, a function of $(\mu_c/\mu_d) \text{Re}^{1/3}$, is the ratio of the speed with which the interface between a sphere and surrounding fluid moves to the speed with which the interface would move if the sphere and fluid were frictionless.

Vir (291) has investigated extraction of acetic acid and propionic acid from trichloroethylene and pentachloroethane in a continuous phase of water at Reynolds numbers of about 1200, and has observed that the nature of mass transfer and its amount can be satisfactorily explained on the basis of an assumption regarding its unsteady state character. The results indicate that in these systems circulation is fully established and contributes towards high rates of mass transfer. On an empirical basis, he has treated the formation stage and the free fall stage as a composite whole, provided an adjustment is made regarding the changing interfacial
area during the drop formation. He has indicated a logarithmically linear relationship between \((0.6 \theta_c + \theta_c)/r^2\) and the fraction of solute extracted in the case of these systems. During the travel stage, the following empirical expression is valid:

\[
\text{Sh} = 0.86 \text{Sc}^{0.33} \text{Re}^{0.8}
\]

Vir has also considered the effect of decreasing driving force for diffusion in case of mass transfer from a growing drop during formation. The theoretical correlation derived on this basis satisfactorily correlates experimental data.

Sawistowski and Goltz (252) have investigated the effect of interface phenomenon on mass transfer coefficients. For this purpose the technique developed by Coulson and Skinner (55) has been used to form and withdraw individual drops of constant volume within a known time. Extraction of acetic acid, acetone and monochloroacetic acid from benzene in continuous phase has been investigated by them. They have found that changes in interfacial tension occurring during mass transfer processes have a significant effect on the rate of transfer. Depending on interfacial tension, two regimes, the diffusional and the turbulent, are separated by a transitional regime. The transfer coefficient in the diffusional regime is independent of solute concentration. In the turbulent regime the rate of transfer is a function of interfacial tension as well as solute concentration. The turbulence created during the formation of a drop, the hydrodynamic behaviour of the drop during its passage through the column and the time of coalescence also affect the coefficient.

Rates of mass transfer from water drops into cyclohexanol and from drops of cyclohexanol, isobutanol, and o-toluidine into
water have been measured by Ward, Trass and Johnson (302). The results published for Reynolds number less than 10 cover a Peclet number range of 0.01 to 5.0 \times 10^5 for non-circulating spheres and 700 to 24 \times 10^5 for circulating spheres. Data for circulating spheres are used to verify the hypothesis that internal circulation affects the external transfer rate. This effect depends on the ratio of continuous to dispersed phase viscosity of the system; a four to six fold enhancement of mass transfer due to internal circulation is found for water drops falling in cyclohexanol.

Marsh and Heidgur (203) have employed a photographic technique to measure the rate of extraction of methyl cortibol out of individual drops of a benzene-carbon tetrachloride mixture dispersed in water. A drop diameter of 0.5 cm and Reynolds number range of 60 to 70 have been studied. It is observed that, after a brief time, the falling drop is either stagnant or shows reduced circulation under the influence of relative phase velocity. For the initial period, they have proposed an expression to find mass transfer coefficients; for the later period, relations of another type are found suitable.

An experimental investigation of the effects of various physical properties on the dispersed phase mass transfer coefficient has been carried out by Skelland and Wellek (270) for non-oscillating and oscillating liquid drops falling in a single stream through stationary continuous liquid phases. The study is limited to systems with low interfacial tension, between 2.5 to 5.8 dynes/cm. Solute transferred into the droplets has been measured for heights ranging from about 2 cm to 103 cm, with precautions taken to minimize end effects. Mass transfer coefficients for
non-oscillating droplets are found to be greater than those predicted by the Kronig and Brink model for non-oscillating drops. Experimental Sherwood numbers are correlated with an average absolute deviation of 34 percent in terms of a relationship involving the dispersed phase Schmidt number, the Weber number and the time group $\frac{4DG}{d^2}$. Experimental results for oscillating droplets are correlated by two correlations with an average absolute deviation of 10.5 percent. The Handlos and Baron model fits the experimental results for oscillating droplets with an average absolute deviation of 38 percent.

Boyadzhiev, Elenkov and Kyuchukov (25) have studied mass transfer in liquid-liquid dispersions in a turbulent flow field for the case where overall transfer is governed by the resistance in the dispersed phase. The system investigated is water-iodine-carbon tetrachloride. The results obtained show that a purely empirical factor $\bar{R} = R^2$, which correlates effective diffusivity with molecular diffusivity, depends strongly on the turbulence of the systems. The results are valid for mass transfer rates in turbulent liquid-liquid dispersions and for some cases of solute diffusion in single oscillating drops.

A photographic technique has been used by Lode and Heideger to evaluate mass transfer rates from single drops in a system expected to exhibit interfacial tension-controlled convection. The extraction of methylcarbitol from organic mixtures of carbon- tetrachloride, benzene, and primol 355 in various proportions into water has been studied. High mass transfer coefficients are observed and explained by assuming that the transfer is controlled by convective rather than molecular transport. It is observed that
the change in molecular diffusivity does not affect the transfer rates. The strong dampening effect of a surfactant on mass transfer rates is also reported.

Hendrix, Dave and Johnson (130) have measured the volumes translated in wake of single drops of organic liquids rising through aqueous media. Organic drops studied include methyl isobutyl ketone, toluene, and toluene-carbon tetrachloride mixtures. Aqueous media include water and sugar solutions. Distance of drop rise varies from 25 to 50 cm. Drop size is varied such that Reynolds numbers of 40 to 600 are obtained. They have reported that for non-oscillating drops volumes translated are nearly independent of distance travelled by the drop but for oscillating drops these decrease rapidly. Transition from non-oscillating to oscillating drops is observed to occur at Reynolds number of 200.

Effect of surface active agents on mass transfer inside drops has been investigated by Huang and Kintner (142) who have proposed a model to account for reduced mass transfer to drops falling through a continuous phase containing a surface active agent. The reduction in transfer is reported to be due to reduction in available interfacial transfer area and to changes in both velocity and pattern of internal circulation. The data for system cyclohexanol-water in presence of Octanol and Zonyl S-13 surfactant agree with the proposed model with a deviation of less than 10 percent.