Rate of Solution of Solid Particles Followed by Chemical Reaction in Agitation Vessel

By

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In this paper, the authors deal with the dissolution of acid anhydride in water followed by the hydrolysis reaction.

Classification may be made of the types of reaction taking place depending upon the relative rates of diffusion and hydrolysis of the acid anhydride.

(1) Diffusion resistance is controlling and the overall rate of reaction depends only on the rate of solution. In this case the higher the agitator speed, the larger the rate of solution.

(2) Diffusion resistance and the chemical resistance to hydrolysis are comparable in magnitude. In this case the overall rate of reaction depends not only on the agitator speed, but also on the rate of hydrolysis.

(3) Chemical resistance to hydrolysis is controlling and the overall rate of reaction is independent of the agitator speed.

The authors derived the generalized rate equation and demonstrated the three types of reaction by the hydrolysis reaction of phthalic acid anhydride and benzoic acid anhydride suspended in water under agitation.

The authors propose the idea of "the degree of transitional saturation" and "the agitation coefficient for heterogeneous reaction".

The latter is useful for the determination of the available agitation intensity for heterogeneous liquid phase reactions.

1. Theoretical Equation for Liquid-Solid Masstransfer Followed by Chemical Reaction.

Referring to the procedures developed by S. Hatta[1] for the chemical absorption of gases, the authors derived the theoretical equation for the rate of hydrolysis of acid anhydride crystals which have only a slight solubility in water.

At first, let the case be considered in which phthalic acid anhydride crystals are suspended and dissolved in water, and subsequently the hydrolysis reaction takes place between the dissolved phthalic acid anhydride and water. The hydrolysis reaction taking place is presented as follows:
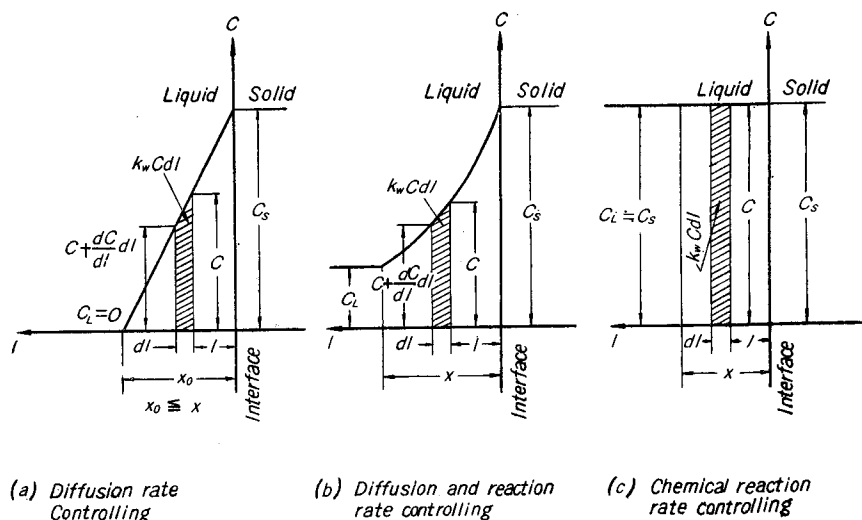
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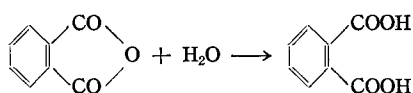
The reaction itself is homogeneous and the rate is expressed as follows:

$$r = kC_wC = k_wC \qquad\qquad (1)$$

where C_w and C are the concentration of water and phthalic acid anhydride respectively. The concentration of water (C_w) is in large excess compared with that of anhydride, so that C_w is taken as constant. Thus the product of k and C_w is expressed as k_w.

Fig. 1 is a schematic diagram which shows the concentration gradient in the

(a) Diffusion rate
    Controlling

(b) Diffusion and reaction
    rate controlling

(c) Chemical reaction
    rate controlling

Fig. 1.   Diagram showing the concentration gradient at the liquid-solid interface
          after a steaey state is attined.

neighbourhood of the liquid-solid interface. **Fig. 1 (a)** corresponds to the case where the amount of water is large and the diffusion resistance is larger than the chemical resistance. **Fig. 1 (b)** corresponds to the case where the amount of water is comparatively small and both the diffusional and chemical resistances are comparable in magnitude. **Fig. 1 (c)** corresponds to the case where the chemical resistance is larger than the diffusional resistance and the main body of water is saturated with phthalic acid anhydride and is maintained in the state of reaction rate controlling.

Taking the material balance in the volume element $(A\,dl)$ (shown by the hatched part in **Fig. 1**), the following differential equation is obtained,

$$\frac{d^2C}{dl^2} = \frac{k_w}{D_f}C \tag{2}$$

Combining with the boundary conditions, $C_{l=0}=C_s$ and $C_{l=x}=C_L$, Eq. (2) is solved to give,

$$C = \frac{1}{\sin h\alpha x}\left\{C_L \sin h\alpha l + C_s \sin h\alpha(x-l)\right\} \tag{3}$$

and

$$\frac{dC}{dl} = \frac{\alpha C_L \cos h\alpha l - \alpha C_s \cos h\alpha(x-l)}{\sin h\alpha x} \tag{4}$$

where $\alpha = (k_w/D_f)^{1/2}$ and D_f is the diffusion coefficient of the anhydride. Therefore the rate of solution of the anhydride (R) (which is equal to the acid produced in the steady state) is,

$$R = -\left(\frac{dW}{d\theta}\right)_{l=0} = -D_f A\left(\frac{dC}{dl}\right)_{l=0} = D_f A\alpha\left\{\frac{\cos h\alpha x}{\sin h\alpha x}C_s - \frac{1}{\sin h\alpha x}C_L\right\}$$

Substituting the notations;

$$\alpha x = \gamma = \sqrt{\frac{k_w}{D_f}}x = \frac{\sqrt{k_w D_f}}{K} \tag{5}$$

$$\beta = \frac{\gamma}{\tan h\gamma} \quad \text{(Hatta number)} \tag{6}$$

$$R = A\beta K\left(C_s - \frac{C_L}{\cos h\gamma}\right) \tag{7}$$

where K is the masstransfer coefficient and is equal to D_f/x. Since the amount of anhydride diffusing into the main body of the water balances with the amount of consumption by the hydrolysis reaction, noting $C=C_L$ at $l \geq x$,

$$-D_f A\left(\frac{dC}{dl}\right)_{l=x} = k_w C_L V \tag{8}$$

Putting $V/A=v$ and substituting the relation;

$$\left(\frac{dC}{dl}\right)_{l=x} = \left(\frac{\alpha C_L \cos h\alpha x}{\sin h\alpha x} - \frac{\alpha C_s}{\sin h\alpha x}\right)$$

in Eq. (8), the following relation is obtained.

$$\frac{C_L}{C_s} = \frac{1}{\cos h\gamma + \alpha v \sin h\gamma} = \emptyset \tag{9}$$

Now the ratio (C_L/C_s) is denoted as $\emptyset$, and the authors have called "the degree of transitional saturation". When the value $\emptyset$ tends to unity, it is useless to increase the degree of agitation any further [refer to **Fig. 1(c)**].

By substituting Eqs. (9) and (6) into Eq. (7) and simplifying, the following relationship is derived,

$$R = \sqrt{k_w D_f}\, A C_s \left\{ 1 + \frac{2}{\left(\dfrac{\alpha v + 1}{\alpha v - 1}\right) e^{2\gamma} - 1} \right\} \tag{10}$$

In Eq. (10), the only value that may be affected by a change in the agitation intensity is γ ($=\alpha x$). Now let the term in the parenthesis be denoted as Ψ.

$$\Psi = \left\{ 1 + \frac{2}{\left(\dfrac{\alpha v + 1}{\alpha v - 1}\right) e^{2\gamma} - 1} \right\} \tag{11}$$

Ψ is a measure which represents the effect of agitation intensity on the overall rate of reaction and the authors have called Ψ "the agitation coefficient for heterogeneous reaction". The authors made numerical calculations for Eq. (11) taking the value αv $[=(k_w/D_f)^{1/2}\, V/A]$ as its parameter and obtained the results shown in **Fig. 2** which shows the relationship between Ψ and $1/\gamma$.

Now let the several cases be considered which are specified by the relative magnitude of $(k_w/D_f)^{1/2}$, V/A and γ.

Case I: $\alpha v \to \infty$

Taking the limitation of $1/\gamma \geq 5$ as an additional condition, the following relation is obtained as is evident from curve (1) in **Fig. 2.**

$$\Psi = 1/\gamma = K/(k_w D_f)^{1/2} \tag{12}$$

Substituting this into Eq. (10), the following rate equation is obtained which shows the type of diffusion controlling reaction.

$$R = KAC_s \tag{13}$$

This corresponds to the case where the rate of chemical reaction is very large (*i.e.*, $k_w \gg D_f$) or that the volume of liquid is very large ($V \gg A$), and is the case of diffusion resistance controlling.

Case II: $1/\gamma \to \infty$ ($\gamma = \alpha x \to 0$)

This is realized under conditions of a very small value of x, *i.e.*, by violent agitation.

Taking the limiting value of Ψ when γ tends to zero, Eq. (11) reduces to,

$$\Psi = \alpha v = \left(\frac{k_w}{D_f}\right)^{1/2} \frac{V}{A} \tag{14}$$

Substituting this relation into Eq. (10), the following equation is derived regardless of the value of αv.

$$R = k_w C_s V \tag{15}$$

The fact that Eq. (10) reduces to Eq. (15) shows that in the case of high agitator speed the value of x tends to zero and the rate of solution of the solid particles

becomes so large that the overall rate of reaction is controlled only by the rate of chemical reaction. The limiting values of Ψ at which the rate of chemical reaction becomes controlling are estimated from **Fig. 2** referring to the various values of av.

Case III: $av = 1 \ [(k_w/D_f)^{1/2} = A/V]$

Substituting the relation into Eq. (11), the value of Ψ is equal to unity regardless of the value of γ and Eq. (10) reduces to,

$$R = (k_w D_f)^{1/2} A C_s = k_w C_s V \tag{16}$$

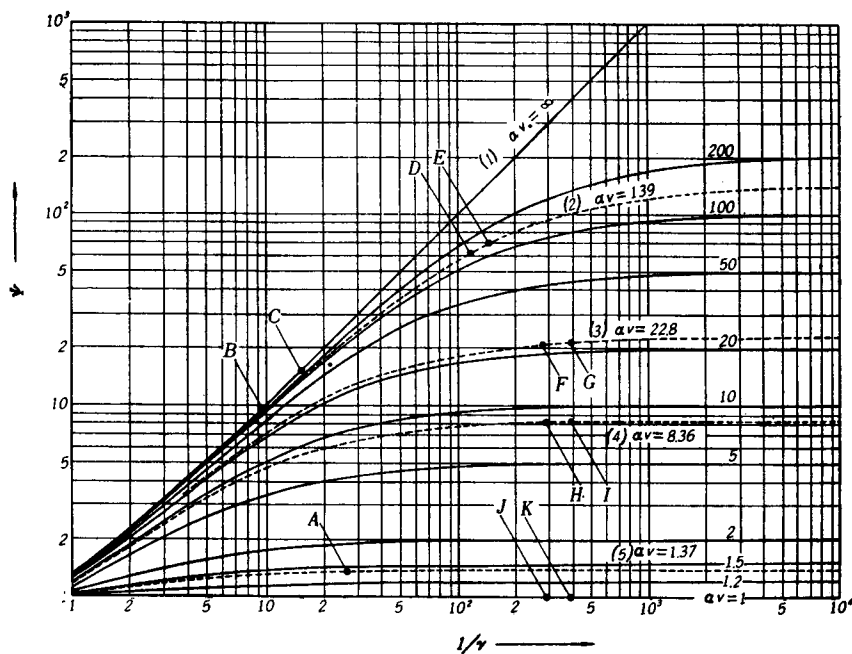This is an extreme case; so long as solid particles are kept in suspension in the

Fig. 2. Diagram showing the relation between ψ and $1/\gamma$, values obtained by numerical calculations taking values of av as the parameter.

liquid, the reaction velocity becomes rate controlling no matter what the agitation intensity may be. It is because of the fact that the interfacial area between solid and liquid is so large compared with the liquid volume that the main body of liquid is saturated with the reactant. This limiting case may also be realized when the value of k_w is so small compared with that of D_f that the rate of chemical reaction becomes rate controlling. For example, in the case of hydrolysis of phthalic acid anhydride, $k_w = 0.598$ [1/min] and $D_f = 7.75 \times 10^{-6}$ [cm²/sec], therefore

$$(k_w/D_f)^{1/2} = \left(\frac{0.598}{60}/7.75 \times 10^{-6}\right)^{1/2} = 35.8 = \frac{A}{V} \, [\text{cm}^2/\text{cm}^3]$$

Hence, to realize this case $(av=1)$, an extremely large amount of solid particles must be suspended in the water in this case.

Case IV : Case other than I, II and III.

This is the case where the diffusion and reaction resistances are comparable in magnitude, *i. e.*, diffusion and reaction rates are controlling, which is the case most unique to heterogeneous reactions.

2. Experimental Results and Comparison with the Theory.
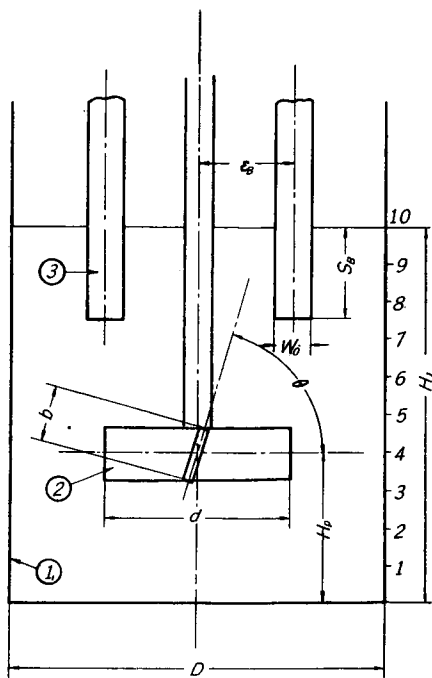
(a) Experimental Apparatus and Procedure.

As the agitation vessel, the authors used a cylindrical glass vessel with a flat bottom. Symbols representing the dimensions for each part of the agitation equipment are shown in **Fig. 3.**

The liquid depth is always chosen equal to the vessel diameter, *i. e.*, $D=H_l$ $=10$ cm. The liquid volume is 785 cc. The impeller used is a four-blade paddle type whose diameter $d=5$ cm, width of the blades $b=1.5$ cm, blade angle $\theta=75°$. The elevation of the impeller $H_p=4$ cm.

For the hydrolysis of phthalic acid anhydride the apparatus without baffle was used, and the hydrolysis of benzoic acid anhydride was performed with the same apparatus with baffle plates, whose conditions are as follows :

① Vessel, ② Impeller, ③ Baffle plates.

Fig. 3. Diagram showing the agitation equipment and the baffled conditions.

Two baffle plates whose width w_0 is 1 cm each, are inserted symmetrically half way between the agitator shaft and the vessel wall, *i. e.*, $\mathcal{E}_B=2.5$ cm. The submersion depth $S_B=2.5$ cm. These baffle plates are useful for dispersing the solid particles into the main body of the liquid which would otherwise float on the liquid surface, being hard to disperse into the main body of liquid. Both the impeller and baffle plates are made of stainless steel (SUS–12).

An electrode made of two platinum plates (1×1 cm wide, 1.5 mm distance) is

placed in the agitated liquid in order to measure directly the electric conductivity of the agitated liquid and thus to trace the change in concentration with time elapsed. The temperature of the liquid is kept constant within $\pm 0.1°C$ by means of a thermostat.

In this report "equivalent particle diameter, calculated from the sphere of equivalent weight, d_p" was used as the mean diameter of the solid particles. This mean diameter was adopted by R. H. Wilhelm, *et al*[2], and is defined by the following relation.

$$d_p = \sqrt{\frac{6}{\pi}\left(\frac{W}{n\,\rho_s}\right)} \tag{17}$$

NO	Symbol	Solid used (g)	Solid sieved range (mesh)	Over-all reaction rate (g-moles/l·min)
(1)	○	5.000	100 under	7.30×10^{-4}
(2)	▲	"	"	7.10 "
(3)	□	0.500	28 ~ 60	2.35 "
(4)	×	"	28 ~ 45	1.45 "
(5)	●	"	"	0.98 "

(4) Equilibrium, $C'_{eq} = 7.70 \times 10^{-4}$ (g-moles/l)

(5) $C'_{eq} = 4.90 \times 10^{-4}$ (g-moles/l)

Separated $C_0 = 5.22 \times 10^{-4}$ (g-moles/l)

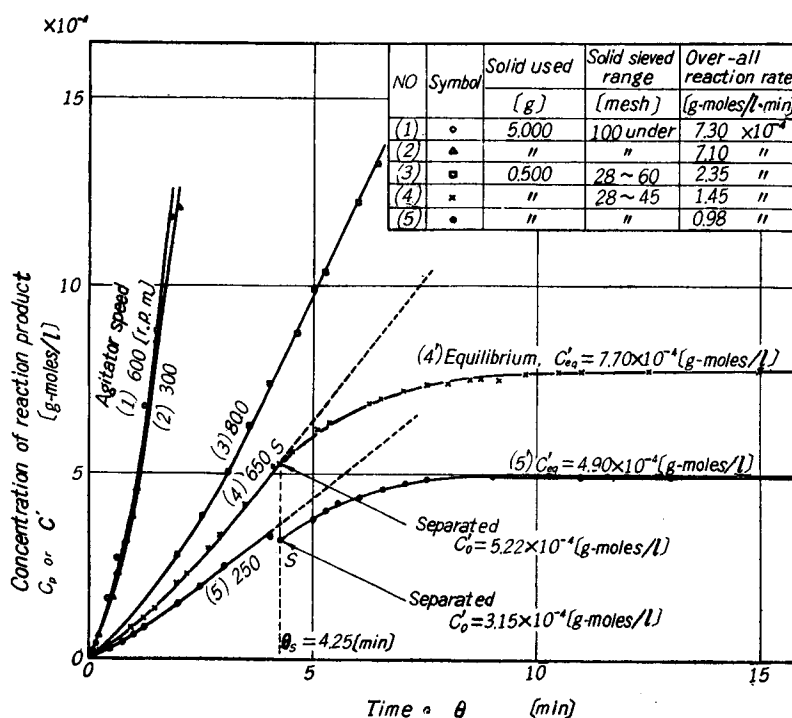Separated $C'_0 = 3.15 \times 10^{-4}$ (g-moles/l)

$\theta_s = 4.25$ (min)

Fig. 4. Reaction rate curves showing the hydrolysis rate of phthalic acid anhydride-water agitation system.

(b) Method to Determine the Overall Rate of Reaction.

The dissolution of phthalic acid anhydride or benzoic acid anhydride in water takes place at the surface of the suspended solids. The hydrolysis reaction takes place in the homogeneous phase. When a steady state is reached in the liquid-solid system under agitation, a pseudo zero order reaction mechanism appears and this mechanism continues as long as the change in the surface area of the solid particles

is negligible as shown by **Fig. 4.** This phenomena may easily be explained by referring to **Fig. 1.**

In the case where the diffusion resistance is controlling, the overall rate of reaction (R) is equal to KAC_s, so that the value R is kept constant as long as the change in A is insignificant. That is the case for both phthalic and benzoic acid anhydride because of their slight solubility [refer to **Fig. 1 (a)**].

In the case where the reaction resistance is controlling, R is equal to $k_w V C_s$, and R is also kept constant [refer to **Fig. 1 (c)**]. In the case where both the resistances are comparable in magnitude, R is equal to the product of k_w, V and C_L, and the liquid-bulk concentration (C_L) remains constant in the steady state, so that the overall rate (R) is also kept constant for a considerable duration of time.

$$R = -D_f A\left(\frac{dC}{dl}\right)_{l=0} = k_w V C_L$$

As shown by the curves (3), (4) and (5) the concentration (C_p) of the phthalic acid produced in the liquid-bulk is proportional to the time of reaction after a few minutes. The overall rate of solution (R/V) is shown in the appended table of **Fig. 4.**

(c) Concentration of Acid Anhydride in the Liquid Bulk.

A certain amount of liquid is withdrawn and filtered through a glass filter. The concentration change of the separated liquid is traced by means of electric conductivity measurements. Curve (4′) in **Fig. 4** is an example. In this case, 0.500 g of phthalic acid anhydride (28–45 mesh) was added to water which had been agitated to a steady state at the agitator speed of $N=650$ r.p.m. After 4.25 min (θ_s), about 15 cc of sample was withdrawn.

As the equilibrium concentration of this sample C'_{eq} is 7.70×10^{-7} [g-moles phthalic acid/l], the difference between C'_{eq} and the concentration C_0' at the instant of separation [refer to point S in **Fig. 4**) is equal to that of phthalic acid anhydride (C_L) at time θ_s.

$$C_L = C'_{eq} - C_0' \tag{18}$$

(d) Reaction Rate Constant of Hydrolysis.

The concentration of phthalic acid anhydride (C) at any time (θ) can be evaluated in a similar way for Eq. (18) as $C = C'_{eq} - C'$. The hydrolysis reaction takes place in dilute solution, therefore the relationship between C and θ is expressed as follows :

$$-\frac{dC}{d\theta} = k_w C$$

or

$$-2.303 \log C = k_w \theta + I \tag{19}$$

Plotting the values of $\log C$ against θ as shown in **Fig. 5** and measuring the slope of the curves, the values of k_w are determined as 0.620 [1/min] for $N=250$ r.p.m. and 0.575 [1/min] for $N=650$ r.p.m. Hence the average value k_w is determined to be 0.598 [1/min].

Referring to the International Critical Tables[3], the hydrolysis reaction rate constant of phthalic acid anhydride at 25°C is given:
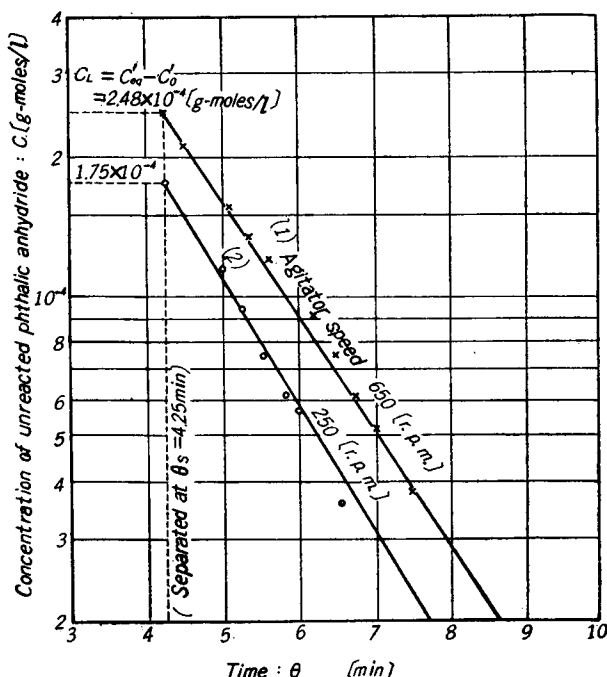
$$k_w = 0.607 \text{ [1/min]} \tag{20}$$

Fig. 5. Diagram used for determining the hydrolysis reaction rate constant of phthalic acid anhydride.

(e) Measurement of the Saturation Concentration of Acid Anhydride.

The solubility of the acid anhydride in water (C_s) may be measured by the procedures mentioned above with a large excess of the anhydride. However it is more reasonable to estimate the value of C_s indirectly by Eq. (15) or (16), substituting the observed value of the overall rate of reaction (R/V) under the conditions where the chemical reaction rate is controlling.

$$C_s = R/k_w V \tag{21}$$

The curves (1) and (2) in **Fig. 4** show the results of experiment in which 5.00 g of fine powders (under 100 mesh) of phthalic acid anhydride are used. These two

curves nearly overlap each other in spite of the great difference in agitator speed because the chemical reaction rate is controlling. The value of R/V is 7.30×10^{-4} [g-moles/l·min] at the agitator speed of 600 r.p.m. In order to check these results, the values of αv and $1/\gamma$ are examined.

The surface area of the particles is taken as that of the spheres of the equivalent diameter of particles, d_p. Assuming $d_p = 0.01$ mm,

$$A = \pi d_p^2 \left(W / \frac{\pi}{6} \rho_s d_p^3 \right) = \frac{6W}{\rho_s d_p}$$
$$= \frac{6 \times 5.00}{1.46 \times 1 \times 10^{-3}} = 2.05 \times 10^4 \quad [\text{cm}^2] \tag{22}$$

Using this value of A, the hydrolysis rate constant as $k_w = 0.598$ [1/min] and the diffusion coefficient as $D_f = 7.75 \times 10^{-6}$ [cm²/sec], we have;

$$\alpha v = \sqrt{\frac{k_w}{D_f} \frac{V}{A}} = \sqrt{\frac{0.598}{7.75 \times 10^{-6} \times 60} \times \frac{785}{2.05 \times 10^4}} = 1.37 \tag{23}$$

The value of $1/\gamma$ was estimated from the preliminary experiment performed with the solution of boric acid crystals ($\rho_s = 1.47$ g/cm³) whose particle size was $d_p = 0.23$ mm (60–100 mesh) and whose shape and density were close to the sample of phthalic acid anhydrid ($\rho_s = 1.46$ g/cm³). Hence,

$$x = \frac{D_{fB}}{K} = D_{fB} / \left(\frac{R/V}{C_s A_B/V} \right) = 1.12 \times 10^{-5} / \left(\frac{16.3/1000 \times 60}{57.5 \times 10^{-3} \times 355/785} \right)$$
$$= 1.07 \times 10^{-3} \quad [\text{cm}] \tag{24*}$$

$$1/\gamma = 1 / \left(\sqrt{\frac{k_w}{D_f}} x \right) = 1 / \left(\sqrt{\frac{0.598}{7.75 \times 10^{-6} \times 60}} \times 1.07 \times 10^{-3} \right) = 26.1 \tag{25}$$

In **Fig. 2,** these values are represented by the point **A.** From the dotted curve (5) the limiting value of Ψ is obtained when $1/\gamma$ tends to infinity with the same value of αv.

From this diagram it is apparent that the over-all rate nearly corresponds to that of the chemical reaction, though not entirely. Substituting the above data in Eq. (21), the value of C_s is given as follows:

$$C_s = 7.30 \times 10^{-4} / 0.598 = 1.22 \times 10^{-3} \quad [\text{g-moles}/l] \tag{26}$$

In order to realize the condition of $\alpha v = 1$, 6.85 g of phthalic acid anhydride should be used for every 785 cc of water.

(f) Degree of Transitional Saturation.

The value of Φ is calculated by measuring the value of C_L and substituting it

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* Since it was difficult to observe the rate of solution of boric acid as fine as 0.01 mm in d_p, the value of K for $d_p = 0.23$ mm was adopted.

into Eq. (9) as mentioned above. However $\varnothing$ is also related to the over-all rate of reaction by the equation

$$R = k_w C_L V = k_w C_s \varnothing V \tag{27}$$

Hence the value of $\varnothing$ is also estimated indirectly from the observed value of the over-all rate (R/V) as follows:

$$\varnothing = (R/V)/k_w C_s \tag{28}$$

In the reaction conditions which result in the curve (4) in **Fig. 4,** the reaction rate (R/V) is 1.45×10^{-4} [g-moles/l·min]. Substituting this value in Eq. (28), we have,

$$\varnothing = 1.45 \times 10^{-4}/(0.598 \times 1 \times 1.22 \times 10^{-3}) = 0.203 \tag{29}$$

On the other hand from the observed value of C_L obtained by direct measurement, we have,

$$\varnothing = \frac{C_L}{C_s} = \frac{7.70 \times 10^{-4} - 5.22 \times 10^{-4}}{1.22 \times 10^{-3}} = 0.202 \tag{30}$$

These results are in good agreement.

In addition, from the experimental result shown by the curve (5) ($N=250$ r.p.m.) in **Fig. 4,** the values of $\varnothing$ are estimated to be 0.134 and 0.143 respectively according to Eqs. (28) and (30).

(g) Effect of Agitation upon the Over-all Reaction Rate.
(1) Demonstration of Case I (diffusional resistance controlling)

The over-all reaction rate for the hydrolysis of phthalic acid anhydride is measured from the slope of the pseudo zero order reaction rate curves in **Fig. 4** after the stationary state is attained. **Fig. 6** is a diagram showing the relation between the observed reaction rate and the agitator speed. In this diagram, curves (1) and (2) show the results obtained by using small amounts of phthalic acid anhydride crystals whose sizes are 10–16 mesh and 16–28 mesh respectively.

As for the particles whose size is 16–28 mesh ($d_p = 0.928$ mm),

$$A = \frac{6W}{d_p \rho_s} = \frac{6 \times 0.300}{9.28 \times 10^{-2} \times 1.46} = 13.3 \ [\text{cm}^2] \tag{31}$$

$$\alpha v = \sqrt{\frac{k_w}{D_f}} \frac{V}{A} = \sqrt{\frac{0.598}{7.75 \times 10^{-6} \times 60}} \frac{785}{13.3} = 2110 \tag{32}$$

The value of $1/\gamma$ is estimated from the data on the solution of boric acid crystals whose d_p is 0.858 mm. For the agitator speed $N=250$ r.p.m., similar calculations as Eqs. (24) and (25) are made.
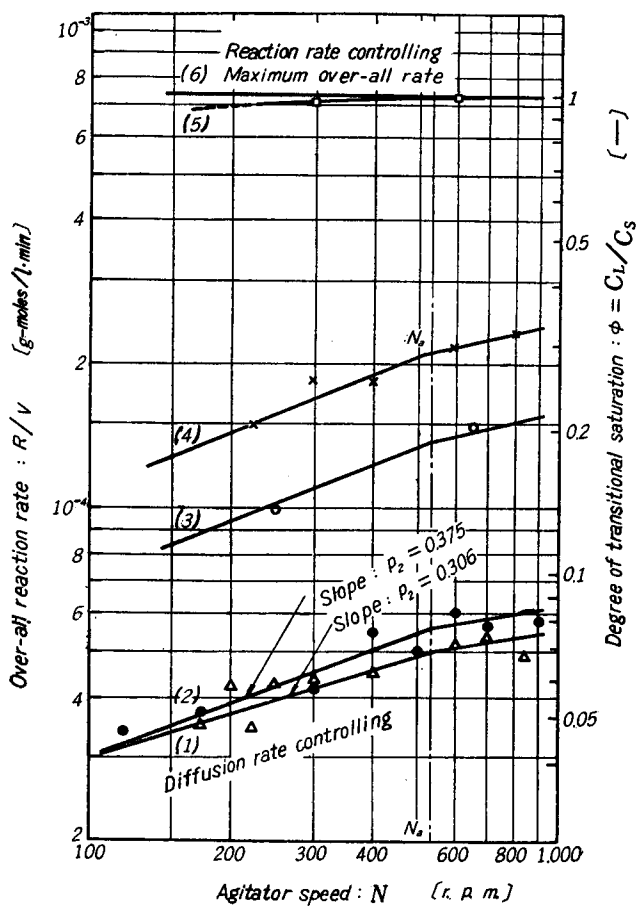
No.	Symbol	Phthalic anhydride crystal			Tempera-ture
		Used	Sieved range	Particle Size(d_p)	
		(g)	$(mesh)$	(mm)	$(°C)$
(1)	△	0.500	16 ~ 10	1.59	26.5
(2)	●	0.300	16 ~ 28	0.928	26.5
(3)	○	0.500	28 ~ 45	—	25.0
(4)	×	0.500	28 ~ 60	—	26.5
(5)	▫	5.000	100 under	0.01	25.0

Fig. 6. Diagram showing the effect of agitation upon the over-all reaction rate of hydrolysis and the degree of transitional saturation (ϕ) in phthalic acid anhydride-water system.

$$x = \frac{D_{fB}}{K} = D_{fB}/\left(\frac{R/V}{C_s A_B/V}\right)$$

$$= 1.12\times10^{-5}/\left(\frac{1.60/1000\times60}{57.5\times10^{-3}\times95.1/785}\right)$$

$$= 2.91\times10^{-3} \;\;[\mathrm{cm}] \tag{33}$$

$$1/\gamma = 1/\left(\sqrt{\frac{k_w}{D_f}}\,x\right) = 1/\left(\sqrt{\frac{0.598}{7.75\times10^{-6}\times60}}\times2.91\times10^{-3}\right)$$

$$= 9.61 \tag{34}$$

For $N=600$ r.p.m.,

$$x = 1.12\times10^{-5}/\left(\frac{2.50/1000\times60}{5.75\times10^{-3}\times95.1/786}\right) = 1.86\times10^{-3} \;\;[\mathrm{cm}] \tag{35}$$

$$1/\gamma = 1/\left(\sqrt{\frac{0.598}{7.75\times10^{-6}\times60}}\times1.86\times10^{-3}\right) = 15.0 \tag{36}$$

These values correspond to the points **B** and **C** respectively in **Fig. 2.** This result shows that the reaction is perfectly in the range of diffusion rate controlling, *i. e.*, in Case I.

The authors made the experiments on the rate of solution of various kinds of crystals in water whose density, particle size and shape are extensively different. Those factors may be correlated by the following relation [Eq. (37)][4].

$$\frac{KD}{D_f} = \frac{D}{x} = \alpha\left(\frac{D^2 n \rho_l}{\mu}\right)^p\left(\frac{\mu}{\rho_l D_f}\right)^q f_1\left(\frac{D^3 g}{\nu^2}\right)f_2\left(\frac{d_p}{D}\right)f_3\left(\frac{\rho_s-\rho_l}{\rho_l}\right)f_4(\varPhi_0) \tag{37}$$

Since the functional relation is so complicated, the authors were forced to give up the determination of all the coefficients and exponents of Eq. (37) and confined themselves to correlating the exponent p with various factors for the time being.

The exponent p in Eq. (37) represents the rate of increase in the masstransfer rate (K) or the rate of decrease in thickness of the effective diffusional film (x) with increase in agitator speed and is an important criterion for the design of agitation equipment.

The generalized correlation of exponent p is presented as follows:

$$p_1 = 0.36\left(\frac{\rho_s-\rho_l}{\rho_l}\right)^{0.22}\left(\frac{d_p}{D}\right)^{-0.23} \tag{38}$$

$$p_2 = 0.48\left[\log\left\{\left(\frac{\rho_s-\rho_l}{\rho_l}\right)+0.043\right\}+1.35\right]\cdot10^{-13.5(d_p/D)} \tag{39}$$

where p_1 and p_2 are the values of p in the range of agitator speed less than and greater than N_f respectively. N_f is the critical agitator speed at which fluidization of all particles takes place. As shown by these equations both the exponents p_1 and p_2 increase with an increase in the difference in densities between liquid and solid and with the decrease in particle size, d_p. The effect of particle shape is not significant.

The details of the derivation of those equations will be reported in the near future.

In the case of phthalic acid anhydride of 16–28 mesh in size, the data of $(\rho_s - \rho_l)/\rho_l = 0.46$ and $d_p/D = 9.28 \times 10^{-3}$ are substituted in Eq. (39) on the assumption that the diffusion rate is controlling, the value of p_2 is calculated to be 0.375. Similarly, in the case of 10–16 mesh, $(\rho_s - \rho_l)/\rho_l = 0.46$, $d_p/D = 1.59 \times 10^{-2}$ and $p_2 = 0.306$. Curves (1) and (2) in **Fig. 6** are drawn with the slope $p_2 = 0.306$ and 0.375 respectively. Both of them agree fairly well with the observed data. Thus the assumption that the diffusion rate is controlling is justified.

(2) Demostration of Case IV (diffusional and chemical resistances are comparable in magnitude)

Curve (1) in **Fig. 7** shows the relation between the overall rate of reaction (R/V) and the agitator speed (N) under the following conditions: benzoic acid anhydride used: 0.500 g, particle size: 28–35 mesh $(d_p = 0.590 \text{ mm})$. At the agitator speed of $N = 300$ r.p.m., the over-all rate is 1.28×10^{-6} [g-moles/$l \cdot$min] and is represented by the point D in **Fig. 7**. Since,

$$A = \frac{6W}{\rho_s d_p} = \frac{6 \times 0.500}{1.20 \times 0.0590} = 42.3 \quad [\text{cm}^2] \tag{40}$$

$$\alpha v = \sqrt{\frac{k_w}{D_f}} \frac{V}{A} = \sqrt{\frac{0.0197/60}{5.87 \times 10^{-6}}} \times \frac{785}{42.3} = 139 \tag{41}$$

The value of $1/\gamma$ was estimated by the data from the solution of crotonic acid crystals $(\rho_s = 1.16 \text{ g/cm}^3)$ whose particle size was $d_p = 0.590$ mm and whose shape and density were close to those of the sample of benzoic acid anhydride $(\rho_s = 1.20 \text{ g/cm}^3)$. Namely,

$$x = \frac{D_{fc}}{K} = D_{fc}/\left(\frac{R/V}{C_s A_c/V}\right) = 9.71 \times 10^{-6}/\left(\frac{2.47/1000 \times 60}{94.0 \times 10^{-3} \times 43.8/785}\right)$$
$$= 1.47 \times 10^{-3} \quad [\text{cm}] \tag{42}$$

$$1/\gamma = 1/\sqrt{\frac{k_w}{D_f}} x = 1/\left(\sqrt{\frac{0.0197/60}{5.87 \times 10^{-6}}} \times 1.47 \times 10^{-3}\right) = 115 \tag{43}$$

These values correspond to the point D in **Fig. 2**. The limit of the dotted curve (2) indicates the limiting value of Ψ when $1/\gamma$ tends to infinity under the same value of αv. When the agitator speed increases to 800 r.p.m., the rate (R/V) becomes 1.53×10^{-6} [g-moles/$l \cdot$min] which corresponds to the point E in **Fig. 7**. The estimated value of $\alpha v = 139$ and $1/\gamma = 143$ (in a similar way for $N = 300$ r.p.m.). These values correspond to the point E in **Fig. 2**. On **Fig. 2**, these two points D and E are still in the range where the diffusion and the reaction rates are both controlling, because the values of Ψ in D and E are much less than the limiting value of $\Psi_{\max} = 139$. The slope of the curve (1) in **Fig. 7** is nearly equal to 0.23 and is smaller than the estimated value of 0.297 calculated by Eq. (39). Thus the overall

rate of reaction increases in accordance with the increase in agitator speed, but not so much as would be expected from the standpoint that diffusion is rate controlling.

As shown by the dotted line (2) in **Fig. 2,** the maximum value of Ψ is equal to 139 and this corresponds to the maximum rate in the state where the reaction rate is controlling. Eq. (10) is written in this case;

$$R_{\max} = \sqrt{k_w D_f}\, A C_s \Psi_{\max} \left[= \sqrt{k_w D_f}\, A C_s\ (139)\right] \tag{44}$$

Fig. 7. Diagram showing the effect of agitation upon the over-all hydrolysis reaction rate and the degree of transitional saturation (Φ) in benzoic acid anhydride-water system.
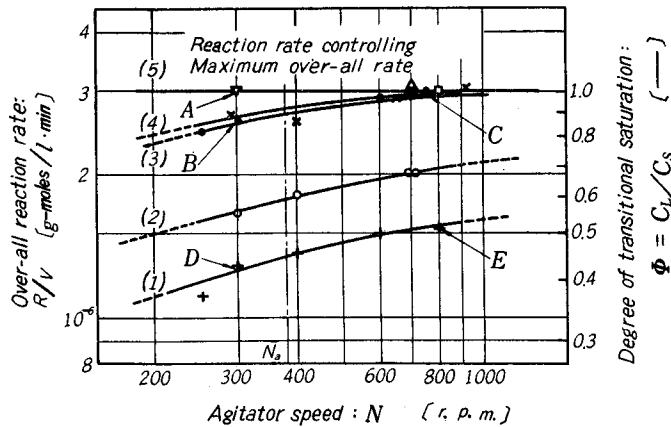
No.	Symbol	Benzoic acid anhydride crystal		
		Used	Sieved range	Particle Size(d_p)
		(g)	(mesh)	(mm)
1	+	0.500	28 ~ 35	0.590
2	o	0.500·	35 ~ 45	0.390
3	×	1,500	28 ~ 45	0.568
4	o	2,000	35 ~ 45	0.390
5	△	2,500	28 ~ 60	0.480
	□	3,000	"	"
	▽	4,000	45 ~ 60	0.285·

Temperature of experiment; 25.0 ℃

In this case, the degree of transitional saturation Φ is equal to unity. The value of Ψ at point **D** in **Fig. 2** is taken to be 60.2.

$$R_D = \sqrt{k_w D_f}\, A C_s \Psi_D \left[= k_w D_f A C_s (60.2)\right] \tag{44'}$$

Therefore the ratio $R_D/R_{\max}$ is given as follows;

$$\frac{R_D}{R_{\max}} = \frac{\Psi_D}{\Psi_{\max}} = \frac{60.2}{139} = 0.432 \tag{45}$$

On the other hand, referring to Eq. (27) R_D and $R_{\max}$ are expressed as follows:

$$R_D = k_w C_L V = k_w C_s V \emptyset \qquad (46)$$

$$R_{\max} = k_w C_s V \qquad (46')$$

Thus, the ratio $R_D/R_{\max}$ is equal to $\emptyset$. Combining this result with Eq. (45') we have;

$$\frac{R_D}{R_{\max}} = \frac{\Psi_D}{\Psi_{\max}} = \frac{C_L}{C_s} = \emptyset \qquad (47)$$

Therefore the ratio $\Psi_D/\Psi_{\max}$ must agree with the value $\emptyset$. Referring to **Fig. 7,** the observed value of $\emptyset$ (see the right hand side ordinate) gives the value of $\emptyset_D = 0.415$ which agrees well with the value of 0.432 [Eq. (45)]. Similarly, the value of Ψ_E is 69.0 from the ordinate scale of **Fig. 2** and the ratio $\Psi_E/\Psi_{\max} = 69.0/139 = 0.497$ which agrees well with the value of $\emptyset_E = 0.505$ in **Fig. 7.**

Hence it is proved that the value of Ψ is proportional to the overall rate of reaction (R/V) and is a measure of the over-all reaction velocity that is attainable by means of agitation.

On this point of view, the authors propose to call the term Ψ "the agitation coefficient for heterogeneous reaction".

As another example, let the following case be considered:

Acid anhydride used: 2.00 g, particle size: 35–45 mesh $(d_p = 0.390$ mm). In this case for the agitator speed of 300 r.p.m., the over-all rate of reaction (R/V) is observed to be 2.57×10^{-6} [g-moles/$l \cdot$min] which is shown by the point B in **Fig. 7** and the estimated value of αv is 22.8 and $1/\gamma$ is 291**. These values correspond to the point F in **Fig. 2.** From curve (3) the limiting value of Ψ can be obtained when $1/\gamma$ tends to infinity under the same value of αv. When the agitator speed is increased to 750 r.p.m. (R/V) becomes 2.95×10^{-6} [g-moles/$l \cdot$min] which is shown by the point C in **Fig. 7** and αv is calculated to be 22.8 and $1/\gamma = 396$**. These values correspond to the point G in **Fig. 2** which is close to the limiting value of curve (3).

From these results it may be seen that under conditions close to those where the reaction rate is the rate controlling step, the ability of agitation to promote the over-all rate of reaction is greatly decreased.

Thus it was found that there is a critical agitator speed at which the over-all rate of reaction reaches a maximum value, *i. e.*, the reaction rate controlling step is realized and any further increase in agitator speed is useless.

(3) Demonstration of Case II and III (chemical reaction rate controlling).

Curve (5) in **Fig. 6** shows the change in the observed values of over-all rate with change in agitator speed by using a much larger quantity of powdered phthalic

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** The value of $1/\gamma$ was estimated from the data on the solution of phenyl acetic acid crystals $(\rho_s = 1.21; d_p = 0.762$ mm).

acid anhydride (5.000 g) whose particle size is less than 100 mesh. The rate of reaction is held nearly constant in spite of the great difference in agitator speed. This condition would be realized in the range corresponding to case II where Eq. (15) is applicable as mentioned above. However under the conditions of the experiment mentioned above, the values of αv and $1/\gamma$ give the point **A** in **Fig. 2** which does not yet reach the range where the reaction rate is controlling.

Since even larger quantities of acid anhydride must be used to realize a reaction rate controlling step with phthalic acid anhydride, the authors used benzoic acid anhydride whose hydrolysis rate is smaller than that of phthalic acid anhydride. Point **A** in **Fig. 7** shows the résult obtained under the following conditions :
benzoic acid anhydride used : 4.00 g, particle size : 45–60 mesh, the agitator speed $N=300$ r.p.m..

In this case the estimated values of αv and $1/\gamma$ are 8.36 and 291** respectively.

These values correspond to the point **H** in **Fig. 2.** Since the value of Ψ at point **H** is nearly equal to the limiting value of curve (4), it is evident that the process is surely in the range where the chemical reaction rate is controlling. The over-all rate of reaction (R/V) under those conditions has its maximum value and is equal to 3.00×10^{-6} [g-moles/l·min].

When the agitator speed is increased to $N=800$ r.p.m. holding all other conditions the same, the value of $1/\gamma$ reaches to 407** which is expressed by the point **I** in **Fig. 2.**

To realize the case III of $\alpha v=1$ with the same sample, the surface area of the solid (A) must be increased a factor of 8.36 and 33 g of benzoic acid anhydride are required in the case of an agitator speed $N=300$ r.p.m. This case is shown by the point **J** in **Fig. 2.**

Thus by means of **Fig. 2.** or Eq. (10), the relation between the change in the over-all rate of reaction (R/V) (*i. e.*, Ψ) and the agitator speed (N) (*i. e.*, $1/\gamma$) was illustrated for all cases including that where the diffusion rate controls (case I), the diffusion and the reaction rates control (case IV) and the reaction rate controls (case II and III).

Acknowledgment

** The value of $1/\gamma$ was estimated from the data on the solution of phenyl acetic acid crystals.

Notation used

A :   total interfacial area   [cm²]

b :   width of the impeller blades   [cm]

C :   concentration of reactant in solution   [g-moles/l]

C' :   concentration of reaction product in the solution after separation
          from the solid   [g-moles/l]

C'_{eq} : concentration of reaction product in the separated solution after
          an infinite time has elapsed   [g-moles/l]

C_L :   concentration of reactant in the liquid bulk   [g-moles/l]

C_p :   concentration of reaction product in the liquid bulk   [g-moles/l]

C_s :   concentration of reactant at saturation with reactant   [g-moles/l]

C_w :   concentration of water   [g-moles/l]

d :   diameter of the impeller   [cm]

d_p :   equivalent particle diameter, calculated from the sphere of
          equivalent weight   [mm] or [cm]

D :   diameter of the agitation vessel   [cm]

D_f :   diffusion coefficient of solute   [cm²/sec]

f_1, f_2, f_3 and f_4: mathematical symbols representing "function of"   [—]

g :   acceleration due to gravity   [cm/sec²]

H_l :   liquid depth   [cm]

H_p :   elevation of the impeller   [cm]

I :   an integration constant   [—]

k :   hydrolysis reaction rate constant for 2nd order reaction   [l/g-moles·min]

$k_w=kC_w$: hydrolysis reaction rate constant multiplied by concentration
          of water C_w [1/min] or [1/sec]

K :   masstransfer coefficient   [cm/min]

l :   distance from liquid-solid interface   [cm]

n :   number of solid particles used   [—]

n :   agitator speed   [r.p.s.]

N :   agitator speed   [r.p.m.]

N_a :   agitator speed at which suction of air occurs   [r.p.m.]

N_f :   agitator speed at which fluidization of particles occurs   [r.p.m.]

p :   exponent of Reynolds number in Eq. (37)   [—]

p_1 :   exponent of R_e or N in the stagnant range   [—]

p_2 :   exponent of R_e or N in the fluidization range   [—]

q :   exponent of Schmidt number   [—]

r :   chemical reaction rate   [g-moles/l·min]

R :   over-all reaction rate   [g-moles/l·min]

$R_e = (D^2 n \rho_l / \mu)$: modified Reynolds number $[-]$

S_B : submerged length of baffle plates (refer to **Fig. 2**) $[cm]$

$v = V/A$: volume of liquid per unit interfacial area $[l/cm^2]$

V : liquid volume $[l]$

w_0 : width of baffle plates $[cm]$

W : total weight of solid particles $[g]$

x : thickness of effective diffusional film $[cm]$

x_0 : net diffusion length for reactant from interface [refer to **Fig. 1 (a)**] $[cm]$

$\alpha = k_w / D_f$ $[1/cm]$

α : a constant $[-]$

$\beta = \gamma / \tan h\gamma$: Hatta number $[-]$

$\gamma = \sqrt{k_w D_f} / K = \alpha x$ $[-]$

ε_B : distance between the baffle plate and the agitator shaft (refer to **Fig. 3**) $[cm]$

θ : angle of impeller blades $[degree]$

θ : time elapsed from interfacial contact $[sec]$ or $[min]$

θ_s : time at the instant of separation measured from interfacial contact $[sec]$ or $[min]$

μ : viscosity of agitated liquid $[c.p.]$

$\nu = \mu / \rho_l$: kinematic viscosity of liquid $[cm^2/sec]$

ρ_l : density of agitated liquid $[g/cm^3]$

ρ_s : density of solid particle $[g/cm^3]$

Φ : degree of transitional saturation for reactant $[-]$

Ψ : agitation coefficient for heterogeneous reaction $[-]$

$\Phi_0 = (36\pi \Phi_v)^{1/3} / \Phi_s$: Wadell's sphericity where Φ_s and Φ_v are surface and volume shape factors respectively[5] $[-]$

Subscript

O : initial value

B : boric acid (with A or D_f)

C : crotonic acid (with A or D_f)

P : phenyl acetic acid (with A or D_f)

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