The Effect of Agitation on Mass Transfer Rates in Liquid - Solid Particle Systems.

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THE EFFECT OF AGITATION ON MASS TRANSFER RATES IN LIQUID - SOLID PARTICLE SYSTEMS

by

Edmund William White

A DISSERTATION
Presented to the Graduate Faculty
of Lehigh University
in Candidacy for the Degree of
Doctor of Philosophy

Lehigh University
1951

CERTIFICATE OF APPROVAL

Approved and recommended for acceptance as a dissertation in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Nov. 15, 1951

D. E. Mack by HAN authorized by letter
Professor in Charge

Accepted, ____________________

Special committee directing the doctoral work of Mr. Edmund William White

H A Neville (for D E Mack) Chairman

C. W. Simmons

M. B. McPherson

ACKNOWLEDGEMENTS

To Professor Darryl E. Mack, for his kind assistance and guidance in all phases of this investigation;

To Dr. Raffaele F. Muraca, for his suggestions and recommendations for analytical procedures;

To Professor Warren W. Ewing and Dr. Frank H. Healey, for their generous permission to use the instruments and facilities of the Physical Chemistry Laboratory;

My sincere appreciation is expressed.

TABLE OF CONTENTS

Summary . . . . pg. 1

Introduction. . . . . pg. 2

A Brief Review of Prior Work. . . . . pg. 6

Theoretical Considerations. . . . . pg. 14

Description of Apparatus. . . . . pg. 20

Procedure . . . . pg. 26

Precision of Measurements . . . . pg. 29

Discussion of Results . . . . pg. 32

Conclusions and Recommendations . . . . pg. 67

Table of Nomenclature . . . . pg. 69

Literature Cited. . . . . pg. 72

Appendix. . . . . pg. 74

LIST OF ILLUSTRATIONS

FIG. 1 - Basic Dimensions of Beaker-Scale Apparatus . . . . pg. 22

FIG. 2 - Dimensions of Ten-Inch Diameter Agitator-Tank . . . . pg. 23

FIG. 3 - Four- and Six-Blade Paddles . . . . pg. 24

FIG. 4 - Basic Dimensions of Thirteen-Inch Agitator-Tank . . . . pg. 25

FIG. 5 - Effect of Impeller Speed on Rate of Reaction. . . . . pg. 33

FIG. 6 - Dissolution of Glassy Borax; Check of Equation. . . . . pg. 37

FIG. 7 - The Adjusted Dissolution Constant as a Function of Impeller Speed. . . . . pg. 48

FIG. 8 - Adjusted Dissolution Constant as a Function of NL. . . . . pg. 55

FIG. 9 - Adjusted Dissolution Constant as a Function of Power per Unit Volume . . . . pg. 61

SUMMARY

The effect of agitation on the rate of mass transfer from solid particles to a liquid was investigated using 60/80 mesh zinc in 0.4 N sulfuric acid and 40/60 mesh glassy borax in tap water. Five impellers (1.81 inch to 6.0 inch diameter, two to six blades) and three baffled tank sizes (4.94 inch to 13 inch diameter) were employed.

The weight of zinc or borax that dissolved in twenty minutes in the corresponding liquids was determined by analysis of a sample. Impeller speeds varied from 121 to 972 rpm.

A break-point in the plot of reaction rate versus impeller speed was characteristic of the two systems investigated. Above the break-point speed, an increased speed of agitation caused a negligible increase in the mass transfer rate. This break-point seems to occur at or near the speed at which full suspension of the particles is attained.

The data could not be correlated by the methods of previous investigators, but the data for glassy borax-water could be correlated in terms of NL.

The power per unit volume of liquid does not appear to be a criterion by which to evaluate the systems studied.

INTRODUCTION

For many thousands of years, agitation and mixing have been utilized in obtaining desired end results. The blending of ingredients in making bread, bricks, or alcoholic beverages are examples of ancient mixing practices. In more modern times, the chemical process industries have made extensive use of the unit operation of mixing. An agitator or scraper is normally an integral part of any apparatus designed for such unit processes as nitration or sulfonation. Gasolines are blended, wax emulsions are prepared, solids are suspended in liquids, powders are blended, and paints are pigmented in various types of mixers or agitators.

Despite this old and continued use of mixing and agitation, the design and selection of devices to produce specific results has remained an art rather than a science. Only in the last twenty-five to thirty years have A. W. Hixson, J. H. Rushton, A. McL. White, D. E. Mack, A. Brothman, E. L. Piret, and a few others managed to develop some fundamental relationships and to apply them to the extremely complicated fluid dynamics of mixing and agitation.

Although "mixing" and "agitation" are often used as more or less synonymous words, "agitation" has in reality a more general context. It refers to any disturbance of the quiescent or equilibrium state of a material - either gaseous, liquid, solid, or any combination thereof. As normally used with reference to the chemical engineering unit operation, "agitation" implies the controlled use of mechanical devices such as propellers, paddles, jets and tumbling drums. In this sense, "mechanical agitation" is often used and is a more limiting and descriptive term.

The engineer and manufacturer are vitally interested in the power (and equivalent cost) required to perform any manufacturing operation. Quite naturally many investigations on the power required to rotate propellers, paddles and turbine agitators in liquids have been conducted. In the most recently published work, the power, expressed as a dimensionless power number ($Pg/N^3L^5\rho$) has been shown to be a function of the Froude number (N^2L/g) as well as the modified Reynolds number ($NL^2\rho/\mu$).

With controlled agitation, three major process results are attained:

1. Mixing.
2. Increasing heat transfer rates.
3. Controlling mass transfer rates.

Obviously these three results are inter-related so that the degree of mixing, the heat transfer rate, or both may influence and control the mass transfer rate in a system.

In "mixing" two or more materials, a particle of one substance is placed as nearly adjacent as practicable to a particle of each of the other substances. Power, time, and cost considerations, as well as the further use to be made of the mixed material, are limiting factors. Certain terms have arisen to describe specific methods or results of mixing. Thus, two batches of gasoline or two powders may be "blended", a solid may be "dispersed" in a liquid or gas to form a "suspension", or two immiscible liquids may be dispersed in one another to produce an "emulsion".

Where heat transfer is involved, agitation acts to reduce the thickness of the stagnant fluid film adjacent to the heat transfer surface and to dissipate the hotter (heating) or colder (cooling) molecules throughout the bulk of the fluid. Early investigators reported overall heat transfer coefficients in specific kettles and tanks. At times these overall coefficients were compared at different agitator speeds in a single apparatus. In other instances, the overall coefficient in the "agitated" tank was compared only with the coefficient in the same tank "unagitated". In 1944 Chilton, Drew and Jebens (1) extended the general method for correlating forced-convection heat transfer data to the cases where an agitated liquid is heated or cooled by a tank coil or a jacket. For a jacketed vessel, it was found:

$$\frac{(h_j D/k)(\mu_j/\mu)^{0.14}}{(c\mu/k)^{1/3}} = 0.36\,(NL^2\rho/\mu)^{2/3}$$

and for a coil:

$$\frac{(h_c D/k)(\mu_c/\mu)^{0.14}}{(c\mu/k)^{1/3}} = 0.87\,(NL^2\rho/\mu)^{0.62}$$

Subsequent investigators have normally used this method of correlation.

It is the primary intent of this investigation to study the effect of agitation on mass transfer rates. Therefore the results and conclusions of some previous investigators are reviewed in the following section.

A BRIEF REVIEW OF PRIOR WORK

All mass transfer phenomena, when examined from the viewpoint of the type of physical phases present, can be assigned to one of seven subdivisions:

1. Gas-gas
2. Gas-liquid
3. Gas-solid
4. Liquid-liquid
5. Liquid-solid
6. Solid-solid
7. Gas-liquid-solid

In the field of mechanical agitation the gas-liquid, liquid-liquid, liquid-solid, and gas-liquid-solid systems have probably been more completely investigated than the other three. The present investigation was limited to liquid-solid systems where the solid was present as a powdered or granular mass; therefore only the prior work in that field will be reviewed.

Murphree (11) in 1923 reported an investigation of the solution of crystalline materials, It was assumed that:

> 1. A definite weight of crystals of nearly uniform size is added to a solute-free solvent and agitated at a uniform rate.
>
> 2. The volume of the solution remains substantially constant.
>
> 3. The rate of solution is proportional to the area of crystals exposed and to the degree of agitation.
>
> 4. The rate of solution at any particular time is proportional to the difference in concentration of the saturated solution and that of the main body of the solution (as shown by A. A. Noyes).

By a series of material balances, differential equations, and integrations, it was shown that:

$$K\theta = \frac{Vk}{nBb}\left[\frac{1}{2}\ln\frac{(k+x_0)^2(k^2-kx+x^2)}{(k+x)^2(k-kx_0+x_0^2)} + \sqrt{3}\tan^{-1}\frac{k\sqrt{3}(2x_0-2x)}{3k^2+(2x_0-k)(2x-k)}\right]$$

For nomenclature see TABLE OF NOMENCLATURE.

For the special case where the amount of crystals is very large compared with the amount necessary to saturate the solvent, the change in the surface area of the crystals is small and may be neglected. Consequently the general equation reduces to:

$$\ln\frac{C_s}{C_s - C} = \frac{KA\theta}{V}$$

where "A" is the surface area.

Hixson and Crowell (5) in 1931 presented an extensive resume of prior work on the effect of agitation on mass transfer rates. These investigators derived the cube root law, an equation differing from that of Murphree only in certain constants. Simplified forms for special cases were also derived.

In subsequent work Hixson and Crowell (6,7) provided experimental substantiation for the cube root law, hence for Murphree's earlier derivation. Further, using the system rock salt-water, the effects of a number of variables were experimentally determined for unbaffled tanks. The results obtained were:

1. The rate of solution increases with an increase in the angular velocity (RPM) of the impeller but the increase is smaller at high angular velocities.

2. In a tank of constant diameter an increase in the length of the impeller, width (1 inch) and angular velocity (83 rpm) constant, produces an increase in the solution rate up to a length equivalent to about 60-70 per cent of the tank diameter; a further increase in impeller diameter produces no increase in solution rate.

3. An increase in the width of an impeller, other factors being held constant, causes an increase in solution rate at the lower (83 rpm) impeller speeds; the effect at higher (240 rpm) angular velocities is appreciable less.

4. An off-center location of the impeller causes increased turbulence and a higher solution rate at a relatively low (83 rpm) angular velocity.

5. As the impeller was moved vertically upward from the bottom of a tank, the rete of solution decreased only to a slight extent at 83 and 240 rpm.

6. For the rock salt-water system, a ten degree Centigrade increase in temperature produced about a 26 per cent increase in the soltuion constant, at a constant (83 rpm) speed of agitation.

7. Increasing the tank diameter results in an increase in soltuion rate (same agitator running at 122 rpm). Since the liquid volume was constant, the liquid height varied so that the increased solution rate is not caused only by the increase in tank diameter.

8. From a study of ten different impellers, it appears that the effect of the impeller (same diameter) is small (about 10 per cent variation) at higher speeds (240 rpm); at a lower speed of 83 rpm the effect is greater (about 41 per cent).

9. A decrease in liquid volume resulted in an increased rate of solution at 83 rpm (tank diameter constant). This is probably the result of more agitation per unit volume.

10. When the amount of solid is large with respect to the area of the bottom of the tank,

> "piling" or "heaping" occurs; this results in a lower solution rate per unit weight of solid.
>
> 11. The effect on solution rate of different particle sizes in two equal weights of a solid, is primarily to change the area of transfer, i.e. the solution constants are proportional to the initial areas (240 rpm).

Hixson and Wilkins (8) in 1933 reported on the application of the Hixson-Crowell cube root law to the dissolution of benzoic acid tablets in water and in several oils. Using seven sizes of tanks from 0.73 to 353 gallons (6 inch to 47 inch i.d.), these investigators concluded that:

> 1. With free rotational agitation (no baffles), "the rate of dissolution depends most markedly upon the stirring speed. . . . The dissolution rate is initially low and rises rapidly to about 85 per cent" (at 125 rpm) "of the value attained at 350 rpm. From 125 rpm to 350 rpm the rate increases much less rapidly but as a straight-line function of the stirring speed. The relation holds for all sizes of vessels studied. The curves are parallel in the straight-line region, and those for the larger vessels lie successively above those for the smaller ones."
>
> 2. "The dissolving rate at 200 rpm rises rapidly throughout the series of small vessels until the 18 inch one is reached, beyond which the increase due to greater size is small. Thus an 18 inch vessel may be used roughly as a model agitator in which to predict the behavior in larger equipment of this type without the necessity of a size correction", for unbaffled tanks.
>
> 3. "Agitation is decreased greatly by an increase in fluid viscosity". The data in one tank are compared by dividing the dissolution constant by the solubility and diffusivity ($K/C_s d$). The data in various tank sizes are correlated as $KD/C_s d$ versus the log ($ND^2\rho/\mu$).
>
> 4. "Effective agitation is reduced by baffle

> introduction to a very great extent in the small sizes, but practically not at all in the plant sizes. The magnitude of this decrease. . . is in inverse ratio to the size of the vessel. More than four baffles produce no additional reduction in the rate of dissolution."
>
> 5. "In the four-baffle system the value of the agitation constant is proportional to the stirring speed. The relation is a straight line which begins at about 125 and continues to about 350 rpm, after which the rate falls off somewhat and tends to approach the horizontal. The curves for several sizes are parallel and arrange themselves. . .with the curves for the larger vessels above those for the smaller ones."
>
> 6. "The effect of size magnification in the four-baffle régime at 200 rpm is much more pronounced than in the free rotational system. The increase is more rapid between the 6-and 24-inch sizes while in the 47-inch tank (plant scale) the solution rate has almost reached its maximum and is practically equal to the effective agitation in the free rotational régime at the same size and speed."
>
> 7. "More effective agitation is found in a shallow vessel than in a deep one at the same stirrer speed", unless the vortex reaches the impeller.
>
> 8. "The power consumption per unit volume of liquid undergoing agitation increases rapidly as the size of the system is increased and as the free rotational flow is deflected by baffles. This means that high speeds in large vessels cannot be used so long as power is of economic importance."

In 1941 Hixson and Baum (2) presented additional experimental data for a number of dissolution systems using the same tanks and 45° impellers as Hixson and Wilkins. A simplified form of the cube root law was derived and shown to give results comparable with the exact expression. By means of dimensional analysis it was predicted that:

$$\frac{KD}{d} = \phi\,(ND^2\rho/\mu)\,\phi'(\mu/\rho d)$$

Therefore the abundant data of the investigators was plotted on log-log paper with the co-ordinates of $(KD/d) / (\mu/\rho d)^{0.5}$ and $(ND^2\rho/\mu)$. Two straight lines were drawn; these supposedly confirmed the existence of a critical Reynolds number. "The points for the system benzoic-acid-methanol are not shown, since this group was the only one which deviated largely from the average line, . . . falling 30-40 per cent below."

In subsequent series of experiments, Hixson and Baum (3) used a similar method for correlating data obtained with a series of marine-type square pitch propellers inserted into the tanks at an angle of 60° to the horizontal. "Comparison is made between the turbine and propeller as an agitating device, and for the range of sizes studied, the turbine, operating without baffles, gives higher values for the dissolution constant in liquid-solid agitation."

In 1944 Hixson and Baum (4) reported on the effect of agitation on the chemical system benzoic acid-sodium hydroxide. A 6-inch diameter tank and a four-bladed turbine-type agitator with a 45° blade angle was used in the experiments. The initial sodium hydroxide concentration was varied from 0.005 to 0.08 M. Using the Nernst-Brunner double-film concept they developed an expression for the total film thickness. Over the range of speeds from 200 to 450 rpm, "the film thickness is linear with speed." Further "the number of (benzoic acid) pellets had no apparent effect on the calculated film thickness except as this factor entered into the definition of surface area."

Mack and Marriner (10) in 1949 used the benzoic acid-sodium hydroxide systems in correlating agitator performance. Two tanks (9.7 and 16.0 inch diameters) and seven flat-bladed impellers (two, four or six blades) of various lengths and widths were used. Three different sizes of benzoic acid pills and two benzoic acid particle sizes were used but the initial sodium hydroxide concentration was held constant (0.0019 N). It was concluded that:

> 1. The performance of dissimilar fully baffled, radial-type impellers, and dissimilar liquid dimensions can be correlated for solid-liquid mass transfer by using the relation
>
> $$\frac{D}{\theta}\left(\frac{H}{D}\right)^{0.15} = \phi\left[\left(\frac{P_g}{N^3L^5}\right)^{0.45} NL^2\right]$$
>
> This may be part of a more general form
>
> $$\left(\frac{\mu}{\rho d}\right)^{a}\left(\frac{kD}{d}\right)\left(\frac{H}{D}\right)^{0.15} = \phi\left[\left(\frac{P_g}{N^3L^5}\right)^{0.45}\left(\frac{NL^2\rho}{\mu}\right)\right]$$
>
> 2. Particle size of the solid phase has no influence on the mass transfer rate.
>
> 3. Size, number and positions of the baffles have no effect on the mass transfer rate so long as fully baffled conditions are maintained.

In an unpublished paper in 1950, Mack (9) proposed that two zones of agitation intensity exist in any agitated system, i.e.

1. A zone of high velocity in or near the impeller.

2. A zone of lower velocity in the main bulk of the tank, -- the "bulk velocity".

"For cases where the film is to be wiped off the surfaces of solid particles free to move with the liquid, we have the 'near impeller' zone affecting the process, since the particles may actually move through the impeller. In fact, the velocity here may be so high compared with the bulk velocity that the 'near impeller' zone performance may control the process." It is further shown that "the Reynolds number for this stream is:

$$Re = (N_p{}^{0.2}L)\ (N_p{}^{0.2}NL)\rho/\mu = N_p{}^{0.4}NL^2\rho/\mu$$

Using this Reynolds number in the usual form of the mass transfer equation we get:

$$\frac{KD/d}{(\mu/\rho d)^{1/3}} = \text{const.} \left(N_p{}^{0.4}\frac{NL^2\rho}{\mu}\right)^f$$

This equation is substantiated by the work of Marriner" and "the work of Hixson".

THEORETICAL CONSIDERATIONS

Mass transfer between a solid and a liquid is often postulated as occuring across a stagnant boundary layer of liquid. Although several rate processes are involved in most cases of mass transfer, the diffusional transfer across this boundary layer is often the slowest, hence the controlling, process. This fact should, of course, be established for each individual case.

An increased flow rate of fluid past the solid surface produces an increased shear and consequently a thinner boundary film and a faster mass transfer rate. Where the solid phase consists of a number of discrete and independent particles, mechanical agitation is often employed to provide the increased fluid flow.

A theoretical examination of such agitated systems is greatly limited by complex fluid dynamics. A single fluid velocity and direction does not exist so that another method of defining shear, hence film thickness, is needed. Previous investigators have employed the impeller speed (N), the speed-diameter (ND), a modified Reynolds number ($ND^2\rho/\mu$ or $NL^2\rho/\mu$), and the power number ($P_g/N^3L^5\rho$) - either singly or in combination. Although such terms provide correlations of data for a particular series of impellers of the same type in the same shape of tank (baffled or unbaffled to the same extent), they fail to correlate satisfactorily the data for different types of impellers, e.g. turbine versus marine propeller, and for different degrees of baffling in the tanks.

Although these functions may serve to define the flow of liquid relative to the impeller or tank, they probably fail to correlate all mass transfer data for solid-liquid systems because they do not define the flow of liquid relative to the solid particles which are free to move with the liquid. For the less complicated case of a particle falling under the influence of gravity through a quiescent liquid, a maximum (or "terminal") velocity is reached at which the gravitational, buoyant and frictional forces are in equilibrium. A steady vertical flow of the liquid does not change the terminal velocity of the particle relative to the liquid.

In a mechanically agitated system, the impeller produces horizontal and rotational, as well as vertical, fluid currents. The trajectory of a particle is dependent upon the net effect of all these forces. Where the local vertical component of flow has a sufficient upward magnitude, the particle will be suspended in the fluid or carried upward. Because the magnitude and direction of the fluid currents vary from point to point within the vessel, the particle will alternately rise and fall. Where the impeller discharges a sufficient volume of liquid, a particle will not reach the bottom of the vessel before horizontal currents carry it to an up-current of sufficient magnitude to stop the downward movement of the solid.

Applying the terminal velocity concept to such two-dimensional systems, it may be reasoned that once suspension has been attained the relative velocity between the liquid and the solid will not change because an increase in the velocity of the liquid only results in a corresponding increase in the absolute particle velocity.

This reasoning is perhaps fully applicable only to particles of very small mass and inertia which are easily suspended in a liquid and which follow every change in direction experienced by the liquid. Larger particles, with greater inertias, will accelerate and decelerate more slowly than the liquid, and will therefore temporarily experience greater velocity differences than that defined by the terminal velocity.

For the smaller particles, the stagnant film which theoretically surrounds each particle should remain constant in magnitude once the particle has been suspended. Any mass transfer limited by diffusion across the film should thus remain approximately constant in rate once complete suspension of the solid has been attained. The inertia of larger particles would permit a temporary additional shear when liquid velocity or direction are changed; a thinner film is temporarily produced.

In general, this means that a break-point will be found in a plot of mass rate versus impeller speed, beyond which an increase in impeller speed is economically unfeasible. (It is assumed that the liquid has a low enough viscosity so that an increase in impeller speed produces an increase in fluid velocity throughout the tank.)

Further, if the terminal velocity concept is valid, the rate of mass transfer should be relatively independent of tank size and impeller dimensions once the plateau following the break-point is attained. This assumes that the weight and area of solid per unit volume of liquid is maintained constant and that the initial concentration of the liquid is also kept the same. In such a case, the concentration of the liquid would be a function of time alone. Obviously the temperature must not be changed.

Probably the same factors determine the terminal velocity of a particle in the two-dimensional agitated system as in the one-dimension gravitational system, i.e.

$$v_m = K_s \sqrt{\frac{(\rho_s - \rho)}{\rho}(D_p)}$$

where K_e combines a friction factor and a shape factor, and D_p is a linear dimension or diameter of the particle.

If the rate of solution in an agitated tank of two equal weights of cubical particles ($D_{p-1} = 2D_{p-2}$) is studied, it would seem at first that the second sample with twice the area should dissolve twice as rapidly as the first. However if both samples are fully suspended the velocity of fluid relative to the particles is proportional to the diameters, i.e.

$$v_{m-1}/v_{m-2} \approx \sqrt{D_{p-1}/D_{p-2}}$$

or

$$v_{m-1} = \sqrt{2}\, v_{m-2} = 1.4\, v_{m-2}$$

The K_{e-1} is slightly less than K_{e-2} so that v_{m-1} will be somewhat less than $\sqrt{2}$ times greater than v_{m-2}. The general prediction is, however, the same i.e. the rate of solution of the second sample will not be twice as great as the rate of solution of the first sample (the factor would probably be about 1.5).

Further examination of this example reveals that the smaller particle is suspended at a lower impeller speed since v_{m-2} is less than v_{m-1}. Consequently the plateau should appear at a lower angular velocity.

Where two or more different sizes of particles are present in the same agitated system, they should act independently except as their rate of solution or reaction is affected by the concentration of the liquid.

DESCRIPTION OF APPARATUS

Three different sizes and shapes of tanks and five different impellers were employed in this investigation. (FIG. 1-4)

Preliminary tests were conducted in a two-liter Pyrex beaker (4.94 inches diameter, D) using a two bladed Lucite paddle, 1.81 inches in diameter, L, by 1.25 inches in width, W, (FIG. 1). Two baffles each 0.92 inch wide (0.19 D) were inserted in the beaker. A clearance of 0.875 inches (0.18 D) was allowed between the bottom center of the beaker and the bottom edge of the impeller.

The second series of tests were conducted in a 10-inch, D, monel tank (FIG. 2). Three different impellers were employed:

1. A two-bladed paddle, 3.66 inch L x 2.50 inch W, representing a scale-up from the beaker tests. (FIG. 2). A clearance of about 2 inches was allowed.

2. A six-bladed paddle, 6.0 inch L x1.375 inch W. The clearance was approximately 3.125 inches. (FIG. 3).

3. A four-bladed paddle, 3.938 inch L x 1.00 inch W. The clearance was about 3.5 inches. (FIG. 3).

Four steel baffles, each 1.0 inch wide (0.10 D), were inserted in the tank, and extended down to approximately the knuckle of the dished bottom.

The third tank (FIG. 4) used in this investigation had the appearance of a truncated cone resting on its smaller base. The top tank diameter was about 14.25 inches and the bottom diameter was approximately 12.25 inches. One impeller was used, a two-bladed paddle 4.84 inch L x 3.31 inch W, which represented a scale-up from the beaker based on a mean tank diameter of 13.25 inches. A clearance of 1.75 inches was allowed. Four steel baffles, each 1.5 inches wide (0.115 D) were inserted in the tank.

A revolution counter was used in all tests to determine the speed of the impeller in revolutions-per-minute. A stop-watch was used in timing all rpm determinations.

BASIC DIMENSIONS OF BEAKER-SCALE APPARATUS

(Scale 6" = 1')

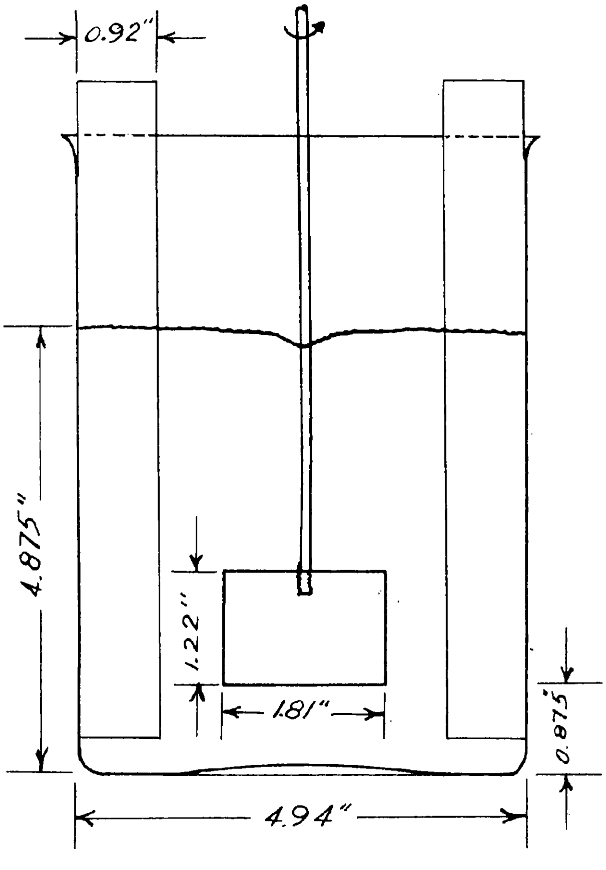
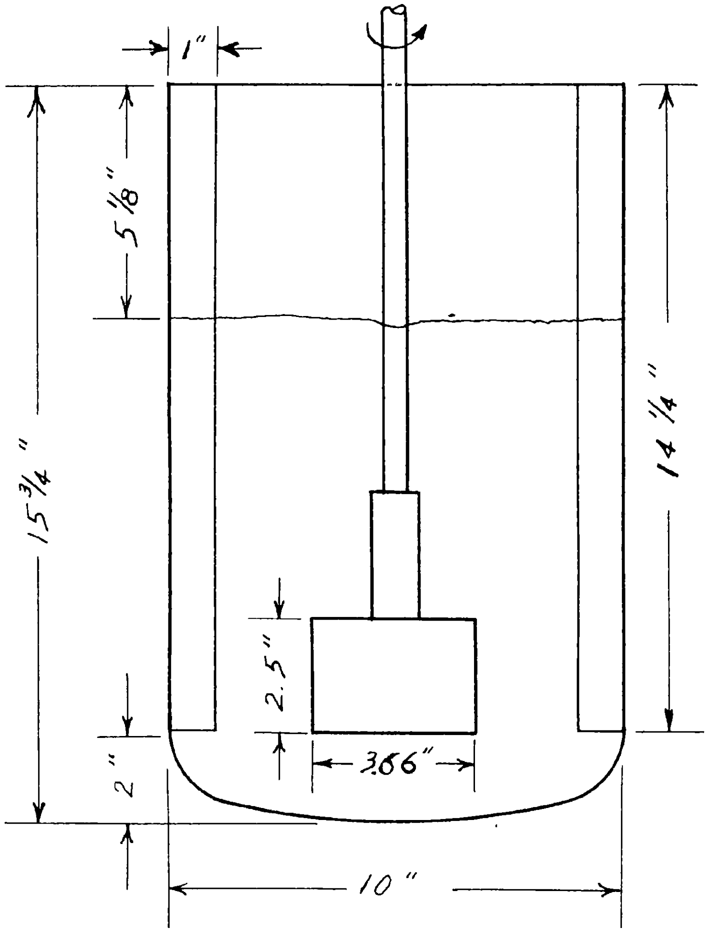


FIG. 1

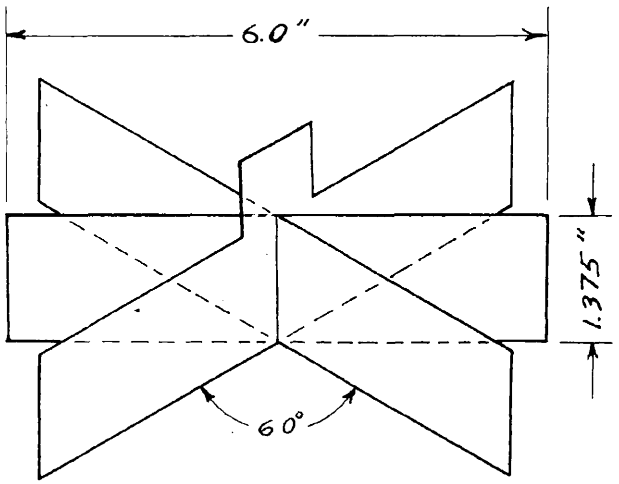
DIMENSIONS OF TEN-INCH DIAMETER
AGITATOR-TANK
(TWO-BLADE PADDLE SHOWN)



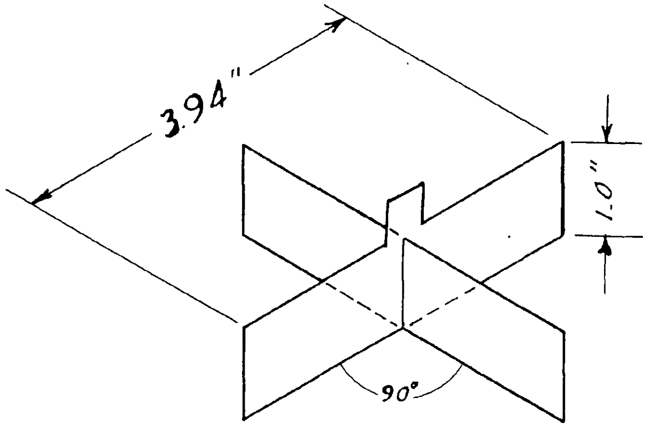
SCALE 3" = 1'

FIG. 2

FOUR- AND SIX-BLADE PADDLES



SIX-BLADE PADDLE



FOUR-BLADE PADDLE

FIG. 3

BASIC DIMENSIONS OF THIRTEEN-INCH AGITATOR TANK

(SCALE 3"=1')

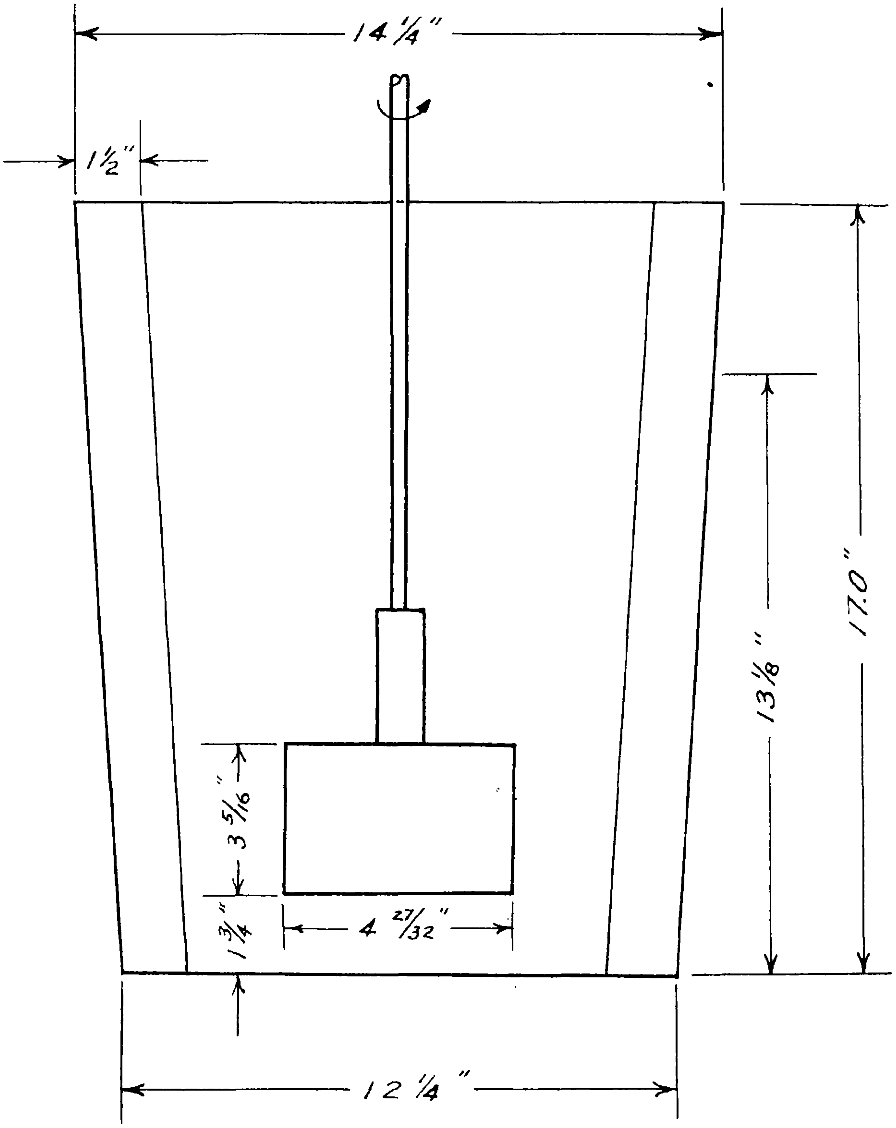


FIG. 4

PROCEDURE

On the beaker scale, two systems of mass transfer were investigated. A 60/80 mesh sieve cut of zinc was dissolved in an approximately 0.41 normal sulfuric acid solution, and a 40/60 mesh sieve cut of fused, glassy borax was dissolved in tap water. In the larger tanks only the borax-water system was investigated; the ratio of borax to water was kept constant in the three sizes of apparatus.

In making tests on the rate of solution of zinc in 0.41 N sulfuric acid, 1500 ml. of acid were transferred from a twenty-liter carboy to the two-liter beaker. The resulting height, H, of the liquid in the beaker was 4.875 inches, i.e. the height of the liquid was about the same as the beaker diameter (H/D = 0.987). The paddle agitator was set at the desired speed and the temperature of the acid was adjusted to 21° ± 0.5° C. by means of a water-ice bath. Twenty-five grams of 60/80 mesh zinc were added and allowed to react with the sulfuric acid for twenty minutes. The acid temperature was measured with a mercury-filled glass thermometer at five minute intervals. The agitator speed was measured two or three times in the course of a twenty minute run (cf. APPENDIX for sample data). At the end of the twenty minutes, a sample of the acid solution was obtained by inserting a 25 ml. pipette (with an enlarged tip) in a rising current of liquid in front of a baffle. This sample was immediately filtered to remove solid particles of zinc. A ten milliliter sample of filtrate was titrated with a standardized potassium ferrocyanide solution using a diphenylamine-potassium ferricyanide indicator and back-titrated with a standardized zinc sulfate solution (cf. APPENDIX).

The dissolution of fused, glassy borax in water was studied in the two-liter beaker, in a ten-inch diameter monel tank and in a 13¼ inch diameter truncated, conical tank (cf. DESCRIPTION OF APPARATUS, FIG. 4). Three different impellers were used in the ten-inch tank; only one impeller was used in the beaker; and only one impeller was used in the largest tank. The same general operating procedure was employed as in the zinc-acid tests. A quantity of water was measured into a tank and its temperature was adjusted to $20.5^\circ \pm 1.5^\circ$ C. with the agitator running at the desired speed. A weighed quantity of borax was added and allowed to dissolve for twenty minutes, at which time the solution was sampled as described above (cf. APPENDIX for sample data). The sample was filtered and ten milliliters of filtrate were titrated to the methyl orange end-point with 0.1 N hydrochloric acid.

The 1.5 liters of tap water used in the beaker runs was measured out in graduated cylinders. The volumes of tap water used in the larger tanks were measured by filling the tank to the level indicated by a mark on one of the baffles. This level was chosen to give a depth of water approximately equal to the tank diameter, with some allowance given to the shape of the tank bottoms. The volumes of water were determined by converting the weights of water, required to fill the tanks to the established marks, into volumes. Approximately the same weight of borax per volume of water was employed in all tests. This data is summarized below:

	Vol.-liters	H/D	Gms./Liter
Beaker	1.50	0.99	33.3
10" Tank	13.12	1.06	33.2
13" Tank	28.66	1.00	33.7

PRECISION OF MEASUREMENT

The average linear dimensions of the tanks and impellers were measured to an estimated ± 0.1 inch with the exception of the impeller clearances, C. Because the bottoms of the three tanks were not perfectly flat, the measurement of the clearances may be in error by ± 0.3 inch.

Solution temperatures were usually measured with a 0° - 100° C. mercury-filled glass-stem thermometer of a type commonly found in chemistry laboratories. It was calibrated in 1° C. intervals and was inserted in the various solutions to about the 5° C. mark. It was not calibrated against a standard thermometer or other temperature-measuring device but the air temperature indicated by this thermometer was in agreement with that indicated by a similar one. No stem corrections were made. In some runs a -4° to 50° C. thermometer, calibrated in 0.1° C. intervals, was employed. The general precision of a temperature measurement is probably ± 0.25° C.

In the course of any one run, the temperature as measured by the thermometer normally varied by less than 1° C., i.e. the average deviation from the mean was less than 0.5° C. The deviation of the average temperature for one run differed from the average temperature of another similar run by less than 1° C. These slight variations in temperature produced negligible changes in mass transfer rates and in the saturation concentration of borax.

The determination of the zinc ion concentration in the zinc-sulfuric acid investigations was subject to the usual errors of sampling and titration. Because the redox reaction used in the titration is based upon the ferricyanide-ferrocyanide equilibrium, the oxidizing action of air produces an end-point somewhat lower than the stoichiometric value. This effect is minimized by standardizing the ferrocyanide solution against a standard zinc solution of approximately the same concentration as the zinc solution produced in the tests. The precision of the analytical method is estimated to be ± 5 per cent with the analytical result normally lower than the actual zinc concentration.

The precision of determinating the borax concentration by titrating with 0.1 N hydrochloric acid is limited by the stoichiometric equality of the alkaline and acid oxides constituting the borax ($Na_2B_4O_7 = Na_2O \cdot 2B_2O_3$). A preliminary investigation indicated that only about 96 per cent of the stoichiometric volume of acid was required. This value was used in converting all titers into weights or concentrations of borax. The final value of concentration is estimated to be in error by not more than one per cent.

Since the rate of mass transfer from a solid to a liquid is proportional to the area of exposed solid, it is imperative that any evaluation of the effect of agitation on mass transfer rates be based upon a unit area. This means that either the initial areas be the same in all tests or that differences in area be completely measurable. In an attempt to maintain identical initial areas, a close screen cut was taken, i.e. the 60/80 zinc cut and the 40/60 borax cut. Because separation was not complete, e.g. from agglomeration of fines, a sieve analysis of the sieve cut was made in several instances. This sieve analysis is subject to errors caused by agglomeration of particles and by breakage or chipping of particles during the sieve analysis. Consequently the results must be employed with caution but they do provide a means of comparison.

The measurement of the revolutions per minute are subject to errors in timing and in the revolution counter. The fluctuation in the two measurements taken during each run provides an estimate of the precision. The maximum deviation noted was 3.8 per cent; the usual deviation was no greater than 0.5 per cent.

DISCUSSION OF RESULTS

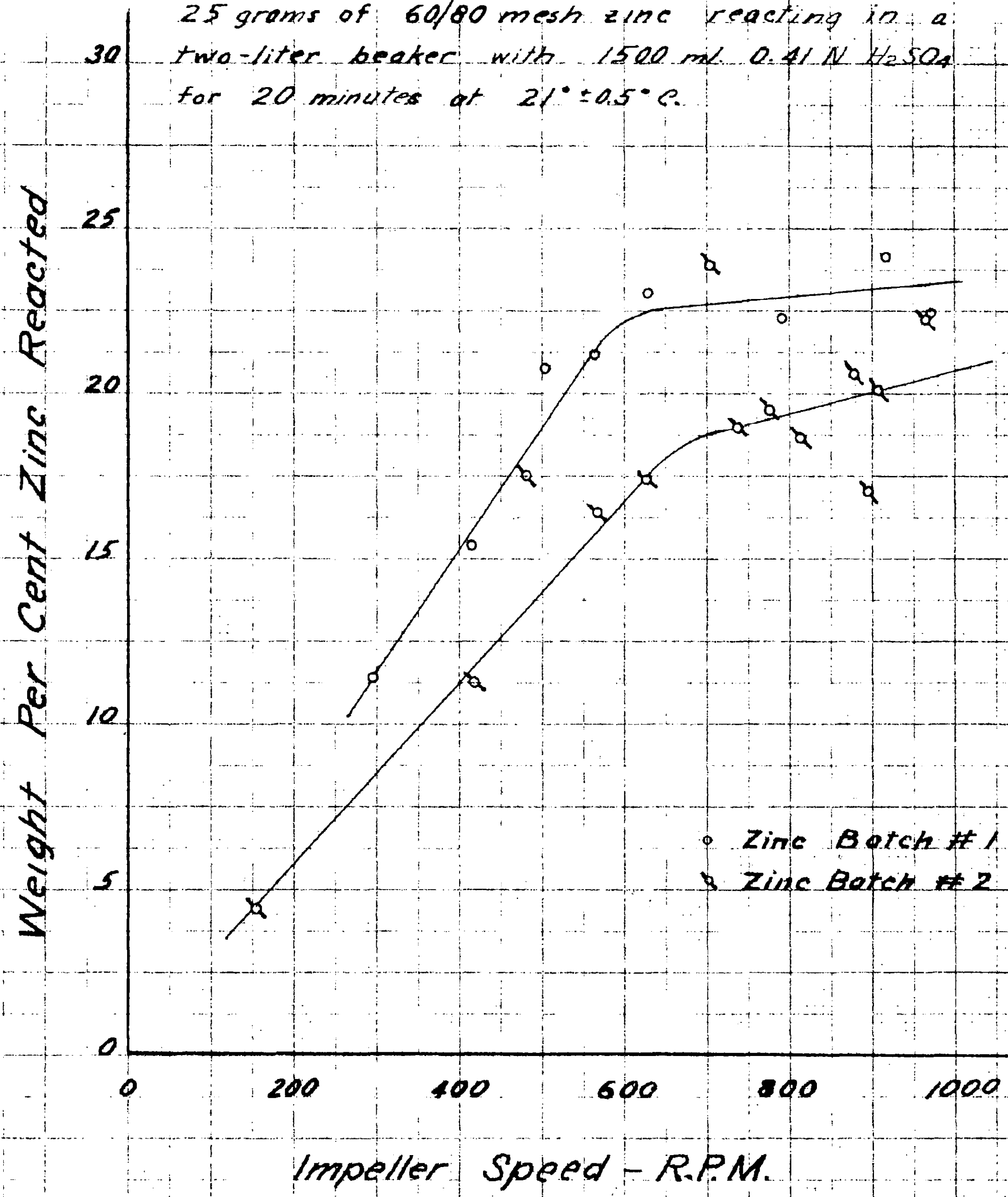
The Zinc-Sulfuric Acid Reaction

The results of the investigation of the effect of agitation intensity upon the rate of reaction of 60/80 mesh zinc with 0.4 N sulfuric acids are presented in TABLES I and II and in FIG. 5. A sample of the data taken during a single run is presented in the APPENDIX.

From FIG. 5 it is evident that the two batches of zinc, received and screened to 60/80 mesh at different times, do not react at the same rate with sulfuric acid. Although all this zinc passed through a U.S. 60 mesh screen and was retained on a U.S. 80 mesh screen, the agglomeration of fines and the distribution of sizes within the 60/80 cut could have resulted in different reaction areas per unit weight of zinc.

Despite the differences in magnitude, both batches of zinc show an appreciable change in the effect on reaction rate of an increase in speed of agitation at the higher angular velocities compared with the lower speeds. The fact that the break-points in the curves occur at or near the impeller speed where full suspension of zinc is visually noted, tends to confirm the theoretical deductions concerning a terminal velocity for particles in agitated

EFFECT OF IMPELLER SPEED ON RATE OF REACTION



25 grams of 60/80 mesh zinc reacting in a two-liter beaker with 1500 ml 0.41 N H_2SO_4 for 20 minutes at 21° ± 0.5° C.

FIG. 5

TABLE I

Reaction of Zinc (Batch #1) with Sulfuric Acid as a Function of Agitator Speed

Zinc	25 grams, 60/80 mesh	Temperature 21.2°C. Avg.
H_2SO_4	1500 ml., 0.4 N.	Beaker scale, 20 min. run

RPM	Per Cent Zn Reacted	Per Cent A_o Left	Average Temperature
295	11.4	92.25	21.3° C.
416	15.4	89.5	21.3
503	20.8	85.6	20.5
567	21.2	85.35	21.3
629*	23.1	84.0	21.2
793	22.3	84.6	21.5
919	24.2	83.2	21.2
974	22.4	84.45	21.3

*Zinc appeared fully suspended at this and higher speeds.

TABLE II

Reaction of Zinc (Batch #2) with Sulfuric Acid as a Function of Agitator Speed

Zinc	25 grams, 60/80 mesh	Temperature 21.0° C. Avg.
H_2SO_4	1500ml., 0.4 N	Beaker scale, 20 min. run

RPM	Per Cent Zn Reacted	Per Cent A_0 Left	Average Temperature
155	4.5	97.0	21.3° C.
418	11.3	92.3	21.1
481	17.5	88.0	21.1
568	16.4	89.8	21.0
629	17.4	88.1	20.6
704*	24.0	83.3	21.1
739	19.0	86.9	20.8
774	19.5	86.6	21.0
811	18.7	87.1	21.0
878	20.6	85.8	21.1
898	17.0	88.3	20.4
907	20.1	86.2	21.3
965	22.3	84.5	20.9

*Apparantly mostly suspended above this speed.

tanks. The lower curve (batch #2) has its break-point at a higher impeller speed than the break-point of the upper curve. This is also consistent with prior reasoning because the larger particles (lower area) require a higher velocity for suspension. The effect of hydrogen evolution on agitation intensity and on effective particle density (by gaseous occlusion) has not been evaluated.

The Dissolution of Glassy Borax

Previous investigators have shown that the instantaneous rate of solution of a solid in a liquid is proportional to the area of solid exposed and to the difference between the concentration of a saturated solution and the solution concentration at that time, that is:

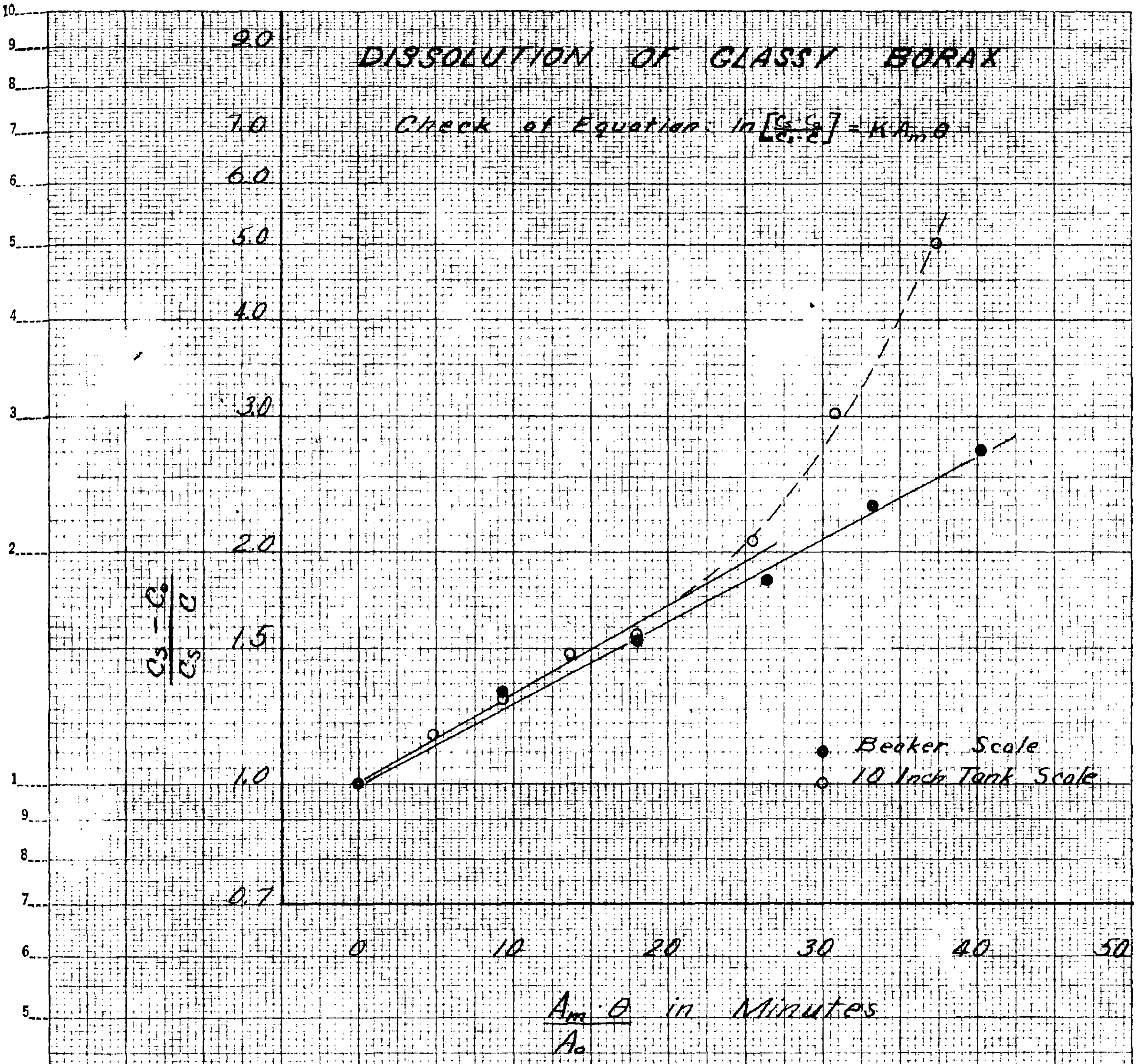
$$\frac{dC}{d\theta} = KA(C_s - C)$$

When the area change is small, a mean value may be used. Integration then gives:

$$\ln\left[\frac{C_s - C_o}{C_s - C}\right] = KA_m\theta$$

A plot of log $(C_s - C_o)/(C_s - C)$ versus $A_m \cdot \theta/A_o$ should result in a straight line.

The results of tests, conducted to determine the applicability of these equations to the glassy borax-



DISSOLUTION OF GLASSY BORAX

Check of Equation: $\ln\left[\frac{C_s - C_o}{C_s - C}\right] = K A_m \theta$

FIG. 6

TABLE III

Dissolution of Glassy Borax (Batch #1) as a Function of Time

Borax	50 grams, 40/60 mesh	Temp. 21.3° C. Avg.	
Water	1,500 milliliters	Beaker scale	

Time θ Minutes	Conc. C Gms/100cc	C_s-C	$\frac{C_s-C_o}{C_s-C}$	Area Per Cent A_o	$A_m\theta/A_o$
0	-----	2.7	1.00	100.0	-----
10	0.660	2.04	1.324	86.4	9.32
20	0.944	1.756	1.538	80.2	18.02
30	1.225	1.475	1.832	73.7	26.05
40	1.528	1.172	2.305	66.4	33.25
50	1.703	0.997	2.71	62.1	40.5

TABLE IV

Dissolution of Glassy Borax (Batch #2)
as a Function of Time

Borax	435 grams, 40/60 mesh	Temp. 20.6° C. Avg.
Water	13,120 milliliters	10 inch Tank

Time θ Minutes	Conc. C Gms/100cc	$C_s - C$	$\frac{C_s - C_o}{C_s - C}$	Area Per Cent A_o	$A_m\theta/A_o$
0	-----	2.7	1.00	100.0	-----
5	0.359	2.341	1.153	92.5	4.81
10	0.606	2.094	1.292	87.5	9.375
15	0.862	1.838	1.468	81.85	13.63
20	0.973	1.727	1.564	79.4	17.94
30	1.392	1.308	2.065	69.6	25.42
40	1.807	0.893	3.025	59.3	31.86
50	2.162	0.538	5.02	49.5	37.4
60	2.465	0.235	11.48	40.4	42.15

water system, are presented in TABLES III and IV, and in FIG. 6. The linearity of the data shown in FIG. 6 indicates that the above relationships are applicable for at least thirty minutes ($A_m \cdot \theta/A_o$ of about 25) under the conditions of the tests. (The rapid increase in log $(C_s-C_o)/(C_s-C)$, found in the 10-inch tank-test beyond thirty minutes, may be caused by attrition and subdivision of the borax particles.) Since all other tests were conducted for only twenty minutes, the linear characteristics were dominant and the rate constant K could be used as a measure of the rate of reaction.

The basic experimental data are presented in TABLES V through IX. The variation in the values of "C" and "K" for different tank and impeller sizes would seem to disprove the prediction (THEORETICAL CONSIDERATIONS) that normally the concentration and dissolution constant would be independent of such changes in tank and impeller dimensions. However, when batch #3 borax was used in three beaker-scale tests (TABLE X), the resulting values of K differed only by about six per cent from those obtained with batch #3 borax in the thirteen-inch tank. This supports the theoretical contention that K is normally independent of tank and impeller sizes once suspension of small particles has been attained. The values of K were therefore adjusted to the same "suspension" or "plateau" value for all batches of borax. Batch #3 was accepted as a standard for this adjustment.

TABLE V

Dissolution of Glassy Borax (Batch #1) in Water as a Function of Agitator Speed

Borax 50 grams, 40/60 mesh Temperature 21.4° C. Avg.

Water 1500 milliliters Beaker Scale, 20 Min. Run

2-Blade Paddle, 1.81"(L) x 1.22"(W)

RPM	Conc. C gms/100 ml	Avg Temp °C	Wt Per Cent Dissolved	C_s-C	Area Per Cent A_0	$Kx10^2$
298	0.642	21.3	19.26	2.058	86.7	1.455
308	0.785	21.4	23.56	1.915	83.6	1.867
379	0.816	21.2	24.44	1.884	83.0	1.965
428	0.934	21.2	28.00	1.766	80.4	2.356
434	0.944	21.2	28.30	1.756	80.2	2.390
498	0.975	21.4	29.24	1.725	79.4	2.496
564	0.970	21.4	29.06	1.730	80.0	2.475
633	0.944	21.4	28.30	1.756	80.2	2.390
684	0.960	21.4	28.80	1.740	79.8	2.445
800	0.996	21.8	29.84	1.704	78.9	2.574
879*	1.022	21.3	30.60	1.678	78.4	2.665
887*	1.052	21.3	31.56	1.648	77.6	2.775
931	1.017	21.7	30.44	1.683	78.6	2.645
939	0.965	21.7	28.94	1.735	79.7	2.460
970	0.991	21.5	29.70	1.709	79.1	2.548
972	0.965	21.4	28.94	1.735	79.7	2.460

*A different 40/60 cut.

TABLE VI

Dissolution of Glassy Borax (Batch #2) in Water as a Function of Agitator Speed

Borax	435 grams, 40/60 mesh	Temperature 20.4° C. Avg.
Water	13,120 milliliters	10-Inch Tank, 20 Min. Run

2-Blade Paddle, 3.66"(L) x 2.5"(W)

RPM	Conc. C gms/100 ml	Avg Temp °C	Wt Per Cent Dissolved	C_s-C	Area Per Cent A_o	$K \times 10^2$
150	0.412	20.3	12.4	2.278	92.0	0.89
194	0.617	20.8	18.6	2.083	87.2	1.38
296	1.152	20.2	34.7	1.548	75.2	3.18
413	1.164	20.2	35.2	1.536	74.8	3.24
556	1.150	20.4	34.7	1.550	75.2	3.17
645	1.148	20.4	34.6	1.552	75.4	3.15
848	1.181	20.8	35.7	1.519	74.5	3.33

TABLE VII

Dissolution of Glassy Borax (Batch #2) in Water as a Function of Agitator Speed

Borax	435 grams, 40/60 mesh	Temperature 20.6° C. Avg.	
Water	13,120 milliliters	10-Inch Tank, 20 Min. Run	

6-Blade Paddle, 6.0"(L) x 1.375"(W)

RPM	Conc. C gms/100 ml	Avg Temp °C.	Wt Per Cent Dissolved	C_s-C	Area Per Cent A_0	$K \times 10^2$
121	0.774	20.2	23.3	1.926	83.8	1.832
147	1.16	20.5	34.9	1.54	75.2	3.215
233*	1.303	21.2	39.2	1.397	71.8	3.74
271	1.202	20.5	36.2	1.498	74.2	3.38
364	1.196	20.7	36.0	1.504	74.3	3.35
458	1.206	20.7	36.3	1.494	74.1	3.40

*Sample delayed. Run was 20½ minutes.

TABLE VIII

Dissolution of Glassy Borax (Batch #2) in Water as a Function of Agitator Speed

Borax 435 grams, 40/60 mesh Temperature 20.8° C. Avg.
Water 13,120 milliliters 10-Inch Tank, 20 Min. Run
4-Blade Paddle, 3.938"(L) x 1.00"(W)

RPM	Conc. C gms/100 ml	Avg Temp °C.	Wt Per Cent Dissolved	C_s-C	Area Per Cent A_o	$K \times 10^2$
202	0.411	20.5	12.4	2.289	91.6	0.82
380	1.232	20.8	37.2	1.468	73.4	3.51
569	1.046	20.9	31.5	1.654	77.7	2.75
676	1.128	21.0	34.0	1.572	75.8	3.08
760	1.227	20.7	36.9	1.473	73.6	3.49
972	1.210	36.5	36.5	1.490	73.9	3.41

TABLE IX

Dissolution of Glassy Borax (Batch #3) in Water as a Function of Agitator Speed

Borax 2.125 lb., 40/60 mesh Temperature 20.0° C. Avg.
Water 28,600 milliliters 13-Inch Tank, 20 Min. Run
2-Blade Paddle, 4.844"(L) x 3.3125"(W)

RPM	Conc. C gms/100 ml	Avg Temp °C.	Wt Per Cent Dissolved	C_s-C	Area Per Cent A_o	$Kx10^2$
130	0.524	20.3	15.6	2.176	89.4	1.08
161	0.80	20.2	23.7	1.900	83.5	1.91
202	1.13	19.6	33.6	1.57	76.2	3.08
285	1.13	19.8	33.6	1.57	76.2	3.08
341	1.113	20.2	33.1	1.587	76.6	3.01
402	1.108	20.2	32.9	1.592	76.6	2.99

TABLE X

Dissolution of Glassy Borax (Batch #3) in Water

Comparison of Beaker Scale with Average Thirteen-Inch Scale Results

Beaker Scale				Thirteem-Inch Scale		
RPM	Conc. C	$K \times 10^2$	% Dev	Conc. C	$K \times 10^2$	% Dev
872	1.027	2.68	5.97	1.130	3.08	1.32
902	1.108	2.99	4.91	1.130	3.08	1.32
972	1.078	2.68	1.05	1.113	3.01	0.99
-	-	-	-	1.108	2.99	1.65
Avg.	1.071	2.85	3.98	1.120	3.04	1.32

Per Cent Difference in Avg. K's $= \frac{(3.04 - 2.85)(100)}{3.04} = 6.25\ \%$

Further qualitative proof for this adjustment is provided by an examination of the sieve analyses for the three batches of borax (APPENDIX). These show that batch #1 had the smallest area per unit weight and batch #2 the largest area. Note that the corresponding unadjusted K's were also in the order $K_1 < K_3 < K_2$. The limitations of a screen analysis do not permit other than a qualitative comparison.

The adjusted data are presented in TABLES XI to XV and are shown as a function of impeller speed, rpm, in FIG. 7. The average deviation from the mean of all data in the plateau region is about 3 per cent. The maximum deviation is 15.3 per cent (for the four-blade paddle at 569 rpm). The largest deviations obtained with the four-blade paddle may have resulted from a vibration of shaft and paddle which developed in some ranges of speed.

In FIG. 7, the portions of the curves where the dissolution constant increases, corresponding to the effect of agitation before suspension is attained, do not coincide. The slopes also differ but this may be more dependent upon particle size distribution than upon agitator and tank dimensions. In an effort to get these portions of the curves to coincide, the usual (ND), the Reynolds-Power number combination, $(NL^2\rho/\mu)(P_g/N^3L^5\rho)^{0.45}$, were employed as abscisses and (K') and $(K'D)$ as ordinate. No satisfact-

THE ADJUSTED DISSOLUTION CONSTANT AS A FUNCTION OF IMPELLER SPEED

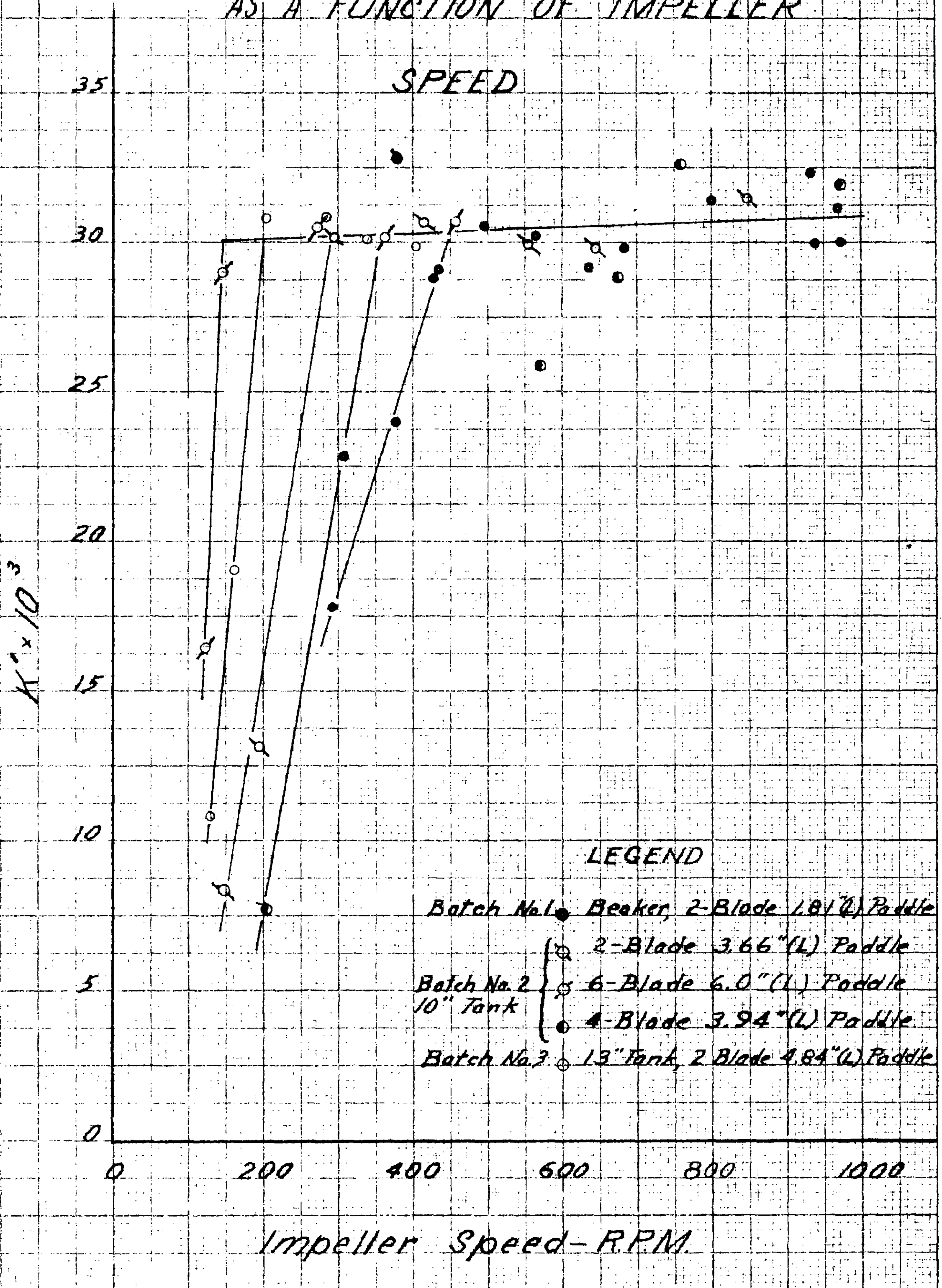


FIG. 7

TABLE XI

Adjusted Dissolution Constants for Glassy Borax (Batch #1) in Water

Borax 50 grams, 40/60 mesh Temperature 21.4° C. Avg.

Water 1500 milliliters Beaker Scale, 20 Min. Run

2-Blade Paddle, 1.81"(L) x 1.22"(W)

RPM	$K' \times 10^2$
298	1.78
308	2.28
379	2.40
428	2.88
434	2.92
498	3.05
564	3.02
633	2.92
684	2.98
800	3.14
931	3.23
939	3.00
970	3.12
972	3.00

TABLE XII

Adjusted Dissolution Constants for Glassy Borax (Batch #2) in Water

Borax	435 grams, 40/60 mesh	Temperature 20.4° C. Avg.
Water	13, 120 milliliters	10-Inch Tank, 20 Min. Run

2-Blade Paddle, 3.66"(L) x 2.5"(W)

RPM	$K' \times 10^2$
150	0.84
194	1.31
296	3.01
413	3.07
556	3.00
645	2.98
848	3.15

TABLE XIII

Adjusted Dissolution Constants for Glassy Borax (Batch #2) in Water

Borax	435 grams, 40/60 mesh	Temperature 20.6° C. Avg.
Water	13,120 milliliters	10-Inch Tank, 20 Min. Run

6-Blade Paddle, 6.0"(L) x 1.375"(W)

RPM	$K' \times 10^2$
121	1.65
147	2.90
271	3.05
364	3.02
458	3.07

TABLE XIV

Adjusted Dissolution Constants for Glassy Borax (Batch #2) in Water

Borax	435 grams, 40/60 mesh	Temperature 20.8° C. Avg.
Water	13,120 milliliters	10-Inch Tank, 20 Min. Run

4-Blade Paddle, 3.938"(L) x 1.00"(W)

RPM	$K' \times 10^2$
202	0.77
380	3.28
569	2.58
676	2.88
760	3.26
972	3.19

TABLE XV

Adjusted Dissolution Constants for Glassy Borax (Batch #3) in Water

Borax	2.125 lb., 40/60 mesh	Temperature 20.0° C. Avg.
Water	28,600 milliliters	13-Inch Tank, 20 Min. Run
	2-Blade Paddle, 4.844"(L) x 3.3125"(W)	

RPM	$K' \times 10^2$
130	1.08
161	1.91
202	3.08
285	3.08
341	3.01
402	2.99

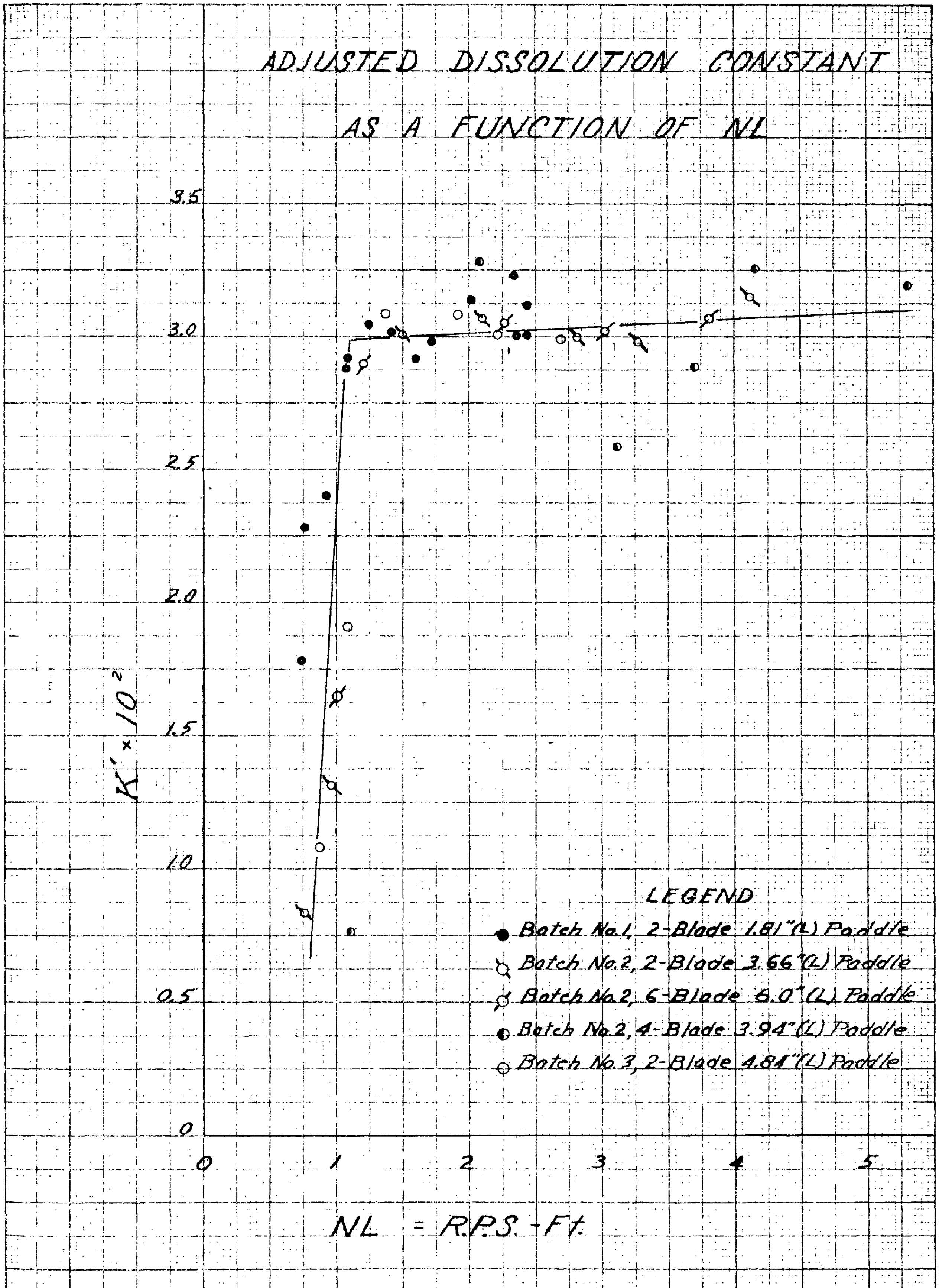
ory correlation was obtained. However, a reasonable correlation of data was obtained by plotting K' as ordinate against NL as abscissa as shown in FIG. 8. The data for this correlation are presented in TABLES XVI to XX.

It has been shown (10) that the effective velocity at which liquid is discharged by an impeller is:

$$v = \text{const.}\ (N_p)^{0.2}(NL)$$

Since, in the present experimental work, the range of power numbers is 3.6 to 8.2, $(N_p)^{0.2}$ varies only from 1.29 to 1.52, i.e. the effect of N_p is small in this work. The effective velocity is thus proportional to NL so that the correlation of K' vs. NL is probably essentially K' vs. v.

Power input per volume of liquid has sometimes served as a rough approximation for accomplishing identical results with different impellers or in different volumes. The concept has been tested in the present work (TABLES XXI to XXV and FIG. 9). From FIG. 9 it appears that the P/V concept is not applicable to the 40/60 mesh borax-water systmm in the apparatus employed. Although the P/V at the break-point of the curves appears to decrease with an increased apparatus size in dimensionally similar systems (scale-up from beaker to 10-inch tank to 13-inch tank), the data are insufficient to correlate P/V with tank diameter or other dimension.



ADJUSTED DISSOLUTION CONSTANT AS A FUNCTION OF NL

FIG. 8

TABLE XVI

Dissolution Constant K' as a Function of NL

Borax 50 grams, 40/60 mesh Temperature 21.4° C. Avg.
Water 1500 milliliters Beaker Scale, 20 Min. Run
2-Blade Paddle, 1.81"(L) x 1.22"(W)

RPM	NL	$K' \times 10^2$
298	0.75	1.78
308	0.77	2.28
379	0.93	2.40
428	1.07	2.88
434	1.09	2.92
498	1.25	3.05
564	1.42	3.02
633	1.59	2.92
684	1.72	2.98
800	2.01	3.14
931	2.34	3.23
939	2.36	3.00
970	2.44	3.12
972	2.44	3.00

TABLE XVII

Dissolution Constant K' as a Function of NL

Borax 435 grams, 40/60 mesh Temperature 20.4° C. Avg.

Water 13,120 milliliters 10-Inch Tank, 20 Min. Run

2-Blade Paddle, 3.66"(L) x 2.5"(W)

RPM	NL	$K' \times 10^2$
150	0.76	0.84
194	0.97	1.31
296	1.51	3.01
413	2.10	3.07
556	2.82	3.00
645	3.28	2.98
848	4.13	3.15

TABLE XVIII

Dissolution Constant K' as a Function of NL

Borax 435 grams, 40/60 mesh Temperature 20.6° C. Avg.
Water 13,120 milliliters 10-Inch Tank, 20 Min. Run
6-Blade Paddle, 6.0"(L) x 1.375"(W)

RPM	NL	$K' \times 10^2$
121	1.01	1.65
147	1.22	2.90
271	2.26	3.05
364	3.03	3.02
458	3.82	3.07

TABLE XIX

Dissolution Constant K' as a Function of NL

Borax 435 grams, 40/60 mesh Temperature 20.8° C. Avg.

Water 13,120 milliliters 10-Inch Tank, 20 Min. Run

4-Blade Paddle, 3.938"(L) x 1.00"(W)

RPM	NL	$K' \times 10^2$
202	1.11	0.77
380	2.08	3.28
569	3.12	2.58
676	3.70	2.88
760	4.16	3.26
972	5.32	3.19

TABLE XX

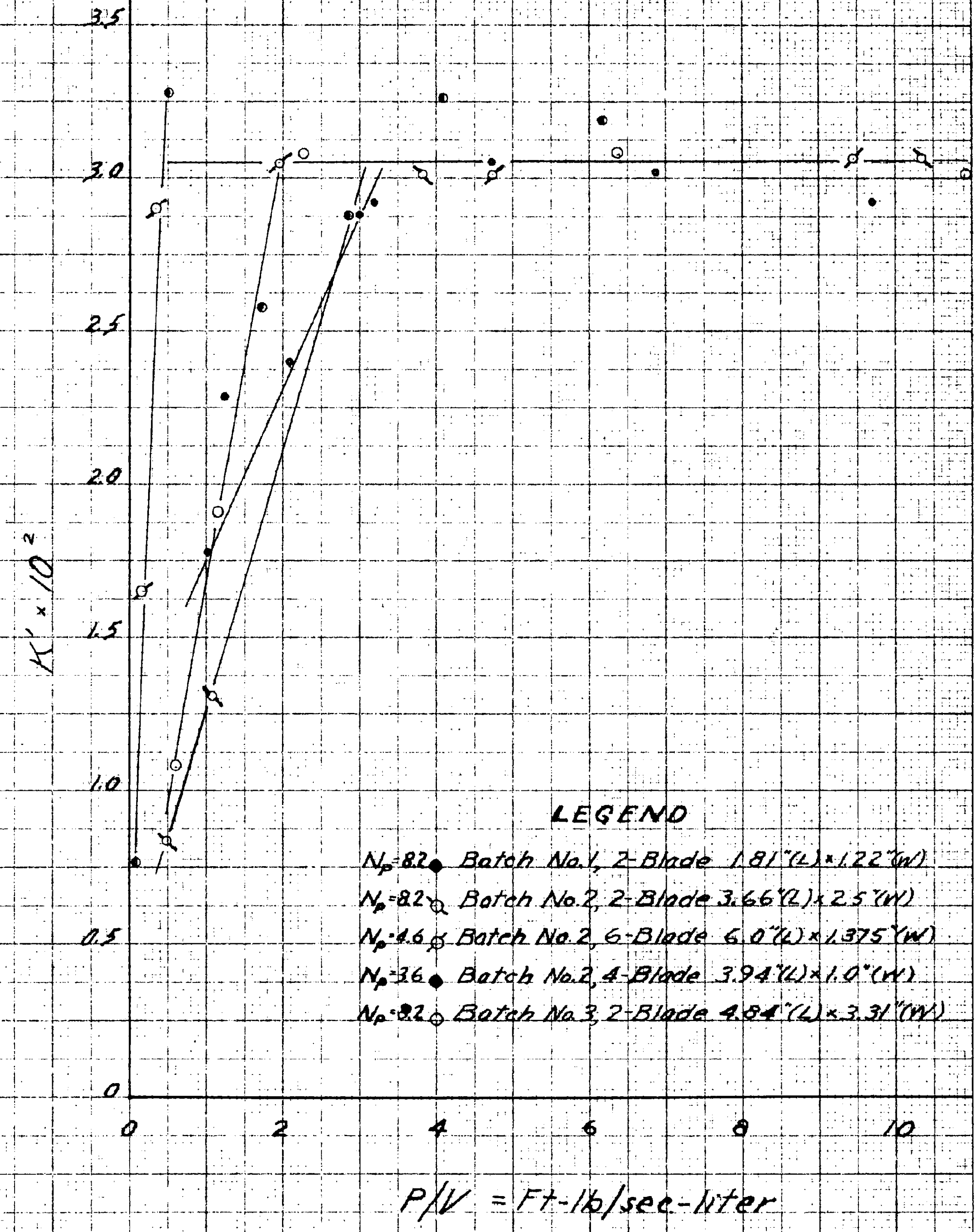
Dissolution Constant K' as a Function of NL

Borax 2.125 lb., 40/60 mesh Temperature 20.0° C. Avg.

Water 28,600 milliliters 13-Inch Tank, 20 Min. Run

2-Blade Paddle, 4.844"(L) x 3.3125"(W)

RPM	NL	$K' \times 10^2$
130	0.88	1.08
161	1.08	1.91
202	1.36	3.08
285	1.92	3.08
341	2.22	3.01
402	2.70	2.99



ADJUSTED DISSOLUTION CONSTANT AS A FUNCTION OF POWER PER UNIT VOLUME

FIG. 9

TABLE XXI

Dissolution Constant as Function of Power per Unit Volume

Borax 50 grams, 40/60 mesh Temperature 21.4 ° C. Avg.
Water 1500 milliliters Beaker Scale, 20 Min. Run
2-Blade Paddle, 1.81"(L) x 1.22"(W), $N_p \doteq 8.2$

N	P*	P/V*	K'
298	1.52×10^{-1}	1.01×10^{-1}	1.78
308	1.68	1.12	2.28
379	3.13	2.09	2.40
428	4.51	3.00	2.88
434	4.80	3.20	2.92
498	7.10	4.73	3.05
564	10.32	6.88	3.02
633	14.57	9.71	2.92
684	18.38	12.27	2.98
800	29.42	19.6	3.14
931	46.3	30.9	3.23
939	47.6	31.8	3.00
970	52.4	34.9	3.12
972	52.8	35.2	3.00

* P in ft-lb/sec and P/V in ft-lb/sec-liter

TABLE XXII

Dissolution Constant as Function of Power per Unit Volume

Borax 435 grams, 40/60 mesh Temperature 20.4° C. Avg.

Water 13,120 milliliters 10-Inch Tank, 20 Min. Run

2-Blade Paddle, 3.66"(L) x 2.5"(W), $N_p = 8.2$

N	P*	P/V*	K'
150	0.65	0.50×10^{-1}	0.84
194	1.41	1.08	1.31
296	4.99	3.81	3.01
413	13.58	10.35	3.07
556	33.15	25.3	3.00
645	51.7	39.4	2.98
848	117.7	89.7	3.15

* P in ft-lb/sec and P/V in ft-lb/sec-liter.

TABLE XXIII

Dissolution Constant as Function of Power per Unit Volume

Borax 435 grams, 40/60 mesh Temperature 20.6° C. Avg.

Water 13,120 milliliters 10-Inch Tank, 20 Min. Run

6-Blade Paddle, 6.0"(L) x 1.375"(W), $N_P = 4.6$

N	P*	P/V*	K'
121	2.32	$0.18x10^{-1}$	1.65
147	4.13	0.32	2.90
271	25.7	1.96	3.05
364	62.2	4.75	3.02
458	124.0	9.47	3.07

* P in ft-lb/sec and P/V in ft-lb/sec-liter.

TABLE XXIV

Dissolution Constant as Function of Power per Unit Volume

Borax 435 grams, 40/60 mesh Temperature 20.8° C. Avg.
Water 13,120 milliliters 10-Inch Tank, 20 Min. Run
4-Blade Paddle, 3.938"(L) x 1.00"(W), N_p = 3.6

N	P*	P/V*	K'
202	1.00	0.08×10^{-1}	0.77
380	6.71	0.51	3.28
569	22.5	1.72	2.58
676	37.8	2.88	2.88
760	53.7	4.10	3.26
972	81.0	6.18	3.19

* P in ft-lb/sec and P/V in ft-lb/sec-liter.

TABLE XXV

Dissolution Constant as Function of Power per Unit Volume

Borax 2.125 lb., 40/60 mesh Temperature 20.0° C. Avg.

Water 28,600 milliliters 13-Inch Tank, 20 Min. Run

2-Blade Paddle, 4.844"(L) x 3.3125"(W), $N_p \doteq 8.2$

N	P*	P/V*	K'
130	1.73	0.61×10^{-1}	1.08
161	3.31	1.16	1.91
202	6.46	2.26	3.08
285	18.2	6.36	3.08
341	31.3	10.94	3.01
402	51.2	17.9	2.99

*P in ft-lb/sec and P/V in ft-lb/sec-liter.

CONCLUSIONS AND RECOMMENDATIONS

1. A "break-point" or "knee" has been shown to be characteristic of several "impeller speed vs. mass transfer rate" curves.

a. At speeds above the break-point, the influence of an increase in impeller rpm is reduced and may become negligible, i.e. K, the mass transfer rate constant, may become a constant (glassy borax-water system).

b. Operation of agitators at speeds much above the break-point rpm is normally economically unfeasible because a greater power input, which increases as the cube of the speed, does not result in a correspondingly greater mass transfer rate.

c. The existence of the break-point is consistant with the "terminal velocity" theory which is advanced for liquid-solid particle systems.

2. The location of the break-point cannot be correlated by impeller speed or by other methods (such as Reynolds number) which have been used by previous investigators to correlate liquid-solid mass transfer systems. However, $K = \phi(NL)$ provides a reasonable correlation of the data for three sizes of tanks and five impellers. This may be part of a more general form:

$$K = \phi(N_p)^{0.2}(NL) = \phi'(V)$$

where "v" is the effective discharge velocity of the impeller.

3. Power per unit volume is not a satisfactory means of correlating the data for the 60/80 mesh glassy borax-water system.

4. It is therefore recommended that liquid-solid particle systems which exhibit the break-point phenomenon be scaled up by maintaining a constant $(N_p)^{0.2}(NL)$ or, if the N_p is to be approximately the same, by keeping (NL) constant. Tests conducted in a two or four liter beaker under fully baffled conditions could ascertain the existence of a break-point.

TABLE OF NOMENCLATURE

A	total surface area of solid particles.
ax^3	weight of one crystal.
B	$\frac{VC_s}{na} - x_o^3$
bx^2	surface area of one crystal.
C	concentration of solution at time Θ, wt/vol e.g. gms/cc.
c	specific heat, Btu/lb-°F.
D	tank diameter, feet unless specified as inches.
D_p	particle diameter.
d	diffusivity.
H	liquid height in tank, feet
h	film heat transfer coefficient, Btu/hr-ft^2-°F.
K	the solution (or "dissolution") constant,-the specific rate of solution per unit area of crystal surface.
K'	a modified or corrected dissolution constant.
K_e	combined shape and friction factor for particle.
k	heat conductivity, Btu/hr-ft^2-°F/ft.
k^3	$\frac{VC_s}{na} - x_o^3 = B$
L	impeller diameter, feet unless specified as inches.
N	impeller velocity, rev/sec unless specified as rpm.
N_p	Power number, P_g/N^3L^5
n	number of crystals; number of particles.
P	power, ft-lb/sec.

Re	Reynolds number, $NL^2\rho/\mu$.
V	volume of solution
v	effective velocity of liquid discharged by impeller
v_m	terminal (or maximum) particle velocity, ft/sec.
W	impeller blade width, feet or inches as specified.
x	linear dimension of a crystal at time θ .
θ	time, minutes or seconds.
μ	viscosity, lb/sec-ft.
ρ	density, lb/ft^3.
ρ_s	density of solid.
ϕ, ϕ'	a function of ---.

Subscripts

c	coil.
j	jacket.
m	terminal or maximum; also, mean.
o	at zero time, initial.
P	power (N_p); particle (D_p).
r	reference size or diameter.
s	saturated condition; also, pertains to solid.
1,2	different particles.

Constants

a,b	constants, the numerical value of which depends upon the shape and density of the crystal.
f	some power.

g gravitational constant, 32.2 ft/sec^2.

$\left.\begin{array}{l} Q \\ Q' \\ q \end{array}\right\}$ proportionality constants.

LITERATURE CITED

1. Chilton, T. H; Drew, T. B.; Jebens, R. H.

"Heat Transfer Coefficients in Agitated Vessels"
Ind. Eng. Chem. 36, 510 (1944)

2. Hixson, A. W. and Baum, S. J.

"Agitation-Mass Transfer Coefficients in Liquid-Solid Agitation Systems"
Ind. Eng. Chem. 33, 478 (1941)

3. Hixson, A. W. and Baum, S. J.

"Agitation-Performance of Propellers in Liquid-Solid Systems"
Ind. Eng. Chem. 34, 120 (1942)

4. Hixson, A. W. and Baum S. J.

"Mass Transfer and Chemical Reaction in Liquid-Solid Agitation"
Ind. Eng. Chem. 36, 528 (1944)

5. Hixson, A. W. and Crowell, J. H.

"Dependence of Reaction Velocity upon Surface and Agitation.---I. Theoretical Considerations"
Ind. Eng. Chem. 23,923 (1931)

6. Hixson, A. W. and Crowell, J. H.

"Dependence of Reaction Velocity upon Surface and Agitation.---II. Experimental Procedure in Study of Surface"
Ind. Eng. Chem. 23, 1002 (1931)

7. Hixson, A. W. and Crowell, J. H.

"Dependence of Reaction Velocity upon Surface and Agitation.---III. Experimental Procedure in Study of Agitation"
Ind. Eng. Chem. 23, 1160 (1931)

8. Hixson, A. W. and Wilkens, G. A.

"Performance of Agitators in Liquid-Solid Chemical Systems"
Ind. Eng. Chem. 25, 1196 (1933)

9. Mack, D. E.

"The Efficiency of Mechanical Agitators"
Unpublished. Lehigh University.

10. Mack, D. E. and Marriner, R. A.

"A Method of Correlating Agitator Performance"
Chem. Eng. Progress 45, 545 (1949)

11. Murphree, E. V.

"Effect of Agitation on the Rate of Solution of Crystals"
Ind. Eng. Chem. 15, 148 (1923)

12. O'Connel, F. P. and Mack, D. E.

"Simple Turbines in Fully Baffled Tanks.--- Power Characteristics"
Chem. Eng. Progress 46, 358 (1950)

APPENDIX

Sample Data for Zinc-Sulfuric Acid Reaction . . . pg. 75

Quantitative Determination of Zinc. . . . . pg. 76

Sample Data for Dissolution of Glassy Borax . . . pg. 81

Analysis of Borax. . . . . pg. 82

Comparison of Three Batches of Nominally 40/60 Mesh Glassy Borax . . . . pg. 84

Biography . . . . pg. 85

SAMPLE DATA FOR ZINC - SULFURIC ACID REACTION

Zinc	25 grams of 60/80 U.S. mesh
H_2SO_4	1500 ml. of 0.406 N
Beaker	#1 (2 liter beaker)
Data:	June 23, 1951

Time-Min	°C	RPM	Remarks
0	21.4	417	1115 o'clock
5	21.7		
10	21.2	414	
15	21.0		
20	21.1		Sample taken
AVG.	21.28	415.5	

Note: The zinc was not fully suspended in this run.

10 ml. Sample

ml. ferrocyanide = 7.0

ml. zinc = 1.0 x 1.55 ml. ferro/ml.zn. = -1.55

Equivalent ml. ferro. = 5.45

QUANTITATIVE DETERMINATION OF ZINC

Reference: "Textbook of Quantitative Inorganic Analysis" pg 548 (I. M. Kolthoff & E. B. Sandell, MacMillan Co. 1936).

1. Determination of zinc by precipitation with standard ferrocyanide solution.

"Zinc ions in neutral or acid medium react with potassium ferrocyanide to form extremely slightly soluble potassium zinc ferrocyanide:

$$2K_4Fe(CN)_6 + 3Zn^{++} \rightarrow K_2Zn_3[Fe(CN)_6]_2 + 6K^+$$

"This reaction has been used for more than sixty years for the determination of zinc. Until recently the end point was detected by means of external indicators such as uranyl nitrate, ammonium molybdate, or ferric chloride. In general the former is the best external indicator. The acidified zinc solution was titrated at 40° with ferrocyanide. In the neighborhood of the end point a drop of the solution was brought in contact with a drop of 1 per cent uranium nitrate on a spot plate and the color observed after 30 seconds. A pale red-brown color (due to the formation of uranyl ferrocyanide) indicated the end point.

"The proper use of an external indicator requires some skill, and it is therefore preferably to use an internal indicator whenever possible. As such, diphenylamine, or diphenylbenzidine, or diphenylamine sodium sulfonate can be used. We have seen (pg 470) that these substances are oxidation-reduction indicators. The oxidation potential of a ferro-ferricyanide solution is given by the equation:

$$E = E_0 \not- 0.060 \log \frac{[Fe(CN)_6^{\equiv}]}{[Fe(CN)_6^{==}]} \qquad @\ 30^\circ C.$$

" An acid solution of a mixture of ferro- and ferricyanide has an oxidation potential much lower than that required to oxidize the indicators to their intensely colored oxidation products. However, if zinc is added to the mixture, the ferrocyanide is precipitated as potassium zinc ferrocyanide. Since ferrocyanide is removed from the solution, the oxidation potential increases. After all the ferrocyanide has reacted, there is a sharp rise in the oxidation potential, and the brilliant blue color of the oxidized form of the indicator developes with the slightest excess of zinc. The mathematical formulation of the process is somewhat complicated by the fact that zinc ferricyanide is also only slightly soluble. Its solubility, however is much greater than that of the ferrocyanide, so that the formation of zinc ferricyanide does not interfere with the color change.

" It is also possible to titrate in the reverse manner. When diphenylamine is added to an acid solution of zinc containing a little ferricyanide, the blue-violet oxidation product is formed. This coloration will persist upon titration with ferrocyanide until all the zinc has been transformed into potassium zinc ferrocyanide. The first excess of ferrocyanide reduces the violet form of the indicator to the colorless form. Use is made of this fact in the determination of zinc with ferrocyanide.

2. Standard solutions

"0.05M potassium ferrocyanide - A C.P. product of $K_4Fe(CN)_6 \cdot 3H_2O$ is recrystallized from water and dried over a saturated solution of sodium bromide dihydrate to constant weight; it then consists of the trihydrate. The sample can also be dehydrated by heating at 100° to constant weight. A 0.05 molar solution is prepared and stablized by the addition of 0.2 gm. of sodium carbonate per liter. Standardize the solution against the standard zinc solution according to the procedure given below.

"0.1 M standard zinc solution. An exactly weighed amount of pure zinc is dissolved in dilute sulfuric acid and diluted to the mark with water in a volumetric flask. The solution should be approximately 0.1 M. From the amount of zinc taken, the exact concentration is calculated.

"Reagents: Potassium ferricyanide solution. 1 per cent solution of C.P. potassium ferricyanide in equilibrium water. It is kept in a dark bottle.

"Indicator: 1 per cent solution of diaphnylamine in concentrated sulfuric acid. Diphenylbenzidine and diphenylamine sodium sulfonate can be used, but a better end point is obtained with diphenylamine.

"<u>Procedure (for standardization and zinc determination in an unknown solution)</u>. To 25 ml. of zinc sulfate solution in a 250 ml. Erlenmeyer flask, add 25 to 75 ml. of water, 2 g. of ammonium sulfate, 10 to 30 ml. of 6N H_2SO_4, 2 or 3 drops of the potassium ferricyanide solution, and 2 or 3 drops of the diphenylamine indicator solution. Wait until the blue color develops, and titrate past the end point with 0.05 M potassium ferrocyanide solution until the blue color changes to a light, creamy yellowish-green. Diminish the speed of titration as the end point is approached, and do not add more than 1 to 2 ml. of ferrocyanide excess. Back titrate slowly with standard zinc solution to the appearance of the purple color. A sharp color change is produced by the addition of one drop of reagent.

"If the end point is overstepped, the excess of zinc can be back-titrated with the standard ferrocyanide solution. An indicator blank of 0.05 ml of 0.05 M ferrocyanide for the 3 drops of indicator should be added to the volume used.

Notes:

"1. Iron and other metals which form insoluble ferrocyanides must be absent.

"2. The appearance of the initial blue color is somewhat facilitated if a few ml. of ferrocyanide solution are added before the addition of the ferricyanide and indicator.

"3. In order to obtain accurate results (within 0.3 per cent) the conditions under which the titration is carried out must be rigidly controlled and should be exactly the same as in the standardization. The speed of titration near the end point and the excess of ferrocyanide added before the back-titration with zinc must be kept uniform. The inaccuracy increases with the amount of ferrocyanide added in excess."

SAMPLE DATA FOR DISSOLUTION OF GLASSY BORAX

Date	July 26, 1951
Borax	435 grams 40/60 U.S. mesh
Water	5 1/8 inch outage from 10 inch tank
Impeller	2-blade, 3.66" (L) x 2.5" (W)

Time-Min	°C	RPM	Remarks
0	20.3	846	1320 o'clock
5	20.8		
10	21.0	850	
15	21.0		
20	21.0		Sample taken
Avg.	20.82	848	

10 ml. of sample = 11.5 ml. 0.1019 N HCl.

ANALYSIS OF BORAX

Reference: (a) "Analytical Chemistry", Treadwell-Hall
Vol. II, 1st ed., pg 471.
(b) "Textbook of Quantitative Inorganic Analysis"
pg 548, I. M. Kolthoff & E. B. Sandell Mac Millan
Co. 1936.

Sodium tetraborate ($Na_2B_4O_7 \cdot 10\ H_2O$ = borax) --- Ref. (b)

Borax in solution can be considered as boric acid which is 50 per cent neutralized:

$$Na_2B_4O_7 + 5\ H_2O \longrightarrow 2\ NaH_2BO_3 + 2\ H_3BO_3$$

The NaH_2BO_3 can be titrated with standard acid (methyl red, bromcresol green, methyl yellow, methyl orange or bromphenol blue as indicators);

$$NaH_2BO_3 + HCl \longrightarrow H_3BO_3 + NaCl$$

or

$$Na_2B_4O_7 + 2\ HCl + 5\ H_2O \longrightarrow 4\ H_3BO_3 + 2\ NaCl$$

Therefore this titration gives the amount of alkali bound to the boric acid.

Another portion of the solution may be titrated against a standard base in the presence of invert suger, glycerol, etc.

Procedure

Weigh out 3 to 5 grams of sample, transfer to 250 ml. volumetric flask and make up to mark.

Titration of the alkali

Pipette 25 ml. of the well-mixed solution into a flask, add three drops of methyl red (or M. O.), and titrate with 0.1 N standard acid until the color changes to orange-red (for the methyl red).

Comparison of Three Batches of Nominally 40/60 Mesh Glassy Borax

U.S. Mesh Cut	Batch No. 1		Batch No. 2		Batch No. 3	
	Wt Per Cent	$\frac{W(D_r)}{W_r(D_p)}$	Wt Per Cent	$\frac{W(D_r)}{W_r(D_p)}$	Wt Per Cent	$\frac{W(D_r)}{W_r(D_p)}$
20/40	1.2	0.007	0.0	0.0	0.1	0.0
40/50*	68.0	0.680	18.0	0.18	36.2	0.32
50/60	26.3	0.345	43.7	0.573	46.2	0.606
60/70	3.2	0.054	30.0	0.467	17.0	0.265
70/80			6.6	0.122	0.9	0.017
80/100	0.3	0.0065	1.3	0.0284	0.1	0.002
- 100	1.0	0.049	0.4	0.0194	0.1	0.215
	100.0	1.1415	100.0	1.3898	100.6	1.215

*This is chosen as reference cut.

$A = qnD_p^2$

$W = QnD_p^3$

$n = W/QD_p^3$

$A = qD^2(W/QD_p^3) = Q'(W/D_p)$

$A/A_r = (W/D_p)/(W_r/D_r) = W(D_r)/W_r(D_p)$

$A_1/A_2 = 1.1415/1.3898 = 0.822$

$A_1/A_3 = 1.1415/1.215 = 0.939$

$A_3/A_1 = 1.215/1.1415 = 1.065$

$A_3/A_2 = 1.215/1.3898 = 0.873$

BIOGRAPHY

1. Born July 8, 1920 in Philadelphia, Pennsylvania, son of Edmund B. and Grace S. (nee Faunce) White.

2. Attended Columbia University in the City of New York from October 1936 until June 1942, receiving the A.B. (6/40), the B.S. (6/41) and Ch.E. (6/42) degrees, and Lehigh University from October 1949 to August 1951.

3. Published "A Short History of Methanol" in CHEMICAL INDUSTRIES, February 1944.

4. Served as a chemical engineer with Westvaco Chlorine Products Corporation (6/42 - 4/44), C. L. Mantell, Ph.D. (11/46 - 2/47) and Diamond Alkali Company (2/47 - 8/49). Served as research assistant (9/49 - 6/50) and graduate teaching assistant (9/50 - 6/51) at Lehigh University.

5. Naval service (4/44 - 9/46) receiving electronics training as an officer.

6. Member American Institute of Chemical Engineers and American Chemical Society. Professional Chemical Engineer (Ohio licence serial 15933).

ProQuest LLC
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