

On the Absorption Velocity of Gases by Liquids.

II. Theoretical Considerations of Gas Absorption due to Chemical Reaction.

By

Sirôzi HATTA—*Kôgakushi.*

Introduction

Of the literature on the theories of gas absorption, the so-called double-film theory of Lewis and Whitman⁽³⁾ seems most remarkable. The fundamental idea of this theory has been discussed in more details by Davis and Crandall.⁽⁴⁾ According to this theory there exist two stationary films of gas and liquid on the respective sides of the boundary interface of the two phases. The gas being absorbed must pass through these films by diffusion. There should be, therefore, a pressure gradient of the gas being absorbed in the gas film, and a concentration gradient of the dissolved gas in the liquid film, as is shown in Fig. 1. Then the absorption velocity can be expressed by:

$$\frac{dW}{Ad\theta} = \frac{D_g}{t_g}(P_g - P_i) \dots\dots\dots (1)$$

$$\frac{dW}{Ad\theta} = \frac{D_l}{t_l}(C_i - C_l) \dots\dots\dots (2)$$

where dW is number of mols of gas being absorbed through area, A , in time, $d\theta$, so that $dW/Ad\theta$ expresses the absorption velocity in mols per unit area per unit time. D_g and D_l are diffusion coefficients in proper units; t_g and t_l are the respective film thicknesses; and P_g and P_i are the partial pressures of the gas being absorbed in the gas bulk at the interface; C_i and C_l are concentrations of dissolved

gas at the interface and in the liquid bulk respectively. Now, at the very interface the liquid is regarded as being always saturated with the gas corresponding to the partial pressure at that place, that is :

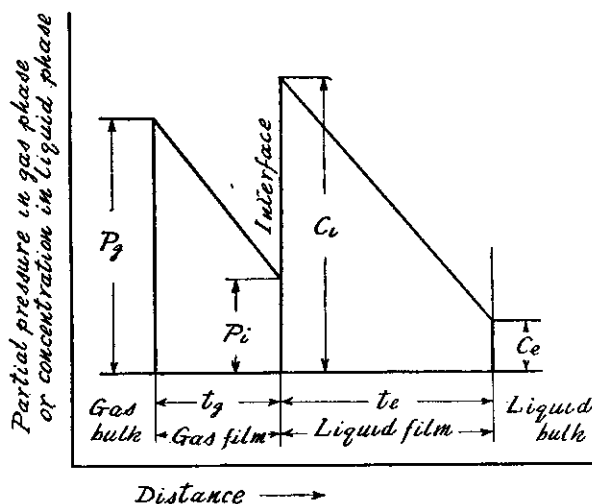


Fig.1. Distribution of partial pressure and concentration in the double film (No chemical reaction)

$$C_i = f(P_i) \dots\dots\dots (3)$$

which is determined by the solubility relation between pressure and concentration. If Henry's law is applicable, (3) becomes :

$$C_i = HP_i \dots\dots\dots (4)$$

where H is solubility coefficient of the gas in mols per atmosphere. From these three equations, (1), (2) and (4), they obtained a theoretical formula of absorption velocity. Particular formulae for very soluble, and for sparingly soluble gases also were derived. Since their original formula and the accompanying explanations seem somewhat complicated, the present author will give it in a somewhat transformed and supplemented by his own ideas. Another more important purpose of this transformation is for studying by comparison with it the formula of absorption velocity due to chemical reactions, which are to be chiefly considered in this paper.

The final formula of absorption velocity, transformed by the author, is :

$$\frac{dW}{Ad\theta} = \frac{HP_g - C_l}{\frac{H}{k_g} + \frac{1}{k_l}} \dots\dots\dots (5)$$

where $k_g = D_g/t_g$ and $k_l = D_l/t_l$, and they are called the film coefficients of the gas and the liquid film respectively. This formula, according to the author, resembles Ohm's law applied to two conductors in series, which is expressed by :

$$I = \frac{E}{R} = \frac{E}{\frac{1}{K_e} + \frac{1}{k_1} + \frac{1}{k_2}} \dots\dots\dots (6)$$

where k_1 , k_2 and K_e are two respective and the overall electric conductances. Comparing (5) and (6) it may be said : The absorption velocity, $dW/Ad\theta$, which corresponds to current, I , is proportional to "absorption potential," $(HP_g - C_l)$, which corresponds to electric potential, E , and is inversely proportional to "absorption resistance," $(H/k_g + 1/k_l)$, which corresponds to electric resistance, $1/K_e$ or $(1/k_1 + 1/k_2)$. By analogy with electric resistance, the absorption resistance is the sum of the respective resistances in series, so that H/k_g represents the resistance of the gas film, and $1/k_l$ that of the liquid film, and the total absorption resistance may be expressed by :

$$\frac{1}{K} = \frac{H}{k_g} + \frac{1}{k_l} \dots\dots\dots (7)$$

where K is called the overall coefficient of the double-film. Then (5) becomes :

$$\frac{dW}{Ad\theta} = K(HP_g - C_l) \dots\dots\dots (8)$$

It is evident by (8) that absorption velocity is zero, when the absorption potential, $(HP_g - C_l)$, is zero, which we call saturation. Let C_∞ be the saturation concentration, then it follows :

$$C_\infty = HP_g \quad \dots\dots\dots (9)$$

From the above general formula the following special cases can be derived.

(a) When the gas is very soluble, i. e., H is very large, (7) and (8) simplify respectively themselves to :

$$K = \frac{k_g}{H} \quad \dots\dots\dots (10)$$

$$\frac{dW}{Ad\theta} = k_g P_g \quad \dots\dots\dots (11)$$

which show that, in this case the liquid film resistance is negligible compared with that of the gas film, and the absorption velocity is proportional to the partial pressure in the gas bulk of the component being absorbed.

(b) When the gas is sparingly soluble, i. e., H is very small, (7) and (8) becomes :

$$K = k_l \quad \dots\dots\dots (12)$$

$$\frac{dW}{Ad\theta} = k_l(HP_g - C_l) \quad \dots\dots\dots (13)$$

which show that, in this case, the gas film resistance may be neglected compared with that of the liquid film.

Miyamoto has recently proposed a new theory of the rate of gas absorption into liquid, which is based on Maxwell's distribution law, and he believes he has derived, without the assumption of stationary boundary film, a formula of absorption velocity, which is substantially the same as (8).⁽⁶⁾ Maxwell's law, however, expresses a state under equilibrium, where the velocity distribution is uniform for all directions. He applies this law to a system, where a change,

i. e., absorption by liquid, is actually occurring, and in the vicinity of the boundary surface molecules having velocity components in the direction perpendicular from the boundary greater than some value are actually, lacking. (Such a non-uniformity of velocity distribution in the vicinity of the boundary is the true meaning of the film concepts). In other words, his calculation is based on the fundamental assumption of neglecting film effects. He also makes no reference to mixed gases of soluble and inert components, where actually the film resistance comes into question. Theories of gas absorption based on film concepts, therefore, are not at all effected by his theory.

Absorption due to Instantaneous Chemical Reaction

So far as purely physical absorption is concerned, the above formulae have been proved to be in satisfactory accord with experimental results. There are, however, many important cases of gas absorption, where the absorption is due to chemical reactions. In such cases the above formulae can no longer be applied.

Absorption of carbon dioxide by potassium hydroxide solutions is one of such cases. The author, assuming the reaction between CO₂ and KOH to occur instantaneously when they meet each other, and combining this with diffusion in the double-film, derived two formulae of this case,⁽¹⁾ which are as follows :

$$\text{For } \frac{x}{2P_g} < \frac{k_g}{sk_l}, \quad \frac{dW}{Ad\theta} = \frac{sx/2 + HP_g}{\frac{H}{k_g} + \frac{1}{k_l}} = K \left(\frac{sx}{2} + HP_g \right) \dots (14)$$

$$\text{For } \frac{x}{2P_g} > \frac{k_g}{sk_l}, \quad \frac{dW}{Ad\theta} = k_g P_g \dots \dots \dots (15)$$

where x is concentration of residual free KOH, and s is the diffusivity ratio of K₂CO₃ and CO₂ in liquid and may be taken as nearly unity. The transition between (14) and (15) is based on the fact

that the pressure of CO_2 , which is minimum at the interface, can not be negative.

Now, comparing (14) with (5) or (8), it will be seen that the effect of the instantaneous reaction is, for this range, equivalent to an increase of the absorption potential by $ax/2$ (C_l is, of course, zero), where $x/2$ may be considered the concentration of K_2O , which combines with CO_2 in molal ratio to form K_2CO_3 . Absorption resistance remains unchanged in this case. Now (15) is substantially the same as (11), which expresses the cases of very soluble gases, and the effect of the reaction of this range is equivalent to making the liquid film resistance zero.

Davis and Crandall have criticized the author's results.⁽⁵⁾ They say the reaction of CO_2 and KOH takes place in two stages. Although they do not show their assumed reactions, according to Fig. 1, Case C, of their paper, the reactions should not be other than as follows :

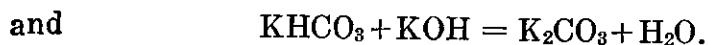
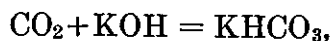
The first stage, $\text{CO}_2 + \text{K}_2\text{CO}_3 + \text{H}_2\text{O} = 2\text{KHCO}_3$, and

the second stage, $2\text{KHCO}_3 + 2\text{KOH} = 2\text{K}_2\text{CO}_3 + 2\text{H}_2\text{O}$.

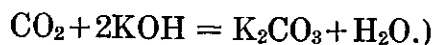
If their consideration were correct, the corresponding absorption velocity could be derived in a similar way to obtain finally :

$$\frac{dW}{Ad\theta} = K \left(\frac{a+x}{2} + HP_g \right) \dots\dots\dots (16)$$

where a is the total concentration of K . According to (16), under the same conditions absorption velocity by pure K_2CO_3 solutions (i.e., $x = 0$) should be somewhat greater than one half of that by pure KOH (i.e., $x = a$). Experimental results by the author disprove this.⁽¹⁾⁽²⁾ Though in these papers cited the author does not emphasize this fact, all the available data and plots show that the velocity by pure K_2CO_3 is much slower than one half of that by pure KOH . (As explained in the previous paper⁽¹⁾ the author is of the opinion, that this reaction occurs in two stages :



Both reactions, however, are very rapid and takes place successively at the same zone in the film, the result of which, therefore, is the same as the direct reaction :



According to the author, (14) and (15) are not limited to the absorption of carbon dioxide by potassium hydroxide solutions; there will be other cases of gas absorption due to similar mechanism.

Absorption due to Chemical Reaction of Moderate Velocity.

As reported in the next paper,⁽²⁾ under the same conditions absorption of CO_2 by K_2CO_3 solutions is much slower than that of the same gas by KOH solutions. The thickness of both films, the solubility, the diffusivity, and other physical properties do not seem to change very much with the replacement of KOH by K_2CO_3 ; the slowness of the absorption by the latter, therefore, should be due chiefly to the chemical reaction velocity. In fact, since OH^- concentration of carbonate solution is very small compared with that of hydroxide solution, it is natural to consider the reaction slow. Based upon these reasons the author considers the mechanism of absorption by K_2CO_3 as follows. CO_2 in gas bulk diffuses at first through the gas film to the interface, where it dissolves into liquid. While the dissolved gas diffuses through the liquid film, it is gradually consumed by reaction with K_2CO_3 to form KHCO_3 , in which form thereafter it diffuses to liquid bulk. Thus, only some fraction of the dissolved CO_2 reaches the bulk in free state, where it is completely reacted upon; this reaction in bulk may be regarded as sufficiently rapid, since the bulk is of a large volume.

According to this consideration pressure and concentration distribution of CO₂ in the double-film will be represented by Fig. 2. Then eqs. (1) and (4) can be applied as above.

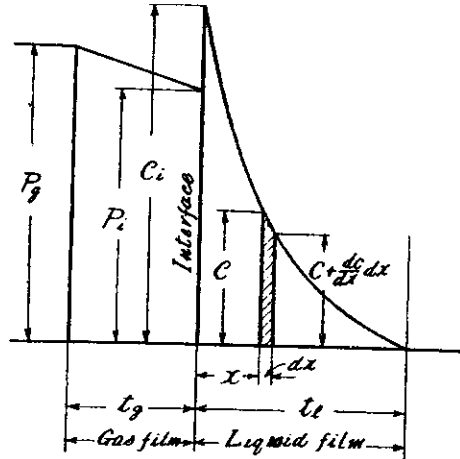


Fig. 2 Distribution of partial pressure and concentration in the double film (Reaction occurring with moderate velocity in liquid film)

$$\frac{dW}{Ad\theta} = \frac{D_g}{t_g}(P_g - P_i) \dots\dots\dots (1)$$

$$C_i = HP_i \dots\dots\dots (4)$$

In the liquid film, however, diffusion and chemical reaction take place simultaneously. The concentration distribution in liquid film shall be considered as follows. Let x be distance from the interface (Here, x is not the KOH concentration), and consider the space between two parallel planes, x and $x + dx$, then :

CO₂ diffusing in from the left side of plane x

$$= -AD_l \left(\frac{dC}{dx} \right) d\theta \dots\dots\dots (17)$$

CO₂ diffusing out to the right side of plane $x + dx$

$$= -AD_l \left(\frac{dC}{dx} + \frac{d^2C}{dx^2} dx \right) d\theta \dots\dots\dots (18)$$

CO₂ consumed in the space between x and $x + dx$

$$= (Adx) k_c C d\theta \dots\dots\dots (19)$$

where the reaction is taken as the first order with respect to CO₂, and k_c includes the velocity constant of the reaction and a term depending upon the mechanism of the reaction, and therefore upon the composition of the solution. By material balance we know that (17) = (18) + (19), therefore we obtain :

$$\frac{d^2C}{dx^2} = \frac{k_c}{D_l} C \dots\dots\dots (20)$$

which is the differential equation of the concentration distribution of CO₂ in the liquid film. Assuming k_c constant throughout the entire film at any instant, and solving (20) we obtain :

$$C = A_1 e^{\alpha x} + A_2 e^{-\alpha x} \dots\dots\dots (21)$$

where $\alpha = \sqrt{\frac{k_c}{D_l}} \dots\dots\dots (22)$

Determine A_1 and A_2 by putting $C = C_i$ at $x = 0$ and $C = 0$ at $x = t_l$, then we obtain :

$$C = \frac{\sinh \alpha (t_l - x)}{\sinh \alpha t_l} C_i \dots\dots\dots (23)$$

Therefore, $\frac{dC}{dx} = -\frac{\cosh \alpha (t_l - x)}{\sinh \alpha t_l} \alpha C_i \dots\dots\dots (24)$

Since at the very interface, $x = 0$, there will not yet be any appreciable chemical reaction and all the dissolved gas diffuses here, we obtain :

$$\frac{dW}{Ad\theta} = -D_l \left(\frac{dC}{dx} \right)_{x=0} = D_l \alpha C_i \frac{\cosh \alpha t_l}{\sinh \alpha t_l} \dots\dots\dots (25)$$

By somewhat transforming (25) we get :

$$\frac{dW}{Ad\theta} = \beta k_l C_i \dots\dots\dots (26)$$

where $\beta = \frac{\gamma}{\tanh \gamma} \dots\dots\dots (27)$

where
$$\gamma = t_l \sqrt{\frac{k_c}{D_l}} = \frac{\sqrt{k_c D_l}}{k_l} \dots \dots \dots (28)$$

Eliminating P_i and C_i from (1), (4) and (26), we finally obtain :

$$\frac{dW}{Ad\theta} = \frac{HP_g}{\frac{H}{k_g} + \frac{1}{\beta k_l}} \dots \dots \dots (29)$$

This equation (29), combined with (27) and (28), is the formula of absorption velocity derived from the above consideration. When the solution has some appreciable vapor pressure of CO_2 , P_i , eq. (23) and the subsequent ones will be somewhat more complicated. So far, however, as P_i is very small compared with P_g , the following modification of (29), which becomes identical with (29) when $P_i = 0$, may be adopted as the general formula of absorption velocity of the above mechanism :

$$\frac{dW}{Ad\theta} = \frac{H(P_g - P_i)}{\frac{H}{k_g} + \frac{1}{\beta k_l}} \dots \dots \dots (30)$$

Now, comparing (30) with (5), which is for purely physical absorption, and noticing that $C_i = HP_i$, it will be seen that the effect of the chemical reaction of moderate velocity within the liquid film is equivalent to multiplying the liquid film coefficient, k_l , by β . This β is connected with γ by (27), which is a purely mathematical equation, and the relation is plotted in Fig. 3. As is seen by the Figure, β is unity at $\gamma = 0$, and it increases very gradually with the increase of γ , while β becomes nearly equal to γ when γ is greater than 3. Furthermore, γ is determined by (28), and it is a dimensionless number (In order to get the correct value of γ , it is necessary to take k_c , D_l , t_l , and k_l in consistent units.) Now by analogy with (7) and (8), the following expressions may be used :

$$\frac{1}{K'} = \frac{H}{k_g} + \frac{1}{\beta k_l} \dots \dots \dots (31)$$

$$\frac{dW}{Ad\theta} = K'H(P_g - P_l) \dots\dots\dots (32)$$

where K' is the overall coefficient of the double-film with chemical reaction of moderate velocity.

It should be remembered, however, that the above derivation assumes the constancy of k_c throughout the entire film, which condition is usually not strictly the case. When the change of k_c within the film is remarkable, the formula cannot give a correct velocity. In such a case, however, the deviation can be at least qualitatively predicted.

As reported in the next paper⁽²⁾, the theoretical formula thus derived satisfies fairly well the experimental results of CO_2 absorption by K_2CO_3 solutions. Some deviation of the formula due to the remarkable change of k_c in the film were also observed, where the deviations were always in the same direction as expected by the theory.

Williamson and Mathews⁽⁷⁾ give the following qualitative expression for the rate of CO_2 absorption by alkaline solutions :

$$\text{Rate} = \frac{P-p}{R+r}$$

where P equals pressure in gas phase ; p , pressure in liquid phase ; R , gas film resistance ; r , liquid film resistance. This expression might seem the same as the author's (30). They mean, however, by r only diffusion resistance ; and therefore their expression is the same as (5), which is for purely physical absorption. They consider the action of alkali to be only to reduce the CO_2 pressure of the liquid phase, p . According to the present author, their expression satisfies experimental results only qualitatively, but not quantitatively.

The author does not mean to say that all cases of gas absorption accompanying chemical reaction of moderate velocity follow the above formula. There may be sometimes appreciable effects of other factors such as adsorption and crystallization. There may also be

quite different kinds of absorption mechanism. Such cases are not considered at all in this paper.

Inspection of the Formula for Moderate Reaction Velocity

The above theoretical formula of absorption velocity due to chemical reaction of moderate velocity is expressed by :

$$\frac{dW}{Ad\theta} = \frac{H(P_g - P_l)}{\frac{H}{k_g} + \frac{1}{\beta k_l}} \dots\dots\dots (30)$$

where $\beta = \frac{\gamma}{\tanh \gamma} \dots\dots\dots (27)$

where $\gamma = t_l \sqrt{\frac{k_c}{D_l}} = \frac{\sqrt{k_c D_l}}{k_l} \dots\dots\dots (28)$

Let us now consider the parameter, γ , in the formula. According to (28), γ becomes small when the reaction velocity is slow (*i.e.*, k_c small) or the film is thin (*i.e.*, t_l small) and γ becomes large when the reaction velocity is rapid or the film is thick. Referring to Fig. 3, *i.e.*, the plot of (27), when γ is very small, say, less than 0.2, β is nearly unity and almost independent of γ . In such a case the absorption formula becomes :

$$\frac{dW}{Ad\theta} = \frac{H(P_g - P_l)}{\frac{H}{k_g} + \frac{1}{k_l}} \dots\dots\dots (33)$$

which is substantially the same as (5), *i.e.*, the formula of purely physical absorption. It can be stated, therefore, that, when the reaction velocity is slow or the film is thin so as to make r less than 0.2, the effect of chemical reaction upon the absorption velocity becomes negligibly small. In the research of the absorption of CO_2 by K_2CO_3 solutions with a bubbling method, which will be reported later, such results were observed at low temperatures, and the

absorption velocity remained almost constant notwithstanding the successive changes of carbonate into bicarbonate; while in the study of absorption of the same gas by the same solutions with an unbroken surface,⁽²⁾ absorption velocity decreased successively with the changes of liquid composition. Such a difference can be easily understood to be due to the difference of γ in the above formula, if we notice the fact that the liquid film is much thinner with bubbles than with an unbroken surface.

When the reaction velocity is rapid or the film is thick so as to make γ great, say greater than 3, β become equal to γ , and the absorption formula becomes:

$$\frac{dW}{Ad\theta} = \frac{H(P_g - P_l)}{\frac{H}{k_g} + \frac{1}{\sqrt{k_e D_l}}} \dots\dots\dots (34)$$

which shows that, in such a case, absorption velocity is independent of the thickness of liquid film. Such results were experimentally verified at high temperatures in the absorption of CO₂ by K₂CO₃ solutions, where the reaction velocity is rapid.⁽²⁾

Now, k_e includes a term depending on the mechanism of the reaction in question. The nature of k_e , therefore, must be studied for each specific case. A particular case of the absorption of CO₂ by K₂CO₃ solutions were studied in the next paper.⁽²⁾

Now it should be noted that, although the boundary between the film and the bulk is actually ambiguous, the conventional idea of a definite film thickness has proved very useful for the conception of such phenomena. It will be interesting, therefore, to calculate the amount of the absorbed gas, which passes through the film and reaches the bulk in free state. This quantity is calculated, as follows, from the concentration gradient at the boundary between the film and the bulk, *i.e.*, at $x = t_l$; that is:

$$\frac{dW'}{Ad\theta} = -D_l \left(\frac{dC}{dx} \right)_{x=t_l} = D_l \alpha C_i \frac{1}{\sinh \alpha t_l} \dots\dots\dots (35)$$

where dW' is this quantity through area, A , in time, $d\theta$. Comparing (35) with (25) we obtain :

$$\delta = \left(\frac{dW'}{Ad\theta} \right) / \left(\frac{dW}{Ad\theta} \right) = \frac{1}{\cosh \gamma} \dots \dots \dots (36)$$

where δ is the fraction of dissolved gas reaching the bulk in free state. Since δ is a function of γ , like β , it is plotted against γ in Fig. 3. According to the plot, $\delta = 0.98$ at $\gamma = 0.2$, *i.e.*, 98% of the total absorbed gas passes through the film in free state; while $\delta = 0.10$ at $\gamma = 3$, *i.e.*, some 90% of total absorption is consumed within the film.

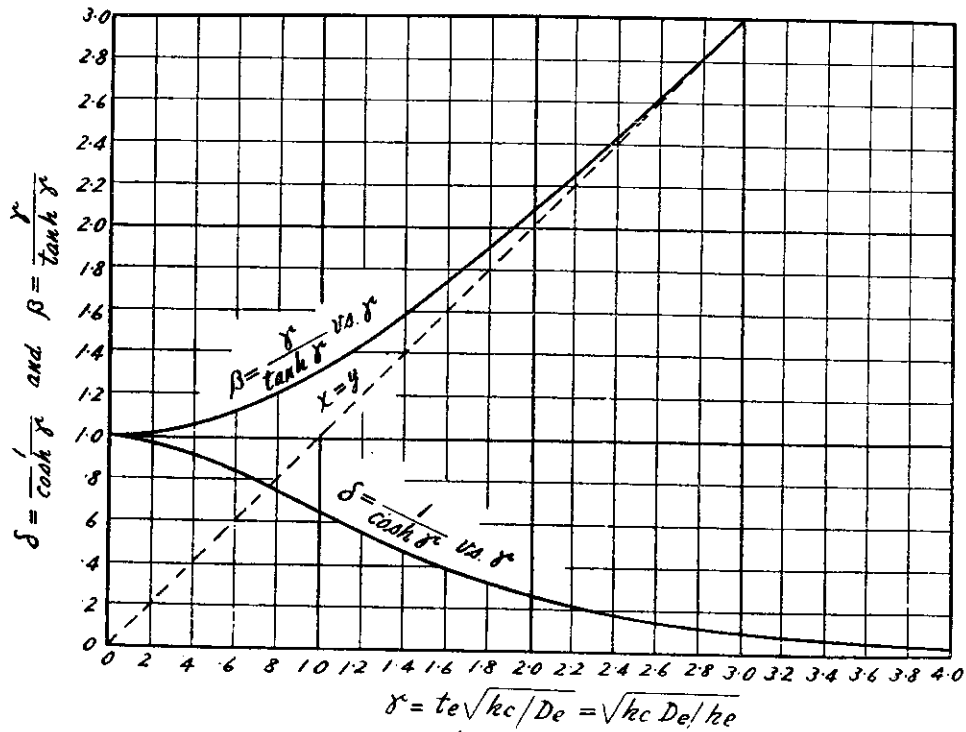


Fig. 3. $\frac{1}{\cosh \gamma}$ and $\frac{\gamma}{\tanh \gamma}$ vs γ

The above results explained by the formulae (33), (34) and (36) may be qualitatively conceivable even without such mathematical formulae. The author, however, has solved the phenomena explicitly by mathematical expressions, not only qualitatively but also quantitatively. He has found the presence of an interesting parameter, γ ,

which is defined by the mechanism and velocity of the chemical reaction, the diffusion coefficient, and the thickness of the liquid film, as expressed by (28).

Summary

(I) Lewis and Whitman's so-called double-film theory was cited, and the formula of absorption velocity of the original authors was somewhat transformed by the present author's own ideas, the result of which is expressed by :

$$\frac{dW}{Ad\theta} = \frac{HP_g - C_l}{\frac{H}{k_g} + \frac{1}{k_l}} \dots\dots\dots (5)$$

By comparing this formula with Ohm's law applied to the case of two conductors in series, and using the terms, "absorption potential" and "absorption resistance," the result was made very clear to conceive. Another more important purpose of this transformation is for studying by comparison with it the formulae of absorption velocity due to chemical reactions, which are to be chiefly studied in this paper.

(II) The formulae of absorption velocity due to instantaneous reactions in liquid film, which had already been reported, were now referred to, that is :

For $\frac{x}{2P_g} < \frac{k_g}{sk_l}$, $\frac{dW}{Ad\theta} = \frac{sx/2 + HP_g}{\frac{H}{k_g} + \frac{1}{k_l}} \dots\dots\dots (14)$

For $\frac{x}{2P_g} > \frac{k_g}{sk_l}$, $\frac{dW}{Ad\theta} = k_g P_g \dots\dots\dots (15)$

where $x/2$ is concentration of the solute reacting in molal ratio with the gas being absorbed, and s is diffusivity ratio of the reaction product and the dissolved gas. The existence of two formulae for different ranges of condition is due to the fact that a pressure cannot

be negative. Noticing that C_l is zero, and by comparing (14) with (5) it will be seen that in this range the absorption resistance remains unchanges, and the effect of the reaction is equivalent to adding $sx/2$ to absorption potential. Comparing (15) with (5) it will be seen that in this range the effect of the reaction is equivalent to reducing liquid film resistance, $1/k_l$, to zero.

(III) A formula of absorption velocity due to chemical reaction of moderate velocity was newly derived. The absorption velocity of this case is expressed by :

$$\frac{dW}{Ad\theta} = \frac{H(P_g - P_l)}{\frac{H}{k_g} + \frac{1}{\beta k_l}} \dots\dots\dots (30)$$

where $\beta = \frac{\gamma}{\tanh \gamma} \dots\dots\dots (27)$

where $\gamma = t_l \sqrt{\frac{k_c}{D_l}} = \frac{\sqrt{k_c D_l}}{k_l} \dots\dots\dots (28)$

According to this result it may be said that the effect of the chemical reaction in this case is equivalent so increasing the liquid film coefficient, k_l , by a certain multiple, β , which is determined by (27) and (28). The term, k_c , depends on the velocity constant and the mechanism of the reaction, so that no general formula of k_c can be given, and the nature of k_c must be studied for each specific case. For the absorption of CO_2 by K_2CO_3 solutions, which is reported in the next paper, the formula of k_c was determined, and at the same time the mechanism of the reaction was made clear. According to the character of (27), if the parameter, γ , is less than 0.2, β becomes nearly unity, and the effect of chemical reaction on the absorption velocity is negligible, and the formula becomes identical with (5), which is for pure physical absorption; while, if γ is greater than 3, β becomes nearly equal to γ , and the formula becomes :

$$\frac{dW}{Ad\theta} = \frac{H(P_g - P_l)}{k_g + \frac{1}{\sqrt{k_c D_l}}} \dots\dots\dots (34)$$

which is independent of the thickness of liquid film.

The fraction of dissolved gas reaching the bulk in free state also was calculated to be :

$$\delta = \frac{1}{\cosh \gamma} \dots\dots\dots (36)$$

According to (36), when γ is 0.2, some 98% passes through the film in free state; while, when γ is 3, about 90% is reacted upon within the film.

The author does not mean to say that all cases of gas absorption due to chemical reactions follow the above formulae. There may be in some cases appreciable effects of some other factors, such as adsorption, crystallization and so on. There may also be quite different kinds of absorption mechanism. Such cases have not been considered at all in this paper. At any rate, experimental results of absorption of CO₂ by K₂CO₃ solutions, which are reported in the next paper, satisfy fairly well the above formula of moderate reaction velocity.

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On the Absorption Velocity of Gases by Liquids.

III. Absorption of Carbon Dioxide by Potassium Carbonate Solution.

By

Sirôzi HATTA—*Kôgakushi.*

Introduction

In the previous paper⁽¹⁾ the author studied the absorption velocity of carbon dioxide by potassium hydroxide solutions, and made clear the mechanism of the absorption. Now he has studied the absorption velocity of the same gas by potassium carbonate solutions. This absorption is industrially used for the manufacture of solid and liquid carbon dioxide from combustion gases. In the literature on the subject we find papers by Riou,⁽²⁾ by Williamson and Mathews,⁽³⁾ and by Sieverts and Fritzsche.⁽⁴⁾ Riou gives plenty of experimental data, but gives no theoretical explanations. Williamson and Mathews used a small tower, and their results are practically interesting, but theoretically are not yet sufficient. Sieverts and Fritzsche used a bubbling method, and consequently there is a great deficiency that they can not know the contact area of the gas and the liquid. There are also some discrepancies among the results of these authors. In this paper the author used the same apparatus with proper modifications as that of the previous paper, and combining both the results he believes he has made clear the mechanism of this absorption.

Apparatus and Experimental Procedure

Fig. 1 shows the main parts of the apparatus (Refer to the previous paper). The absorber is a vertical cylinder, i.d. 8 cm., of Monel metal, containing a definite volume of K_2CO_3 solution.

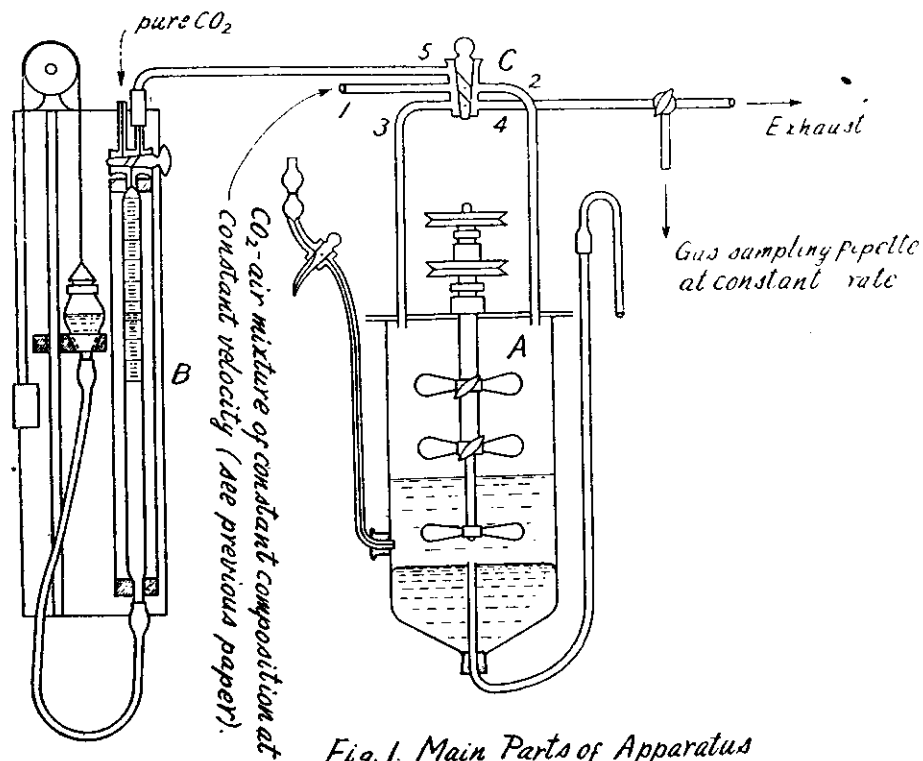


Fig. 1. Main Parts of Apparatus

Liquid and gas phases are stirred with respective stirrers rotating at mutually independent velocities. Carbon dioxide and air mixture of a definite composition, previously brought to the experimental temperature and moderately humidified, is supplied at a constant rate to the absorber, and the excess leaves it. The rate of the gas supply is sufficiently large to avoid a change of gas composition in the absorber due to the change of the absorption velocity. Thus, absorption takes place at a definite area of contact surface, 0.50 sq.dm. At first, the temperature, velocities of both stirrers, and the rate of gas supplies are all adjusted to the required conditions before charging the solution. Then a definite volume, 125 c.c., of potassium carbonate solution is introduced (Actually, most experiments were started from KOH solutions, the reason being explained later). According to the progress of absorption, carbonate is transformed into bicarbonate, and the composition of the solution changes successively. It is the main object of each experiment to study the change

of absorption velocity according to this change of solution composition.

Since the absorption by K_2CO_3 is found to be much slower than that by KOH , a smaller amount of solution is used, and in order to keep unchanged as much as possible the position and the other conditions of the liquid surface, a certain volume of mercury was charged at the bottom of the absorber. To get sufficiently reliable data at the range of absorption velocity of this paper, the measuring methods are all necessarily changed from those of the previous paper. The new methods are as follows.

For the measurement of the absorption velocity, the absorber, *A*, is connected with a special cock, *C*, to a gas burette, *B*. Except at the velocity measuring time, the cock, *C*, is turned to such a position that the burette is closed, and the CO_2 -air mixture is supplied to the absorber, and the excess of gas leaves it to waste. To make velocity measurement the cock is turned to the position as shown in the Figure. CO_2 -air mixture is now wasted directly, while the absorber is connected with the burette, *B*, in which pure CO_2 is stored over a saturated solution of $NaCl$, which has been previously saturated with CO_2 . Now, the volume decrease of CO_2 in the burette in a definite time interval, usually one minute, is carefully read, from which the absorption velocity is calculated.

The composition of the solution at any instant, that is, the proportion of carbonate and bicarbonate, is determined by a special gas-volumetric method, i.e., by measuring the CO_2 gas volume, which is evolved by the action of sulphuric acid on a definite volume of liquid sample. Details of this method will be reported in a separate paper.⁽³⁾ Using always a constant volume of the acid of a definite concentration, and making a proper correction to the observed volume due to a moderate solubility of CO_2 , this method gives a fairly satisfactory result, and it takes only a few minutes. Generally the velocity measurement and the liquid sampling were made alternately.

Such experiments were made under various conditions of temperature, CO₂ percent in gas phase, velocity of either stirrer, and concentration of the solution.

Example of Measurements and Velocity Calculations

An example of measurements and velocity calculation therefrom is shown in Table 1, where the experiment was started from KOH, and the conditions are as given in the Table. The second column, V in c.c., is CO₂ volume obtained by the gas-volumetric analysis from the sample taken at the time of the first column. The fourth column, v in c.c., is CO₂ volume absorbed in one minute beginning at the time of the third column. The fifth column, absorption velocity, $dW/Ad\theta$, in mols CO₂ per hour per sq. dm., was calculated from v by:

$$\frac{dw}{Ad\theta} = 60(v) \left(\frac{273}{273+t} \right) \left(\frac{B-p}{760} \right) \left(\frac{1}{mA} \right),$$

where B is barometric pressure; p , vapor pressure of saturated NaCl solution, which is about 77% of water; A , contact area, 0.50 sq. dm.; and m , molal volume of CO₂ at N.T.P., 22,260 c.c.

While there still remained free hydroxide the absorption velocity was too rapid to be measured by the same burette unchanged. The absorption velocity of this range, therefore, was calculated by the successive differences of V of the second column. The sixth column, V_{mean} , is the successive mean of V , and corresponds to the time of the velocity measurement. The seventh column, X , is ratio of the total CO₂ and the total potassium concentrations in the solution, and was calculated by:

$$X = V_{mean} \left(\frac{273}{273+t} \right) \left(\frac{B-p}{760} \right) \left(\frac{1}{mc} \right),$$

where c is c.c. of N/10-HCl solution used for the titration of the same volume at that for the gas-volumetric analysis, methyl-orange being an indicator, and it measures the total alkali, or total potassium in the sample. Now c was 0.206 c.c. in this experiments.

Consider now the meaning of $X = [\text{CO}_2]_{\text{total}} / [\text{K}]_{\text{total}}$. It is evident that $X = 0, 0.5$ and 1 for pure $\text{KOH}, \text{K}_2\text{CO}_3$ and KHCO_3 respectively; X lies between 0 and 0.5 for $\text{KOH-K}_2\text{CO}_3$ mixtures, and between 0.5 and 1 for $\text{K}_2\text{CO}_3\text{-KHCO}_3$ mixtures. Let the total alkali concentration, i.e., $[\text{K}]_{\text{total}}$ be a , then by definition of X , $[\text{CO}_2]_{\text{total}} = aX$. Let further for $\text{KOH-K}_2\text{CO}_3$ mixtures, $[\text{KOH}] = x$ and $[\text{K}_2\text{CO}_3] = y$, then

$$\left. \begin{aligned} x &= a(1-2X) \\ y &= aX \end{aligned} \right\} \dots\dots\dots (1)$$

where x lies between 0 and 0.5 . Let also be for $\text{K}_2\text{CO}_3\text{-KHCO}_3$ mixtures, $[\text{K}_2\text{CO}_3] = y$ and $[\text{KHCO}_3] = z$, then

$$\left. \begin{aligned} y &= a(1-X) \\ z &= a(2X-1) \end{aligned} \right\} \dots\dots\dots (2)$$

where x lies between 0.5 and 1 .

According to these equations for both $\text{KOH-K}_2\text{CO}_3$ and $\text{K}_2\text{CO}_3\text{-KHCO}_3$ mixtures together, the concentration of either component, and therefore the composition of the solution, can be expressed conveniently by this term, X . This method of expression is used in this paper and in the subsequent ones.

Thus, the results of Table 1 are shown graphically in Fig. 2, where the abscissa is X , and the ordinate is the absorption velocity, $dW/Ad\theta$. For illustration, $[\text{KOH}], [\text{K}_2\text{CO}_3]$, and $[\text{KHCO}_3]$ given by (1) and (2) are recorded in abscissa. Absorption velocity for the range of X less than 0.5 , i.e., absorption by KOH has already been studied.⁽¹⁾ The absorption velocity for X greater than 0.5 , i.e., absorption by K_2CO_3 , will be seen to be much slower than that by KOH . The velocity by carbonate solution decreases with the increase of X at first rapidly, then somewhat gradually, and at last again rapidly, so that the form of the curve seems to indicate that the relation between the absorption velocity and X is not very simple.

Table 1.

An Example of Measurements and Velocity Calculations.

(Exp. No. 39, started from 1*N*-KOH solution, liquid volume 125 c.c., CO₂ in gas 98%, liquid and gas stirrers 93 and 350 r.p.m. respectively, liquid sample 0.2060 c.c., gas measured at 11°C., $B-p = 763-7 = 756$ mm.)

Time	V	Time	v	$\frac{dW}{Ad\theta}$	V_{mean}	X
3'	0.96					
8'	1.40	—	—	0.272	1.18	0.246
13'	1.74	—	—	0.210	1.57	0.327
18'	2.00	—	—	0.161	1.87	0.390
27'	2.32	—	—	0.110	2.16	0.450
39'	2.60	32.5'	14.45	0.0745	2.46	0.512
51'	2.84	44.5'	12.30	0.0633	2.72	0.566
1h 6'	3.08	58'	10.52	0.0542	2.96	0.616
21'	3.30	1h 13'	9.38	0.0483	3.19	0.665
36'	3.58	28'	8.53	0.0439	3.44	0.716
51'	3.75	43'	7.70	0.0396	3.67	0.765
2h 6'	3.96	58'	7.02	0.0362	3.84	0.800
21'	4.06	2h 13'	6.38	0.0329	4.00	0.834
36'	4.21	28'	5.86	0.0302	4.14	0.863
51'	4.32	43'	5.38	0.0277	4.27	0.890
3h 6'	4.40	58'	4.91	0.0253	4.36	0.908
21'	4.46	3h 13'	4.31	0.0222	4.43	0.923

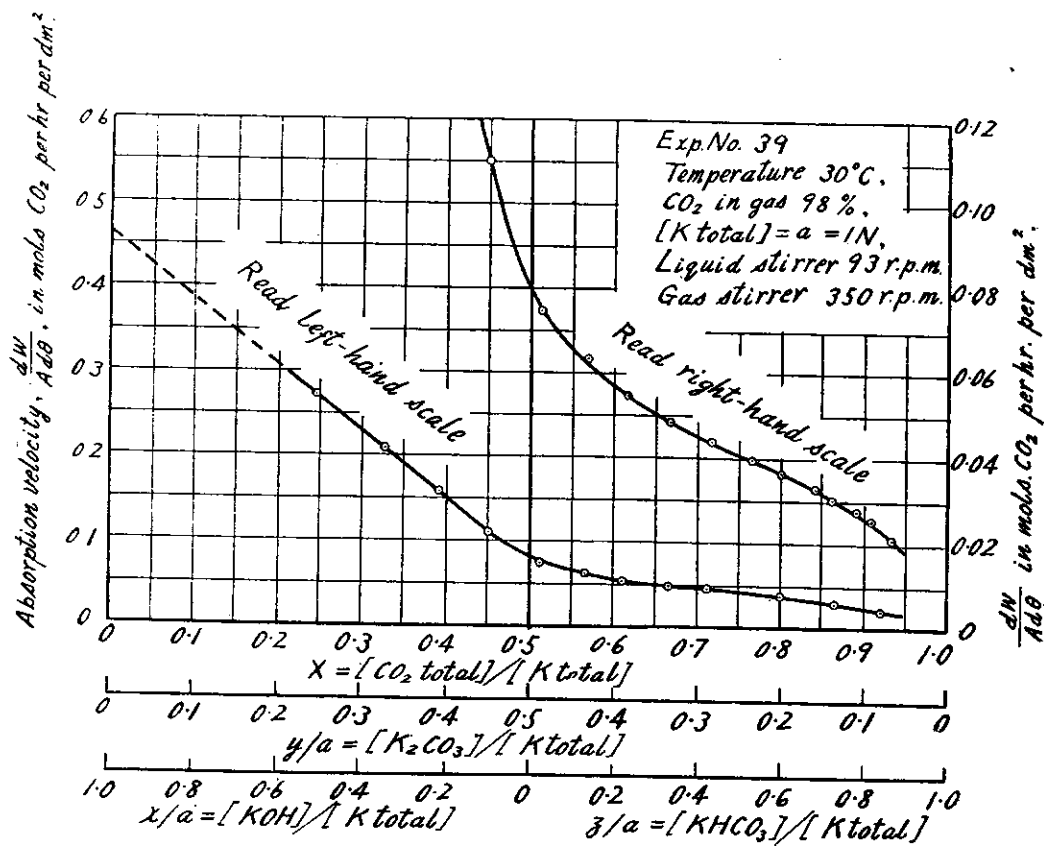


Fig 2 An example of observed absorption velocity vs. liquid composition.

Theoretical Considerations

The absorption mechanism of CO_2 by KOH solutions has been already made clear by the author⁽¹⁾ by combining the double-film theory of Lewis and Whitman⁽⁴⁾ and the chemical reaction velocity, in which the reaction between CO_2 and KOH was regarded as taking place instantaneously as soon as they meet each other. The theoretical formula of absorption velocity consists of two equations for different ranges of conditions, one of which is:

$$\left(\frac{dW}{Ad\theta}\right)_{\text{KOH}} = \frac{HP_g + sx/2}{\frac{H}{k_g} + \frac{1}{k_l}} \dots\dots\dots (3)$$

where P_g is the partial pressure of CO_2 in the gas phase; H , solubility coefficient of CO_2 in mols per atmosphere; k_g and k_l , film coefficients of the gas and liquid films respectively. Putting x of (1) in (3) we obtain:

$$\left(\frac{dW}{Ad\theta}\right)_{\text{KOH}} = \frac{HP_g + (1-2X)sa/2}{\frac{H}{k_g} + \frac{1}{k_l}} \dots\dots\dots (4)$$

which represents the straight line in Fig. 2 in the range of X between 0 and 0.5, and its slope, m , is expressed by:

$$m = -\frac{sa}{\frac{H}{k_g} + \frac{1}{k_l}} \dots\dots\dots (5)$$

As will be seen later, the value of m under a definite condition is necessary for the theoretical treatment of the absorption velocity by K_2CO_3 under the same condition.

Now, as to the range of X greater than 0.5, i.e., absorption by carbonate, the thickness of both films, the dissolution, the diffusion and other physical phenomena will remain almost unchanged. The slowness of the absorption by K_2CO_3 should be due, therefore, chiefly