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Archiefexemplaar

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Absorption studies in the light of the penetration theory

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Ten geleide.

Het afstudeerwerk, wat in samenwerking met S. Lynn is verricht, behelst de absorptie van SO_2 in vallende vloeistoffilms.

In de hierna volgende concept publicaties, waarin dit werk is samengevat is een scheiding gemaakt tussen de absorptiemetingen aan een relatief lange natte wand kolom, een korte natte wand kolom en de absorptie aan vloeistofilms, die langs bollen en langs een rij van onder elkaar geplaatste bollen vallen.

De absorptiesnelheden, die bij deze proeven zijn gemeten, kunnen nu behoudens enkele correcties voor bepaalde effecten geheel voorspeld worden met de penetratie theorie. Tevens is door deze metingen een beter inzicht verkregen hoe men zich de absorptie van een gas in vloeistof in een gepakte kolom moet voorstellen.

Aan het eind van deze concept publicaties vindt men een korte toelichting bij de foto's, die gemaakt zijn van het eindeffect, waarvan in deel II literatuuraanwijzing [5] sprake is.

pag. 6.

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Absorption studies in the light of the penetration theory.

I. Long wetted-wall columns.

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Summary.

The absorption of SO_2 by water and by aqueous solutions of HCl, $NaHSO_3$ and NaCl using relatively long wetted-wall columns (12 to 22 cm) with no gas phase resistance has been investigated. The results of the investigation show (1) that in the presence of small concentrations of a surface active material (here "Teepol", an alkyl sulfate wetting agent) the rate of absorption is very well predicted by the penetration theory, (2) that the primary function of the wetting agent is to prevent the formation of ripples in a falling film of the heights used and (3) that the hydrolysis reaction of the system SO_2-H_2O is very rapid relative to the contact times involved, so that absorption of SO_2 by water may be considered as physical absorption.

The data obtainable with this type of absorber may be used to calculate a rather reliable value of the product $C^* \sqrt{D}$ in the case of physical absorption. If this product is known, the absorber may be used to study reaction rates in chemical absorption.

Resumé.

On a étudié l'absorption de SO_2 pure dans l'eau et dans des solutions aqueuses de HCl, $NaHSO_3$ et NaCl avec une colonne à parvis mouillées, de 12 à 22 cm, de longueur. Lex expériences démontrent (1) qu'en présence de faibles concentrations d'un détergent ("Teepol") la vitesse

d'absorption peut-être prédite avec la theorie simple de diffusion non-stationnaire, (2) que la fonction primaire du détergent est de supprimer les ondulations à la surface du liquide, et (3) que la réaction d'hydrolyse du système SO_2-H_2O est très rapide auprès les temps de contact utilisés (entre 0,1 et 1 seconde).

Pour l'absorption physique, des expériences dans un absorbeur comme utilisé ici peuvent fournir une valeur assez sûre du produit $C^*\sqrt{D}$. Au cas où cette valeur soit connue, l'absorbeur peut être utilisé pour l'étude de vitesses de réaction chez l'absorption avec réaction chimique.

1. Introduction.

The penetration theory of absorption in the absence of gas-phase resistance, first proposed by Higbie [1] in 1935, has long been recognized as being intuitively more reasonable than the stagnant liquid film concept which is used so widely in practical design work. While many investigators [2, 3,4] have used the penetration theory to correlate their data, however, attempts to verify the theory quantitatively have not been highly succesful. Reasons for this have been the appearance of ripples on the liquid films, unknown end- and begin-effects, inexact methods of analysis and various other complications. As a result, the precision of the data has generally been low. The present investigation was undertaken in an attempt to verify the penetration theory quantitatively for a very simple flow situation.

As applied to the case of a falling liquid film the basic assumptions of the penetration theory are as follows: Gas is absorbed by an element of area on the surface of the film as if the surface element were saturated during the first instant of exposure, and as if the liquid behind the element were an infinitely deep stagnant layer during the time, t_c, in which the element moves from the top of the column to the bottom. Thus, the velocity of that part of the film through which the solute diffuses during t_c is considered to be constant, and the diffusion in the direction of flow is assumed to be negligible. These assumptions are expressed in the following familiar differential equation and its boundry conditions

$$D\frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t} \qquad \begin{array}{lll} c = c_0 & \text{for} & x > 0, t = 0 \\ c = C^* & \text{"} & x = 0, t \geq 0 \quad (1) \\ c = C_0 & \text{"} & x = \infty, t \geq 0 \end{array}$$

where D = diffusivity of the solute in the liquid, cm^2/sec,

c = concentration of diffusing solute, g/cm^3,

C^+ = concentration of solute at saturation, g/cm^3,
C_0 = initial concentration of solute in bulk of liquid, g/cm^3,
x = coordinate in the direction of diffusion, cm,
t = time, sec.

The rate of absorption, Φ_m (g/sec), of an element of area at time t is then

$$\frac{d\Phi_m}{dA} = (C^+ - C_0)\sqrt{\frac{D}{\pi t}}$$

and the average rate of absorption per unit area, Φ_m'' (g/cm^{2}sec), for the whole column can be shown to be

$$\Phi_m'' = \frac{1}{t_c}\int_0^{t_c}(C^+ - C_0)\sqrt{\frac{D}{\pi t}}\,dt$$

$$= 2(C^+ - C_0)\sqrt{\frac{D}{\pi t_c}} \qquad (2)$$

where t_c is the total contact time of an element of area.

For the case of a film formed on the outside of a cylindrical tube, the area, A, of the film surface is

$$A = 2\pi(r + \delta)h_e \qquad (3)$$

where h_e = the effective height of the column,
r = the radius of the tube,
δ = the thickness of the film.

The thickness of the film is determined by the density and viscosity of the liquid and by the flow rate. For laminar flow it is given by

$$\delta = \sqrt[3]{\frac{3\nu\Gamma_v}{g}} \qquad (4)$$

where ν = kinematic viscosity, cm^2/sec,
Γ_v = volumetric rate of flow per cm, cm^3/cm sec,
g = acceleration due to gravity, 981 cm/sec^2.

The velocity of the surface of the film is similarly determined by the nature of the liquid and the flow conditions and for laminar flow is

$$V_i = \frac{3}{2}\,\frac{\Gamma_v}{\delta} \qquad (5)$$

The flow has been found to be essentially laminar [5] for values of Re below 1200 when Re is defined as

$$Re = \frac{4\Gamma_v}{\nu}$$

The time during which an element of area on the surface of the film is in contact with the gas as it moves from the top of the column to the bottom is

$$t_e = \frac{h_e}{V_i} = \frac{2}{3}\,\frac{\delta h_e}{\Gamma_v} \qquad (6)$$

Thus, the average rate of absorption per unit area for the column becomes

$$\phi_m'' = \frac{\phi_m}{2\pi(r+\delta)h_e} = 2(c^*-c_0)\sqrt{\frac{3D\Gamma_v}{2\pi\delta h_e}}$$

$$= 2(c^*-c_0)\left(\frac{3D}{2\pi}\right)^{1/2}\left(\frac{g}{3\nu}\right)^{1/6}\cdot\Gamma_v^{1/3}\cdot h_e^{-1/2} \qquad (7)$$

Danckwerts [6] has provided a means of estimating the conditions under which the assumptions of an infinitely thick layer moving at a constant velocity are no longer approximately valid. From a graphical solution of the differential equation for diffusion in a finite film moving with a parabolic velocity profile he found that the effect of the wall and the velocity gradient did not change the rate of absorption by more than 5% so long as the value of the dimensionless group+) is less than 0.1 (the substition of eqs. (4) and (5) in this group yields $\frac{1}{4}\frac{h}{V_i}\Big/\frac{\delta^2}{2D}$ or, in other words, the ratio $\frac{\text{residence time}}{\text{diffusion time constant}}$ must be less than 0.4). For the smallest value of Γ_v used in this set experiments the corresponding value of h should thus be less than 200 cm, a condition which is met with quite a wide margin of safety in these experiments.

+) $\frac{h\,D\,\nu}{g\,\delta^4}$

2. Description of equipment.

A schematic diagram of the equipment is shown in Fig.1. Water was throttled through a valve from a pressure of two atmospheres through a rotameter and into the absorber. The purpose of having the water supplied under pressure was to prevent small changes of pressure in the absorber from affecting the liquid flow rate.

The water flowed into the absorber through a vertical tube made of stainless steel with an outer diameter of 15 mm. The surface of the tube was roughened slightly by sand blasting to facilitate wetting by water, and the tube wall was slightly rounded at the top. The water entered at the bottom of the tube and flowed out over the top and down the sides as a falling film. The liquid level in the receiver at the bottom of the film was kept constant, the height of the column being varied by moving the tube rather than by changing the liquid level.

SO_2 from a cylinder flowed first through a large rotameter and was then saturated with water before being admitted into the absorber. The incoming flow rate of the SO_2 was always greater than the rate at which the gas was being absorbed, and the excess passed out through a second, much smaller rotameter in the outlet line. The flow through the smaller rotameter was about 5% of the incoming flow. By thus maintaining a small steady stream of gas through the absorber, the accumulation of insoluble gaseous impurities at the liquid interface was prevented. The temperatures of the incoming gas stream, of the water in the saturator, and of the incoming and outgoing liquid streams, and the pressure in the absorber and before the gas rotameter were measured for each experimental point. Small adjustments of the data were then applied to obtain the rate of absorption at 20°C and a partial pressure of SO_2 of 750mm Hg. These adjustments will be discussed in more detail in another section.

Ordinary distilled water was used. Preliminary experiments indicated that the amount of air dissolved in the water as the result of the pressurization of the feed vessel had no measurable effect on the gas absorption. The SO_2 used was 99.9% pure, the impurities being H_2O and SO_3. The solutions of sodium bisulfite were made from the purest commercially available sypply of that salt. The normality of the solutions was determined by acidimetric titration. The sodium chloride solutions were made up by weight.

3. Treatment of data.

For ease of comparison, the data obtained were all adjusted to a constant value of the surface temperature of the water film and a constant value of the partial pressure of SO_2 within the absorber. The average temperature of the surface of the film was assumed to be 1.3°C above the average of the inlet and outlet temperatures. (see section 5). The rate of absorption at the average temperature of the experiment (16°, 20°, or 24°C) was then calculated by assuming the thermal coefficient of absorption to be -1.6%/°C, a value which is based on the penetration theory (see section 4,A) and which was verified by experiment. Thus, the rate of absorption observed, for example, at an average surface temperature of 20.5° was increased by 0.8% to obtain the value for 20°. The adjustments made in this manner rarely exceeded 2% and were usually less than 1%.

The partial pressure of the SO_2 in the absorption vessel was computed by subtracting the vapor pressure of water at the temperature of the water in the saturator from the absolute pressure in the vessel.

The concentration of SO_2 at the surface of the film and hence the rate of absorption of SO_2 in the liquid, was assumed to be directly proportional to the partial pressure of SO_2 in the vessel. Thus, the rate of absorption observed, for example, at a partial pressure of SO_2 of 755 mm Hg was decreased by 0.67% to obtain the rate at 750 mm Hg. These adjustments too, were usually less than 1%.

4. Results and Conclusions.

A. Agreement of the data with the penetration theory.

If, for a certain gas-liquid system, one has dependable values for all of the parameters of equation (7), one may test the penetration theory quantitatively for that system. Lacking one of the parameters, one may use the absorption data of the system as a means of determining its value by assuming the theory to hold. In the present case, a combination of these two procedures was employed.

The terms in equation (7) subject to the most uncertainty for the SO_2-water system are, of course, C^* and D. Values of the former found in the literature disagree by about 7%, those found for the latter disagree by nearly 50%. Since it was thus necessary to make an arbitrary choice of the parameters used, we chose the following procedure. Absorption data were taken with the flow rate, column height, and temperature as independent variables. A value of C^* was selected from the literature, and a value of D was then calculated from the data for one height and temperature. Since the temperature coefficients of D and C^* are fairly well known, it was then possible to check the penetration theory by the variation of the absorption with temperature and column height.

The data on the solubility and dissociation of SO_2 in water were taken entirely from the work of Johnstone and Leppla [7]. Their results are presented in terms of an ionization constant and a Henry's law constant which are given as functions of the temperature. Their values for these constants and the total solubility differ from those given by other authors. They are used here, however, because they are consistent with each other and can easily be used in calculating the effect of temperature on the rate of absorption.

In Fig.2 are shown the data for the rate of absorption of SO_2 by a solution of 0.0050 wt.% surface active material (Teepol) in water for columns of different heights. The effective height, h_e, of the column was obtained by measuring the actual height, h, and adjusting for the entry effect in the following manner: The area of the liquid surface on the top of the tube is more than πr^2 and less than $2\pi r^2$, i.e., the surface area is between that of a circle and a hemisphere. It was taken arbitrarily to be $3/2\,\pi r^2$, which can be expressed in terms of an increase in the height, Δh, of $3/4\,r$. The liquid in the receptor, being relatively stagnant, was assumed to absorb SO_2 at a negligible rate.

The solid lines in Fig.2 were calculated from equation (7). For C^+ at 20°C a value of 0.0995 g SO_2/cm^3 (data of Johnstone and Lepple [7]) was taken. It was found that a value of D at 20°C of 1.46×10^{-5} cm^2/sec fits all the experimental data. This value is in the same range as those found by other investigators. Kolthoff and Miller [8] reported 1.73×10^{-5}, Peaceman [2] found 1.55×10^{-5}, Whitney and Vivian [9], as will be mentioned later, based their calculations on a value of 1.66×10^{-5}, and Groothuis and Kramers [10] found 1.4×10^{-5} cm^2/sec.*) The above values have been interpolated, where necessary, to 20°C by assuming $D\mu/T$ to be a constant.

The scatter of the data in Fig.2 is remarkably low for absorption work. The straight portions of curves drawn through the experimental points in Fig.2 would lie within 1/2% of the respective theoretical lines. Since a deviation of the experimental points from the theoretical curves of only 2% would be significant, it is felt that the agreement of the two over a range of column heights of slightly less than a factor two provides a sufficiently rigorous test of the theory for the purposes of this paper.

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*) The authors' value also agrees very well with the semi-empirical correlation of Scheibel (Ind. Eng. Chem. 1954 46 2007) and Wilke (Chem. Eng. Prog. 1949 45 218).

~~the purposes of this paper~~.

Furthermore, as can be seen in Fig.3, equation (7) equally well predicts the change in absorption with temperature, caused by variations in C^*, D and μ.

The departure of the curves of Figs.2 and 3 from linearity at the higher flow rates is believed to be due primarily to the increasingly greater effect of the entrance conditions. This effect is relatively more important for the shorter columns, as would be expected. The deviation of the points from the theoretical line becomes important at increasingly lower flow rates as the height of the column is decreased. The minimum height of the type of column used in these experiments was thus determined by these entry effects.

B. The effect of the presence of Teepol.

Many observers studying absorption and desorption with wetted-wall columns have reported that at certain flow rates and column heights the rates of absorption measured are much higher than those predicted by the penetration theory. This effect has generally been attributed to ripples on the film surface. These ripples are always observable when the rate of absorption is abnormally high, and are not found when the rate of absorption is normal. Emmert and Pigford [3], as well as others, found that the addition of a small amount of an alkyl sulfonate ("Petrowet") eliminated the ripples and decreased the absorption. They also found, however, that as the concentration of this wetting agent was increased the rate of absorption went through a minimum, showing an optimum concentration for the elimination of ripples. Zernovskaya and Belopolskii [11] found that the presence of a minimum depended on the type of surface active material used.

The effect of the ripples on the gas absorption depends a great deal on the height of the column being used. At low flow rates the ripples appear quite close to the top of the column, and the amplitude of the ripples is relatively high. As the flow rate is increased, the ripples begin to form at points increasingly farther from the entrance, and the amplitude of the ripples decreases. A column of any height could presumably be ripple-free at sufficiently high flow rates if it were not for the onset of turbulence in the film.

The addition of a surface active material to the water lowers the point on the column at which the ripples begin to form. The effect of the wetting agent used, an alkyl sulfate marketed under the trade name of "Teepol", on the absorption is shown in Fig.4. The hump in the absorption curve of pure water is gradually ironed out as the Teepol concentration is increased. At the highest flow rates, where even the pure water does not exibit ripples, it is seen that the absorption by the water is nearly the same as that of the Teepol solutions.

C. The hydrolysis of SO_2 in aqueous solution.

According to *Roth* [12], in a saturated solution of SO_2 in water the SO_2 is present in three forms: unhydrated, hydrated and ionized. *Johnstone* and *Leppla* [7] reported that the concentration of unionized SO_2 in aqueous solution varied with the partial pressure of SO_2 in accordance with Henry's law, and gave values for the Henry's law constant which were based on their measurements of the solubility and the values of the ionization constant which they had chosen. As the result of measurements made with a packed column, Whitney and Vivian [9] suggested that the rate of the ionization reaction might be slow in relation to the contact times involved in their column. This assumption can be checked by comparing the rate of absorption in water with the rate of absorption in a solution which suppressed the ionization reaction. One should find a distinctly lower rate of absorption by an acid, for instance, if the ionization reaction were fast, and very little difference in the rates of absorption if the ionization reaction were slow.

A saturated solution of SO_2 at normal pressure and temperature is about 1.6 M in SO_2 and about 0.18 N in hydrogen ion, i.e., about 11% ionized. Because the saturated solution is so concentrated, it is necessary to use acid or bisulfite solutions of high ionic strength in order to suppress the ionization by a measureable amount. Therefore, absorption measurements were carried out with 3 N HCl, and 1 N and 0.2 N $NaHSO_3$. In addition, solutions of 1 N and 0.2 N NaCl were used in order to provide, for comparison, an idea of the effect of ionic strength alone. It is assumed that NaCl forms no complexes with SO_2. All the solutions contained 0.0050 wt.% Teepol.

The results of these tests are shown in Fig.5. The lines on the figure represent equation (7) for water and the sulfite solutions. To make the calculations, the concentration of unionized SO_2 in the sulfite solutions was assumed to be the same, when expressed in grams per thousand grams of water, as it is in pure water. The partial specific volume of SO_2 was assumed to be the same in the sulfite solutions as in water, and the term $D\mu$ was assumed to be a constant. A summation of the pertinent physical and chemical properties of the solutions, measured and calculated, is given in Table I.

(Table I)

The rate of absorption by the 1 N bisulfite solution is retarded even more than is predicted on the basis of reduced ionization and a smaller diffusion coefficient. This is not surprising, since one would expect a certain salting-out effect by the $NaHSO_3$ on the unionized SO_2, and the predicted change in the diffusivity coefficient is little more than a guess. The magnitude of these two effects may be estimated by comparison to the absorption by NaCl solutions. As is seen in Fig.5, 0.2 N NaCl absorbs at nearly as great a rate as water, while 1 N NaCl absorbs at a rate which is about 5% smaller.

The rate of absorption by 3 N HCl was found to be the same as that of water. This is surprising, since one would expect both a lower solubility of SO_2 (due to retarded ionization) and a lower diffusivity (because of a higher viscosity) in the acid. Rough solubility measurements indicated, however, that the equilibrium concentration of SO_2 in 3 N HCl is about 15% greater than that of water. It thus appears that the agreement in the rates of absorption is simply a coincidence.

The evidence given above, in favour of a fast hydrolysis reaction, is persuasive but not conclusive. The data could all be interpreted as being in accord with the concept of a slow hydrolysis reaction if it were assumed that the diffusion coefficients in the bisulfite solutions were reduced much more than the change in viscosity would indicate. Such an assumption, while drastic, can not be dismissed, a priori, as an impossibility.

Additional data, however, obtained by a completely separate method, appear to settle the question beyond doubt. An apparatus was constructed which permitted the rapid mixing of a stream of water and a stream of liquid SO_2, and the subsequent measurement of the electrical conductivity of the solution obtained. In the steady-state flow obtaining, complete mixing was produced in a time interval of 0.1 second, and the conductivity was measured for times between 0.1 and 1.0 second. Using the conductivity data of Morgan and Maass [14], it was found that even at temperatures as low as 4°C, the hydrolysis reaction was at least 90% complete within the shortest time interval which could be measured.

Whitney and Vivian made their assumption of a slow hydrolysis reaction in order to correlate their absorption data with that of other investigators. Their data can be correlated just as easily by assuming a lower value of the diffusion cefficient than they used. As is mentioned above, the variations in the values of D found in the literature are sufficiently wide to give one a great deal of freedom in making a choice of a value to use.

In the light of the data and arguments presented above, it appears that the rate of the hydrolysis reaction of SO_2 in water is fast relative to the diffusion process. Thus, one may assume that the surface of a water film is instantaneously saturated at the equilibrium concentration upon exposure to SO_2. It follows that the absorption of SO_2 in water may be treated as physical absorption.

5. Discussion of errors.

The random error, as can be seen from the plots of the experimental data, is quite small, about ± 1%. It arises from uncertainties in reading the rotameters and thermometers and in determining the heihgt of the column.

The systematic errors include both the uncertainties in the calibration of the equipment and also the uncertainties in the assumptions involved in the estimation of the surface on the top of the column, of the changes in solubility due to temperature and pressure (i.e. of the corrections made to present the data for a standard temperature and pressure), and of the surface temperature of the film.

The estimation of the equivalent height of the column involves a two-fold assumption; first an estimation of the surface of the liquid on the top of the column and second an estimation of the velocity at the surface. Both are necessary in order to estimate the time of contact of an element of surface area. However, the value of Δ h amounts to only 5-10% of h, so that a relatively large error in the estimation of h will not greatly alter the relationship of the gas absorption to height, since this varies with $h_e^{\frac{1}{2}}$.

The estimation of the actual temperature of the interface is subject to the most uncertainty of all of the assumptions involved. If the film actually behaved as a semi-infinite stagnant layer, the surface temperature would remain constant. However, the thermal diffusivity of water is of the order of a hundred times greater than the diffusivity of SO_2 in water, so that, whereas the assumption of constant velocity and infinite depth is justifiable for the diffusion of material in the films considered, it is not at all justifiable for the diffusion of thermal energy.

One can calculate the temperature rise of the surface of the film due to the absorption of SO_2 (Danckwerts [14]). If one takes the heat of solution of SO_2

in a saturated solution to be 6.7 Kcal/mol (Roth [12]) this rise is found to be about 1,6°C. For want of a better assumption the average temperature of the surface of the film was taken as the average of the inlet and outlet water temperatures plus 1,6°C.

It is estimated that the total uncertainty due to systematic errors is ± 5%, the greatest part being due to the temperature of the surface of the film.

6. Limits of applicability.

The conditions studied here were for effective column heights between 12.5 and 22.5 cm. and for Reynolds numbers between 123 and 1150. This corresponds to contact times between 0.13 and 0.98 seconds. Lower flow rates were not studied because of the difficulty in keeping the tube completely wet by the solution. Measurements with shorter tube lengths were not included because of the increasing relative importance not only of the entrance effect but also of an exit effect.

This exit effect is evidenced by the appearance of a band of ripples about a centimeter above the level of the liquid in the receptor. Preliminary, qualitative experiments indicate that the surface of the falling film below this band of ripples is nearly stagnant, and that the height of the band of ripples varies inversely with the velocity of the falling film. A similar phenomenon has been reported by Matsuyama [15], who studied absorption by short liquid jets. This effect will be discussed in Part II of this paper.

Acknowledgement.

The authors wish to acknowledge the contributions to this paper by A. Kessler, who developed the absorption apparatus, and to R.A.T.O. Nijsing, who helped with part of the taking of the data.

Notation.

A	Area of film surface, cm^2.
C	Concentration of diffusing solute, g/cm^3.
C_0	Initial concentration of solute in bulk of liquid, g/cm^3.
C^+	Concentration of solute in saturated solution, g/cm^3.
D	Diffusivity of solute in liquid, cm^2/sec.
g	Acceleration due to gravity, 981 cm/sec^2.
h	Height of column, cm.
Δh	Increment in height to account for entry effect, cm.
h_e	Effective height of column, h + h, cm.
r	Radius of tube, cm.
Re	Reynolds' number of film.
T	Absolute temperature, $^\circ$K.
t	Time, sec.
t_c	Contact time of an element of area in the column, sec.
v_i	Velocity of the surface of the liquid film, cm/sec.
x	Coördinate in the direction of diffusion, cm.
Γ_v	Volumetric rate of flow per centimeter, cm^3/cm sec.
$\gamma_\pm$	Mean activity coefficient of positive and negative ions.
δ	Thickness of liquid film on wall of column, cm.
μ	Dynamic viscosity, g/sec cm.
ν	Kinematic viscosity, cm^2/sec.
Φ_m	Rate of absorption, g/sec.
Φ_m''	Rate of absorption per unit area, g/cm^2 sec.

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Table I

Pertinent physical and chemical properties of solutions used.

Solution	$\gamma_{\pm}$	$C^*_{H^+}$ (calc)	$C^*_{HSO_3^-}$ (calc)	$C^*_{H_2SO_3}$ (calc)	$\mu, 20^\circ C$ g/cm sec	$D, 20^\circ C$ 10^{-5} cm^2/sec	$\rho, 20^\circ C$ g/cm^3	$\left[2(C^*-C_0)\left(\frac{2D}{2\pi}\right)^{\frac{1}{2}}\left(\frac{\mu}{\rho D}\right)^{\frac{1}{6}}\right] \times 10^3$ (calc)	(exp)
H_2O	0.82	0.0108	0.0108	0.0887	0.0100	1.46	0.998	2.97	
0.2 N NaCl	0.74	-	-	-	0.0102	1.43	1.004	-	2.95
1.0 N NaCl	0.66	-	-	-	0.0109	1.34	1.038	-	2.77
2.84 N HCl	-	-	-	-	-	-	1.045	-	3.00
0.196 N $NaHSO_3$	0.74	0.0075	-	0.0885	0.0104	1.40	1.011	2.78	2.80
1.087 N $NaHSO_3$	0.66	0.0025	-	0.0865	0.0117	1.25	1.075	2.43	2.26

$$\log_{10} H = \frac{1268.43}{T} - 7.37566 \qquad H = \frac{\text{moles } SO_2}{1000 \text{ g } H_2O} \Big/ p_{SO_2} \text{ (mm Hg)}$$

$$\log_{10} K = \frac{893.32}{T} - 4.71507 \qquad K = \frac{[H^+][HSO_3^-]}{[H_2SO_3]}, \quad [\ ] = \frac{\text{moles}}{1000 \text{ g } H_2O}$$

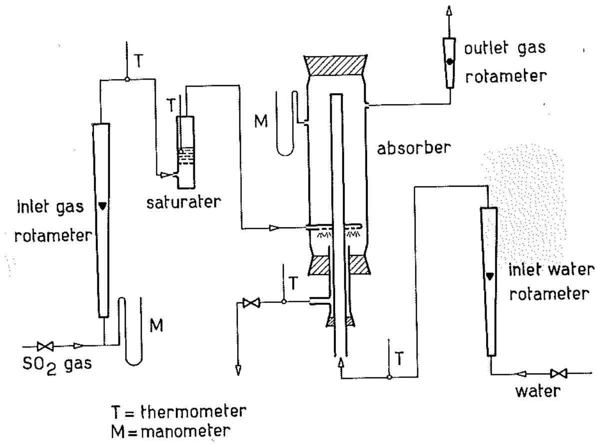

Fig.1
Sketch of absorption apparatus.

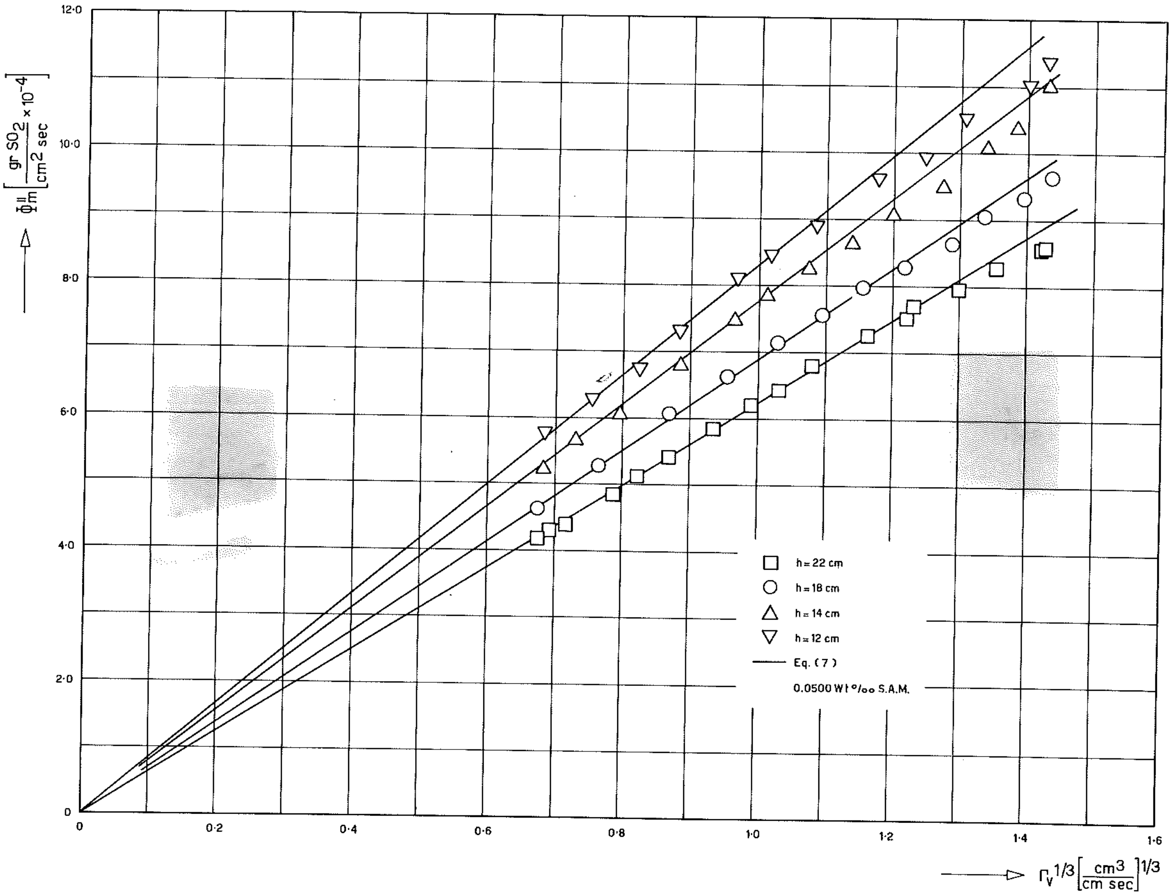

Fig.2
Rates of absorption for different heights of column.

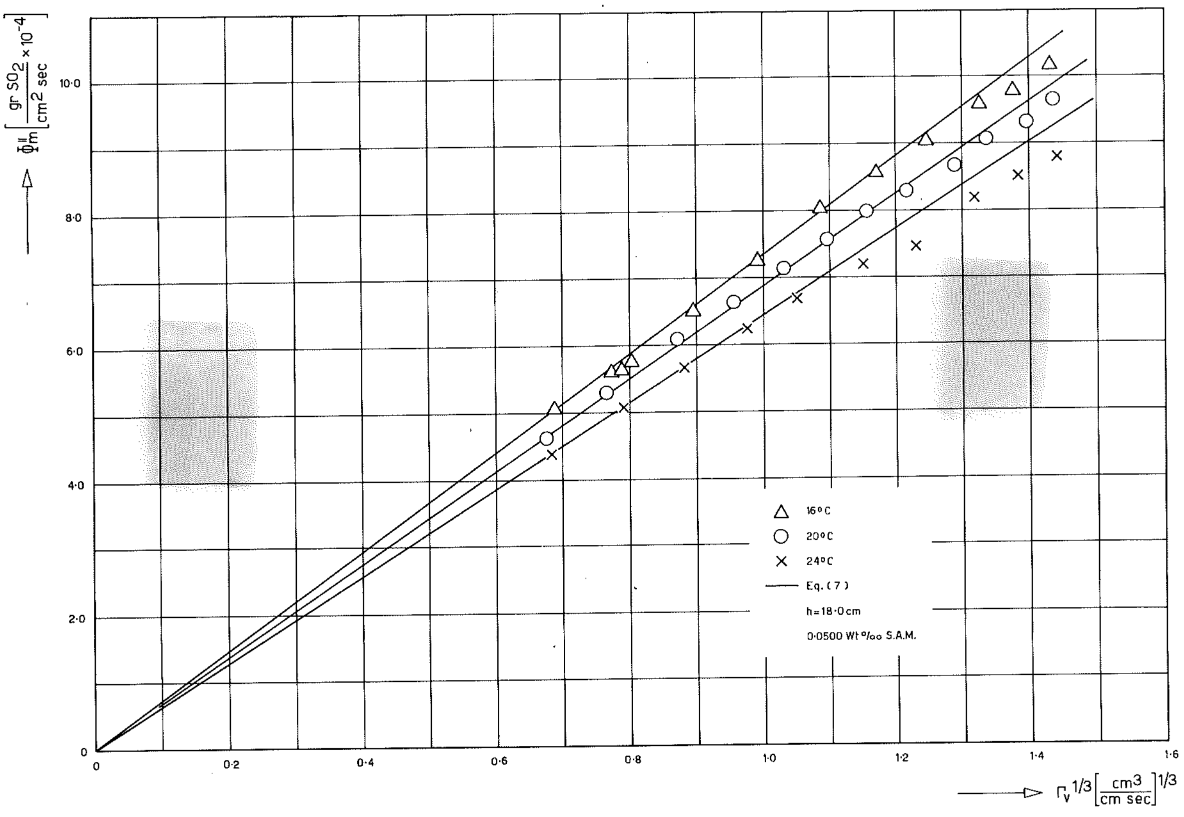

Fig.3

Rates of absorption at different temperatures.

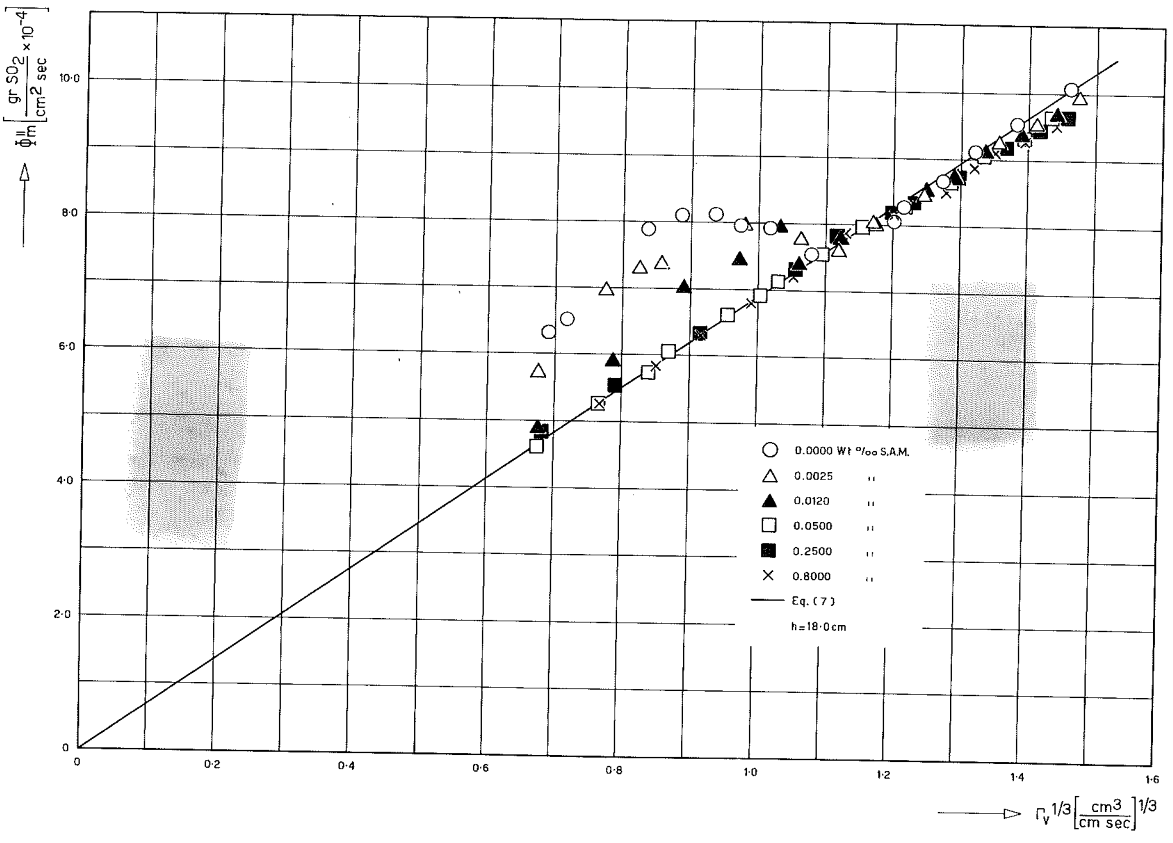

Fig.4

Effect of surface active material on the rate of absorption of SO_2 in water.

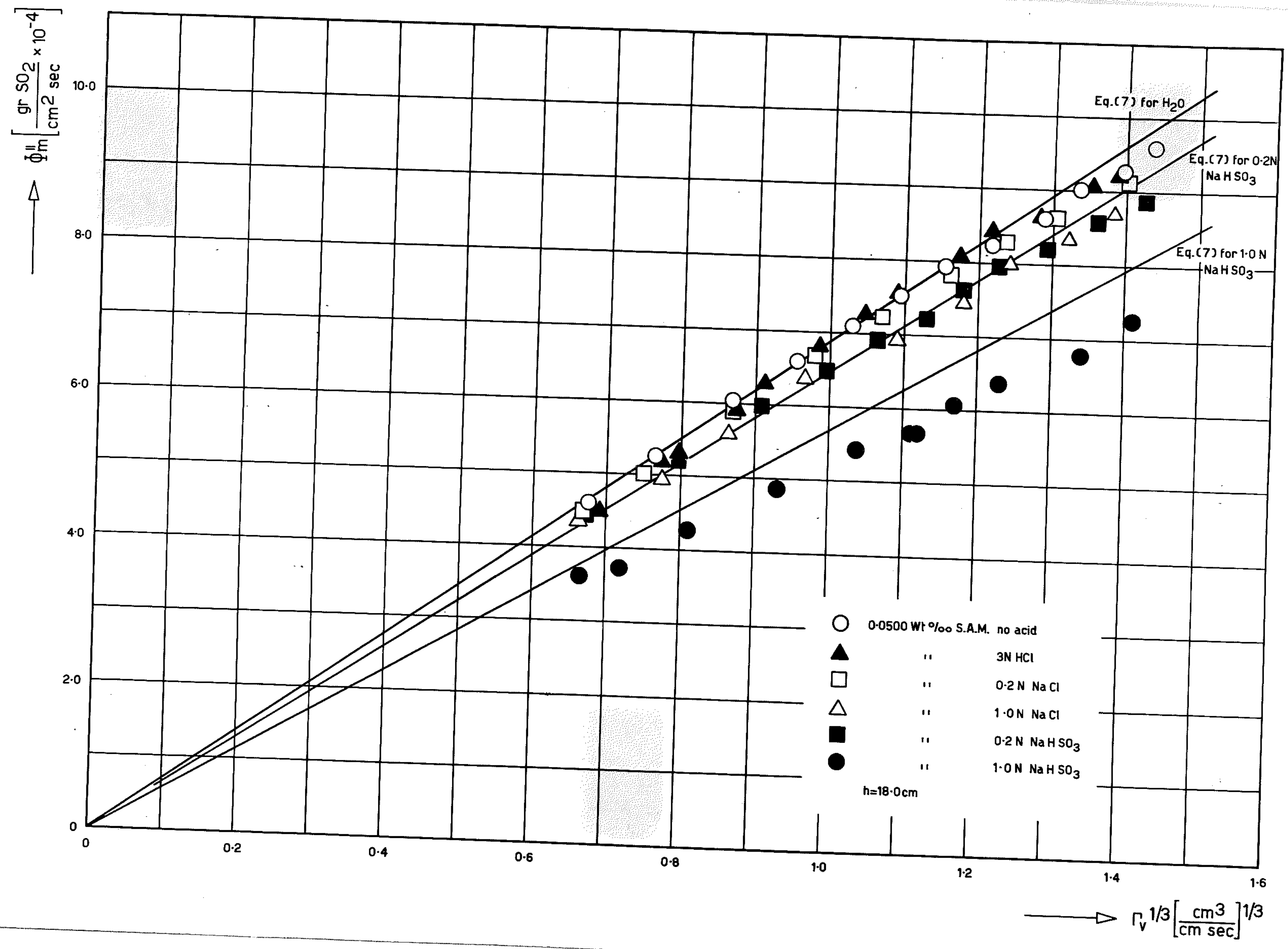

Fig.5

Comparison of the rates of absorption of SO_2 in water and in solutions of $NaHSO_3$, NaCl and HCl.

Absorption studies in the light of the penetration theory.

II. Absorption by short wetted-wall columns.

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Summary.

The rate of absorption of SO_2 by water in short wetted-wall columns (heights of 1 to 5 cm) with no gas phase resistance has been investigated. When the liquid film emerges through a slit of appropriate width, the entrance effect is negligible and need not be considered in applying the penetration theory to the rate of absorption. However, there is a considerable end-effect which is evidenced by a thickening of the film, accompanied by an apparent stagnation of the surface, on the lower one centimeter of the column. The rate of absorption by this part of the film is relatively low. This phenomenum complicates the analysis of data obtained with short wetted-wall columns, or other equipment with films flowing over small distances.

Résumé.

On a mesuré la vitesse d'absorption de SO_2 pure dans l'eau dans un absorbeur à paroi moillée avec un hauteur de 1 à 5 cm. Si l'eau est alimenté par une fissure d'une largeur appropriée, la correction qu'il faudrait introduire dans la theorie de la "pénétration" pour calculer l'absorption, parait être negligeable. D'autre part, il se produit une région

avec une grande resistance pour l'absorption à la partie inférieure de la surface de l'eau. En certains cas cette partie peut avoir une hauteur de 2 cm. L'apparition de cet effet est visible par une faible augmentation de l'épaisseur de la couche, qui est accompagné par une corrugation de la surface. Par l'effet signalé ici l'analyse de la résistance de la phase liquide à l'absorption se complique, surtout quand il s'agit d'un appareil, où des couches de liquide parcourent des trajets courts.

1. Introduction.

In the first article of this series [1], the absorption of SO_2 by water using relatively long wetted-wall columns was discussed. Columns with effective heights between 12.5 and 22.5 cm were studied using pure SO_2 (thus no gas-phase resistance), and were found to obey the penetration theory quantitatively. It was shown that the film behaved as a semi-infinite layer with the surface suddenly saturated with SO_2, and that the rate of absorption, Φ_m (g/sec), for the column was expressed by the following formula:

$$\Phi_m = 2(C^+ - C_0) A \sqrt{\frac{D}{\pi t_c}} \qquad (1)$$

where C^+ = concentration of solute at the surface - g/cm^3

C_0 = initial concentration of solute in bulk of liquid - g/cm^3

A = area of film surface - cm^2

t_c = time during which an element of area on the surface is exposed to gas - sec.

In the previous study the water flowed down the outside of a vertical tube which was open at the top. This produced an entry effect whose magnitude could not be estimated with great accuracy. For the study of short columns the top was covered with an accurately centered cap, which formed an entry-section for the film of water. The distance required for the surface of the film to accelerate to 90% of the equilibrium velocity was estimated by the use of a scaled-up model and found to be about 12 times the film thickness. Thus, the entry-effect is negligible and need not be considered in applying the penetration theory to the rate of absorption.

In the course of the experiments with both the long and the short columns, it was found that at a certain height above the surface of the stagnant liquid in the receiver, into which the film of water flowed, the thickness of the film increased from the normal to a slightly greater value. This was accompanied by the appearance of a narrow, horizontal band of ripples at the top of the thickened portion of the film. The height of this end-effect was found to vary in an inverse manner with the velocity of the film, from 2 cm for the lowest flow rate used to 0.1 cm for the highest. An effect similar to this has been observed by *Matsuyama* [2], who studied absorption by a short jet of liquid. However, the effect apparently escaped the attention of *Peaceman* [3] and *Emmert* and *Pigford* [4], who have also worked with short columns.

Qualitative experiments indicate that the surface of the film below the ripples is nearly stagnant. A light powder (lycopodium seed) blown onto the surface of the film circles lazily instead of being swept immediately into the liquid receiver. A coloured liquid introduced in the surface layers of the film accumulates to form a dark-coloured band below the ripples [5].

If the surface of the film below the ripples were actually stagnant, the rate at which that area absorbed gas would be very much lower than that of the much fresher liquid above the ripples. One may consider two extremes: (1) when the area of this end-effect is a comparitively small fraction of the total film area and (2) when the end-effect has reached the top of the column so that the surface of the entire film is apparently stagnant.

In the first situation, the rate of absorption of the area below the ripples may be neglected relative to that of the fresher surface. The column may thus be considered to be shorter by the height of the end-effect, h_r. Using the relationship between the contact time, t_c, and the liquid flow rate, acceleration of gravity, and the physical properties of the fluid given in [1], equation (1) then becomes

$$\Phi_m = 4(C^+-C_0)(r+\delta)\left(\frac{\pi D}{2}\right)^{1/2}\left(\frac{gg}{\nu}\right)^{1/6}\Gamma_v^{1/3}h_e^{1/2} \qquad (2)$$

where h_e = effective height of column, $(h-h_r)$, cm.

In the second situation it is assumed that the liquid issuing from the entry-section remains in full parabolic flow, with zero velocity at the surface. It is thus analogous to the case of heat transfer to a liquid in laminar flow between parallel plates when the liquid enters a section where one plate has a different, constant temperature and the other is perfectly insulated. So far as is known, the literature contains no solution of the differential equation obtaining in this case.

However, for sufficiently low values of the term $hD/\delta\Gamma_v$, the solution may be approximated from the solution for the symmetrical case when the liquid enters a section where both plates have the same different, constant temperature. The rate of heat transfer in the former case will be just half that in the latter case, in the first approximation (in reality it will be somewhat greater than half). The solution for the latter case has been calculated by Prins, Mulder and Schenk [6]. Using the notation of this paper, their results may be expressed in the following formula:

$$\frac{\Phi_m}{2\pi r(C^{*}-C_0)\Gamma_v} = F\left(\frac{hD}{\delta\Gamma_v}\right) \tag{3}$$

where δ, for flow due to gravity between vertical parallel plates, is

$$\delta = \sqrt[3]{\frac{12\nu\Gamma_v}{g}}$$

The value of the term $\frac{\Phi_m}{2\pi r(C^{*}-C_0)\Gamma_v}$ as a function of $\frac{hD}{\delta\Gamma_v}$, calculated from the work of Prins, etal., is given in the following table.

Table I

$4\frac{hD}{\delta\Gamma_v}$	$\frac{\Phi_m}{2\pi r(C^{*}-C_0)\Gamma_v}$
0.01	0.025
0.02	0.040
0.05	0.075
0.10	0.120

2. Description of equipment.

The equipment has been described in detail in [1]. The chief modification for the purposes of this paper was the introduction of the water through a narrow slit at the top of the column. A second alteration was the addition of a plastic cover to the liquid receiver. The liquid in the receiver was kept in contact with the cover during a run so that the surface exposed to the SO_2 was greatly reduced. A sketch of the absorber, showing the changes mentioned, is given in Figure 1. For further details of the equipment the reader is referred to [1].

3. Treatment of data.

The data were reduced to the common basis of a partial pressure of SO_2 of 750 mm Hg and a surface temperature of the water film of 20°C. The manner in which these adjustments were made has been described in [1]. In all experiments pure (99.9%) SO_2 was absorbed in distilled water. In some cases a surface-active agent ("Teepol") was added. The height of the band of ripples was measured with a millimeter scale mounted inside the absorber with a precision of about a half a millimeter. This measurement was made while gas was being absorbed.

4. Discussion of results.

Gas absorption measurements were made at column heights of 5, 3, 2, and 1 cm using pure water and dilute solutions of Teepol of various concentrations. These data are plotted in Fig.2 as Φ_m versus $\Gamma_v^{1/3}$. For comparison, equation (2), with $h_r = 0$, has been drawn in for the four column heights, and equation (3) has been drawn in for a height of 2 cm. The values of C^+ and D used were taken from [1]. For the shorter columns equation (2) was drawn in only for values of $\Gamma_v^{1/3}$ above $1.2 \left[\frac{cm^3}{cm\ sec}\right]^{1/3}$ to avoid confusion with regard to which points should approach which lines.

In Fig.2 the effect of the stagnation of the surface of the film below the band of ripples is quite apparent. As the flow rate increases, the height of the band of ripples decreases, and the measured rate of absorption approaches the calculated rate.

The height of the end-effect is not affected by the height of the column (see Fig.3). For this reason the fraction of the total area of the column which is below the band of ripples at a given liquid flow rate will be greater for the shorter columns. This is reflected in the rate of absorption, as shown in Fig.2. The deviation of the points from the theoretical lines shows a consistent increase as the column height decreases.

Various Teepol concentrations were used with the 3-cm column. It is seen that, within the experimental error, there is no observable effect of the addition of the Teepol.

For both the 1- and the 2-cm columns the band of ripples reaches the top of the column at a certain flow rate below which the entire surface of the film appears to be nearly stagnant. [illegible]

The absorption data for the two columns show distinct breaks at those flow rates.

Absorption data for the 2-cm column were taken at exceptionally low flow rates, in the region where the entire column is covered with the stagnant film. As seen in Fig.2, the points lie consistently 15 to 20% above the curve of equation (3). It is interesting, however, that the agreement is as good as this considering the assumptions involved in the derivation of the equation.

In Fig.3 is a plot of $\sqrt{h_r}$ versus $\Gamma_v^{1/3}$. It is seen that the height of the end-effect does not depend upon the height of the column, but is influenced by the Teepol concentration. As Teepol is added, the band of ripples becomes fainter and more difficult to observe. At low Teepol concentrations h_r is somewhat greater than with water, while at high Teepol concentrations it is appreciably lower. As mentioned before, however, the addition of the Teepol had no measureable effect on the gas absorption. For this reason, the line shown in Fig.3 was drawn through the points for water without regard to the points for the Teepol solutions.

The straight line in Fig.3 was used to correlate the data for various columns in Fig.4, where Φ_m is plotted versus $\Gamma_v^{1/3}(h-h_r)^{1/2}$. Equation (2) is again drawn in the figure, and it is seen that the correlation is remarkably good. From the agreement of the data with the calculated line it must be concluded that the stagnant lower part of the film indeed absorbs gas at a greatly reduced rate.

In Fig.5 the data for the 1-cm and the 5-cm columns are plotted on a log-log scale to show the interpretation that one might be led to from such a presentation. ([illegible])

The points for the 5-cm column lie on a rather nice straight line having a slope of 0.39. If one discards two of the points for the 1-cm column, the other six form a line with a slope of 0.97. The data for the other columns can be plotted similarly to obtain values for the exponent n in the equation

$$\Phi_m \sim \Gamma_r^{\,n} \qquad (4)$$

which lie between the two mentioned above. It is possible that the presence of stagnant regions on the liquid films flowing in packed columns is responsible for the well-known facts that the exponent in equation (4) is usually about twice the value of 1/3 predicted by the penetration theory, and that the value of this exponent depends upon packing shape and size and the nature of the absorbing liquid.

The presence of such stagnant regions can be demonstrated by introducing lycopodium powder into a laboratory-size packed column. Whirling groups of powder particles can then be seen, and the residence time of the powder in the column is found to be far greater than that of the liquid.

5. Discussion of errors.

The work presented in this article is subject to the same errors and uncertainties discussed in [1]. Because the rate of gas absorption by the short columns is smaller than by the long columns, the percentage deviation of the experimental points from a smooth curve drawn through them is somewhat greater in this work.

6. Limits of applicability.

The conditions studied here were for column heights between 1 and 5 cm and for Reynolds' numbers between 20 and 1150. This corresponds to contact times between 0.01 and 0.22 seconds neglecting the stagnation effect.

Acknowledgement.

The authors wish to acknowledge the contribution to this paper made by A.J. de Graaf, who made part of the measurements presented here.

Notation.

A	Area of film surface, cm^2
C_o	Initial concentration of solute in bulk of liquid, $\mathrm{g/cm}^3$
C^*	Concentration of solute in saturated solution, $\mathrm{g/cm}^3$
D	Diffusivity of solute in liquid, $\mathrm{cm}^2/\mathrm{sec}$
g	Acceleration due to gravity, 981 $\mathrm{cm/sec}^2$
h	Height of column, cm
h_r	Height of band of ripples, cm
h_e	Effective height of column, $(h - h_r)$, cm
r	Radius of tube, cm
Re	Reynolds' number of film
t_c	Contact time of an element of area in the column, sec
Γ_v	Volumetric rate of flow per centimeter, $\frac{\mathrm{cm}^3}{\mathrm{cm\ sec}}$
δ	Thickness of liquid film on wall of column, cm
ν	Kinematic viscosity, $\mathrm{cm}^2/\mathrm{sec}$
Φ_m	Rate of absorption, g/sec.

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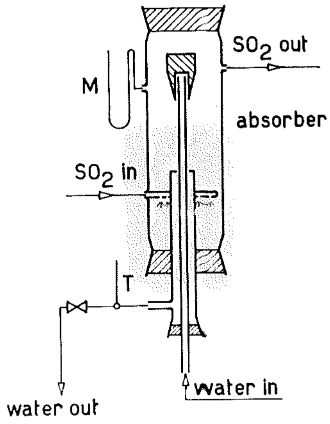


Fig.1
Sketch of modified absorber.

Fig.2
Rates of absorption for different heights of column as functions of flow rate.

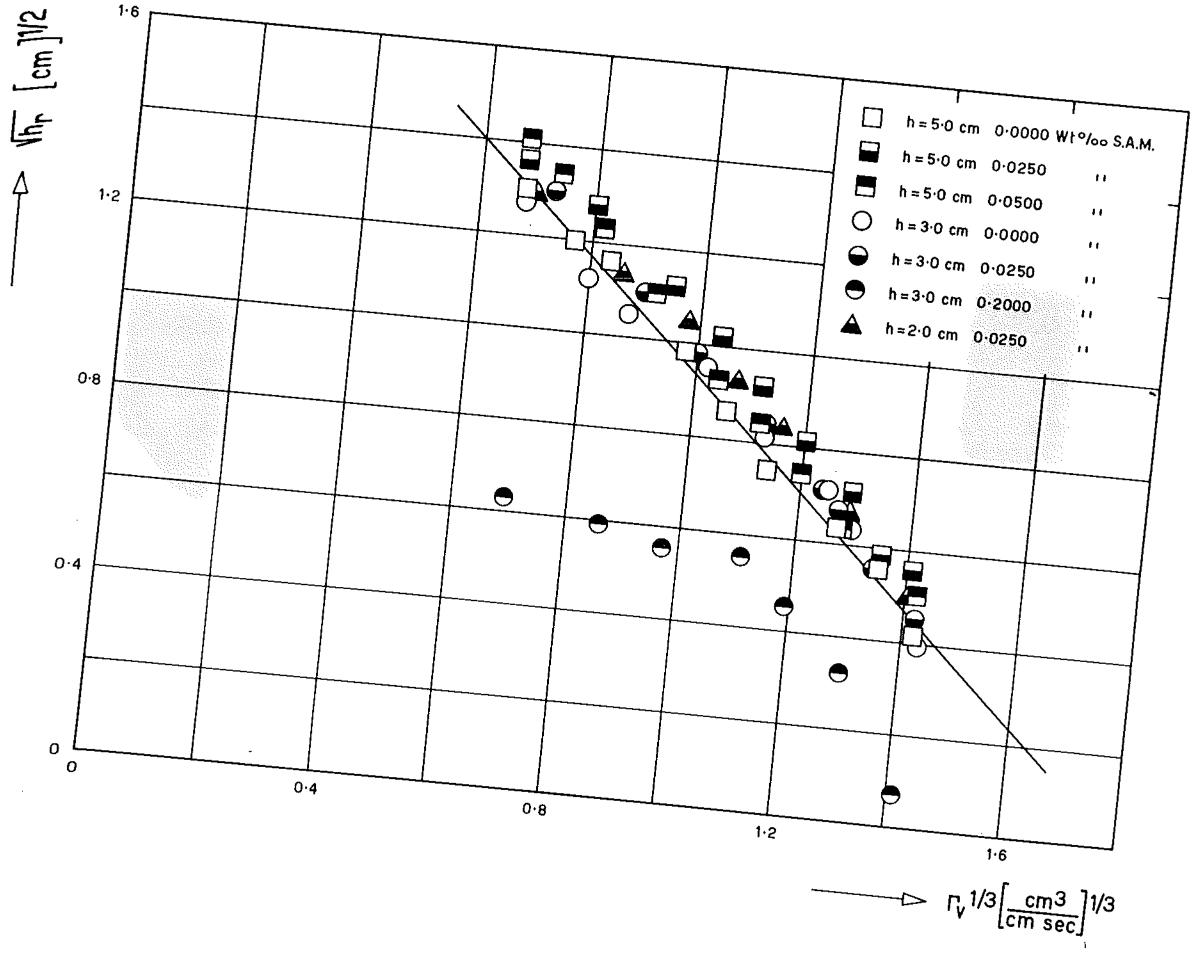
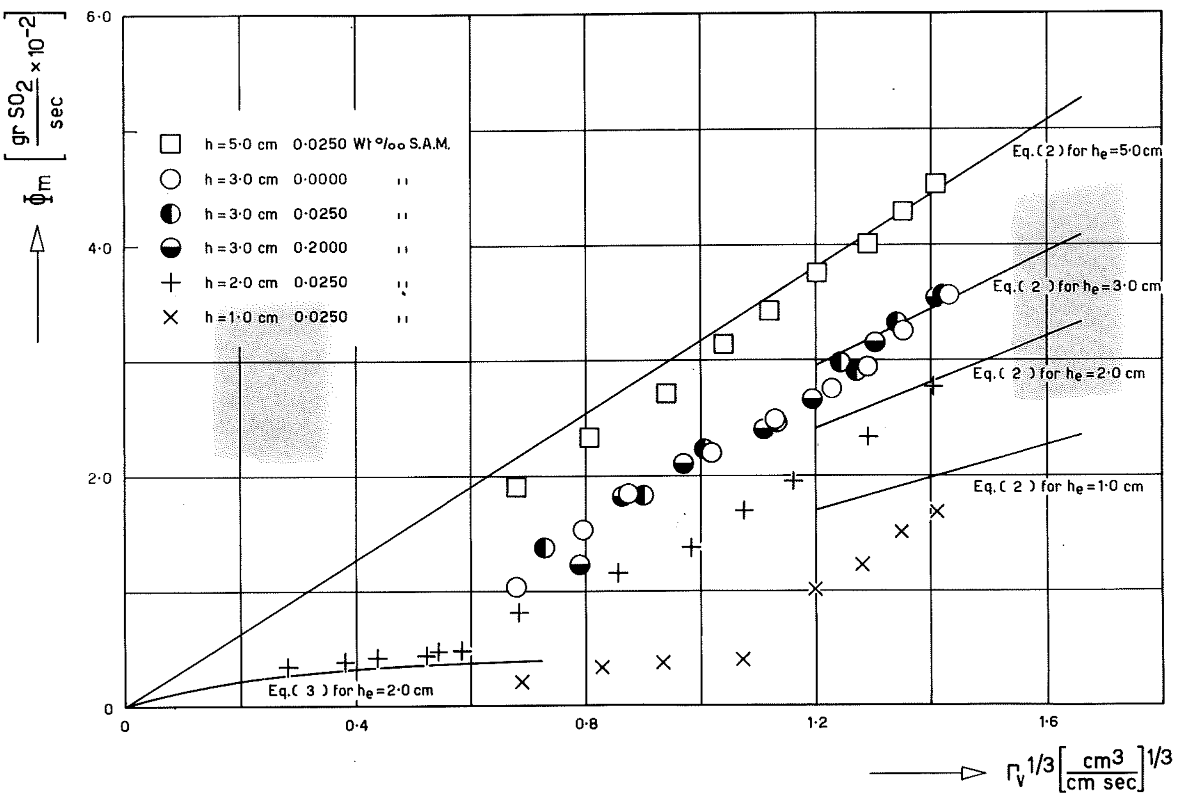
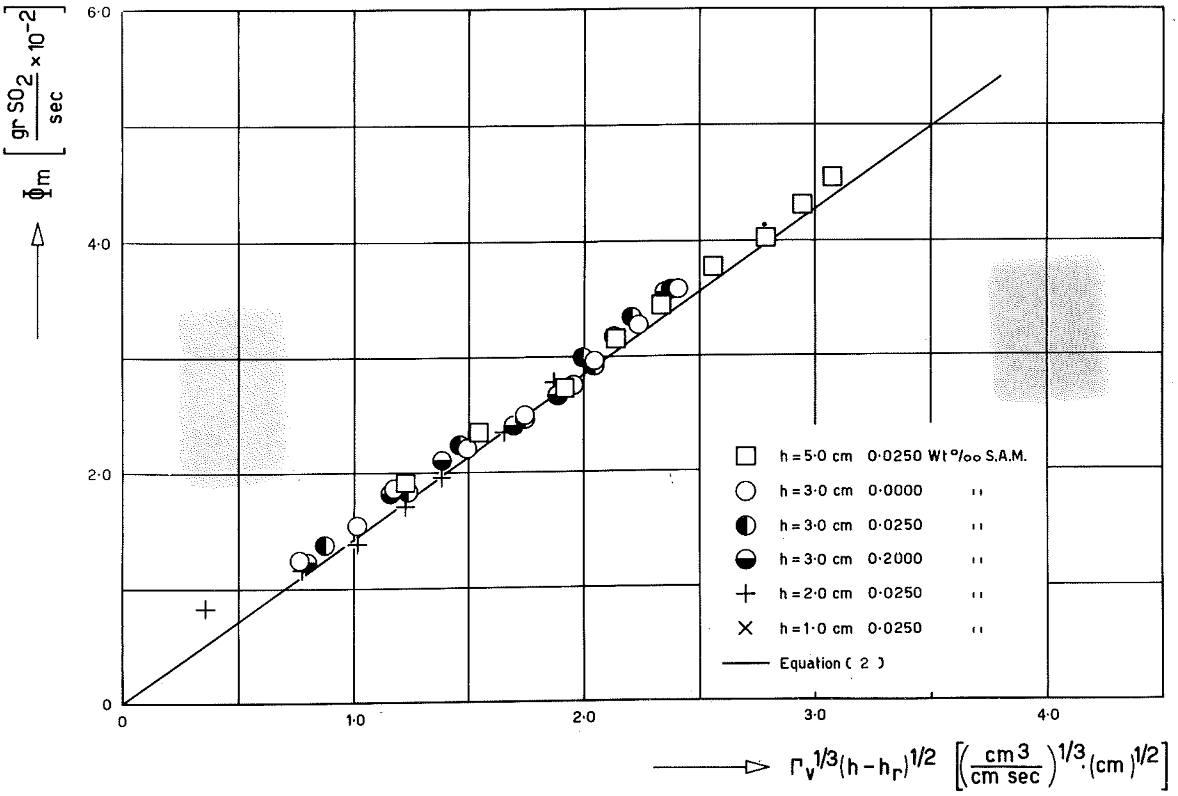

√h_r [cm]^1/2
1·6
1·2
0·8
0·4
0
0
0·4
0·8
1·2
1·6
Γ_v 1/3 [cm3 / cm sec] 1/3
h = 5·0 cm 0·0000 Wt°/oo S.A.M.
h = 5·0 cm 0·0250 ''
h = 5·0 cm 0·0500 ''
h = 3·0 cm 0·0000 ''
h = 3·0 cm 0·0250 ''
h = 3·0 cm 0·2000 ''
h = 2·0 cm 0·0250 ''

Fig.3
Height of the end-effect as a function of flow rate.

Fig.4
Correlation of rates of absorption for different columns by subtracting stagnant area.


$\Phi_m \left[\frac{gr\ SO_2}{sec} \times 10^{-2}\right]$
6·0
4·0
2·0
0
0
0·4
0·8
1·2
1·6
$\Gamma_v^{1/3} \left[\frac{cm^3}{cm\ sec}\right]^{1/3}$
h = 5·0 cm 0·0250 Wt °/oo S.A.M.
h = 3·0 cm 0·0000 ''
h = 3·0 cm 0·0250 ''
h = 3·0 cm 0·2000 ''
h = 2·0 cm 0·0250 ''
h = 1·0 cm 0·0250 ''
Eq.(2) for h_e = 5·0 cm
Eq.(2) for h_e = 3·0 cm
Eq.(2) for h_e = 2·0 cm
Eq.(2) for h_e = 1·0 cm
Eq.(3) for h_e = 2·0 cm


$\Phi_m \left[\frac{gr\ SO_2}{sec} \times 10^{-2}\right]$
6·0
4·0
2·0
0
0
1·0
2·0
3·0
4·0
$\Gamma_v^{1/3}(h-h_r)^{1/2} \left[\left(\frac{cm^3}{cm\ sec}\right)^{1/3} \cdot (cm)^{1/2}\right]$
h = 5·0 cm 0·0250 Wt °/oo S.A.M.
h = 3·0 cm 0·0000 ''
h = 3·0 cm 0·0250 ''
h = 3·0 cm 0·2000 ''
h = 2·0 cm 0·0250 ''
h = 1·0 cm 0·0250 ''
Equation (2)

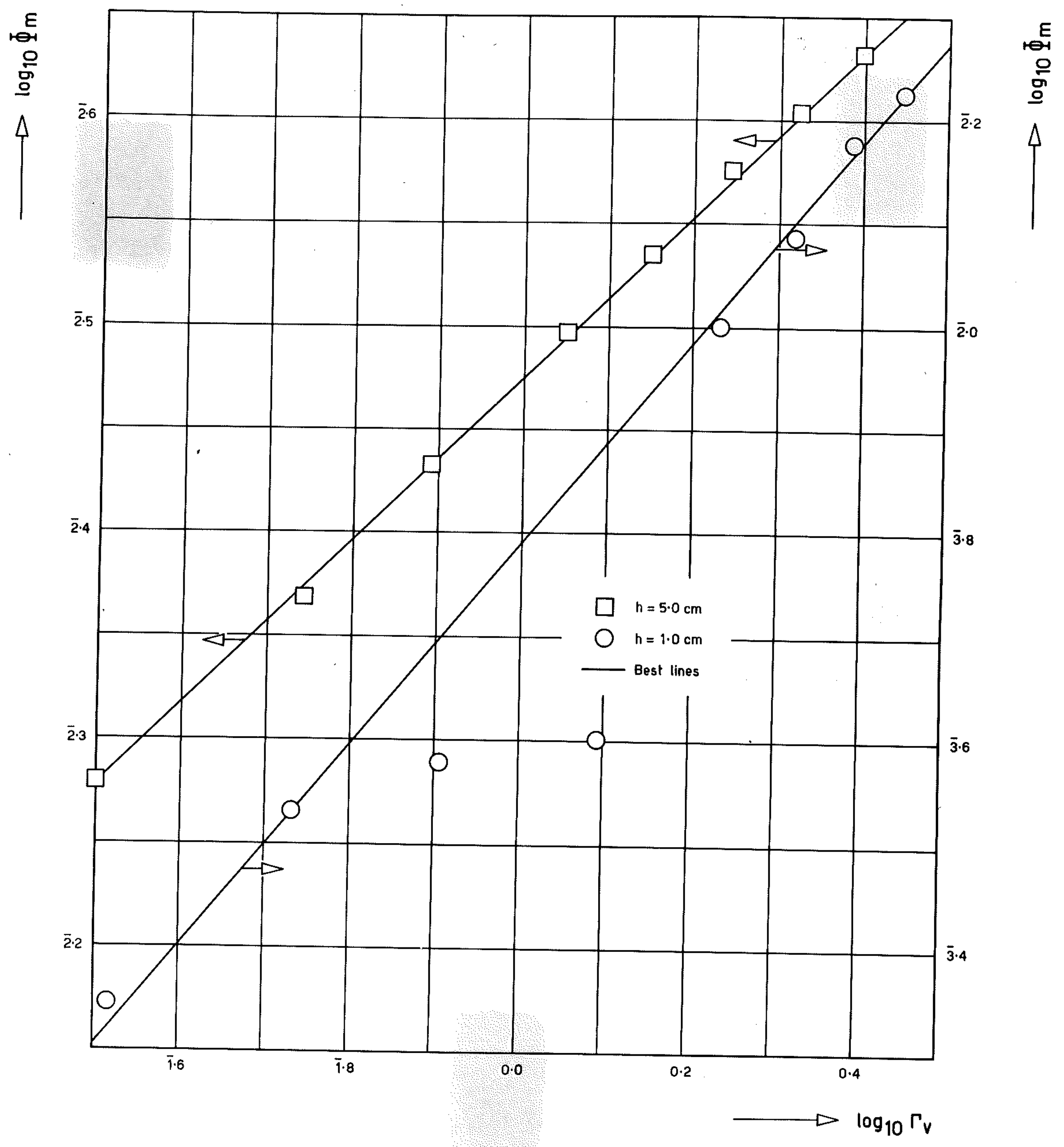


Fig.5

Log-log plot of absorption data to demonstrate weakness of this form of presentation.

Absorption studies in the light of the penetration theory.

III. Absorption by wetted spheres, singly and in columns.

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Summary.

A study has been made of the absorption of SO_2 by water flowing in a laminar film over the surface of single spheres and columns of spheres. By means of the penetration theory it is possible to correlate the data for spheres of radii from 1 to 3 cm, and for columns containing up to fourteen spheres. It appears that these is little or no mixing of the surface layers with the bulk of the liquid as it flows from one sphere to the next in a vertical row.

Résumé.

On a étudié l'absorption de SO_2 par eau, qui coule en couche laminaire sur la surface d'une sphère et d'une colonne formée par sphères superposées. Il a paru possible de trouver une correlation satisfaisante entre la vitesse d'absorption et la dimension des sphères (2 à 6 cm. diamètre), leur nombre (1 à 14) et le debit d'eau (0.5 à 7.5 cm^3/sec). Cette correlation peut être prédite au moyen de la theorie de diffusion non-stationnaire. Les expériences démontrent qu'il ne se produit pas un melange entre la surface et l'intérieur du liquide quand celui-ci passe d'une sphère à l'autre.

1. Introduction.

In the first article of this series [1] it was found that for physical absorption without gas phase resistance in a wetted-wall column the simple theory of transient diffusion into a stagnant layer of liquid (penetration theory) is valid for contact times up to 1 second. In the case of a film of liquid flowing over a sphere a similar mathematical treatment is greatly complicated if one attempts to consider the stretching of the film, and the consequent distortion of the concentration gradients, as it flows from the top of the sphere to the bottom. This stretching will have the effect of increasing the concentration gradients on the upper half of the sphere and of decreasing them on the lower half. Because the film on the upper half of the sphere, being fresher, absorbs faster than when it is on the lower half, one would expect the net effect of the stretching and contracting of the film to be an increased rate of absorption. Without considering these effects, the following calculation can be made:

Consider a sphere of radius R (cm) with an angular coordinate α which is zero at the top of the sphere and π at the bottom. Liquid flows over the sphere in a laminar film, with a total volumetric flow rate of Φ_v (cm^3/sec). It is assumed that the thickness of the film, δ, at any latitude on the sphere is the same as it would be for the same flow rate per unit length, Γ_v (cm^3/cm sec), on a plane surface making the same angle with the vertical. Thus:

$$\delta = \sqrt[3]{\frac{3\nu\Gamma_v}{g\sin\alpha}}$$

$$= \sqrt[3]{\frac{3\nu\Phi_v}{2\pi R g\sin^2\alpha}} \qquad (1)$$

where ν = kinematic viscosity, cm^2/sec
g = acceleration due to gravity, 981 cm/sec^2

It follows from the above assumption that a half-parabolic velocity profile will exist at all latitudes on the sphere, so that the velocity of the surface of the film, v_i (cm/sec), is given by the following equation:

$$v_i = \frac{3}{2}\frac{\Gamma_v}{\delta}$$

$$= \left(\frac{9g}{32\nu\pi^2}\right)^{1/3} \Phi_v^{2/3} R^{-2/3} \sin^{-1/3}\alpha \qquad (2)$$

The rate of absorption of a differential unit of area on the film is

$$d\Phi_m = (C^+ - C_0)\sqrt{\frac{D}{\pi t}}\, dA \qquad (3)$$

where Φ_m = rate of gas absorption, g/sec
C^+ = concentration of solute in saturated solution, g/cm^3
C_0 = initial concentration of solute in bulk of liquid, g/cm^3
D = diffusivity of solute in liquid, cm^2/sec
t = time during which the element of area has been exposed to the gas, sec.

The "age" of an element of area at latitude α is

$$t = \int_0^\alpha \frac{R\, d\alpha}{v_i}$$

$$= \left(\frac{32\nu\pi^2}{9g}\right)^{1/3} \Phi_v^{-2/3} R^{5/3} \int_0^\alpha \sin^{1/3}\alpha\, d\alpha$$

and an element of area can be expressed as

$$dA = 2\pi R^2 \sin\alpha\, d\alpha$$

Thus, the rate of absorption for the whole sphere becomes

$$\Phi_m = (C^{*}-C_0)\sqrt{D}\left(\frac{18g\pi}{\nu}\right)^{1/6}\Phi_v^{1/3}R^{7/6}\int_0^{\pi}\frac{\sin\alpha\, d\alpha}{\left[\int_0^{\alpha}\sin^{1/3}\alpha\, d\alpha\right]^{1/2}} \qquad (4)$$

The value of the term

$$\int_0^{\pi}\frac{\sin\alpha\, d\alpha}{\left[\int_0^{\alpha}\sin^{1/3}\alpha\, d\alpha\right]^{1/2}} \qquad \text{is } 2.33$$

and the value of

$$\int_0^{\pi}\sin^{1/3}\alpha\, d\alpha \qquad \text{is } 2.58, \text{ as}$$

determined by numerical integration.

For the absorption of SO_2 in water when the partial pressure of the SO_2 is 750 mm Hg and the temperature of the surface of the water film is 20°C, equation (4) can be expressed as

$$\Phi_m = K R^{7/6}\Phi_v^{1/3} \qquad (4a)$$

The value of K obtained using the values of the pertinent physical properties listed in [1] is 1.19×10^{-2} $[g\ SO_2/sec.\ cm^{-7/6}.(cm^3 H_2O/sec)^{-1/3}]$. This value can only be considered as an approximation because the flow conditions at the top and bottom of the sphere have been idealized and the effect of the stretching and contracting of the film has been disregarded.

The derivation above has been for single spheres. For spheres mounted in a column one must consider whether the streamlines of the flowing film are effectively mixed as the liquid passes from one sphere to the next. ([illegible])

As has been shown above, the rate of absorption in the case of one sphere is

$$\Phi_m \sim (C^{+} - C_0)\frac{A}{\sqrt{t_c}}$$

where t_c is the time in which an element of area is exposed to the gas in moving from the top of the sphere to the bottom. If there is complete mixing of the streamlines of the fluid at the points between the spheres, and if the concentration of the dissolved gas in the out-going liquid is small relative to C^{+}, the rate of absorption for N spheres will be approximately:

$$[\Phi_m]_{\text{N spheres}} \cong N \cdot [\Phi_m]_{\text{1 sphere}}$$

If there is no mixing of the streamlines in the flow from one sphere to the next, the contact time for the liquid flowing down a row of N spheres will be $N \cdot t_c$, the total area exposed to the gas will be $N \cdot A$ and the rate of gas absorption will be

$$[\Phi_m]_{\text{N spheres}} = \sqrt{N} \cdot [\Phi_m]_{\text{1 sphere}}$$

or from equation (4a),

$$\Phi_m = K\sqrt{N}\,R^{7/6}\,\Phi_v^{1/3} \qquad (5)$$

It should be remembered that the derivation of these equations rests on the assumption that film can be considered as a semi-infinite medium. With other words, the "depth of penetration" of the solute must be small, and the relative saturation of the out-going liquid will be low.

2. Description of equipment.

The equipment used was the same as that described in [1] and [2] except that the absorber was modified to permit the placement of the spheres, as shown in Fig.1. Single spheres having radii of 1.00, 1.50, 1.90, and 2.95 cm were used. Vertical rows of 3, 5, 10, and 14 spheres having radii of 1.00 cm were also studied. The bottom of the lowest sphere was set 2 cm above the level of the liquid in the receiver to minimize the influence of the end-effect described in [2]. The liquid receiver was equipped with a plastic cover, also described in [2]. For further details of the equipment the reader is referred to [1].

3. Treatment of data.

The data were reduced to the common basis of a partial pressure of SO_2 of 750 mm Hg and a surface temperature of the water film of 20°C. The manner in which these adjustments were made has been described in [1]. In all experiments pure (99.9%) SO_2 was absorbed in distilled water to which a surface-active material ("Teepol") had been added. The spheres were made from steel ball-bearings and were mounted on a stainless steel rod.

The results presented here are subject to the same errors and uncertainties discussed in [1] and [2]. The average deviation of the points in Fig.2 from the solid line is 0.11×10^{-2} g SO_2/sec.

4. Discussion of results.

The rate of absorption using single wetted spheres is shown in Fig.2, plotted against $\sqrt{N}\, R^{7/6}\, \Phi_v^{1/3}$ The slope of the solid line through the points is about 7.6% greater than the value of K calculated from the penetration theory. This disagreement is probably due to the stretching effect, which was neglected in the derivation of equation (5), and is actually smaller than might have been expected. Of more importance is that the data for the four spheres all fall on the same straight line when plotted in the manner suggested by the penetration theory.

The solid line of Fig.2 is also drawn in Fig.3, where it is seen to represent the data for vertical rows containing up to 14 spheres with good precision at sufficiently low flow rates. It is seen that the data for the 5-sphere column begin to deviate appreciably from the ~~best~~ solid line at a flow rate of 4.2 cm^3/sec. Those for the 10-sphere column begin to deviate at 2.0 cm^3/sec, and those for the 14-sphere column begin to deviate at 1.9 cm^3/sec. This effect is due to the increasingly great tendency of the liquid film to ripple at a given liquid flow rate as the number of spheres in the column is increased. The instability of the flow over the lower spheres in a column is observed as a tendency for the liquid stream to "dance" back and forth at the points where the spheres are joined to each other. This tendency is decreased, but not eliminated, by the addition of 0.050‰ ~~0.025%~~ of a surface-active material ("Teepol"). With concentrations of Teepol either greater or less than this the tendency to ripple is greater.

The fact that the data for the columns of spheres fall on a straight line when plotted in the manner of Fig.3 is a strong indication that there is essentially no mixing of the streamlines in the film as it flows from one sphere to the next.

These results suggest that liquid in laminar flow in a packed column may frequently travel over many pieces of packing before effective mixing of the surface layers and the bulk of the liquid occurs. The average liquid-side resistance to absorption would then be greater than if mixing were taking place at each juncture between the pieces of packing. However, as has been indicated in [2], at the places where such mixing does occur, there is a stagnant surface over the region one to two cm above the point of mixing, again resulting in a reduction of the absorption rate. In the practical case, the effects described in this paper and in [2] are counteracted by turbulent regions in the film, which are produced by local uneven wetting of the packing and by the stream of gas. This turbulence tends to decrease the liquid-side resistance.

5. Limits of applicability.

The conditions studied here were for single spheres with radii between 1.00 and 2.95 cm, for columns containing up to 14 spheres having radii of 1.00 cm, and for flow rates between 0.5 and 7.5 $cm^3 H_2O/sec$. This corresponds to contact times between 0.29 and 0.05 sec. for the 1 cm-radius sphere and between 1.78 and 0.29 sec. for the 3 cm-radius sphere.

Acknowledgement.

The authors wish to achnowledge the contributions to this paper made by A.J. de Graaf and J.C. Hoogeveen, who took part in the investigation.

Notation.

A	Area of sphere, cm^2
C^+	Concentration of solute at saturation, g/cm^3
C_o	Initial concentration of solute in bulk of liquid, g/cm^3
D	Diffusivity of solute in liquid, cm^2/sec
g	Acceleration due to gravity, 981 cm/sec^2
K	Constant in equation (4a)
N	Number of spheres in a column
R	Radius of sphere, cm
t	Time of contact with gas of an element of area, sec
t_c	Time of contact with gas of an element of area in moving over one sphere, sec
v_i	Velocity of surface of film, cm/sec
α	Angular coordinate on sphere
Γ_v	Liquid flow rate per unit length, $cm^3/cm\ sec$
δ	Film thickness, cm
ν	Kinematic viscosity, cm^2/sec
Φ_m	Rate of absorption of gas, g/sec
Φ_v	Liquid flow rate, cm^3/sec.

References.

(1) Lynn, S., Straatemeier, J.R., and Kramers, H.; Chem.Eng.Sci.

(2) Lynn, S., Straatemeier, J.R., and Kramers, H.: Chem.Eng.Sci.

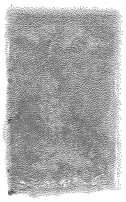


Fig.1
Sketch of modified absorber.

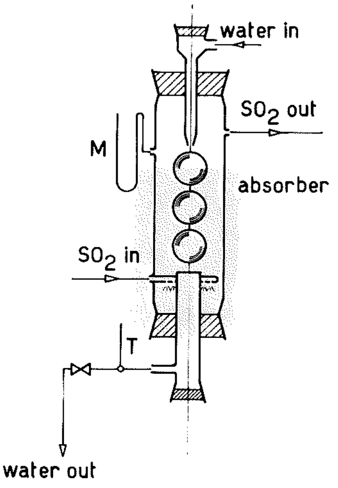


Fig.1
Sketch of modified absorber.

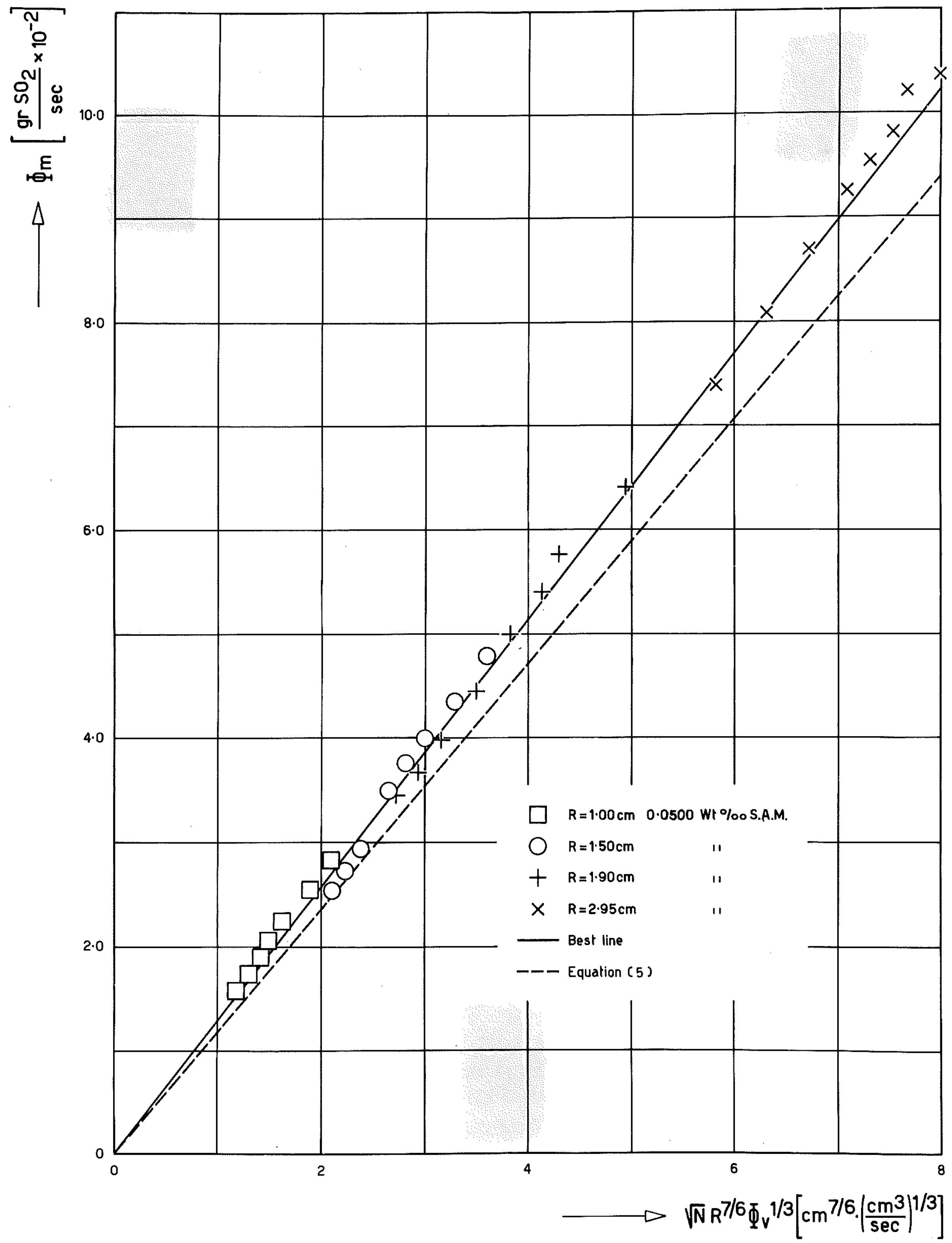


Fig.2
Gas absorption by single spheres.

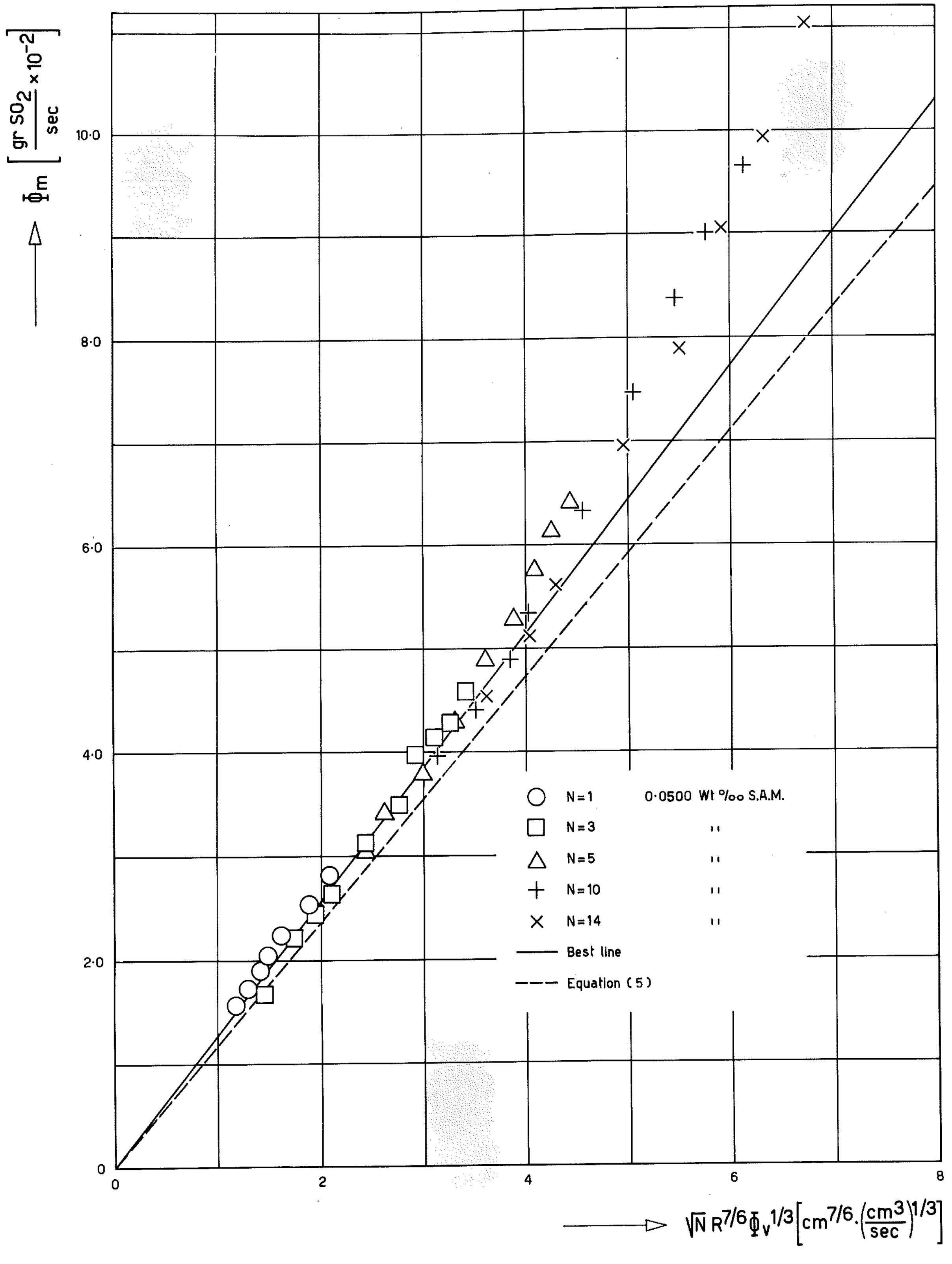


Fig.3

Gas absorption by columns of spheres, R = 1.00 cm.

Korte toelichting bij de foto's van het eindeffect.

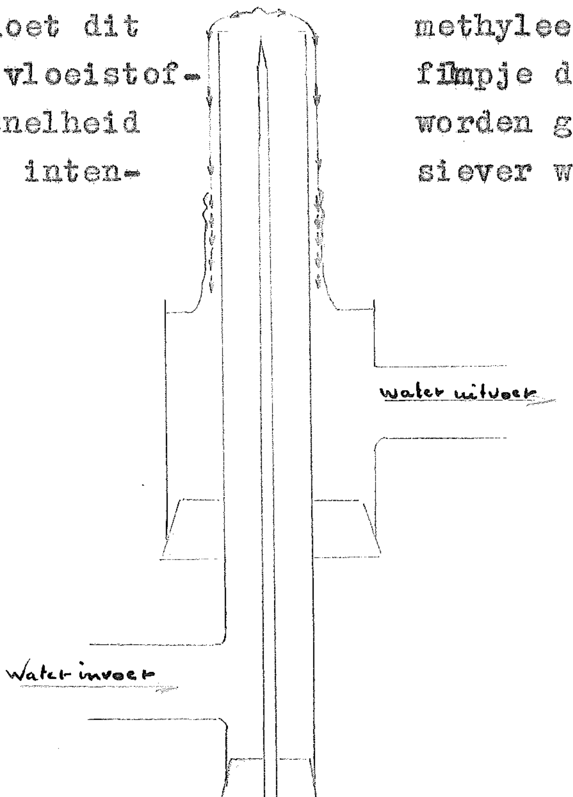
Het eindeffect, wat in deel II van dit verslag besproken is en waarbij de invloed hiervan op de absorptie is gemeten, is door kleuren van het vloeistofoppervlak duidelijk waarneembaar gemaakt en op de foto's vastgelegd.

Door verschillende proefjes is gebleken dat dit effect alleen optreedt wanneer het water filmpje in een stilstaand poeltje valt. Stroomt bijv. een dergelijk filmpje langs de onder elkaar geplaatste bollen in een vloeistofontvangertje (zie deel III) dan zal dit effect tussen de bollen niet, maar onder de laatst geplaatste bol wèl te zien zijn.

In onderstaand schetsje is aangegeven op welke wijze dit effect met een kleurstof, een methyleenblauw oplossing, is aangetoond.

Deze kleurstof wordt hier m.b.v. een capillair zodanig in het water geinjecteerd dat zij voor een groot gedeelte aan het oppervlak van het waterfilmpje naar beneden stroomt.

Ontmoet dit methyleenblauw nu het "starre" vloeistoffilmpje dan zal haar neerwaartse snelheid worden geremd en de kleur zal intensiever worden.



Op de hier volgende foto's 1 en 2 is dit duidelijk te zien. Men kan ook duidelijk waarnemen, dat de hoogte van dit effect groter wordt naarmate men de vloeistofbelasting vermindert.

Dat dit grote intensiteitsverschil niet veroorzaakt wordt door het feit, dat de filmdikte ter plaatse van dit eindeffect iets groter is dan daar boven, is met foto 3 aangetoond.

Hier is de kleurstof niet geinjecteerd zodat zij aan het oppervlak van de film komt, maar aan het water van te voren toegevoegd. De hierbij gebruikte concentratie van de kleurstof was dezelfde als de afvoer van de vorige gefotografeerde proefjes.

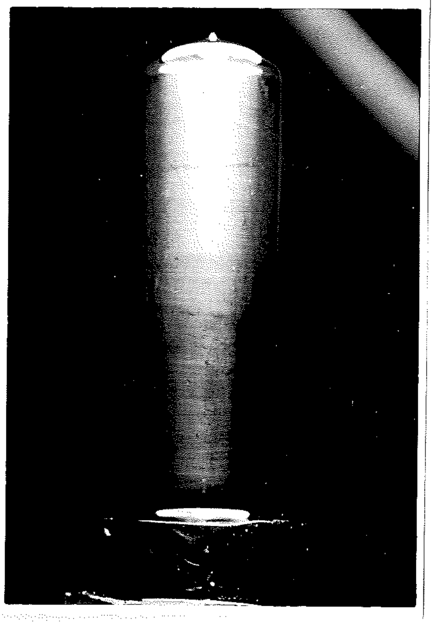
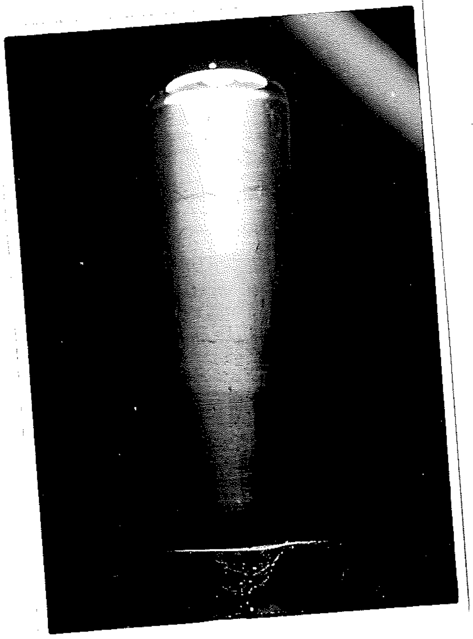


Fig.1
hoogte kolom 4,8 cm
hoogte eindeffect 2,2 cm
$\Gamma_v = 0{,}53 \frac{cm^3}{cm\ sec}$



Fig,2
hoogte kolom 4,8 cm
hoogte eindeffect 1,6 cm
$\Gamma_v = 0{,}76 \frac{cm^3}{cm\ sec}$

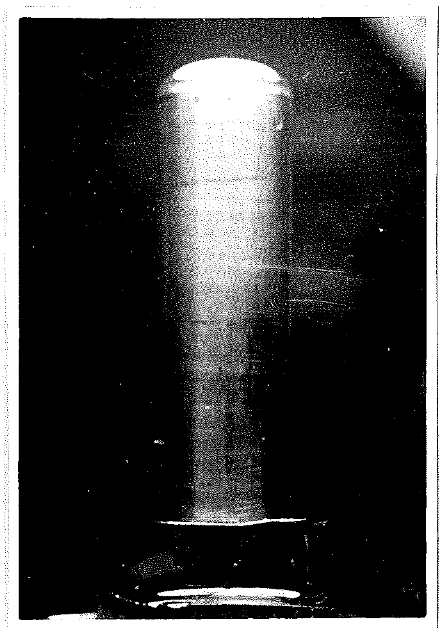


Fig.3

Kleurstof niet geinjecteerd.