CXXVI.—*The Rate of Evolution of Carbon Dioxide from Solution in Presence of Colloids.*

By ALEXANDER FINDLAY and OWEN RHYS HOWELL.

THE rate at which a gas escapes from a supersaturated solution has been shown by Findlay and King (T., 1913, **103**, 1170; 1914, **105**, 1297) to be influenced by the presence of colloids. The method employed in investigating the process, however, involved a rather complicated arrangement of apparatus and considerable manipulative skill, and it seemed to be desirable to obtain some other and more simple method of studying the problem. We have therefore investigated the rate of desaturation of a solution of carbon dioxide when an indifferent gas is bubbled through the solution, the progress of de-aeration being followed by means of measurements of electrical conductivity (compare Perman, T., 1895, **67**, 868, 892; 1898, **73**, 511; Knox, *Ann. Physik*, 1895, **54**, 44; Meyer, *Z. Elektrochem.*, 1909, **15**, 249; Bohr, *Ann. Physik*, 1899, **68**, 500; Steele, T., 1903, **83**, 1470; Carlson, *J. Chim. Phys.*, 1911, **9**, 228). The method is essentially different from that employed by Findlay and King, and a precisely comparable behaviour is not to be looked for; but it is simple to carry out, and the results obtained, we believe, throw some further light on the behaviour of colloids.

Apparatus and Method.—The conductivity cell was a cylindrical

vessel made of resistance glass, 12.5 cm. high and 3.4 cm. in diameter, which could readily be connected with the gas inlet and outlet tubes by means of glass tubes with tapered and ground ends.

The carbon dioxide used in the experiments was prepared by the action of pure hydrochloric acid on white marble, and was washed by passage through solutions of potassium permanganate and sodium hydrogen carbonate, and then through distilled water. Before entering the conductivity cell, in which distilled water or water containing colloid was placed, the carbon dioxide was passed through a fourth wash-bottle, placed in the thermostat and containing the same solution as the conductivity cell. In this way alteration of the concentration of the solution in the conductivity cell was avoided.

For desaturation, a current of air was drawn at a constant rate through the solution. The air was freed from carbon dioxide by passage through a long tube containing soda-lime, and then through two wash-bottles containing potassium hydroxide and distilled water, and lastly through a flask, immersed in the thermostat and containing a quantity of the solution used in the conductivity cell. Before entering the conductivity cell, the air was brought to the temperature of the thermostat by passage through about 8 feet of narrow copper tubing wound in spiral form and immersed in the thermostat. This precaution was found to be necessary in order to prevent the cooling of the solution by the stream of air.

All measurements were carried out at 25°. Fifty c.c. of the solution were introduced into the conductivity cell and its conductivity was determined. It was then saturated with carbon dioxide and the conductivity again determined. Air was aspirated through the solution and the conductivity determined every half-minute.

Calculation of Results.—As each air-bubble enters the solution the carbon dioxide diffuses into it at a rate which may be represented

by the expression $-\frac{dC}{dt} = \frac{\Delta \cdot s}{l} (C_1 - C_2)$, where Δ is a diffusion

coefficient (*see later*), s the area of the surface of the bubble, l the thickness of the surface layer, C_1 and C_2 the concentration of carbon dioxide in the solution and in the bubble, respectively. If the bubbles pass through the solution at a constant and sufficiently rapid rate, the area, s , may be regarded as constant, and the concentration C_2 as zero. We may therefore write, since $\Delta \cdot s/l$ is constant for a given solution, $-dC/dt = kC_t$ where C_t is the concentration of the carbon dioxide in the solution at any time t . On integration, this yields the expression $k = \frac{1}{t} \log_e C/C_t$. In the case of weak acids, the conductivity, κ , is approximately proportional

to the square root of the concentration, expressed in gram-equivalents per litre, and we may therefore write $k = \frac{1}{t} \log_e \kappa^2 / \kappa_t^2$.

The conductivities of the solutions of carbon dioxide were corrected by subtracting the conductivity of the water (in the case of pure aqueous solutions), or of the colloidal sol employed. The velocity coefficient was then calculated from these corrected values.

EXPERIMENTAL.

1. *Pure Aqueous Solutions of Carbon Dioxide*.—As the result of a large number of experiments, it was found that the desaturation of a pure aqueous solution of carbon dioxide proceeds in the same manner irrespective of the rate at which the current of air is passed. The rate of desaturation increases, it is true, with increase in the rate of passage of the air, but for a given rate the velocity coefficient remains practically constant until desaturation is nearly complete. In all our final measurements, therefore, a constant rate of air current was maintained. In Table I are given the results of one out of the many determinations of the velocity of desaturation of an aqueous solution of carbon dioxide. In this table, t represents time in minutes, κ the conductivity of the solution, κ_c the corrected conductivity obtained by subtracting the conductivity of the water from the conductivity of the solution of carbon dioxide, and k is the velocity coefficient.

TABLE I.
Conductivity of water, 2×10^{-6} reciprocal ohms.

t .	$\kappa_c \times 10^6$.	$\kappa_c^2 \times 10^{12}$.	$0.43 k$.
0	47.10	2218	
0.5	41.96	1760	0.201
1.0	37.88	1427	0.192
2.0	30.41	924.7	0.190
4.0	19.46	378.6	0.192
6.0	12.35	152.5	0.194
8.0	7.72	59.6	0.196
10.0	4.75	22.56	0.199

Mean = 0.195

It was found, in agreement with the results obtained by Findlay and King (*loc. cit.*), that the velocity of desaturation was quite independent of the time during which the carbon dioxide had been kept in solution.

2. *Solutions containing Starch*.—In these experiments Kahlbaum's soluble starch was employed. The starch was repeatedly washed with alcohol and with water in order to remove any soluble salts present. The solutions were prepared by adding boiling conductivity water to starch paste, and the mixture was then warmed on the water-bath for ten minutes, when it became clear. Starch

solutions of different concentration were employed, and it was found that the rate of desaturation of solutions of carbon dioxide in presence of starch is considerably greater than in the case of pure aqueous solutions, and that it increases somewhat, although not markedly, as desaturation proceeds. This behaviour was found with all the starch solutions investigated, and is more pronounced the greater the concentration of the starch. Even when the process of saturation and desaturation was repeatedly carried out with the same starch solution, there was no change in the general behaviour of the solutions. The results obtained with starch solutions of different concentration were as follow :

(a) One per cent. solution of starch; initial conductivity, 24.40×10^{-6} reciprocal ohms. $0.43k$: mean value = 0.292 (extreme values = 0.289 and 0.314).

(b) 2.5 Per cent. solution of starch; initial conductivity, 56.10×10^{-6} reciprocal ohms. $0.43k$: mean value = 0.338 (extreme values = 0.289 and 0.402).

3. *Solutions containing Dextrin.*—Kahlbaum's dextrin was used and was purified by dialysing an 8 per cent. solution for about a week against conductivity water, a little toluene being added to prevent the growth of moulds. The results given in (c), (d), and (e) are selected from a large number of determinations, all of which gave similar values :

(c) 1.64 Per cent. solution of dextrin; initial conductivity, 27.55×10^{-6} reciprocal ohms. $0.43k$: mean value = 0.256 (extreme values = 0.242 and 0.278).

(d) 3.28 Per cent. solution of dextrin; initial conductivity, 48.81×10^{-6} reciprocal ohms. $0.43k$: mean value = 0.242 (extreme values = 0.232 and 0.245).

(e) 6.56 Per cent. solution of dextrin; initial conductivity, 83.92×10^{-6} reciprocal ohms. $0.43k$: mean value = 0.216 (extreme values = 0.217 and 0.226).

4. *Solutions containing Gelatin.*—French sheet gelatin was used. Before use it was cut up into small pieces and allowed to soak for several days in repeatedly changed conductivity water. Owing to the excessive frothing which took place during desaturation of the carbon dioxide solutions, only dilute solutions of gelatin could be employed. The results given in (f) are typical of those obtained in other cases :

(f) 0.25 Per cent. solution of gelatin; initial conductivity, 18.20×10^{-6} reciprocal ohms. $0.43k$: mean value = 0.117 (extreme values = 0.069 and 0.119).

5. *Solutions containing Ferric Hydroxide.*—A dialysed sol of ferric hydroxide was employed. A large number of determinations

have been made, and the results given in (g) and (h) are representative of all:

(g) 0.69 Per cent. solution of ferric hydroxide; initial conductivity, 321.1×10^{-6} reciprocal ohms. $0.43k$: mean value = 0.155 (extreme values = 0.130 and 0.153; maximum value = 0.174).

(h) 1.39 Per cent. solution of ferric hydroxide; initial conductivity, 510.2×10^{-6} reciprocal ohms. $0.43k$: mean value = 0.192 (extreme values = 0.166 and 0.162; maximum value = 0.222).

Discussion.

When one considers the results detailed above, it will be observed that the presence of a colloid has a distinct influence on the rate of desaturation of a solution by the bubbling method. In the case of solutions of starch and of dextrin, the velocity coefficient of desaturation is greater, and in the case of ferric hydroxide and of gelatin, the velocity coefficient is smaller than that of pure aqueous solutions of carbon dioxide. As a rule, also, in the case of the colloid sols the values of the velocity coefficient are less constant than in the case of pure aqueous solutions, and generally show a trend towards increasing values as the desaturation proceeds. This increase in the velocity coefficient, which is specially marked in the case of gelatin solutions, may perhaps find its explanation in the changes which the colloid undergoes under the influence of carbon dioxide, and in consequent changes of surface tension of the solutions.

Although the values of the velocity coefficient show a definite trend, we have, for the purpose of comparison, taken the mean of the values, as indicated in Table I and in (a)—(h). These values we have collected together in Table II, column 2.

TABLE II.

Velocity coefficients of desaturation of solutions of carbon dioxide.

Solvent.		Velocity coefficient (Findlay and King).	
		$0.43 k$.	
1. Starch solution,	1 per cent.	0.292	
2. " " solution,	2.5 " "	0.338	(3 per cent.) 0.037
" " "	1.64 " "	0.256	
" " "	3.28 " "	0.244	(3 " ") 0.057
" " "	6.56 " "	0.216	
3. Water		0.195	0.065
4. Ferric hydroxide solution,	0.69 " "	0.154	
" " "	1.39 " "	0.192	(1.35 " ") 0.067
5. Gelatin solution,	0.25 " "	0.117	(0.05 " ") 0.150

To find an explanation of the varying values of the velocity coefficient of desaturation by the bubbling method, we must consider the expression used in calculating these values (p. 1047). This expression involves the factor $\Delta \cdot s/l$, where Δ represents a diffusion coefficient

cient of carbon dioxide across the boundary layer between solution and air bubble, or, perhaps, we ought more correctly to say that Δ represents the coefficient of evolution or escape of the gas from the boundary surface of the solution into the air bubble. It would seem that we are dealing here, not with a true diffusion coefficient of a gas across a film, for in that case we should expect that the value of Δ and therefore the value of the velocity coefficient of desaturation would be greatest in the case of the solution in which carbon dioxide is most soluble (compare Exner, *Sitzungsber. Akad. Wiss. Wien*, 1874, **70**, ii, 465; Wiesner and Molisch, *ibid.*, 1889, **98**, i, 670). This, however, is not the case, for addition of gelatin raises the solvent power of water for carbon dioxide, and addition of starch and of dextrin diminishes the solvent power (Findlay and Creighton, *T.*, 1910, **97**, 536).

We come back, therefore, to the question, What is the property of the solution which determines the value of Δ and therefore the value of the velocity coefficient of desaturation? It was suggested by Findlay and King (*T.*, 1913, **103**, 1170) that the velocity of evolution of carbon dioxide from supersaturated solution on being vigorously shaken might be brought into relation with the surface tension of the solution, and that the lower the surface tension the more rapid would be the evolution of the gas. In the case of Findlay and King's experiments, this conclusion seems to be borne out, as a glance at column 3 of Table II will show; for starch and dextrin raise the surface tension of water, whereas gelatin lowers the surface tension. In our experiments, however, we find the inverse relationship between velocity of desaturation and surface tension of the solution; the velocity coefficient of desaturation varies synbatically, not antibatically, with the surface tension.

Since substances which lower the surface tension of a liquid become concentrated in the surface layer, we might regard the colloid as exercising a sort of blocking action and in this way retarding the escape of carbon dioxide from the solution. This explanation, however, would scarcely hold in the case of those colloids which, like starch, raise the surface tension of water, and for which the velocity of desaturation is greater than for water. We are inclined to believe, therefore, that it is not the surface tension of the solution which determines the rate of escape of a gas, but rather the internal pressure of the solution which varies synbatically with the surface tension. Determinations of the rate of desaturation of a gas solution by the bubbling method would therefore give a measure of the internal pressure of the solution. It will be of interest to find whether this is true for solutions of carbon dioxide in different, non-colloidal solvents.

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It may also be pointed out that since it has been found (Skirrow, *Z. physikal. Chem.*, 1902, **41**, 139; Christoff, *ibid.*, 1905, **53**, 321; **55**, 622) that solvent power for a gas varies antibatically with the surface tension, we shall expect that the velocity coefficients of desaturation by the bubbling method will vary antibatically with the solvent power of the solutions for carbon dioxide. As indicated above, this has been found to be the case.

CHEMISTRY DEPARTMENT,
UNIVERSITY OF ABERDEEN.

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