In a later note in *Nature* we shall offer proof that nitric acid in sulphuric acid as solvent is in fact converted completely into NO_2^+. Reactions (5) thereby become consistent with kinetics (1) for nitration in sulphuric acid. Bennett and Williams have shown that the bisulphate ion is the principal proton acceptor in this case[3].

Reactions (6) likewise correspond to kinetics (2) and (3) for nitration in organic solvents. Sufficiently reactive aromatic compounds remove the NO_2^+ as fast as it is formed, whereas much less reactive compounds allow it to approach a small equilibrium concentration. Both the zeroth- and first-order rate constants are reduced by added nitrate ions, according to a law of the same hyperbolic form. This can be explained by equations (6), essentially as a consequence of the assumed preliminary proton transfer leading to the nitracidium ion, $H_2NO_3^+$. Both the zeroth- and first-order reactions are retarded by 'nitrous acid', but this effect we refer back to that observed with nitrate ion.

The connexion between the two effects emerged in the course of another investigation, which was undertaken jointly with Mrs. F. M. Garforth, in order to elucidate the nature of 'nitrous acid' in solvents containing nitric acid. Studies by the methods of optical absorption and electrical conductivity have led to the conclusion that the condition of 'nitrous acid' is essentially the same as that of added N_2O_4, but that this exists as a binary electrolyte, one of its ions being the nitrate ion.

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Structure of Catalytic Metal Films

EVAPORATION of metals on to the walls of a glass tube at room temperature is known to yield films of high catalytic activity in many instances. In the case of tungsten a film of apparent area 140 cm.² and estimated weight of order 1 mgm. was found[1] by two methods to possess an area of 450 cm.². It was concluded "that the film was probably not microcrystalline to any great extent", but this conclusion is now found to be invalid. These results, together with other data, are best explained by assuming that the film is microcrystalline, in accordance with the results of electron diffraction[2]. The crystallites of a sputtered platinum film have a side of ~ 0·005 μ by the latter method. Taking a simple model of equal spheres exposing all their surface to the reacting gas, we calculate for the above tungsten film a crystal diameter of 0·007 μ. By itself, of course, the chemical evidence cannot decide whether the particles are crystalline or amorphous.

The results of Beeck, Smith and Wheeler[3] would seem to allow an extension of the argument. They found that films of nickel on glass formed by evaporation in high vacuum showed crystalline electron diffraction patterns, and that the true area measured by the chemisorption of hydrogen or carbon monoxide increased *linearly* with the weight of metal deposited, over the range examined (5–50 mgm.). The 50 mgm. film had an area of 4,200 cm.², which they discuss in terms of pore structure. On our view, complementary to theirs, the film is made up of approximately uniform crystallites of diameter 0·043 μ. During evaporation, once a crystal reaches this diameter approximately, it ceases to grow and a new nucleus starts, this diameter probably being a function of the experimental conditions.

The 0·1 mgm. nickel film of A. and L. Farkas[4] possessed a true area of 150 cm.², corresponding to a particle diameter of 0·005 μ. The first crystallites in this film (average thickness 1 atom) may still be in the growing stage. On the other hand, the difference from 0·043 μ may reside in the conditions of deposition, and traces of a strongly chemisorbed gas may well have a profound effect here. It may be calculated for the case of hydrogen on tungsten (taking Roberts's value of ΔH^5) that adsorption from a pressure of 10^{-6} mm. might lower the surface tension of the metal by as much as 500 dynes/cm. This may well help to increase the degree of dispersion of the film.

It is seen that the relatively small ratio of true to apparent area observed with films of only a few atoms average thickness is, in fact, misleading. The present view is in much better accord with the physical evidence.

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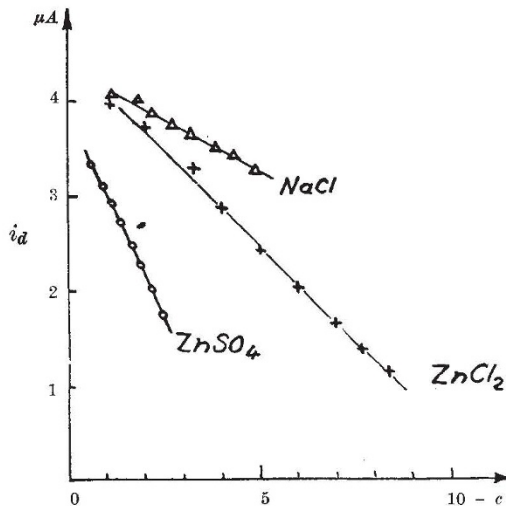[5] Roberts, J. K., "Some Problems in Adsorption" (Cambridge, 1939), 19.

Influence of the Nature and Concentration of Supporting Electrolyte on Polarographic Diffusion Current

WHEN determining traces of impurities in zinc alloys it was found to be of interest to study the behaviour of the diffusion current in supporting electrolytes of high concentration.

Shaikind[1] has found that the diffusion current of Pb^{2+} and Cd^{2+}, when present at constant concentration, decreases with increasing concentration of supporting electrolyte, when the latter is $ZnCl_2$ or $ZnSO_4$, but remains constant when it is KCl or Na_2SO_4. He ascribes the decrease in current to the increase in viscosity, but has not made any direct measurements concerning this.

Gentry[2] has investigated the relation between the diffusion current of Tl^+ and viscosity in ethylene glycol – water mixtures, and has found the product of the diffusion current and the square root of the viscosity of the medium to be constant. This paper was not published until our investigation was finished.

We have studied the systems set out in the accompanying table.

Supporting electrolyte	Concentration range of supporting electrolyte moles/lit.	Metal
$ZnCl_2$	1·5–10	Cd, Pb, Bi, Tl
$ZnSO_4$	0·3–2·4	Cd
$Zn(NO_3)_2$	0·5–4·8	Cd, Pb
NaCl	0·9–4·6	Cd
NH_4Cl	0·9–4·6	Cd
Na_2SO_4	0·1–0·9	Cd
$MgCl_2$	0·5–4·2	Cd
$CaCl_2$	0·5–4·0	Cd
$AlCl_3$	0·3–2·7	Cd
KSCN	1·0–9·2	Ni

All measurements have been carried out in a thermostat at 25·0° C. The solutions were freed from oxygen, and gelatin was added in some cases at a concentration of 0·005 per cent as a maximum suppressor.

The concentration of the metal is given by x, and that of the supporting electrolyte by c.

In all the cases investigated, a strict linear relationship was found between x and the diffusion current i_d, when c was constant.

The experiments were carried out in two different ways: (1) Varying c, keeping x constant. (2) Varying c, keeping $x/c = p$ (a constant).

(1) In the first series the diffusion current was found to be a linear function of c, i_d in most cases decreasing with increasing c (Fig. 1).

Fig. 1. Cd^{2+} IN VARIOUS SUPPORTING ELECTROLYTES (x IS CONSTANT)

The fundamental Ilkovic equation may in this case be written:

$$i_d = \text{const.}\ D^{1/2} \quad . \quad . \quad . \quad (1)$$

where D is the diffusion coefficient. According to Stokes–Einstein

$$D.\eta = \text{const.} \quad . \quad . \quad . \quad (2)$$

where η is the viscosity coefficient of the medium.

Measurements of viscosity have shown that there is a linear relationship between $\eta^{-1/2}$ and c in the concentration ranges given above:

$$\eta^{-1/2} = -a.c + b \quad . \quad . \quad . \quad (3)$$

where a and b are constants depending on the nature of the supporting electrolyte.

Combining (1), (2) and (3) we obtain

$$i_d = \text{const.}\ (-a.c + b) \quad . \quad . \quad (4)$$

In most cases it has been verified experimentally that the constants a and b are the same for any given supporting electrolyte, whether determined by polarographic or viscosimetric measurements.

It is interesting to note that in the case of a supporting electrolyte of NH_4Cl, where η decreases with increasing c, the diffusion current of Cd^{2+} also increases with increasing c, as was to be expected.