

SUMMARY

1. Concentrated, acid solutions of ferric nitrate supercool with respect to the primary phase (crystalline ferric nitrate nonahydrate).
2. Non-isomorphous solid impurities are inert towards nucleation of the supercooled primary phase.
3. Isomorphous solid impurities actively influence the crystallisation of the primary phase.

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EFFECT OF THE COMPOSITION OF SOLUTION ON THE RATE OF DIFFUSION OF ELECTROLYTIC HYDROGEN THROUGH METAL MEMBRANES. II. DIFFUSION OF HYDROGEN THROUGH PALLADIUM MEMBRANES

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The previous paper¹ analysed possible schemes for the diffusion of electrolytic hydrogen through metal membranes taking into account different mechanisms for the removal of atomic hydrogen from the electrode surface, and gave experimental results on the effect of the composition of the solution and the surface state of an iron membrane on the rate of diffusion of hydrogen through the latter.

We have now investigated the way in which the rate of diffusion of hydrogen through palladium membranes is affected by the halide anion I^- and the tetrabutylammonium cation $(C_4H_9)_4N^+$ separately and jointly, and also by poisoning of the palladium with mercury, when they act on the polarisation and the diffusion sides of the diaphragm. Furthermore, determinations have been made of the variation in potential of a palladium electrode in various solutions with the quantity of molecular hydrogen removed from its surface.

EXPERIMENTAL

A palladium diaphragm 40 μ thick was clamped between the flat ground edges of two vessels A and B (Fig. 1). The system was made airtight and watertight by means of two thick Plexiglas plates, into which was inserted the apparatus and which were drawn together by four bolts, the joint being thus made a tight fit. Such an arrangement enabled grease to be dispensed with on the plane-parallel ground joint, and thus ensured uncontaminated conditions. Both polarisation and diffusion cells were fitted with horizontal burettes, in which the volumes of hydrogen evolved on both sides of the membrane could be measured from the advance of the solution meniscus. The palladium membranes were treated with ethyl alcohol, hot concentrated sulphuric acid, and strong alkali, washed with twice distilled water, dried, and clamped in the plane-parallel ground joint as described above. The apparent surface area of one side of the electrode was 1 cm^2 . The membrane was activated by polarising both sides with an anodic current of 2×10^{-3} A cm^{-2} in 1 N H_2SO_4 until the start of visible oxygen evolution. After the anodic activation, cells A and B were filled with 1 N H_2SO_4 freshly saturated with H_2 , in which both sides of the membrane were cathodically polarised at 2×10^{-3} A cm^{-2} for 16–18 h, until the palladium was completely saturated with hydrogen. After this, the polarisation of one side of the diaphragm, which we shall call the diffusion side, was discontinued, while that of the other side, the polarisation side, was continued at a higher current density (5×10^{-3} A $\times cm^{-2}$) until a constant rate of diffusion of hydrogen was established.

The potential thus established on the diffusion side was 50–60 mV more negative than the reversible hydrogen potential in the same solution. This deviation from the equilibrium value on active electrodes is due mainly² to supersaturation with molecular hydrogen of the layer adjacent to the electrode, owing to the slowness of its diffusion into the bulk of the solution. When polarisation of the polarisation side of the membrane was terminated, its potential became equal to that of the diffusion side, and both sides slowly approached a value corresponding to the reversible hydrogen electrode, which was then maintained for a long time. The quantity of hydrogen diffusing in our experiments was approximately half that being evolved by cathodic polarisation of the polarisation side. The effects of additives in the solution, and of poisoning the electrode with mercury, on diffusion and the hydrogen overpotential were investigated at a cathodic polarisation of the polarisation side $i_p = 5 \times 10^{-3}$ A cm^{-2} and of the diffusion side $i_d = 0$. The reagents employed were subjected to redistillation, recrystallisation, or electrolytic purification, as appropriate.

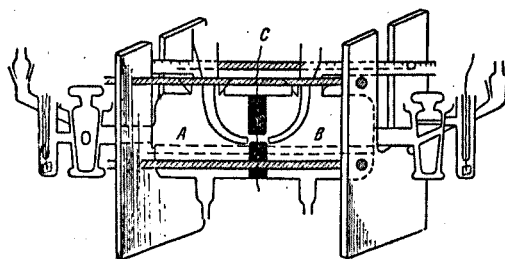


Fig. 1. Diagram of apparatus.

RESULTS

Fig. 2 shows polarisation curves obtained on both sides of the membrane in 1 N H_2SO_4 by a rapid method, in which the cathodic polarisation of the electrode was not maintained constant long enough for equilibrium to be reached between the quantity of hydrogen dissolved in the palladium and the current density (curves 1 and 1'). In acid polarisation curves obtained by rapid and slow methods coincide. The coincidence of curves 1 and 1' indicates that the two sides of the membrane have the same electrochemical activity. Over the range 10^{-3} – 10^{-2} A cm^{-2} a linear relation is observed between η and $\log i$ with $b = 0.09$, in good agreement with the results of Frumkin and Aladzhalova², but differing from those of Schuldiner³, who probably worked with more active electrodes.

Fig. 3 shows the effect of adding 0.03 N KI to 1 N H_2SO_4 in the polarisation and diffusion cells on the diffusion of hydrogen and on the hydrogen overpotential on both sides.

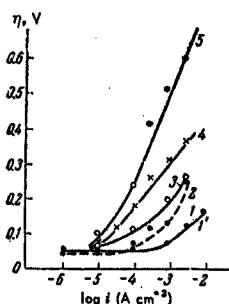


Fig. 2. Polarisation curves for palladium in solutions of: 1) and 1') 1 N H_2SO_4 ; 2) 1 N H_2SO_4 + 0.005 M $[(\text{C}_4\text{H}_9)_4\text{N}]_2\text{SO}_4$; 3) 1 N H_2SO_4 + 0.03 N KI; 4) 1 N H_2SO_4 + 0.03 N KI (after immersion of unpolarised electrode in same solution); 5) 1 N H_2SO_4 + 0.03 N KI + saturated $(\text{C}_4\text{H}_9)_4\text{NI}$.

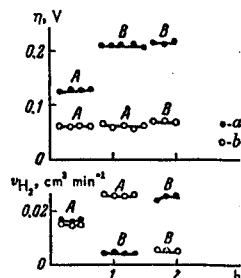


Fig. 3. Effect of addition of 0.03 N KI to 1 N H_2SO_4 , on the polarisation and diffusion sides of the membrane, on η_p , η_d , v_p , and v_d : a) polarisation side; b) diffusion side; A) 1 N H_2SO_4 ; B) 1 N H_2SO_4 + 0.03 N KI.

The abscissae represent times in hours, and the ordinates the overpotentials η_p and η_d on both sides of the membrane and the amounts of hydrogen, in $\text{cm}^3 \text{min}^{-1}$, evolved from the polarisation and diffusion sides of the membrane, v_p and v_d respectively, when the polarisation side is cathodically polarised at a current $i_p = 5 \times 10^{-3}$ A cm^{-2} ($i_d = 0$). The letters on the graphs indicate the composition of the solutions. When 1 N H_2SO_4 in the polarisation cell is replaced by 1 N H_2SO_4 + 0.03 N KI solution, with continuous cathodic polarisation of the polarisation side, η_p increases abruptly by ~ 80 mV, and then increases very slowly with time. The value of v_d also rises suddenly†, and then remains substantially constant. The increase in v_d results in a further rise in η_d by 3–4 mV. When 0.03 N KI is added to 1 N H_2SO_4 on the diffusion side, v_d drops sharply to 10–50% of its value, and hence v_p increases. Fig. 3 shows that an increase in v_p by a factor of 6–7 is accompanied by an increase in η_p of 5–7 mV. The potential on the diffusion side also becomes somewhat more negative (η_d increases), in spite of the diminished quantity of hydrogen removed from the surface‡. The 50% increase in the quantity of hydrogen removed from the polarisation side in 1 N H_2SO_4 produced by adding 0.03 N KI to the 1 N H_2SO_4 on the diffusion side leads to an increase in η_p by 4–7 mV. The polarisation curve obtained in 1 N H_2SO_4 + 0.03 N KI solution (Fig. 2, curve 3) is displaced towards higher overpotentials relative to the curve obtained in 1 N H_2SO_4 .

If the polarisation side of the membrane, previously polarised by the above procedure in 1 N H_2SO_4 + 0.03 N KI at 5×10^{-3} A cm^{-2} , is left in the solution without a current passing for 16–18 h, subsequent application of cathodic polarisation at the former current density gives a higher value of η_p (Fig. 4, curve B'), which rises rapidly with time, while v_d , after reaching its previous value, begins to fall, and hence v_p increases. The crosses on this diagram show values of η_p for continuous cathodic polarisation of the polarisation side in 1 N H_2SO_4 + 0.03 N KI during the same period. The polarisation curve obtained in 1 N H_2SO_4 + 0.03 N KI after preliminary standing of the electrode in the solution without polarisation is displaced towards still higher overpotentials, and has a very steep slope (Fig. 2, curve 4).

Fig. 5 shows that 0.005 M $[(\text{C}_4\text{H}_9)_4\text{N}]_2\text{SO}_4$ increases η_p by 100–120 mV, but does not affect v_d , while η_d remains unchanged. Addition of 0.03 N KI on the diffusion side diminishes v_d , and hence v_p increases. The greater amount of hydrogen evolved from the polarisation side does not result in any appreciable change in η_p .

Addition of $(\text{C}_4\text{H}_9)_4\text{NI}$ to 1 N H_2SO_4 + 0.03 N KI on the polarisation side results in a further increase in η_p compared with the acid KI solution, while v_d somewhat diminishes (Fig. 6). The increase in v_p on addition of 0.03 N KI to the solution on the diffusion side does not result in any appreciable change in η_p in the 1 N H_2SO_4 + 0.03 N KI + saturated $(\text{C}_4\text{H}_9)_4\text{NI}$ solution. The polarisation curve for this latter solution is shown in Fig. 2 (curve 5).

† KI also increases v_d in the case of the diffusion of hydrogen from aqueous alkali, but the effect is far weaker than in aqueous acid.

‡ An increase in η_d with decrease in v_d can be observed only when access of atmospheric oxygen to the diffusion cell is excluded.

§ $(\text{C}_4\text{H}_9)_4\text{NI}$ is very sparingly soluble in water. We always added an excess of it, and worked with solutions which were saturated with respect to this salt.

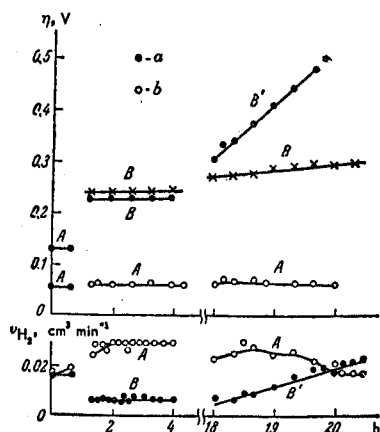


Fig. 4. Effect on η_p , η_d , v_p , and v_d of addition of 0.03 N KI to 1 N H₂SO₄ on the polarisation side: a) polarisation side; b) diffusion side; A) 1 N H₂SO₄; B) 1 N H₂SO₄ + 0.03 N KI; B') 1 N H₂SO₄ + 0.03 N KI after prolonged immersion of unpolarised electrode.

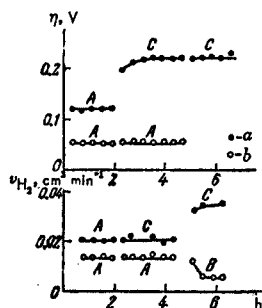


Fig. 5. Effect on η_p , η_d , v_p , and v_d of addition of 0.005 M [(C₄H₉)₄N]₂SO₄ to 1 N H₂SO₄ on the polarisation side and of 0.03 N KI to 1 N H₂SO₄ on the diffusion side: a) polarisation side; b) diffusion side; A) 1 N H₂SO₄; B) 1 N H₂SO₄ + 0.03 N KI; C) 1 N H₂SO₄ + 0.005 M [(C₄H₉)₄N]₂SO₄.

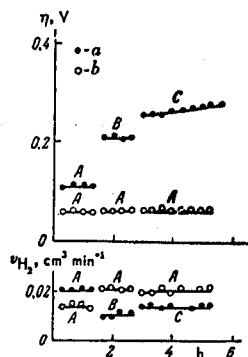


Fig. 6. Effect on η_p , η_d , v_p , and v_d of addition of (C₄H₉)₄NI to 1 N H₂SO₄ + 0.03 N KI on the polarisation side: a) polarisation side; b) diffusion side; A) 1 N H₂SO₄; B) 1 N H₂SO₄ + 0.03 N KI; C) 1 N H₂SO₄ + 0.03 N KI + saturated (C₄H₉)₄NI.

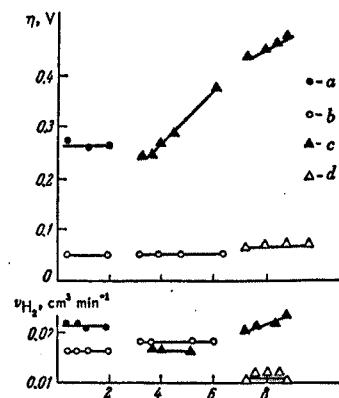


Fig. 7. Effect on η_p , η_d , v_p , and v_d of poisoning with mercury of the polarisation and diffusion sides of the membrane in 1 N H₂SO₄: a) polarisation side; b) diffusion side; c) polarisation side poisoned with mercury; d) diffusion side poisoned with mercury.

Poisoning of the polarisation side with mercury is accompanied by increases in η_p and in v_d (Fig. 7)†. The rise in η_p with time on the introduction of mercury into the solution on the polarisation side is probably associated with the increasing extent of poisoning of the electrode surface by the mercury. When the diffusion side is poisoned with mercury, the rate of diffusion of hydrogen falls†, and hence v_p increases. In spite of the decreased quantity of hydrogen which diffuses, the potential of the diffusion side becomes somewhat more negative (by ~12 mV).

DISCUSSION

The results obtained in the present work (see Table) indicate that the anion I⁻ and poisoning of the palladium with mercury exert antagonistic effects on the diffusion of hydrogen according as to how they act on the polarisation or the diffusion side of the membrane. Addition of KI to the dilute H₂SO₄ on the polarisation side or poisoning of this side with mercury results in an increase in v_d . It is interesting that, when KI is added to the solution on the polarisation side, only one-sixth of the hydrogen discharged on this side begins to be evolved there, while five-sixths diffuse to the opposite side. When I⁻ or Hg acts on the palladium on the diffusion side, v_d falls, the effect being consistent with the influence of these agents on the M-H_{ads} bonding energy w and the hydrogen overpotential. The adsorption of I⁻ on palladium diminishes w .⁴ By analogy with platinum⁵, the poisoning of palladium with mercury should also decrease w . The diminution in the M-H_{ads} bonding energy slows down both the discharge stage and the removal of H_{ads} by recombination. At the same time the penetration of atomic hydrogen into the metal is facilitated, and its escape at the opposite surface impeded.

† In contrast to the previous experiments, those on the effect of poisoning the palladium with mercury on the diffusion of hydrogen were carried out with relatively inactive palladium.

† The diffusion of hydrogen is inhibited by poisoning the diffusion side with mercury also in the case of diffusion into a solution of alkali.

TABLE. Effect of the composition of solution, on the polarisation and diffusion sides of the membrane, on the rate of diffusion of hydrogen v_d through the latter and on the hydrogen overpotential η .

η	Polarisation side	Diffusion side
$\eta_{H_2SO_4} < \eta_{H_2SO_4 + KI}$	$v_{H_2SO_4} < v_{H_2SO_4 + KI}$	$v_{H_2SO_4} > v_{H_2SO_4 + KI}$
$\eta_{H_2SO_4} < \eta_{H_2SO_4 + KI + (C_4H_9)_4NI}$	$v_{H_2SO_4 + KI} > v_{H_2SO_4 + KI + (C_4H_9)_4NI}$	-
$\eta_{H_2SO_4} < \eta_{H_2SO_4 + [(C_4H_9)_4N]_2SO_4}$	$v_{H_2SO_4} = v_{H_2SO_4 + [(C_4H_9)_4N]_2SO_4}$	-
$\eta_{Pd \text{ in } H_2SO_4} < \eta_{Pd \text{ poisoned with Hg in } H_2SO_4}$	$v_{Pd \text{ in } H_2SO_4} < v_{Pd \text{ poisoned with Hg in } H_2SO_4}$	$v_{Pd \text{ in } H_2SO_4} > v_{Pd \text{ poisoned with Hg in } H_2SO_4}$

The effect of I^- on η and v_d after prolonged immersion of the electrode without cathodic polarisation in 1 N H_2SO_4 + 0.03 N KI solution, when a steady increase in η is accompanied by a fall in v_d (Fig. 4), does not fit into such a simple scheme. Comparison of the effects of I^- on η and the diffusion of hydrogen through palladium during continuous cathodic polarisation of the electrode with the corresponding effects after prolonged standing of the electrode without polarisation indicates the probable existence of two types of poisoning of palladium by iodide, "mild" and "severe". With the former, the growth in η is accompanied by an increase in v_d ; with severe poisoning, a quite rapid rise in η with time is accompanied by a slow fall in the rate of diffusion of hydrogen. In order to explain the latter effect, it must be assumed that on palladium, as on iron, the hydrogen enters the metal in the same elementary act as that in which the hydrogen ion is discharged. In other words, in this case the intermediate state, through which hydrogen passes on entering the metal lattice, is not identical with the steady state of hydrogen adsorbed on the metal surface, which is discussed in the theory of hydrogen overpotential. Transition between these two states is obviously possible, but it involves sufficient activation energy for the evolution of hydrogen during electrolysis and its penetration into the metal to be regarded as mutually independent. It is possible that penetration into the lattice occurs only at certain points on the surface, for example, where lattice dislocations emerge. On this view, mild iodide poisoning represents mainly the poisoning of active sites on the palladium surface, at which discharge of the hydrogen ion involves its transition to the adsorbed state. Severe iodide poisoning of palladium, occurring relatively slowly with time, involves poisoning of the whole surface of the palladium, in which sites through which the discharged hydrogen penetrates into the metal are especially strongly poisoned. Perhaps the slight decrease in the flux of diffusing hydrogen on addition of $(C_4H_9)_4NI$ to the 1 N H_2SO_4 + 0.03 N KI solution on the polarisation side (Fig. 6) is associated with a partial conversion of mild into severe iodide poisoning of the palladium under the influence of increased adsorption of I^- in the presence of $(C_4H_9)_4N^+$.

The mechanism of the action of the $(C_4H_9)_4N^+$ cation on the hydrogen overpotential and on the diffusion of hydrogen from 1 N H_2SO_4 through palladium can be explained by the fact² that the overpotential of palladium is the sum of two quantities: $\eta = \eta_i + \eta_\theta$, where η_i is governed by the rate of discharge of hydrogen ions when the palladium surface is covered with H_{ads} corresponding to molecular hydrogen at 1 atm, and η_θ by the rate of removal of hydrogen from the surface. The $(C_4H_9)_4N^+$ cation, on being adsorbed on

the electrode surface, makes the Ψ' potential more positive, diminishes the hydrogen ion concentration in the double layer, and thereby slows down the discharge of hydrogen ions, as a result of which the hydrogen overpotential increases.

The effect of $(C_4H_9)_4N^+$ would obviously be the same on all portions of the surface, so that v_d remains unchanged (Fig. 5).

The increase in the overpotential η of palladium accompanying adsorption of I^- and poisoning with mercury is due not so much to the slowing down of the removal of H_{ads} from the electrode surface as to the retardation of the discharge of hydrogen ions, also caused by the decrease in w accompanying such adsorption and poisoning. This follows from the relatively small change in η of palladium in 1 N H_2SO_4 + 0.03 N KI, and of palladium poisoned with mercury in 1 N H_2SO_4 , with variation in the total quantity of atomic hydrogen removed from the electrode surface. Frumkin has shown⁷ that the change in η produced by additional amounts of atomic hydrogen introduced into the reaction zone on the electrode surface serves as a measure of the rate of removal of H_{ads} : the more slowly is atomic hydrogen removed from the electrode surface, the more will η grow under the influence of additional quantities of atomic hydrogen. This conclusion has been confirmed experimentally for iron in a solution of alkali⁸. With palladium, as mentioned above, a 50% increase in the quantity of hydrogen evolved from the polarisation side at $i_p = 5 \times 10^{-3}$ A cm⁻² is accompanied by an increase in η on the polarisation side in 1 N H_2SO_4 by 4–7 mV, whereas in 1 N H_2SO_4 + 0.03 N KI solution the increase of the latter is 5–7 mV for a sevenfold increase in the quantity of hydrogen evolved (Fig. 3). These data indicate that, under these conditions, η is determined mainly by the discharge stage.

At more positive potentials removal of H_{ads} has a greater effect on η , in conformity with theory⁷. The experiment illustrated in Fig. 3 shows that addition of 0.03 N KI to 1 N H_2SO_4 makes the potential on the diffusion side 5 mV more negative, in spite of the quantity of hydrogen removed from the surface decreasing by a factor of 5–6. Poisoning the palladium with mercury retards the removal of H_{ads} to an appreciably greater extent. Poisoning the diffusion side with mercury is accompanied by an increase in η of 12 mV (Fig. 7), in spite of a diminution by a factor of 5–6 in the amount of hydrogen removed from this side. Thus I^- and especially Hg, by decreasing the value of w , activate the H_{ads} and promote the ionisation $H_{ads} \rightarrow H^+ + e$, which is responsible for the increase in η in spite of the decreased concentration of H_{ads} .

As mentioned above, the high values of η in the presence of the $(C_4H_9)_4N^+$ cation are associated with a slowing down of the discharge stage. In conformity with this, we observed no change in η in $1\text{ N H}_2\text{SO}_4 + 0.005\text{ M }[(C_4H_9)_4N]_2\text{SO}_4$ (Fig. 5) when the quantity of hydrogen evolved from the polarisation side approximately doubled.

The irreversibility of the hydrogen ion discharge stage on palladium is illustrated also by the different values of η_p and η_d in solutions of the same composition under conditions such that the amounts of molecular hydrogen removed from each side of the membrane are equal. Fig. 3 shows that in $1\text{ N H}_2\text{SO}_4$ $v_p \approx v_d \approx \frac{1}{2}i_p$ and $\eta_p \approx 0.13$, whereas $\eta_d \approx 0.06$. The higher value of η_p on the polarisation side is obviously due to the occurrence of the discharge $H^+ + e \rightarrow H_{ad}$, at the rate $i_p = 5 \times 10^{-3}\text{ A cm}^{-2}$.

We wish to express our deep thanks to Academician A. N. Frumkin for valuable advice and hints in the course of this work, and for discussing the results obtained.

SUMMARY

1. A study has been made of the way in which the rate of diffusion of hydrogen through palladium is affected by poisoning the latter with mercury and by the composition of the solution — $1\text{ N H}_2\text{SO}_4$, $1\text{ N H}_2\text{SO}_4 + 0.03\text{ N KI}$, $1\text{ N H}_2\text{SO}_4 + 0.005\text{ M }[(C_4H_9)_4N]_2\text{SO}_4$, and $1\text{ N H}_2\text{SO}_4 + 0.03\text{ N KI} + \text{saturated } (C_4H_9)_4\text{NL}$.
2. Palladium can be poisoned by iodide in two ways, which have different effects on the rate of diffusion of hydrogen.
3. Penetration of hydrogen into the poisoned palladium probably occurs in the same elementary act as the discharge of a hydrogen ion.
4. Determinations have been made of the effect of a change in the quantity of molecular hydrogen removed from the surface of a palladium electrode on the hydrogen overpotential of the latter in the above three solutions and of palladium poisoned with mercury in $1\text{ N H}_2\text{SO}_4$. The results indicate the irreversibility of both the discharge stage and the removal of adsorbed hydrogen.

EFFECT OF CALCIUM SULPHIDE ON THE SURFACE TENSION AND DENSITY OF CALCIUM-MAGNESIUM SILICATE MELTS

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The present study, which forms part of a more general investigation¹, was undertaken because of the scarcity of relevant data. Surface tension and density were measured for three groups of melts of basicity, defined as the molar ratio $(\text{CaO} + \text{MgO} + \text{CaS})/(\text{SiO}_2)$, 0.8, 1.0, and 1.2 respectively. The concentration of MgO was varied in 5% steps, within each group, from 0 to 15 wt.%. Calcium sulphide was added in amounts not exceeding 10 wt.%. Calcium oxide was replaced by equivalent amounts of magnesium oxide and calcium sulphide, keeping the basicity of the melt constant.

The measurements were carried out in a graphite resistance furnace, using graphite crucibles and an inert (nitrogen) atmosphere. The surface tension and the density of the melts were measured by the maximum gas bubble pressure method, already described¹, with graphite capillaries of bore 6.5 and 4.5 mm, and purified argon or helium as the carrier gas. Surface tensions were measured by the maximum bubble pressure observed with the capillary just below the liquid surface; densities were measured by the variation of the maximum bubble pressure with depth of immersion, given by a micrometer adjustment. The precision of the two measurements was $\pm 4-5\%$ and $\pm 8-10\%$ respectively.

Replacement of calcium oxide by an equimolar amount of calcium sulphide invariably affected the surface tension (Figs. 1-3), the magnitude of the effect increasing with MgO concentration. Thus a 4% addition of calcium sulphide to melts of basicity 1.0 containing 5% of MgO lowered the surface tension from 478 to 388 erg cm^{-2} , whereas in the presence of 15% MgO the same amount of CaS decreased the surface tension of melts of basicity 1.0 from 482 to 329 erg cm^{-2} (Fig. 2). Much the same behaviour was observed in melts of basicity 0.8 and 1.2 (Figs. 1 and 3). Successive additions of calcium sulphide did not affect the surface tension of silicate melts by the same amount: the first 4% addition of CaS to melts of basicity 1.0 and containing 5 wt.% of MgO lowered the surface tension by 90 erg cm^{-2} , whereas the following 4% addition lowered the surface tension only by a further 18 erg cm^{-2} (Fig. 2). In other words, the surface tension becomes relatively insensitive to additions of calcium sulphide at high concentrations of the additive. All melt compositions studied in this work showed the same qualitative variation of surface tension with percentage of CaS (Figs. 1-3).

An entirely analogous variation of surface tension with CaS concentration had been previously observed in the $\text{CaO}-\text{SiO}_2$ system¹. The effect is a clear manifestation of the limited solubility^{2,3} of CaS in magnesia-lime-silicate melts. The first additions of calcium sulphide dissolve in the melt and lower the intermolecular and intramolecular forces, the larger sulphur ions residing mostly in the outer shell of the complex anions. Thus the surface tension of the melts is very significantly lowered by the first few increments of calcium sulphide.

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