Int. J. Heat Mass Transfer. Vol. 5, pp. 429–433. Pergamon Press 1962. Printed in Great Britain.

PIONEER PAPERS IN CONVECTIVE MASS TRANSFER

5. W. G. WHITMAN: The two-film theory of gas absorption, *Chemical and Metallurgical Engineering* **29**, 146–148 (1923). Reprinted with permission from *Chemical Engineering*, Copyright 1923, McGraw-Hill Publishing Co.

Editor's Foreword

In the preface to their book *Absorption and Extraction* (McGraw-Hill, 1951), Sherwood and Pigford state: "Methods of applying the Whitman 'two-film' theory to various design problems have been extended and refined, but it is curious that after 28 years the theory itself has never been adequately checked experimentally". Whatever may be meant by an "adequate check" in this case, their remark at least shows the central position which the Whitman idea has occupied in the thinking of chemical engineers. Now that "films" have been replaced by "boundary layers" in the mass transfer literature, it is interesting to note that Whitman was quite clear in 1923 that the film of definite thickness was a fiction, as witness his phrase: "actually no such sharp demarcation exists".

D.B.S.

A Preliminary Experimental Confirmation of

THE TWO-FILM THEORY OF GAS ABSORPTION*

It Seems to Explain Satisfactorily the Well-Recognized Differences of Absorption Rate for Varying Concentrations

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THE various theories for the mechanism of gas absorption proposed within the past 8 years agree on the general form for the absorption equation. Essentially these all assume that the rate of absorption is proportional to a potential factor multiplied by certain coefficients which are dependent upon the construction and size of the absorbing apparatus and the operating conditions.

$$\frac{dW}{d\theta} = \text{coefficient times driving potential} \quad (1)$$

where

W = amount of gas absorbed

θ = time for this absorption.

A considerable divergence is noted, however, in formulations of the potential factor. In all cases, this driving potential is proportional to the difference between actual conditions and conditions at equilibrium—i.e. it is proportional to the distance from equilibrium. Certain writers [Lewis, *J. Ind. Eng. Chem.*, vol. 8, p. 825 (1916); Whitman and Keats, *J. Ind. Eng. Chem.*, vol. 14, p. 185 (1922)] have expressed the potential as the difference between the partial pressure of solute in the gas and the partial pressure of solute exerted by the liquid. Others [Donnan and Masson, *J. Soc. Chem. Ind.*, vol. 39, p. 236T

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* Few subjects are creating more interest both theoretically and practically than gas absorption. For years entirely empirical in its applications and even yet preponderantly so, there have been developed several theories that seem to shed some light on its mechanism. This paper clears up some of the fog around the potential factor. It will contribute in helping to put this unit process on a substantial basis. One of the slogans should perhaps be, "No more monstrosities as absorption towers!" No more of the old formula, "Let's make it a foot bigger in diameter and 5 ft higher just for good luck".

(1920); Van Arsdel, *Chem. & Met.*, vol. 23, p. 1115 (1920), and vol. 28, p. 889 (1923)] picture the potential as a difference between the concentration of solute in the gas (converted into concentration in the liquid by the solubility relationship) and the concentration in the liquid. These two concepts may be expressed as follows:

$$\text{Driving potential} = p_g - p_l = p \tag{2}$$

$$\text{Driving potential} = c_g - c_l = c \tag{3}$$

where p_l = the partial pressure of solute exerted by the liquid, and

c_g = the concentration of liquid which would be in equilibrium with the gas.

The two different formulations give the same result for the specific case of absorption at constant temperature using a solute which obeys Henry's law—i.e., $p = kc$. Under these conditions, $\Delta p = k\Delta c$, and either expression would be permissible.

Consideration of the physical significance of these terms shows the cause of this divergence. In all cases (except where a slow chemical reaction is involved) the rate of absorption is controlled by the rate of diffusion through the surface films at the gas-liquid boundary. The first concept pictures diffusion through a gas film, actuated by a difference in the partial pressure of the solute at the outside of the film (in the main body of gas) and the inside of the film (in equilibrium with the liquid). The other concept considers diffusion through a liquid film on the surface of the main body of liquid with diffusion controlled by a difference in concentration between the outside of the film (in equilibrium with the gas) and the inside (the true liquid concentration). Actually, the choice between these two theories has been made in the past by selecting the one which gave most consistent results in the experiments under investigation at the time.

In 1922, Keats and the author published experiments (Whitman and Keats, *J. Ind. Eng. Chem.*, vol. 14, p. 185) contrasting the processes of humidification and dehumidification, and comparing heat transfer with absorption in general. From the work on humidification and dehumidification it was shown that the rate of diffusion is controlled by two surface films, an exterior gas film surrounding the liquid, and a liquid film on the surface of the liquid. The relative importance of these two films varied with the experimental conditions, the liquid film resistance being eliminated in humidification processes and amounting to 75 per cent of the total for certain dehumidification runs. Furthermore, the effect of such variables as liquid and gas velocities on the resistances of the separate films differed to a considerable extent.

In the article referred to, no attempt was made to point out the significance of the two-film theory in absorption problems. It is the purpose of this paper to present this view of the absorption process and illustrate its application.

Fig. 1 shows a liquid in contact with gas from which the solute is being absorbed. The gas and liquid films at the boundary can be indicated as having a definite thickness, although actually no such sharp demarcation exists. Conditions at the outside of the gas film (1) are the same as in the main body of gas, while those at the inside of the liquid film (3) are the same as in the main body of liquid. The gas and liquid at the boundary between the two films (2) are in equilibrium. Absorption occurs therefore through two films in series. Diffusion through the gas film should

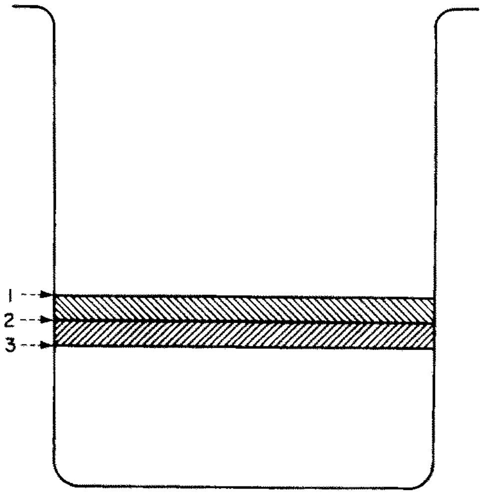


FIG. 1. Contact of gas and liquid phase.

be determined by a partial pressure gradient of the solute—i.e., (by $p_1 - p_2$) and through the liquid film by a concentration gradient ($c_2 - c_3$). The following equations represent the process:

$$\frac{\mathrm{d}W}{\mathrm{d}\theta} = k_p(p_1 - p_2) = k_c(c_2 - c_3) \qquad (4)$$

where k_p = the coefficient of diffusion through the gas film, and

k_c = the coefficient of diffusion through the liquid film.

The values of k_p and k_c will, of course, be dependent on experimental conditions.

Comparison of this equation with the two previously proposed:

$$\frac{\mathrm{d}W}{\mathrm{d}\theta} = K_p(p_1 - p_3) \qquad (5)$$

$$\frac{\mathrm{d}W}{\mathrm{d}\theta} = K_c(c_1 - c_3) \qquad (6)$$

(where K_p and K_c are overall coefficients) explains why neither of the latter have broad application. Theoretically equations 5 and 6 should apply only when the concentration is directly proportional to the pressure. Under other conditions it is usually not permissible to use an overall coefficient K_p or K_c with an overall potential ($p_1 - p_3$) or ($c_1 - c_3$), since there are two separate potential factors involved and there is no direct proportionality between them.

Many cases cannot be handled by such arbitrary simplifications. For example, if the deviation from Henry's law or if the temperature range is considerable, a simplification based on direct proportionality between p and c would be unjustified and the overall coefficients K_c or K_p would have no significance.

Such a case is illustrated in the absorption of hydrochloric acid. A series of absorption experiments with this gas were made at a constant temperature of gas and liquid of 30 deg. C. The pressure solubility relations at this temperature are shown in Fig. 2 on co-ordinate and in Fig. 3 on semi-log plots.

It is important to note that the partial pressure of HCl over aqueous solutions of the acid is negligible up to concentrations of approximately 250 g/l, but that it rises rapidly with increase in acid concentration above this range.

Since for acid concentrations up to about 250 g/l the partial pressure of HCl is negligible, it follows that acids the surface concentration of which is below this figure will absorb gas as rapidly as it can reach the surface—i.e. rate of absorption is determined solely by rate of diffusion through the gas film and the equation for absorption rate becomes $\mathrm{d}W/\mathrm{d}t = K_p p_1$. Furthermore, K_p is in this case identical with k_p.

However, at high concentrations of acid, the equilibrium pressure on the surface becomes large and also changes rapidly with the concentration. Consequently the absorption of a small amount of acid into the surface brings the surface into substantial equilibrium with the gas, thereby preventing absorption until the absorbed acid has diffused through the liquid film into the interior. However, owing to the shape of c–p curve, the available concentration gradient is slight and consequently the rate of diffusion slow. This explains the well-recognized fact that for the same pressure gradient the rate of absorption into the dilute towers of a hydrochloric acid system is far more rapid than in those towers containing strong acid.

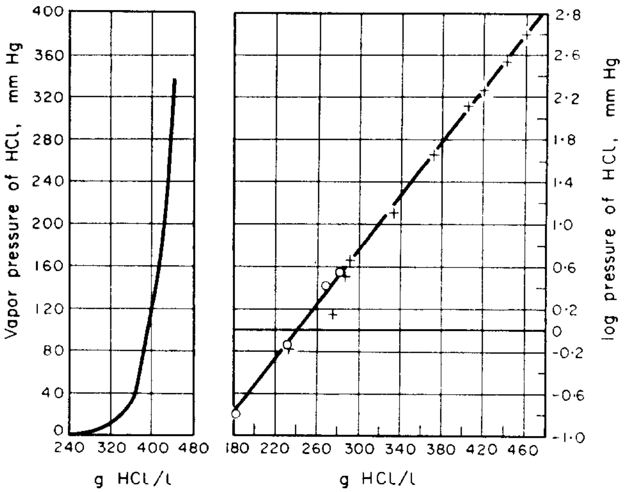
Table 1 presents data obtained in absorption runs under different concentrations and pressures, and the coefficients which should be

Table 1

Run	$\frac{\mathrm{d}W}{\mathrm{d}\theta}$	P_1	P_3	Δp	C_1	C_3	Δc	K_p	K_c
		mm Hg			g/l				
1	41·0	225	55	170	425	378	47	0·24	0·87
2	24·0	41	0·3	40·7	368	204	164	0·59	0·146
3	24·1	41	0	41·0	368	9	359	0·59	0·067

obtained by assuming either a gas or a liquid diffusion alone.

Comparison of runs Nos. 1 and 2 shows that K_p increases nearly two and one-half fold in the latter case. The values for K_c vary even more, that for the first run being twelvefold that for run 3. It will be noted that the values of K_p for runs 2 and 3 are identical, although those for K_c differ more than twofold. The conditions of these runs represent a specific limiting case where treatment by the pressure potential alone is permissible.



FIGS. 2 and 3.
FIG. 2. (At left)—Pressure–solubility relationship at 30 deg. C. FIG. 3 (At right)—Semi-log plot of Fig. 2. The crosses in Fig. 3 represent data by Dolezalek, *Z. ph. ch.*, vol. 26, p. 334 (1898). and the circles are data by Bates and Kirschman, *J. Am. Chem. Soc.*, vol. 41, 1897 (1919).

These data can be treated from the two-film concept as follows. From equations 4 and 5

$$\frac{k_c}{k_p} = \frac{p_1 - p_2}{c_2 - c_3} \tag{7}$$

and

$$\frac{K_p}{k_p} = \frac{p_1 - p_2}{p_1 - p_3} \tag{8}$$

By assuming that the value of K_p from run 3 (where the liquid is so dilute that the back pressure p_2 is practically zero) equals k_p, run 1 can be used to calculate k_c.

$$\frac{K_p}{k_p} = \frac{0{\cdot}24}{0{\cdot}59} = \frac{225 - p_2}{225 - 55}$$

$$p_2 = 156 \text{ mm}$$

and the corresponding concentration, c_2, from Fig. 3, is 412 g/l.

$$k_c = \frac{W}{\theta}(c_2 - c_3) = \frac{41{\cdot}0}{412 - 378} = 1{\cdot}2$$

It is now possible to check these figures in a general way by applying them to run 2.

$$\frac{k_c}{k_p} = \frac{1{\cdot}2}{0{\cdot}59} = \frac{p_1 - p_2}{c_2 - c_3} = \frac{41 - p_2}{c_2 - 204}$$

Referring again to Fig. 3 for corresponding values of p_2 and c_2, the equation is satisfied by $p_2 = 0{\cdot}6$ mm and $c_2 = 224$ g/l.
Therefore,

$$\frac{dW}{d\theta} = k_c(c_2 - c_3) = 1{\cdot}2 \times 20 = 24 \text{ g/h},$$

checking with the observed value in Table 1.

It is recognized that the data presented in this illustration are insufficient to prove definitely the truth of the two-film theory, and further work has been started along the same lines. It does, however, show clearly that the methods formerly proposed are entirely incapable of handling cases of this nature, and that the concept of a single gas or liquid film is permissible only when the relationship between concentration and pressure is approximately a direct proportion. For the more complicated problems, the two-film theory seems fundamentally sound and the preliminary experiments have afforded checks as to its validity.