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.

(1) $\dfrac{dW}{d\theta}$ = coefficient times driving potential

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 (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:

(2) Driving potential = $p_g - p_l = p$
(3) Driving potential = $c_g - c_l = c$

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 demarkation exists. Conditions at the outside of the gas film (1)

> 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."

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.
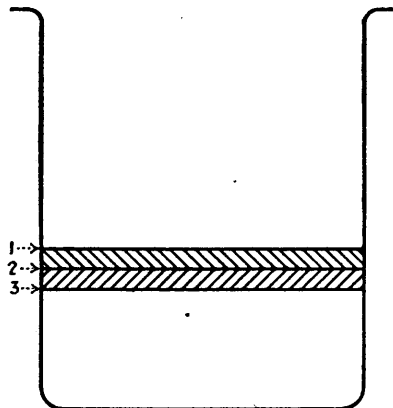

FIG. 1—CONTACT OF GAS AND LIQUID PHASE

Diffusion through the gas film should 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:

$$(4) \quad \frac{dW}{d\theta} = k_p(p_1 - p_2) = k_c(c_2 - c_3)$$

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:

$$(5) \quad \frac{dW}{d\theta} = K_p(p_1 - p_3)$$

$$(6) \quad \frac{dW}{d\theta} = K_c(c_1 - c_3)$$

(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 grams per liter, but that it rises rapidly with increase in acid concentration above this range.

Since for acid concentrations up to about 250 grams per liter 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 $dW/d\theta = K_p p_1$. 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 I presents data obtained in absorption runs under different concentrations and pressures, and the coefficients which should be obtained by assuming either a gas or a liquid diffusion alone.

TABLE I

Run	$\frac{dW}{d\theta}$	P_1	P_3	Δp	C_1	C_3	Δc	K_p	K_c
		mm. Hg			gms. per liter				
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

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
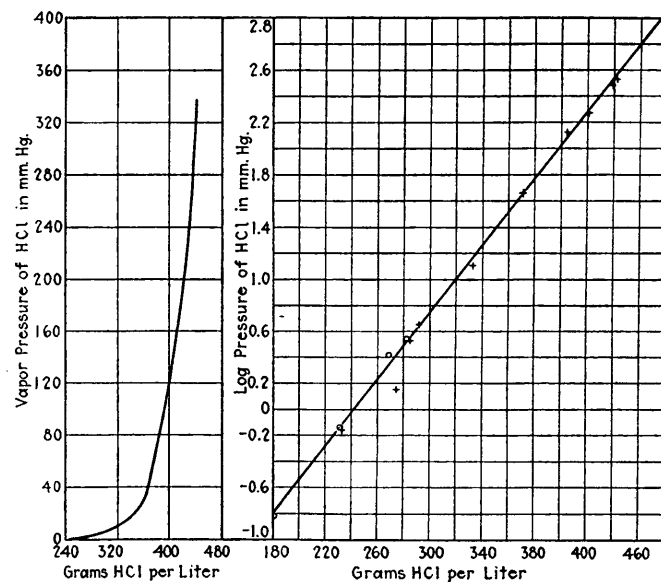
FIGS. 2 AND 3

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 circled crosses are data by Bates and Kirschman, *J. Am. Chem Soc.*, vol. 41, 1897 (1919).

where treatment by the pressure potential alone is permissible.

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

$$(7) \quad \frac{k_c}{k_p} = \frac{p_1 - p_2}{c_2 - c_3} \quad \text{and} \quad (8) \quad \frac{K_p}{k_p} = \frac{p_1 - p_2}{p_1 - p_3}$$

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.

$$\frac{K_p}{k_p} = \frac{0.24}{0.59} = \frac{225 - p_2}{225 - 55}$$

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

and the corresponding concentration, c_2, from Fig. 3, is 412 grams per liter.

$$k_c = \frac{W}{\theta} / (c_2 - c_3) = \frac{41.0}{412 - 378} = 1.2$$

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

$$\frac{k_c}{k_p} = \frac{1.2}{0.59} = \frac{p_1 - p_2}{c_2 - c_3} = \frac{41 - p_2}{c_2 - 204}$$

Referring again to Fig. 3 for corresponding values of p_2 and c_2, the equation is satisfied by $p_2 = 0.6$ mm. and $c_2 = 224$ grams per liter.
Therefore,

$$\frac{dW}{d\theta} = k_c(c_2 - c_3) = 1.2 \times 20 = 24 \text{ grams per hour,}$$

checking with the observed value in Table I.

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.

A New Filtration Principle

An Outstanding British Development in Chemical Engineering—An Improvement in China Clay Mining Is Noted

BY OUR LONDON CORRESPONDENT

ONCE AGAIN an engineer without any pretensions to chemical knowledge has brought to the notice of the chemical industry an invention which may find extensive application. Dr. Hele-Shaw is well known for his plate clutch and other mechanical inventions and researches. He conceived the idea of filtration through the edges of a large number of sheets of rough impervious paper pressed tightly together, this being an entirely different conception to the usual one of filtration through the surface of a sheet. Each sheet of the waterproof paper is perforated with an identical number of holes (forming tubes when the sheets are superimposed) in such a way that large and small holes are in alternate rows. The filter exhibited contained about 4,000 sheets and had a capacity of about 150 gal. per hour. The liquid to be filtered is forced in from one end through one series of holes and passes out through the other series after leaving behind in the interstices between the sheets the matter previously held in suspension. The residue can be removed from the "inlet tubes" without opening the filter and if necessary the operation can be made continuous.

Demonstrations were made on muddy water, mixtures of oil and water, dyestuffs, and dirty engine and paraffine oil. The muddy water gave an absolutely clear liquid, the oil and water were completely separated and the dyestuff was completely removed after passing through the filter. The capacity of these filters depends largely on the viscosity of the fluid and the dimensions of the holes, the area of the filter surface and the pressure that can safely be applied. The essential points are that a pack of paper is inexpensive, that each pair of holes constitutes a miniature filter and that twenty-four "packs" occupying a total volume of less than 100 cu.ft. would deal with 3,600 gal. of water per hour. This new principle of "edge filtration," originally designed for purification of condensing water, is not intended to replace ordinary types of filters. It will probably be suitable for colloidal suspensions, sugar solutions and even for removal of bacteria. Interesting developments should result from collaboration with chemical engineers in the further development of this new tool.

A FURTHER IMPROVEMENT IN THE CHINA CLAY INDUSTRY

In your correspondent's letter of December last, published in January, reference is made to the substantial recovery shown by the china clay industry. A further improvement has since occurred, bringing the output of the Cornish mines back to the pre-war figure, and the future appears to be very bright. There is little doubt that even now a considerable portion of the more valuable grades of china clay is wasted, and this not on account of inefficiency at the mine. Owing to inferior grading, the clay used in certain less discriminating industries contains a much higher proportion of the finer grades than is necessary, so that to all intents and purposes valuable clay is lost. With improved grading methods and elimination of such waste, there is a prospect of increased revenue for the mines. The future may possibly lie with a more extended use of high-grade clay, some of which may be obtained by conversion of the low-grade material in colloid or "liquid shear" mills. It has been shown that such machinery can cleave the secondary muscovite in china clay, which is so finely divided that further grinding by ordinary means is impracticable and yet is in particles large enough to make it a disagreeable constituent for ordinary purposes. There is no doubt that a really fine china clay, high in potash, has a big future in the pottery industry and it may be noted that such clay, found naturally in the Far East, was the origin of Chinese porcelain and was used as mined without the addition of feldspathic or other fluxes. Modern machinery may therefore enable manufacturers to place upon the market the equivalent of the natural porcelain clay of the East.

PERSONAL NOTES

Sir George Beilby has been succeeded by Dr. C. H. Lander as director of fuel research at the Fuel Research Board and Sir R. Threlfall has been appointed chairman. The new chair of chemical engineering at University College has been filled by the appointment of E. C. Williams of Leeds University and formerly of the National Benzol Research Association and the British Dyestuffs Corporation.