Distribution of dissolution rate of marble in hydrochloric acid, under natural convection conditions

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The dependence of the rate of dissolution of marble rods, immersed vertically in a hydrochloric acid bath, on the distance from the leading edge is investigated experimentally. An inversely proportional to the fourth root of the distance dependence is found only as a limiting case. The deviation from this law at finite concentrations should be attributed to the disruptive effect of the carbon dioxide bubbles on the diffusion layer. A correlation between the rate of dissolution, at a certain distance from the leading edge, and the concentration is also given.

Boguski (1) first showed that the rate of dissolution of marble in solution of acids is proportional to the molar concentration of the acid and it is the same for several strong acids.

Spring (2) found that the rate of dissolution of marble in strong acids is not unimolecular over the entire range of concentration and that different faces of Iceland spar crystals dissolve at different rates.

Brunner (3) reported that the dissolution of marble in strong acids obeys his well known diffusion rate theory and that it dissolves somewhat faster than magnesia.

King (4) showed that the rate of dissolution of metallic oxides, hydroxides and carbonates in strong acids is controlled by the diffusion rate theory and that the higher values found for marble might be explained by the disruptive effect of carbon dioxide bubbles on the diffusion layer. In a later work King (5) measured the rate of dissolution of a marble cylinder rotating in dilute solutions of a number of acids and acid mixtures. He concluded that the rate of dissolution follows the usual criteria of the diffusion rate theory, but that the original theory must be modified in several aspects in the case of weak acids. He also showed that the rates are not unimolecular.

In the original rate diffusion theory Nernst (6) postulated a stationary layer of liquid in contact with the dissolving solid. Within the layer only diffusion is operative, while outside the layer the concentration is maintained at a constant value.

In recent years the above concept of the diffusion layer has been modified. The basic element of the new treatment is that it takes into account a well defined convective flow as a result of density changes which accompany concentration changes in the region of the interface. It is to be noted that all the new theoretical treatments of the diffusion layer are referred almost always to cathodic electrolytic prosesses and usually to vertical electrodes.

It has been shown theoretically (7—14) and confirmed experimentally (9,11,13) that the diffusion layer formed across an electrode under natural convection conditions is generally thicker with increasing distance from the leading edge of the electrode and that, under limiting current conditions, the current density (or the reciprocal of the thickness of the diffusion layer) is inversely proportional to the fourth root of the distance from the leading edge.

It is the purpose of this paper to investigate experimentally if the above mentioned condition of the theory can equally well be applied to the case of dissolution processes controlled by the diffusion rate theory.

For this investigation we chose the case of dissolution of marble in dilute hydrochloric acid solutions. Our first step was the experimental confirmation of the existence and the direction of the density current along prismatic rods of marble, immersed vertically in an unstirred solution, and secondly the dissolution rate dependence upon the distance from the leading edge of the rod where the flow of the solution originates.

Experimental

In order to prove the existence and the direction of the density current the following experiment was performed: A cylindrical plastic cell, shown schematically in Fig. 1, was divided by means of a plastic partition, in two equal compartments. The partition was 3 cm. thick and was provided with a rectangular opening the cross section of which was approximately 1.7×1 cm. The specimens of marble were made in the form of prismatic rods 20 cm. long and of such cross section so that they could pass through the opening with a tolerance of about 2.5 mm. Each rod was cut in two halves, which after having been cleaned and dried were weighted separately. The two pieces were rejoined by means of Duco cement. The cell was filled with hydrochloric acid solution of the desired concentration and the rod was inserted in it through the

opening. The portion of the rod immersed in each compartment was about the same. One hour after the immersion of the specimen in the cell the solution of the
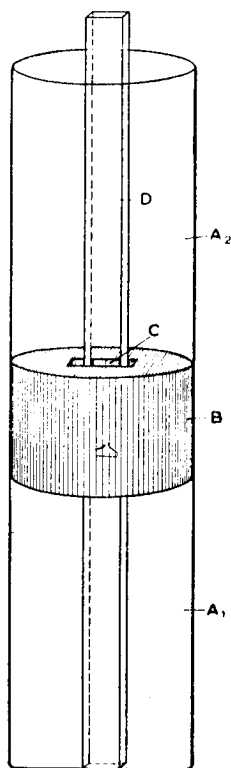

Fig. 1. Cell used for the experimental investigation of the density current. A_1 lower compartment, A_2 upper compartment, B partition, C opening and D rod of marble.

upper compartment was withdrawn first and then the rod was removed. The rod was cut at the point of the junction and after having been cleaned and dried the two halves were weighted. The content of the two compartments was analyzed for hydrochloric acid and calcium.

Experiments were made with 0.1, 0.05, 0.02 and 0.01 m HCl acid solution. The results are summarized in Table I.

For the investigation of the dependence of the rate of dissolution of marble (or the reciprocal of the thickness of the diffusion layer) on the distance from

the leading edge, a method similar to that used by Wagner (9) was adopted. Prismatic rods of marble with the following dimensions : length 16cm, breadth 1 cm and width 0.72 cm were prepared. The rods were cut in eight pieces, each of about 2 cm of lentgh. The pieces after having been cleaned and dried were weighted. The original rod was reconstructed by putting the pieces together in the same order in which they were cut. The rod thus reconstructed was tightly clamped by means of a plastic frame, as it is shown schematically in Fig. 2. The rod was then immersed vertically in the HCl acid bath of the desired concentration. In all the experiments a 25 liters bath was used. Under these conditions the concentration of the hydrochloric acid remained practically constant. The following concentrations of acid were used : 0.1, 0.066, 0.05,
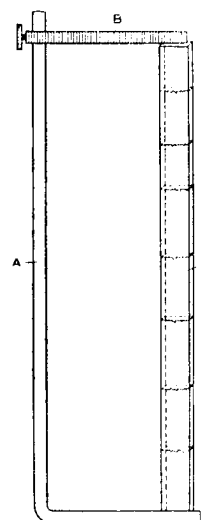

Fig. 2. Rod consisting of 8 pieces of marble as it was used for the study of dependence of dissolution rate on the distance from the leading edge.

0.04, 0.033, 0.020, 0.014, 0.01 and 0.007 m. The time of attack was 2 hours for the first four concentrations and 4 hours for the rest. In all the experiments the temperature was about 25 5 Cº.

Results and discussion.

As shown in Table I neither the loss in

Table I. Measurements showing the existence of a density current.

Initial concentration of HCl in moles/lit	Loss of calcium in g			Loss of calcium as calculated from the consumption of HCl in g			Calcium found in the solution in g		
	Upper Comptm.	Lower Comptm.	total	Upper Comptm.	Lower Comptm.	total	Upper Comptm.	Lower Comptm.	total
0.10	0.1910	0.1946	0.3856	0.1928	0.1790	0.3718	0.2000	0.1835	0.3840
0.05	0.0613	0.0466	0.1079	0.0334	0.0782	0.1116	0.0253	0.0897	0.1150
0.02	0.0267	0.0150	0.0417	0.0086	0.0316	0.0402	0.0092	0.0368	0.0460
0.01	0.0108	0.0092	0.0200	0.0063	0.0175	0.0238	0.0046	0.0161	0.0207

weight of the marble rods, nor the concentration of the solution was uniform throughout the cell. The portion of the rod in the upper compartment dissolved more, but more calcium was found in the lower compartment.

Moreover the concentration of hydrochloric acid was higher in the upper compartment, in spite of the fact that in this compartment more hydrochloric acid was consumed to dissolve the marble.

These results show clearly that a downward density current exists by means of which some solution, mainly from the interface region, is transported from the upper to the lower compartment. This solution is of course richer in calcium and poorer in acid. On the other hand solution of the bulk concentration of the down compartment is forced upwards. Under the experimental conditions the diffusional stream is rather weak. In the case of 0.1 m acid the results are inconsistent. This should be attributed to the higher evolution of carbon dioxide bubbles. The higher dissolution rate of the marble in the upper compartment is, at least qualitatively, in agreement with the theory, since the direction of the flow is downwards.
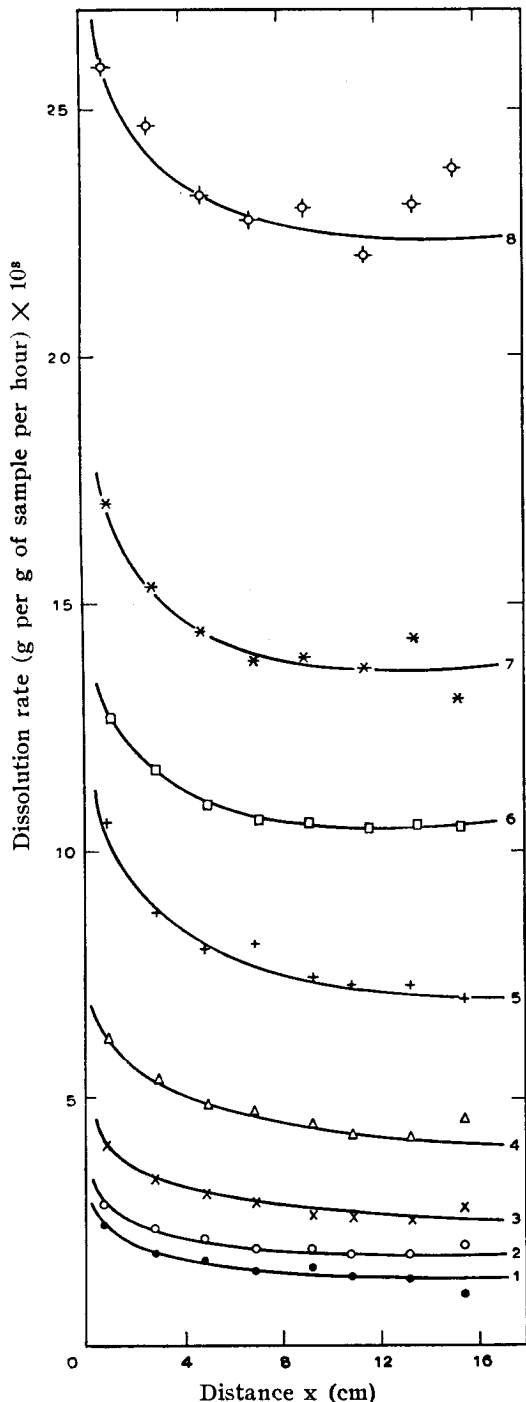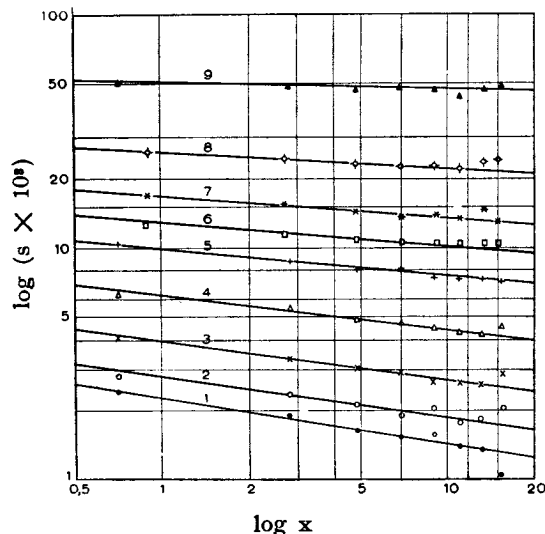
The dependence of the dissolution rate on

Fig. 4. Log of dissolution rate vs. log of distance for the same concentrations as in Fig. 3.

the distance from the leading edge is shown in Fig. 3, where the dissolution rates in grams of calcium carbonate per hour per gram of sample are plotted against the distance from the leading edge for various concentrations of acid.* Plots of the log of the dissolution rate(s)vs. the log of the distance, for the same concentrations, are given in Fig. 4. The slopes n of the straight li-

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* In all plots the mean values of the dissolution rates for each piece of marble were used as true values at the middle of each piece. The error introduced this way is appreciable only for the first piece from the leading edge, and it also depends on the value of the exponent n (see below) being larger the higher the values of n. For instance with n=0.25 the error in the first piece is $37^o/o$ becoming inappreciable for the next piece already ($2^o/o$).

Fig. 3. Observed dissolution rate dependence on the distance from the leading edge.

Curve No	1	2	3	4	5	6	7	8
Conc. HCl	0.007	0.01	0.014	0.02	0.033	0.04	0.05	0.066

nes calculated from these plots are given in Table II.

Table II. Values of n at various concentrations of hydrochloric acid.

Conc. HCl moles/lit	n
0.100	0.195
0.066	0.18
0.050	0.16
0.040	0.15
0.033	0.12
0.020	0.11
0.014	0.09
0.010	0.07
0.007	0.03

The equation of dependence of the dissolution rate s on the distance from the leading edge is of the form

$$s = \frac{K}{x^n} \tag{1}$$

where K and n are constants for a given concentration.

In Fig. 5 a plot of n vs. the square root of the concentration is given. From this plot the limiting value of n was found equal to 0.25. This
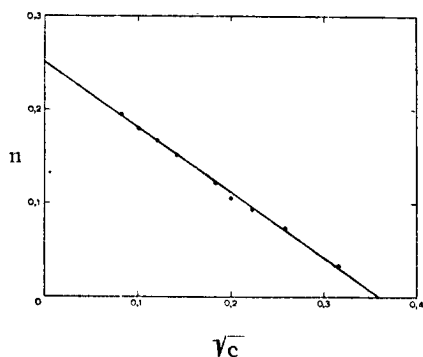

Fig. 5. Plot of exponent n, Eq. (1), vs. square root of concentration.

means that in the case of dissolution of marble rods, immersed vertically in the acid bath, only at a very low concentration of acid an inversely proportional to the fourth root ot the distance dependence of the dissolution rate should be expected. The deviation from this limiting value of n must be attributed to the disruptive effect of CO_2 bubbles on the diffusion layer, especially at higher concentrations.

From the foregoing discussion it is obvious that two factors determine the dependence of the dissolution rate on the distance from the leading edge: the natural convection effect and

the stirring effect of the bubbles. In view of this, Eq. (1) may be written in the form:

$$s = \frac{K'}{x^{1/4}} + Z \tag{2}$$

In this Equation the first term of the right side represents the pure convectional effect and
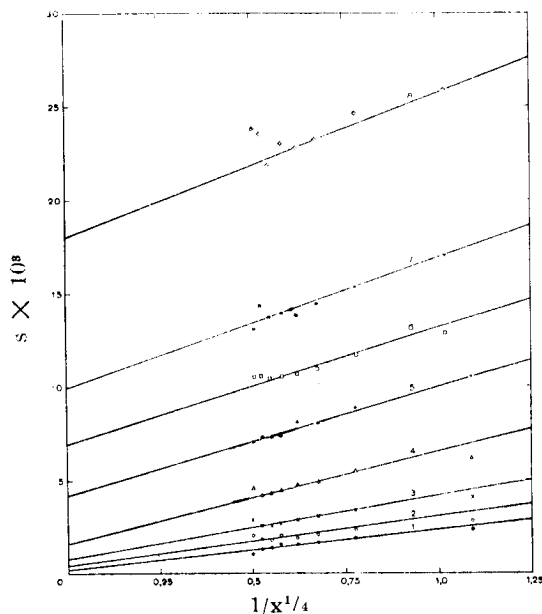

Fig. 6. Plot of dissolution rate vs. $1/x^{1/4}$ for the same concentrations as in Fig. 3.

the second term the stirring effect of the bubbles.

In Fig. 6 a plot of s vs. $\frac{1}{x^{1/4}}$ is given. From this plot the values of K' and Z for each concentration were calculated. In Figures 7 and 8 the
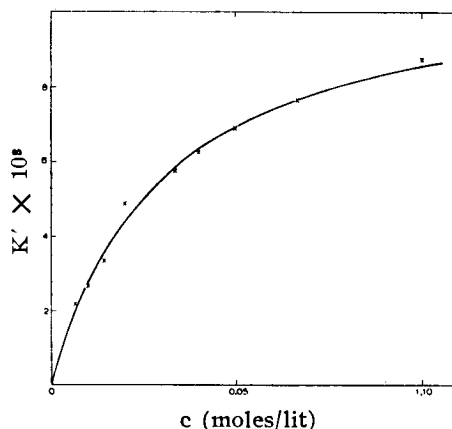

Fig. 7. Plot of K', Eq. (3) vs. concentration.

dependence of K' and Z on the concentration is shown. The functions expressing these curves are:

$$K' = \frac{c}{a + bc} \tag{3} \qquad , \qquad Z = kc^2 \tag{4}$$

The following values of the constants in (3) and (4) were found: a=2.7, b=90 and k=4.

Thus Eq. (2) may be written:

$$s = \frac{\dfrac{c}{a+bc}}{x^{1/4}} + kc^2 \qquad (5)$$

In Fig. 9 Eq. (5) is graphically represen-

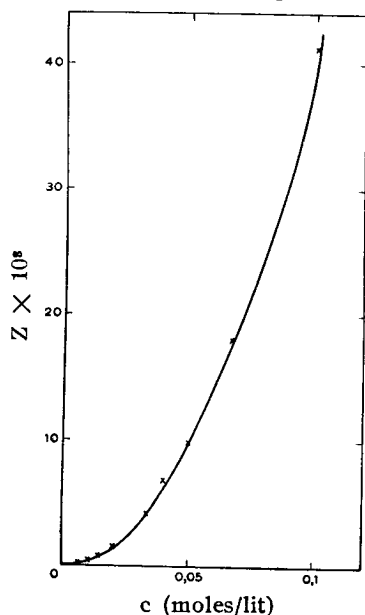Fig. 8. Plot of Z, Eq. (4), vs. concentration.

ted with the values of a, b and k given above and for a distance x=6.5 cm.

Experimental values of s (for the same distance) are also shown in this diagram.

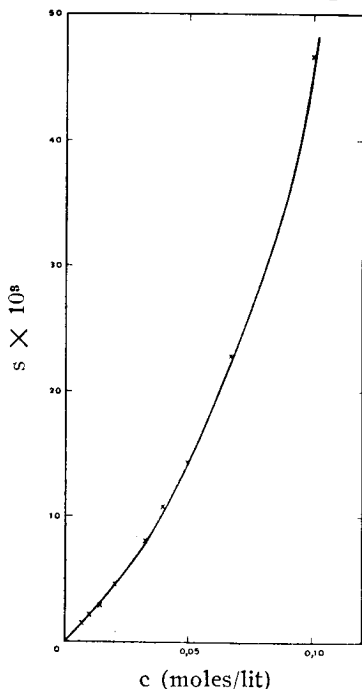Fig. 9. Plot of Eq. (5), with experimental values on it, for a distance x = 6.5 cm

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ΠΕΡΙΛΗΨΙΣ

Κατανομὴ τῆς ταχύτητος διαλύσεως μαρμάρου εἰς ὑδατικὰ διαλύματα ὑδροχλωρικοῦ ὀξέος, ὑπὸ συνθήκας φυσικῆς ἀναταράξεως.

Υπο Θ. ΓΙΑΝΝΑΚΟΠΟΥΛΟΥ καὶ Μ. ΠΙΠΙΝΗ

Ἡ ταχύτης ἀποθέσεως μετάλλων ἐλέγχεται ἀποκλειστικῶς ἢ μερικῶς ἐκ τῆς ταχύτητος μεταφορᾶς τῶν ἰόντων τοῦ μετάλλου ἐπὶ τῆς καθόδου. Ἐδείχθη θεωρητικῶς καὶ διεπιστώθη πειραματικῶς ὅτι εἰς περιπτώσεις κατακορύφων ἠλεκτροδίων καὶ ὑπὸ συνθήκας φυσικῆς ἀναταράξεως, ἡ ὁριακὴ πυκνότης ρεύματος εἶναι ἀντιστρόφως ἀνάλογος τῆς τετάρτης ρίζης τῆς ἀποστάσεως ἐκ τοῦ ἄκρου τοῦ ἠλεκτροδίου ἐκ τοῦ ὁποίου ἄρχεται τὸ ρεῦμα πυκνότητος, τὸ ὀφειλόμενον εἰς τὴν ὑπάρχουσαν διαφορὰν συγκεντρώσεως μεταξὺ μεσεπιφανείας καὶ ἐσωτερικοῦ τοῦ λουτροῦ.

Εἰς τὴν προκειμένην ἐργασίαν ἐπεκτείνονται αἱ ὡς ἄνω διαπιστώσεις εἰς περιπτώσεις φαινομένων διαλύσεως ἐκπληρούντων τὰ γενικὰ κριτήρια τῆς θεωρίας διαχύσεως. Οὕτω, ἐρευνᾶται ἡ περίπτωσις διαλύσεως πρισματικῶν ράβδων μαρμάρου βυθιζομένων κατακορύφως εἰς λουτρὸν ἀραιοῦ ὑδροχλωρικοῦ ὀξέος. Ἐν πρώτοις διαπιστοῦται πειραματικῶς ἡ ὕπαρξις ρεύματος πυκνότητος κατὰ μῆκος τῆς μεσεπιφανείας μὲ ἀφετηρίαν τὸ ἄνω ἄκρον τῆς ράβδου. Ἀκολούθως ἐρευνᾶται πειραματικῶς ἡ ἐξάρτησις τῆς ταχύτητος διαλύσεως τοῦ μαρμάρου ἐκ τῆς ἀποστάσεως ἀπὸ τὴν ἀφετηρίαν τοῦ ρεύματος πυκνότητος, διὰ διαφόρους συγκεντρώσεις ὀξέος. Διαπιστοῦται ὅτι, ὡς ὁριακὴ περίπτωσις διὰ χαμηλὰς συγκεντρώσεις ὀξέος, ἡ ταχύτης διαλύσεως εἶναι ἀντιστρόφως ἀνάλογος τῆς τετάρτης ρίζης τῆς ἀποστάσεως ἐκ τῆς ἀφετηρίας τοῦ ρεύματος πυκνότητος. Μὲ αὔξουσαν συγκέντρωσιν καὶ διὰ τὴν ἐρευνηθεῖσαν περιοχήν, ἡ ταχύτης καθίσταται μᾶλλον ὁμοιόμορφος. Τὸ τελευταῖον ἑρμηνεύεται ἐκ τοῦ γεγονότος ὅτι ἡ ἐκ τῆς αὐξανομένης ἐκλύσεως φυσαλλίδων διοξειδίου τοῦ ἄνθρακος προκαλουμένη ἀνατάραξις τείνει νὰ ὑποκαταστήσῃ τὴν φυσικὴν τοιαύτην.

Τέλος παρέχεται ἐμπειρικὴ ἐξίσωσις ἀποδίδουσα τὴν ταχύτητα διαλύσεως εἰς δεδομένον ὕψος τῆς ράβδου, ἀπὸ τὴν συγκέντρωσιν τοῦ ὀξέος.

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