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The Motion of Solid and Liquid Metallic Bodies in Solutions of Electrolytes.

II. Motion in the field of gravity

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1. Falling drops

In the present paper we shall consider the electrical phenomena which arise when drops of a metal move through solutions of electrolytes in the field of gravity.

The fall of drops in a liquid medium was investigated by Hadamard[1] and Smoluchowski[2]. They showed that for small Reynolds numbers a drop falls without changing its spherical shape, the motion of the liquid within it having the character, in cross section, of two eddies.

The velocity of fall of the drop is given by the formula:

$$U = \frac{2}{3\mu} \frac{(\rho - \rho') a^2 g (\mu + \mu')}{2\mu + 3\mu'} \qquad (1)$$

The notations are the same as in Part I[3].

We see from (1) that the velocity of fall of a liquid drop is greater than that of a solid sphere, the latter being given by the well-known Stokes formula:

$$U = \frac{2}{9} \frac{(\rho - \rho') g a^2}{\mu} \qquad (2)$$

In the case of mercury drops in water the difference between the two velocities should be about 15%.

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[1] Hadamard, C. R., **152**, 1735 (1911).

[2] Smoluchowski, Proc. Math. Congress, Cambridge, 1912, p.192.

[3] A. Frumkin and B. Levich, Acta Phys. Chim., **20**, 769(1945).

Let us now consider the fall of a drop of mercury in an electrolyte solution. It is clear that the motion of the liquid at the mercury-solution interface drags along the outer ions of the double layer, thus giving rise to a convection current over the surface of the drop. The ions will be carried to the rear end of the drop and as a result of their accumulation an electric field will be set up.

This field should, evidently, send the ions back over the surface of the particle. On the other hand, the potential difference which has arisen between the fore and rear ends of the drop can be evened out by currents flowing through the bulk of the solution along the lines of force. Two limiting cases are obviously possible here.

1. The potential difference is evened up through the solution so rapidly that the convection current of ions along the surface is compensated by currents through the adjacent layers of solution without any noticeable accumulation of charges at the rear end of the drop. In this case the transfer of ions over the surface by convection proceeds freely and the resulting electric field does not retard the motion of the liquid along the surface. Hence the velocity of fall of the drop is determined, as in the absence of electrolytes, by formula (1).

2. The potential is practically not equalized at all and ions continually accumulate at the rear end of the drop until the resulting electric field completely stops their further transfer over the surface by convection[4].

In other words, in this case, the resulting electric field will completely stop the motion of mercury at the surface of the drop, which will thus fall as if it were solid. The velocity of fall of such a «solidified» drop is given by the Stokes law [2].

An exact computation, carried out by B. Levich [5] brings to the following general expression for the velocity of fall of an ideally polarizable drop:

$$U = \frac{2}{3} \frac{(\rho - \rho') g a^2}{\mu} \frac{\mu + \mu' + \frac{\varepsilon^2}{3\varkappa}}{2\mu + 3\mu' + \frac{\varepsilon^2}{\varkappa}} \tag{3}$$

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[4] Strictly speaking, besides currents through the bulk of the solution the concentration of ions on the surface can also be evened up by surface diffusion and surface conductivity, but here too, as in Part I, we shall neglect this small effect.

[5] Part III, to appear shortly.

It may be seen from (3) that the first limiting case is realized when $\frac{\varepsilon^2}{\varkappa} \ll \mu + \mu'$, and the second—when the reverse inequality is fulfilled. Thus, here too, as in the case of motion in an electric field, an increase in the surface density of charge completely damps the motion.

The transfer of the ions of the double layer by the flow of the liquid is accompanied by the appearance of an electric field in the space surrounding the drop.

Computations yield the following expression for the distribution of potential in the neighbourhood of an ideally polarizable drop falling in a liquid unbounded by walls:

$$\varphi = \frac{\varepsilon(\rho - \rho')ga}{3\varkappa\left(2\mu + 3\mu' + \frac{\varepsilon^2}{\varkappa}\right)} \frac{a^3}{r^2} \cos\theta \tag{4}$$

where θ is the angle between the radius vector and the direction of fall of the drop (Part III).

Smoluchowski derived an equation similar to (4) but with a different value of the coefficient of $\frac{\cos\theta}{r^2}$ for the case of a solid particle[6].

Equation (4) is valid at distances which are small compared to the diameter of the tube. The potential difference between the fore and rear ends of the drop, according to equation (3) and (4), equals:

$$\Delta\Phi = \frac{U\varepsilon\mu}{\varkappa\left(\mu + \mu' + \frac{\varepsilon^2}{3\varkappa}\right)} \tag{5}$$

Equation (5) could be obtained, except for the numerical coefficients, from considerations of dimensions. Denote by V the velocity of the liquid at the surface of the drop with respect to coordinate axes fixed in the centre of the drop, and let V be positive for upward motion. Then the force with which the external medium acts on 1 cm² of the surface of the drop is equal in order of magnitude to $\frac{(U-V)\mu}{a}$. This force is counterbalanced by the viscous strain inside the drop $\frac{V'\mu'}{a}$ and the retarding action of the electric field $\frac{\varepsilon\Delta\Phi}{a}$. Hence, in order of magnitude

$$\frac{V\mu'}{a} + \frac{\varepsilon\Delta\Phi}{a} \sim \frac{(U-V)\mu}{a}.$$

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[6] Smoluchowski, Graetz, Hand. der Elektriz. und des Magnetismus, 2, 385 (1914).

But, as it was pointed out in Section 4, Part I, we have in order of magnitude

$$\Delta\Phi \sim \frac{V\varepsilon}{\varkappa},$$

whence

$$\Delta\Phi \sim \frac{U\varepsilon\mu}{\varkappa\left(\mu+\mu'+\frac{\varepsilon^2}{\varkappa}\right)}.$$

When a shower of drops falls through a solution, a potential difference — called sedimentation potential — will obviously be set up along the height of fall.

Let the number of drops per unit volume of solution be sufficiently small, so that the distance between the drops is large compared to their dimensions. It can then be assumed that each drop falls independently of the others and that the electric fields of the drops are superposed additively. In this case the sedimentation potential can be calculated exactly.

Let us, first, consider more in detail a single drop falling through a column of liquid. We shall find the mean value of the potential $\overline{\varphi_u}$ in a plane S which lies above the drop at a distance small compared to the radius of the column, but does not intersect the drop; the linear dimensions of the plane are large compared to those of the drop and to the distance from it. The origin of coordinates will be taken in the centre of the drop. The surface area of the part of the plane intercepted between the angles θ and $\theta+d\theta$ is equal to $\frac{2\pi r^2 \sin\theta}{\cos\theta}\, d\theta$; hence, using equation (4), we obtain:

$$\overline{\varphi_u} = \frac{1}{S}\int_{\frac{\pi}{2}}^{\pi} \frac{2\pi r^2 \sin\theta}{\cos\theta}\,\varphi\, d\theta = \frac{2\pi}{S}\,\frac{\varepsilon(\rho-\rho')\,ga^4}{3\varkappa\left(2\mu+3\mu'+\frac{\varepsilon^2}{\varkappa}\right)}\int_{\frac{\pi}{2}}^{\pi}\sin\theta\, d\theta =$$

$$= -\frac{2\pi}{S}\,\frac{\varepsilon(\rho-\rho')\,ga^4}{3\varkappa\left(2\mu+3\mu'+\frac{\varepsilon^2}{\varkappa}\right)}.$$

In similar manner we find for the part of the surface lying below the drop

$$\overline{\varphi_d} = \frac{2\pi}{S} \frac{\varepsilon (\rho - \rho') g a^4}{3\varkappa \left(2\mu + 3\mu' + \frac{\varepsilon^2}{\varkappa} \right)} \, .$$

Hence the sedimentation potential caused by the fall of a drop in a column of liquid equals:

$$\overline{\varphi_d} - \overline{\varphi_u} = \frac{4\pi}{S} \frac{\varepsilon (\rho - \rho') g a^4}{3\varkappa \left(2\mu + 3\mu' + \frac{\varepsilon^2}{\varkappa} \right)} \, .$$

Let us denote by n the average number of drops per unit volume. The sedimentation potential E per unit length in the column of liquid, through which the drops are falling, will evidently equal

$$E = nS (\overline{\varphi_d} - \overline{\varphi_u}) = \frac{4\pi n \varepsilon (\rho - \rho') g a^4}{3\varkappa \left(2\mu + 3\mu' + \frac{\varepsilon^2}{\varkappa} \right)} = \frac{2\pi a^2 \mu U \varepsilon n}{\varkappa \left(\mu + \mu' + \frac{\varepsilon^2}{3\varkappa} \right)} =$$

$$= \frac{a \varepsilon n P}{(2\mu + 3\mu') \varkappa + \varepsilon^2} \, , \tag{6}$$

where P is the weight of the drop, and S — the cross section of the tube in which the drops are falling. Similarly to the mobility of a drop in an external electric field [see Part I, equation (32)], the quantity E passes through a maximum at $\varepsilon_{\max} = \sqrt{\varkappa (2\mu + 3\mu')}$. The last expression in equation (6) is obtained from equation (8), Part I, similarly to the case of the corresponding relations for the mobility in an electric field, by substituting $2\mu + 3\mu'$ for μ and a for d.

If the ends of a column of liquid of length L and cross-section S are connected with an external resistance W, the potential difference is equalized through the external circuit, so that a current I flows through the liquid and the external resistance and is superimposed on the system of local currents of the falling drops. Since the e. m. f. of the circuit equals EL,

$$I = \frac{EL}{\frac{L}{S\varkappa} + W} = \frac{I_0 \frac{L}{S\varkappa}}{\frac{L}{S\varkappa} + W} \tag{7}$$

where I_0 is the «current of falling drops», which flows when $W = 0$, *i. e.* when the column is short-circuited. According to (6) and (7)

$$I_0 = ES\varkappa = \frac{4\pi n S\varepsilon(\rho-\rho')ga^4}{3\left(2\mu+3\mu'+\frac{\varepsilon^2}{\varkappa}\right)} = \frac{2\pi a^2 n S U\varepsilon\mu}{\mu+\mu'+\frac{\varepsilon^2}{3\varkappa}} \tag{8}$$

In the case of positively charged particles the current in the external circuit flows from the bottom of the column to the top, and in the column itself, consequently, from top to bottom, *i. e.* in a direction opposite to the local currents near each drop. Indeed, connecting the ends of the column of liquid is equivalent to impressing an external potential difference equal in magnitude and opposite in sign to the total sedimentation potential EL. The potential determined by equation (4) thereby decreases and we shall find the value of this decrease for the case when it is most important, *viz.* when the drop is in the first regime of motion $\left(\frac{\varepsilon^2}{\varkappa} \ll 2\mu+3\mu'\right)$. In this case, according to equation (9), Part I, the potential in the column of liquid near the drop due to the current I_0 equals

$$-E\left\{r+\frac{1}{2}\frac{a^3}{r^2}\right\}\cos\theta$$

so that instead of (4) we obtain:

$$\varphi = \frac{\varepsilon(\rho-\rho')ga\cos\theta}{3\varkappa(2\mu+3\mu')}\left\{\frac{a^3}{r^2} - 4\pi n a^3\left(r+\frac{1}{2}\frac{a^3}{r^2}\right)\right\} \tag{9}$$

At the surface of the drop ($r=a$) the ratio of the second to the first term in equation (9) is $6\pi n a^3$, *i. e.* under our assumptions (distance between the drops large as compared to their radius) this ratio is small. In other words, connecting the external circuit does not essentially affect the distribution of potential in the immediate vicinity of each drop; hence, the substitution into equation (8) of the value of E from (6) is justified.

When the external circuit is open, the total current through each horizontal cross-section of the column of liquid is zero; in other words, the quantities of electricity transported by the convection current due to the motion of the outer sheets of the double layer and by the conductivity currents are equal in magnitude and opposite in sign. One could imagine that the sum of the conductivity currents is exactly equal to the «current of falling drops» which flows in the external circuit and in the column of liquid when the latter is short-circuited. In this case the total quantity of electricity transported through each cross-section of the column of liquid by electrical conduction would be equal to zero. In reality this is not so, as can easily be seen from the following computation. Let us draw a horizontal plane intersecting the drop and denote by θ_a the angle formed by the vertical and the radius vector drawn from the centre of the drop to a point of intersection of the surface of the drop with this plane. The conductivity current, which emerges from the lower part of the drop and enters the upper part, and, therefore, passes through the cross-section of the solution indicated, equals

$$I' = -\varkappa \int\limits_0^{\theta_a} \frac{\partial \varphi}{\partial r}\, 2\pi a^2 \sin\theta\, d\theta = \frac{2\pi\varepsilon(\rho-\rho')ga^3}{3\left(2\mu+3\mu'+\dfrac{\varepsilon^2}{\varkappa}\right)} \sin^2\theta_a .$$

The number of drops in the tube for which θ_a lies between θ and $\theta + d\theta$ is $nSa \sin\theta d\theta$ and, hence, the total conductivity current equals

$$I'' = \int\limits_0^{\pi} I' nSa \sin\theta\, d\theta = \frac{8}{9} \frac{\pi\varepsilon(\rho-\rho')ga^4 nS}{2\mu+3\mu'+\dfrac{\varepsilon^2}{\varkappa}} = \frac{2}{3} I_0 .$$

The reason for the difference between I'' and I_0 becomes clear if one bears in mind that the current I_0 which is superimposed on the local currents when the column is short-circuited, and the sum of the conductivity currents flowing, when the circuit is open, correspond to potential differences between the ends of the column which are equal in magnitude; but whereas with respect to the current I_0 the solution acts practically as a homogeneous conductor, the lines of the current I'' composed of the local currents of the individual drops deviate markedly from shortest distances.

It follows from equation (7) for the first limiting case of motion that

$$I_0 = 2\pi n\varepsilon a^2 S\mu(\mu+\mu')^{-1} U .$$

Inasmuch as the quantity $4\pi\varepsilon a^2 nSU$ expresses the total charge of the inner sheet of the double layer on the drops passing through a cross section of the tube in unit time, the current due to the fall of the drops differs in this case only by the coefficient $\frac{\mu}{2}(\mu+\mu')^{-1}\sim 0.2$ [7] from the value which it would have for falling spheres with a free charge equal to the total charge of the inner sheet of the double layer.

The above reasoning loses its force in the case of a «dense» shower of mercury drops when the distances between the drops are no longer large compared with their radii, *i. e.* $n^{1/3}\sim a$. In this case, which is of purely theoretical interest being difficult to realize experimentally, the electric fields near each drop can no longer be considered independently of one another and the local deviations from equipotentiality are averaged out. This corresponds to an apparent increase in the electrical conductivity of the medium surrounding the drop, as a result of which the retarding action of the charge on the motion of the surface of the drop is weakened. Moreover, under these conditions the external circuit now substantially affects the distribution of potential near each drop, and in the limiting case of a very «dense» shower the retarding action of the charge should disappear entirely when the external resistance is short-circuited, similarly to what occurs when a liquid is forced through a solid diaphragm. In the case of a «dense» shower, connecting the external circuit must also affect the velocity of fall of the drops.

The strict application of equation (4) entails imposing a number of conditions whose exprimental realization may present some difficulty. Thus the Reynolds number should be less than unity, whereas in the case of mercury drops falling in water $U\sim 30$ cm/sec. and $a = 10^{-2}$, whence $\mathrm{Re}\sim 30$. Furthermore, the change in the potential difference at the surface of the drop should be small compared to the initial potential difference and hence

$$\frac{\varepsilon(\rho-\rho')ga^2}{3\varkappa\left(2\mu+3\mu'+\frac{\varepsilon^2}{\varkappa}\right)}=\frac{1}{2}\,\frac{\varepsilon U\mu}{\varkappa\left(\mu+\mu'+\frac{\varepsilon^2}{3\varkappa}\right)}<\frac{\varepsilon}{C},$$

$$\frac{1}{2}\,\frac{U\mu}{\varkappa(\mu+\mu')+\frac{\varepsilon^2}{3}}<\frac{1}{C} \tag{10}$$

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[7] On first thought such a result seems surprising; however, it will readily be understood that in the first limiting case the convection current transfers a quantity of electricity of the order of $2\pi aU\varepsilon$ from the lower to the upper part of the drop, *i.e.* through a distance a. The product of these two quantities $2\pi a^2U\varepsilon$ is of the same order of magnitude as the product of the velocity of fall by the total charge of the sphere $4\pi a^2\varepsilon$.

where C is the capacity of the double layer. Condition (10) can be fulfilled with small values of the concentration ($10^{-3}N$ and less) only if ε is not too small.

All the above formulae refer to the case of an ideally polarizable drop. In the presence of mercury ions the changes in the potential drop in the double layer due to the convection current are partially evened up through discharge of the mercury surface; this causes a decrease in the sedimentation potential and a simultaneous decrease in the effect of retardation of the motion. Due to the complicated relationship between the limiting diffusion current and the angle θ, an exact calculation is impossible, just as in the similar case discussed in Section 4 Part I. If the limiting diffusion current were independent of θ, then in the case of incompletely polarizable drops equation (6) would have to be replaced (see Part I) by

$$E=\frac{4\pi}{3}\,\frac{n\varepsilon(\rho-\rho')\,ga^4k^{-1}}{\varkappa(2\mu+3\mu')+\varepsilon^2k^{-1}}=\frac{4}{3}\,\frac{\pi n\varepsilon(\rho-\rho')\,ga^4}{\varkappa k(2\mu+3\mu')+\varepsilon^2} \tag{11}$$

where $k=1+\frac{a}{2\varkappa w}$. This expression, at any rate, allows of an approximate estimate of the decrease in the sedimentation potential due to incomplete polarizability of the drops. Similarly equation (3) must be replaced by

$$U=\frac{2}{3}\,\frac{(\rho-\rho')\,ga^2}{\mu}\,\frac{k(\mu+\mu')+\frac{\varepsilon^2}{3\varkappa}}{k(2\mu+3\mu')+\frac{\varepsilon^2}{\varkappa}}$$

The fall of mercury drops in a liquid containing mercury ions, besides bringing to a separation of electric charges should also cause a change in the concentration of the mercury ions. With positively charged drops the concentration will increase in the upper part of the column and decrease in the lower part. This should bring to a potential difference between mercury electrodes of the first type in contact with the solution, whose sign is opposite to that of the sedimentation potential. In contradistinction from the sedimentation potential this effect does not disappear when the fall of the drops through the solution ceases, but remains until the difference in concentration in the column of liquid is evened up by diffusion. If the mercury drops are formed in the upper part of the column of liquid and merge together in the lower part this too brings about changes in the concentration such as are familiar from the theory of the dropping electrode. In this case, however, the concentration of mercury ions falls off in the upper part of the column and increases in the lower part, *i. e.* the change in the concentration is opposite in sign to the change induced by the falling process itself. This may possibly explain some of the phenomena observed by Billitzer[8] in his experiments with dropping electrodes.

The relations derived in this paper can be compared with the results of measurements of currents of falling drops carried out by N. Bach[9]. In these experiments the shower of drops was obtained by forcing mercury through a glass diaphragm at the rate of 3.1 cm^3 mercury per second. The drops fell through a column of oxygen-free solution 90 cm high and 3 cm in diameter of composition $x\ KNO_3 + 10^{-6} N\ Hg_2(NO_3)_2 + 2 \times 10^{-7}\ N\ HNO_3$, and merged into one continuous mass of mercury at the bottom of the column. By means of two calomel electrodes a side circuit of resistance W was connected to the column of liquid to allow of maesuring the current I.

N. Bach's paper gives the values of the current of falling drops I_0, calculated from I and W by equation (7) for x varying from $1N$ to $10^{-5} N$. In one experiment measurements were made of the dropping electrode current which set in, when the mercury above the glass diaphragm was short-circuited with the lower mercury surface, while the charge of the mercury which passed through the diaphragm was found from the electrocapillary curve using the potential measured under the same conditions. The surface area of the drops formed in unit time was calculated from the current and the charge, while from the surface area and the volume flow of mercury per second the average value of the radius of the drops was found to be $a = 1.1 \times 10^{-2}$ cm. The application of equation (7) to these experiments involves a number of difficulties.

1. Under the conditions of the experiment $U \sim 30$ cm/sec., hence the Reynolds number $\mathrm{Re} \sim \frac{30 \times 1 \cdot 1 \times 10^{-2}}{10^{-2}} \sim 30$, *i. e.*, much greater than unity. Direct observation showed that the motion of the liquid was of a turbulent character and the paths of the drops deviated from the vertical.

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[8] Billitzer, Z. physik. Chem., **48**, 513 (1904).
[9] N. Bach, Acta Phys. Chim., **1**, 27 (1934).

2. At the beginning of the fall, when the charge of a drop was still small, condition (10) was not fulfilled in dilute solutions.

3. The expressions derived refer to a shower of drops of equal dimensions. This condition was not satisfied in the experiments of N. Bach, and the quantity $a = 1.1 \times 10^{-2}$ cm expresses an average value of a $\left(\text{computed according to the formula } \frac{\Sigma a^3}{\Sigma a^2}\right)$. Moreover a was not determined individually for each solution, although due to the dependence of the interfacial tension on the composition of the solution, the conditions of formation of the drops varied somewhat in the different cases.

4. In the derivation of equations (6) and (7) it was assumed that the charge of the drops ε remains constant throughout the motion. In N. Bach's measurements of the current of falling drops the mercury emerging from the diaphragm was not connected with any other electrode so that the charge of the drops upon leaving the diaphragm was zero. After falling through a solution containing $Hg_2^{\cdot\cdot}$ ions drops acquired a positive charge; in other words, ε increased during the motion. It is not difficult to modify equation (7) so that it holds in the case of a linear growth of ε with the path of the drop l. Since the quantity $\frac{4}{3}\pi a^3 nSu$ equals the volume of mercury γ which passes through a cross-section of the column in unit time, it follows from equations (6) and (7) that

$$I_0 = \frac{3}{2}\,\frac{\gamma\varepsilon\mu}{a\left(\mu + \mu' + \frac{\varepsilon^2}{3\kappa}\right)} \tag{12}$$

Suppose now that ε increases linearly with l and denotes by ε_L the value of ε, which the drop acquires on passing through a column of length L. Then

$$I = \frac{3\gamma\mu}{2a}\cdot\frac{1}{L}\int_0^L \frac{\varepsilon\, d}{\mu + \mu' + \frac{\varepsilon}{3\kappa}} = \frac{3\gamma\mu}{2a}\,\frac{1}{L}\int_0^L \frac{\varepsilon_L \frac{l}{L}\, dl}{\mu + \mu' + \frac{l^2}{L^2}\cdot\frac{\varepsilon^2{}_L}{3\kappa}} =$$

$$= \frac{9\gamma\mu}{4a}\,\frac{\kappa}{\varepsilon_L}\ln\left(\frac{\mu + \mu' + \frac{\varepsilon^2}{3\kappa}}{\mu + \mu'}\right). \tag{13}$$

In N. Bach's experiments $\gamma = 3.1$ cm³ per sec, $\mu = 0.0105$, $\mu' = 0.015$, $a = 1.1 \times 10^{-2}$. Inserting these values in equation (13), and going over to practical units we can write:

$$I = 15.3 \times 10^{-7} \frac{\varkappa}{\varepsilon_L} \lg (1 + 1.27 \times 10^8 \varepsilon_L^2 \varkappa^{-1}). \tag{13a}$$

If, after passing through a column of liquid of length L, a drop acquires a charge ε_{L_1}, which then grows according to a linear law up to a value corresponding to a length L, then it is easily shown that for a section of the path $L - L_1$ we obtain instead of (14):

$$I = \frac{9\gamma\mu}{4a} \frac{\varkappa}{\varepsilon_L - \varepsilon_{L_1}} \ln \frac{\mu + \mu' + \frac{\varepsilon_L^2}{3\varkappa}}{\mu + \mu' + \frac{\varepsilon_L^2}{3\varkappa}} = 15.3 \times 10^{-7} \frac{\varkappa}{\varepsilon_L - \varepsilon_{L_1}} \times$$
$$\times \lg \frac{1 + 1.27 \times 10^8 \varepsilon_L^2 \varkappa^{-1}}{1 + 1.27 \times 10^8 \varepsilon_{L_1}^2 \varkappa^{-1}}. \tag{14}$$

In order to apply equation (13) it is necessary to know the charge acquired by the drop at the end of its path.

One of us (B. Levich) found the following expressions for the diffusion current per unit area of the surface of a spherical particle moving in a solution[10]

$$(j_d)_l = 0.85 \left(\frac{DU}{a}\right)^{1/2} n_k F c_k \tag{15}$$

in the case of a liquid drop, and

$$(j_d)_s = 1.1 \left(\frac{D^2 U}{a^2}\right)^{1/3} n_k F c_k \tag{16}$$

for a solid particle; D denotes the diffusion coefficient, n_k — the valency and c_k — the concentration of the diffusing substance (in moles per cm³). In the present case $D = 0.78 \times 10^{-5}$ (from the mobility of mercury ions at 25° — 68.6 recalculated for 18) and $n_k c_k = 10^{-9}$.

As shown above the regime of a mercury drop in a solution of an electrolyte corresponds to the regime of fall of a liquid drop if $\varepsilon \ll \varepsilon_{\max}$, and to that of a solid spherical particle if $\varepsilon \gg \varepsilon_{\max}$, where $\varepsilon_{\max} = \varkappa^{1/2} (2\mu + 3\mu')^{1/2}$. Since the dependence of j_d on U is not known for intermediate values of ε, an approxi-

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[10] Acta Phys. Chim., to appear shortly.

mate assumption was made in computing ε, according to which j_d is given by equation (15) for all values of $\varepsilon < \varepsilon_{\max}$ and by equation (16) for $\varepsilon > \varepsilon_{\max}$. U was computed in the first case from equation (1) and in the second—from equation (2). Hence, applying equations (15) and (16) we obtain:

$$(j_d)_l = 13 \times 10^{-6}\ a/\text{cm}^2 \text{ and } (j_d)_s = 2.7 \times 10^{-6}\ a/\text{cm}^2.$$

When the total concentration of the solution is less than $10^{-2}\ N$ one can assume that throughout the time of fall the condition $\varepsilon > \varepsilon_{\max}$ is practically fulfilled. In this case ε_L was computed according to the formula

$$\varepsilon_L = \frac{L}{U_2}\,(j_d)_s = 7.6 \times 10^{-6}\,\frac{\text{coul.}}{\text{cm}^2}\,.$$

For the most dilute of the solutions investigated with $\varkappa = 2.5 \times 10^{-6}$, a correction must be made for incomplete polarizability, since in this case the quantity $k = 1 + \frac{a}{2\varkappa W}$ was different from unity. Indeed, according to the equation $W = RT/2Fj_d$, for $j_d = 2.7 \times 10^{-6}$, $W = 4.7 \times 10^{-3}$ and $k = 1.5$. In this case, on the basis of equation (11) the quantity $(\mu + \mu')$ in equation (13) must be replaced by $(\mu + \mu')\,k$; this, however hardly affects the result which is determined in the main by the coefficient preceding the logarithm. For a $10^{-4}\ N\text{KNO}_3$ solution ($\varkappa = 1.4 \times 10^{-5}$) $k = 1.08$ and the correction for incomplete polarizability has no practical importance.

In the case of solutions with a total concentration equalling $10^{-2}\ N$ and $10^{-1}\ N$ in a considerable part of the path of the drop $\varepsilon < \varepsilon_{\max}$. In such cases the computations were carried out as follows. The value of $\varepsilon_{\max}$ was calculated for each solution; then the expression

$$\varepsilon_{\max} = \varepsilon_{L_1} = \frac{L_1}{U_1}\,(j_d)_l$$

was used to determine the path L_1 which a drop must traverse in order to acquire a charge equal to $\varepsilon_{\max}$. The charge which the drop possessed at the end of its fall was found from the equation

$$\varepsilon^L - \varepsilon_{\max} = \frac{L - L_1}{U_2}\,(j_d)_s.$$

Substituting these values of ε_{L_1} and ε_{L_2} in equations (13) and (14) it is easy to find the values of I_1 and I_2 corresponding to the first and second parts of the path and hence from the equation $I_0 = \frac{I_0 L_1 + I_2 (L - L_1)}{L}$ to determine ~~the total~~ value of I_0. In the case of a normal KNO_3 solution such computations lead to values of ε exceeding the possible equilibrium value in the given system. The equilibrium potential of mercury in $N\,KNO_3 + 10^{-6}\,N\ Hg_2(NO_3)_2$ equals 0.63 and is 0.91 away from the maximum of the electrocapillary curve. The average capacity on the positive branch of the electrocapillary curve of KNO_3 according to Krüger's data [11] is 29×10^{-6}, whence for the equilibrium value of ε in this solution we obtain $\varepsilon = 26 \times 10^{-6}$. The drop could have acquired this value in $\frac{26 \times 10^{-6}}{13 \times 10^{-6}} = 2$ sec. over a path of 73 cm; on the remainder of the path the value of ε should have remained constant. In this case I_1 was computed for the first part of the path by equation (13) and I_2 for the second part by equation (12) with a value of $\varepsilon = 26 \times 10^{-6}$; the total value of I_0 was found from I_1 and I_2 as described above. The method of computing ε is not entirely reliable, however, this circumstance introduces a much smaller element of indefiniteness into the

Table 1

Currents of falling drops $x\ KNO_3 + 10^{-6}\,N Hg_2(NO_3)_2 + 2 \times 10^{-7}\,N HNO_3$ solutions

x	$\varkappa$	ε_L	$I_{0\,calc.}$	I_0 obs. (according to N. Bach)
1 N	8.05×10^{-2}	26×10^{-6}	1.6×10^{-3}	2.3×10^{-3}
$10^{-1} N$	1.05×10^{-2}	14×10^{-6}	6.9×10^{-4}	3.2×10^{-4}
$10^{-2} N$	1.18×10^{-3}	9.8×10^{-6}	2×10^{-4}	1×10^{-4}
$10^{-3} N$	1.26×10^{-4}	7.6×10^{-6}	4.5×10^{-5}	1.9×10^{-5}
$10^{-4} N$	1.4×10^{-5} *	7.6×10^{-6}	7.5×10^{-6}	4.3×10^{-6}
$10^{-5} N$	2.5×10^{-6} *	7.6×10^{-6}	17×10^{-7}	9.3×10^{-7}

*Corrected for the electrical conductivity of the initial water 1×10^{-6}.

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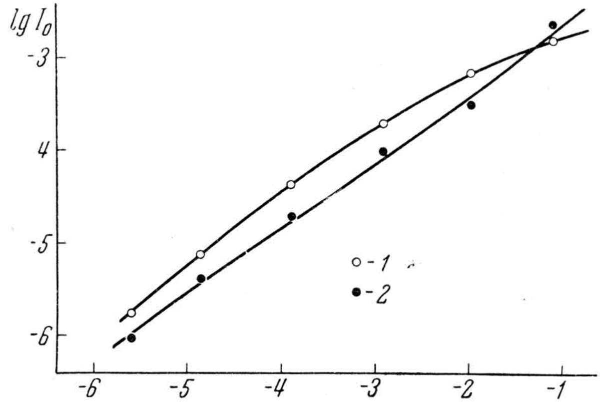
[11] Krüger u. Krumreich, Z. Elektrochem., **19**, 617 (1913).

calculation of I than might at first appear, since the variation of ε within certain limits does not affect the value of I very strongly. The final results of the calculations are summarized in Table 1. The third column gives the calculated values of ε at the end of the path of the drop.



Abscissae—lg $\varkappa$

Fig. 1. Currents of falling drops in acidulated KNO_3 solutions of different conductivity: 1—calculated values; 2—experimental values of N. Bach.

Fig. 1 shows the dependence of I on $\varkappa$ in the logarithmic scale. If it is taken into consideration that the conditions of the experiment differed markedly from those strictly demanded by the theory, and that the computation of ε_L was not entirely reliable the agreement between theory and experiment may be regarded as quite satisfactory. At any rate, the theory gives the correct order of magnitude of I_0 and the dependence of I_0 on the electrical conductivity over a wide range of values. It should be borne in mind that in the case of solid particles I_0 should increase, not decrease, with dilution of the solution.

2. The flow of mercury from a capillary

Antweiler[12] observed that when water flows out of a capillary tube the liquid in the drop describes a turbulent motion. The velocity of this motion is naturally greater, the greater the velocity of the liquid jet emerging from the capillary. When mercury

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[12] Antweiler, Z. Elektrochem., **47**, 839 (1938).

drops emerge into solutions of electrolytes similar motions should arise. However, the familiar Ilkovic-Rideal-McGillavry formula which forms the basis of polarographic analysis is derived on the assumption that a drop grows like a rubber balloon, only by radial displacements, and the wide applicability of this formula shows that in many cases the tangential motion of the liquid can be disregarded. Krjukova and Kabanov [13] obtained polarographic curves in sufficiently concentrated solutions of electrolytes which reveal the presence of motions connected with the flow of mercury from a capillary and observed these motions directly. They are represented schematically in Fig. 2 (according to Krjukova). These motions can give rise to additional maxima on the polarographic curves which to distinguish them from the ordinary maxima connected with the unequal polarization of the mercury surface, can be called polarographic maxima of second kind. We shall not, however, dwell any further here on the theory of these maxima, but shall limit ourselves to the case when the growth of the drop in the electrolytic solution proceeds in the absence of a current, *i. e.* unaccompanied by electrolysis. The motions on a mercury electrode will be discussed in a subsequent paper.

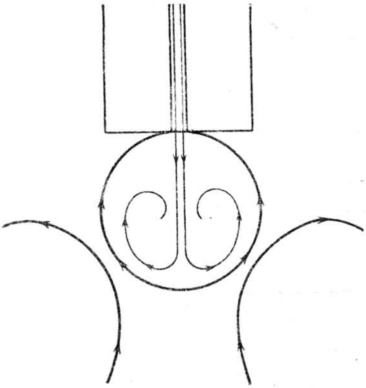

Fig. 2. Flow of mercury from a capillary tube according to T. Krjukova.

The motions which arise in a drop upon emergence from a capilary should carry back the charges of the double layer to the upper part of the drop and the resulting electric field should retard the motion, especially in the case of large charges and small electrical conductivity of the solution. Inasmuch as the phenomenon is qualitatively fully similar to the case of falling drops already discussed, it is superfluous to dwell on it any longer. The complexity of the dyna-

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[13] Krjukova and Kabanov, J. Phys. Chem. (Russ.), **13**, 1454 (1939); ibid., **15**, 775 (1941).

mical conditions in the case of flow from a capillary renders difficult the development of a strict quantitative theory. However, the theory of the current caused by falling drops contains one relationship, which can be applied with benefit to the present case. The velocity v at some point of the surface of an ideally polarizable drop $\left(e.\ g.\ \text{at}\ \theta=\frac{\pi}{2}\right)$ relative to a coordinate system fixed in the drop is equal, as will be shown in Part III, to

$$v=\frac{1}{3}\,\frac{(\rho-\rho')\,ga^3}{2\mu+3\mu'+\frac{\varepsilon^2}{\varkappa}} \tag{17}$$

If we denote by v_0 the value of v with the same μ and μ' but with $\varepsilon=0$, we have, accordingly:

$$\frac{v}{v_0}=\frac{(2\mu+3\mu')}{\left(2\mu+3\mu'+\frac{\varepsilon^2}{\varkappa}\right)} \tag{18}$$

It is clear from the qualitative analysis of the phenomena occurring in the motion of a charged surface, which was given in Section 1, that a relation similar to (18) should also apply to the flow of a drop from a capillary, the difference in the dynamic conditions merely causing a change in the numerical coefficients. When a drop flows out of a capillary the motion of the mercury surface is communicated to the adjacent layers of the solution, as depicted in Fig. 2, and can be observed, *e. g.*, if particles of carbon powder are suspended in the solution. It was in this manner that equation (13) was subjected to a semi-quantitative analysis by T. Krjukova, who kindly permitted us to utilize her results. The flow of mercury took place at the rate of 10.8 mg per second at constant potentials in an oxygen-free solution; the diameter of the drops was 1.1 mm; the drop time $\tau=0.9$ sec. A comparative estimate of the velocity of the particles suspended in the solution was made by visual observation through a microscope of the region near the lower surface of the drop where the velocity is greatest. The maximal velocity was 4—5 mm per second. The relative values of the velocity, *i. e.* the values of $\frac{v}{v_0}$, estimated at various concentrations and potentials, are represented in Fig. 3 by arrows. After these measurements were made the values of the function $f=\frac{2\mu+3\mu'}{2\mu+3\mu'+\frac{\varepsilon}{\varkappa}}$ were calculated. Introducing the numerical values of μ and μ' and expressing ε and $\varkappa$ in practical units, we obtain:

$$f=\frac{0.068}{0.068\times 10^7\varepsilon^2\varkappa^{-1}}\,.$$

The values of ε were calculated from direct measurements of the capacity of the mercury surface in KCl solutions. For solutions of N, 0.1 N and 0.01 N KCl we used unpublished data of T. Borisova (Karpov Institute, Moscow); for 0.0001 N KCl—data of Vorsina[14] and for 0.001 N KCl—values averaged from the data of Vorsina and Borisova. To calculate ε from the measured capacity it is necessary to know the potential of zero charge ($\varepsilon=0$). This latter can be determined from electrocapillary measurements or (in dilute solutions) from the position of the minimum on the capacity-concentration curve. The curves in Fig. 3 represent the calculated values of f as a function of the potential; the mercury potentials on the axis of abscissae refer to the normal calomel electrode. The circles on the axis of abscissae denote the positions of the zero charge potentials for the corresponding solutions (—0.56 in N KCl;—0.52 in 0.1 N, 0.01 N and 0.01 N KCl;—0.51 in 0.0001 N KCl). As may be seen from the figure, the calculated curves render correctly the

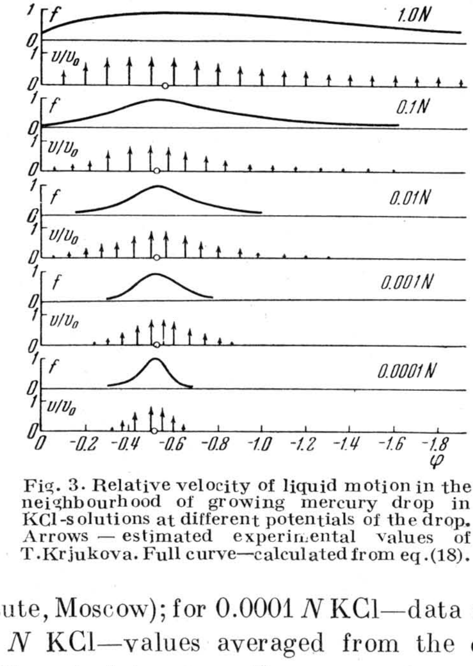

Fig. 3. Relative velocity of liquid motion in the neighbourhood of growing mercury drop in KCl-solutions at different potentials of the drop. Arrows — estimated experimental values of T. Krjukova. Full curve—calculated from eq. (18).

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[14] Vorsina and Frumkin, C. R. Acad. Sci., **24**, 918 (1939).

experimental dependence of the velocity of motion on the potential and concentration of the solution. Whereas in the well conducting solution N KCl the drop behaves like a liquid at all the potentials investigated, as the electrical conductivity of the solution decreases, the range of potentials in which tangential motions can still be observed becomes narrower and narrower, and in dilute solutions these motions are observed only in the immediate vicinity of the maximum of the electrocapillary curve. At other potentials the mercury surface acts as if it were solid, or rather, as if it were an elastic membrane and the growth of the drop is accompanied only by radial displacements of the mercury. The curves v/v_0 *vs.* potential also clearly reveal especially in more concentrated solutions a more rapid decrease of the velocity of motion on passing from the zero charge point towards more positive potentials as compared to the range of more negative potentials. This is due to the greater capacity of the positively charged mercury surface.

On going over from falling to growing drops we ignored one circumstance, which now demands the introduction of a correction into the theory here developed. In order that the potential of the growing drop remain constant, a charging current of average density $\varepsilon\tau^{-1}$ must flow through it, so that in contradistinction to a falling drop the total current on a growing drop is not equal to zero. Due to a slightly higher resistance of the solution with respect to the lines of current flowing towards the surface of the drop near the end of the capillary as compared with those flowing towards the lower surface of the drop, the charging of the drop does not take place quite uniformly; as a result, differences of potential and of interfacial tension should arise, and hence also motions tending to even up these differences. It will easily be seen that in contradistinction to the motions previously considered, the rôle of the latter motions should be the more important, the greater the charge and the lower the electrical conductivity of the solution. In view of the smallness of the charging current, however, this effect is small and has not as yet been detected experimentally.

It is interesting to consider the case of mercury dropping into a solution containing mercury ions or the analogous case of an amalgam in a solution containing ions of the corresponding metal. Under these conditions the quantity $\frac{\varepsilon^2}{\varkappa}$ in equation (19) should be divided by a «depolarization factor» $k = 1 + \frac{a}{2\varkappa W}$ the significance of which was explained above:

$$\frac{v}{v_0} = \frac{(2\mu + 3\mu')}{2\mu + 3\mu' + \frac{1}{k}\frac{\varepsilon^2}{\varkappa}} \tag{19}$$

It follows from equation (19) that in the case of depolarization tangential motions should occur at higher values of ε as well. This conclusion has not yet been checked experimentally.

A further verification of equations (18) and (19) is planned by means of quantitative measurements of the velocity v at different potentials and concentrations, it is also proposed to make measurements in presence of substances exerting an additional retarding action on motions of the surface, such as multivalent cations, surface active substances, *etc.*

Summary

1. The dependence of the sedimentation potential and the current caused by the fall of mercury drops in an electrolyte solution on the radius of the drops, charge density, electrical conductivity and viscosity of the solution is determined; it is shown that the behaviour of the drop varies depending on the value of the dimensionless quantity $\frac{\varepsilon^2}{\varkappa(2\mu + 3\mu')}$. At small values of this number the mercury drops behave like liquid drops, whereas at large values the electric fields set up retard the motion of the surface and the drops act as if they were solid. The derived relations were borne out by the results of measurements of currents caused by falling mercury drops obtained by N. Bach.

2. It is shown that the process of flow of a mercury drop into a solution also depends on the value of the same number. At small values the flow will be accompanied by eddy motions of the mercury inside the drop, the mercury on the surface flowing from the lower to the upper part of the drop. At large values the drop will grow only by radial motion of the liquid, as is usually assumed in the theory of polarographic analysis. These conclusions were checked by data of T. Krjukova on the motion of the liquid when mercury flows into KCl solutions of various concentrations.

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