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THE VELOCITY OF FALL OF MERCURY DROPS IN A VISCOUS MEDIUM

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The velocity of fall u_s of solid sphere of radius a in a viscous medium is given by the well-known formula of Stokes. Hadamard (1) and Rybczinski (2) have shown that the velocity of fall of a liquid drop is greater than u_s

$$u = u_s \frac{3\mu + 3\mu'}{2\mu + 3\mu'} \tag{1}$$

where μ is the viscosity of the surrounding medium, and μ', the viscosity of the drop. If $\mu \gg \mu'$

$$u = \frac{3}{2} u_s \tag{2}$$

The difference between u and u_s is due to the fact that for a falling liquid drop the tangential velocity at the interface is not zero. A vortical kind of motion arises in the falling drop, which makes particles of the liquid continually flow from the interior to the surface in the lower (front) part of the drop, and from the surface to the interior in the upper (rear) part.

A number of authors have checked the formula of Hadamard — Rybczinski (3). The observed velocities are usually smaller than those computed from equation (2). In a careful investigation Lebedev (4) could find no appreciable difference between the velocities of fall in castor oil of solid spheres and mercury drops up to 0.15 cm in radius. Hower, Volarovich and Leontieva (5) report that drops of molted lead fall in B_2O_3 according to equation (2). Bond and Newton (6) find that there is a critical radius of the drop $\bar{a}$. At $a \ll \bar{a}$ the drops fall according to Stokes' formula, and at $a \gg \bar{a}$, according to equation (1). Bond and Newton explain the existence of a critical radius by the action of the interfacial tension σ which hinders the tangential motion. They have found on dimensional considerations

$$\bar{a} \sim \frac{\sigma^{1/2}}{(\rho - \rho')^{1/2} g^{1/2}} \tag{3}$$

However, as the surface area of drop remains constant during the time of fall, as long as the surface layer remains in equilibrium with the volume phases, the transition of molecules from the interior to the surface and *vice versa* cannot be accompanied by a change in the free energy and cannot give rise to forces at the interface. Boussinesq (7) proposed the equation

$$u = u_s \frac{3\mu + 3\mu' + ea^{-1}}{2\mu + 3\mu' + ea^{-1}} \tag{4}$$

where e is the ratio of the change in the interfacial tension to the rate of change of the area of the liquid surface upon its deformation; it can be regarded as a measure of a certain surface viscosity. At small a Boussinesq's equation reduces to Stokes' formula; at large a, to the equation of Hadamard — Rybczinski. However, the existence of a measurable surface viscosity for a pure liquid surface at the rates of deformation which occur in measurements of the velocity of falling drops has never been confirmed.

Frumkin and Levich (8) have shown that in the presence of a double electric layer at the liquid — liquid interface the tangential motion gives rise to a potential difference between the front and rear parts of the drop, which retards the fall. According to this theory, the velocity of fall of a charged metal drop is

$$u = u_s \frac{3\mu + 3\mu' + \frac{\varepsilon^2}{\varkappa}}{2\mu + 3\mu' + \frac{\varepsilon^2}{\varkappa}} \qquad (5)$$

where ε is the charge per unit surface of the drop, *i. e.* of the inner shell of the double layer, and $\varkappa$ the specific electric conductivity of the solution. At $\frac{\varepsilon^2}{\varkappa(\mu+\mu')} \ll 1$, equation (5) reduces to equation (1), and at $\frac{\varepsilon^2}{\varkappa(\mu+\mu')} \gg 1$, to Stokes' formula. In the deduction of equation (5) it is assumed that the surface is «ideally polarizable», *i. e.* that the ions of the solution can neither be formed nor disappear on the surface of the drop. At $\mu \gg \mu'$ (mercury in glycerine)

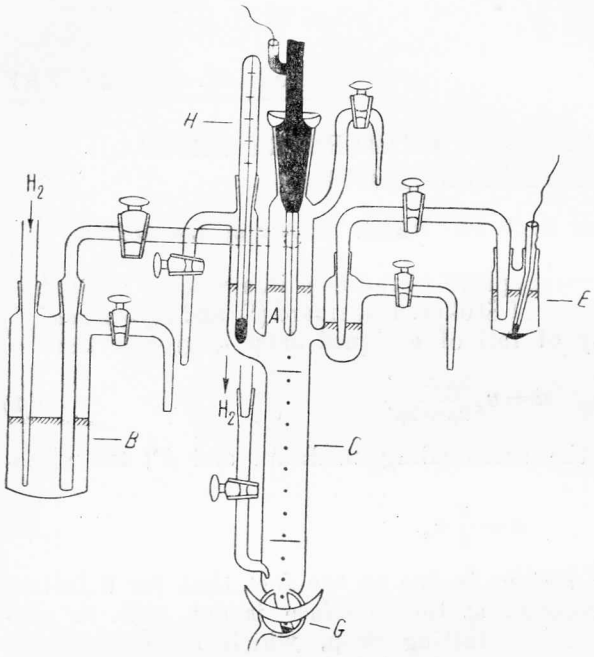

Fig. 1.

$$u = u_s \frac{3\mu + 3\mu' \frac{\varepsilon^2}{\varkappa}}{2\mu + \frac{\varepsilon^2}{\varkappa}} \qquad (5a)$$

It can be easily shown that $a\varepsilon^2/\varkappa$ in order of magnitude expresses the change in the interfacial tension at unit rate of deformation of the drop surface. In this sense the term $\varepsilon^2/\varkappa$ in equation (5) plays the same rôle as e/a in equation (4), although the two expressions have completely different physical meanings.

In the present investigation equation (5a) was checked experimentally. The apparatus used in these experiments is schematically depicted in Fig. 1. Under the pressure of a column of mercury, drops of mercury 0.4—0.5 mm in radius flowed from the capillary A into a solution of an electrolyte in glycerine containing a small quantity of water (1—3 per cent). The dropping time was approximately 0.5 sec.; the viscosity of the solution at 20° was 5—7 poise, the velocity of fall was approximately 1 cm/sec. Prior to the measurements the heated solution in the side vessel B was saturated with hydrogen for 20 hours and then forced into the measuring vessel C which has also been preliminarily filled with hydrogen. Several experiments were also carried out on single drops; in such cases the drops were thrown into the solution from a glass plate wetted by the solution. In these cases as well

as in some experiments with drops flowing from the capillary, the dissolved air was not removed from the solution. The solutions were prepared from c. p. glycerine of an American brand. The electrolytes were Na_2SO_4 and KBr, twice recrystallized and ignited. The solutions were prepared directly in the vessel B. The velocity of fall of the drops in the tube C was determined by the time of fall between two marks made on the glass at a distance of 5 cm.

The drops were given a definite charge by an external source of e. m. f. inserted into the circuit consisting of an auxiliary mercury electrode E, the solution and the growing drop. The magnitude of ε was calculated from the formula $\varepsilon = i/s$, where i is the average current and s is the surface area of the drops formed in unit time. The latter was computed from the dropping time and the radius of the drops. The radius under the given conditions of dropping was determined by weighing 150 drops which were collected in the lower part of the tube C and then removed by way of the stopcock G. The radius varied slightly with ε throughout one series of measurements. The values of a given below correspond to $\varepsilon = 0$. The value of the charge and of u_s for each point were calculated using the value of a found for that particular point experimentally.

The temperature of the solution was read on the thermometer H. The viscosity and electric conductivity of the solution were determined preliminarily for several adjacent temperatures, and the value corresponding to the temperature of the experiment found by interpolation.

Equation (5a) was checked by comparing $\alpha_{obs} = \frac{u}{u_s}$ with $\alpha_{calc} = \frac{3\mu + \varepsilon^2 \varkappa^{-1}}{2\mu + \varepsilon^2 \varkappa^{-1}}$. However, the value of the velocity u in equation (5a) is given for a single drop falling in an unlimited liquid, whereas the experimental value u'' is influenced by the proximity of the walls and the hydrodynamical interaction of the falling drops in the column. In the case of «solid» drops for which $\alpha_{calc} = 1$, the correction for the influence of the walls was computed according to Faxen's formula

$$u = u' \frac{1}{1 - k_1 a R^{-1}}$$

where R is the radius of the tube C equal to 7.6 mm; $k_1 = 2.1$; u' is the observed velocity of the single drop.

In order to determine the correction for the interaction of the drops in the column several series of measurements were carried out at the value of the charge which a drop acquired from contact with the dissolved air and which satisfied the condition $\alpha_{calc} = 1$ (the experiment was performed without introducing the electrolyte and $\varkappa$ was very small). The velocity u' of a single drop and the velocity u'' of the drops in the column were determined for different dropping times, and hence, for different intervals d between the falling drops. It was assumed further that if u'' and u' are reduced to the same radius, there exists between them a simple linear relation

$$u' = u''(1 - k_2 a d^{-1})$$

where k_2 is a coefficient which was determined graphically from the experiment. In three runs of 15 measurements each we found the values $k_2 = 0.97$, 1.13, 1.20, giving an average $k_2 = 1.1$.

For «liquid» drops where $\alpha \neq 1$ Bond (9) puts $k_1 = 2.4/\alpha$. We did not succeed in experimentally determining the value of k_2 for this case. Following Bond, we put $k_2 = 1.1/\alpha$ for the general case. Such an assumption appears justified, since at great distances from the drop the velocity of the liquid relative to a stationary point falls off as $1/\alpha r$, where r is the distance from the centre of the drop, and hence the transition from the case $\alpha = 1$ to the case $\alpha \neq 1$ corresponds to an α fold increase in the

linear dimensions at large distances*. Taking into consideration all the corrections we obtain the relation

$$u = u'' \frac{1 - \frac{1.1\,a}{\alpha d}}{1 - \frac{2.1\,a}{\alpha R}} \qquad (6)$$

from which we calculated u after first substituting for α the quantity u/u_s. Using the value of u thus obtained we found the corrected value of α which was again substituted into equation (6). The two corrections to u to a certain extent cancel out, so that the difference between u and u'' does not exceed 5 per cent. The main results obtained after the introduction of the correction are given below. Altogether 25 runs of 12—15 points each were made.

1. Velocity of Fall in the Presence of Dissolved Air. When the drops come into contact with the dissolved oxygen of the air, they acquire a considerable positive charge. *E. g.*, in a solution of KBr with $\varkappa = 3.5 \cdot 10^{-4}$, $\mu = 8.1$, the value of ε was $24.2 \cdot 10^{-6}$ coul./cm^2, as determined from the current intensity in the circuit consisting of the dropping mercury, the solution and the mercury electrode, which had been exposed to the air for a long time ([10]). In this solution $\alpha_{obs} = 1.21$, $\alpha_{calc} = 1.24$.

In the presence of dissolved oxygen and at small electrical conductivity of the solution single drops fell in exact agreement with Stockes' formula; $\alpha_{obs} = 1.00—1.03$, with an average of 1.01. Under these conditions the charge on the drop after a certain time of contact with the solution is independent of its initial value. Thus, despite the fact that the initial value of the charge was varied over a wide range by sending current through, α_{obs} remained constant within the limits 0.99—1.02 for drops falling from a capillary into a solution of 0.03 N KBr ($\varkappa = 2.3 \cdot 10^{-5}$, $\mu = 5.2$).

2. Velocity of Fall of Drops in Solutions Saturated with Hydrogen. After the dissolved oxygen has been removed, the velocity of fall is a function of the charge on the drop before it breaks away. Fig. 2 gives the values of α_{obs} and α_{calc} for drops falling from a capillary into two solutions with widely differing values of $\varkappa$. It can be seen that in agreement with the theory, α varies between 1.03 and 1.47, depending on the charge of the drop; as $|\varepsilon|$ increases, the velocity approaches u_s, and at small charges $^3/_2\, u_s$. The decrease of α with growing $|\varepsilon|$ proceeds more slowly at greater values of $\varkappa$. There is however a slight deviation of the calculated from the observed dependence of α on ε, namely, the entire curve α_{obs} is slightly displaced towards the negative values of ε with respect to the curve α_{calc}. It was thought at first that the low values of α observed at positive ε as compared with the theory are due to some adsorption process. However, experiments carried out with Na_2SO_4 and KBr showed that the position of the curves does not depend on the nature of the anion. Neither did the addition of surface-active substances, like amyl and octyl alcohols, to the glycerine cause any appreciable change in the form of the curve. With increasing dilution of the solution the displacement of the maximum of α_{obs} with respect to the point of zero charge remained practically constant. These facts lead us to believe that the observed deviation is due to some other cause; that it is to be explained by the variation of the charge during the fall of the drop, caused by traces of dissolved oxygen from the air which were not removed from the solution. By applying to a falling «liquid» drop a formula deduced by V. Levich for the rate of diffusion of a dissolved substance, it can be shown that at $2—3 \cdot 10^{-6}$ oxygen content (which can be considered as a very satisfactory result of purification of the solution with hydrogen) the change in ε during the time of fall through 5 cm is $\sim 4 \cdot 10^{-6}$. Under such conditions an initial negative charge of $2 \cdot 10^{-6}$

* This consideration was formulated by V. G. Levich.

becomes zero when the falling drop is in the middle of the above distance, which corresponds to a maximum of α_{obs}. Assuming roughly that the magnitude of the charge varies linearly with the distance travelled by the drop, one can easily obtain from equation (5a) the following expression for the average velocity of fall $\bar{u}$ on a given portion of the path of the drop

$$\frac{\bar{u}}{u_s} = \left[1 - \frac{1}{3\left(\frac{\varepsilon_l}{\sqrt{3\mu\varkappa}} - \frac{\varepsilon_0}{\sqrt{3\mu\varkappa}}\right)}\left(\operatorname{arc\,tg}\frac{\varepsilon_l}{\sqrt{3\mu\varkappa}} - \operatorname{arc\,tg}\frac{\varepsilon_0}{\sqrt{3\mu\varkappa}}\right)\right]^{-1} \qquad (7)$$

where ε_0 and ε_l are the values of the charge corresponding to the beginning and the end of the given interval. By means of this equation and assuming $\varepsilon_l - \varepsilon_0$ equal to $8\cdot10^{-6}$ and $3.4\cdot10^{-6}$ resp., we calculated the dotted curves in Figs. 2a and 2b. It can be seen that the agreement of the theory with experiment is satisfactory.

On first thought it is difficult to understand the rôle played by the radius of the drop in the experiments of earlier investigators, since this quantity does not figure in equation (5) and (5a). It can be shown, however, that with

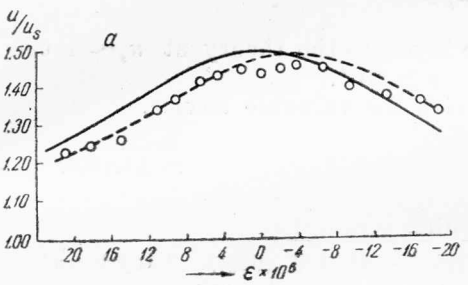

Fig. 2a. $\sim 1N$ KBr in glycerine, $\varkappa = 5\cdot10^{-4}$, $\mu = 4.8$, $a = 0.434$ mm. Full-line curve α calculated from equation (5a), dotted curve α calculated from equation (7) with $\varepsilon_l - \varepsilon_0 = 8\cdot10^{-6}$.

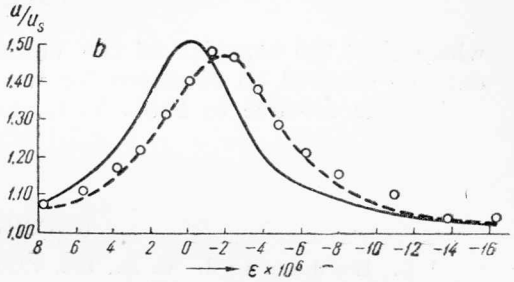

Fig. 2b. Sat. Na_2SO_4 in glycerine, $\varkappa = 8.1\cdot10^{-6}$, $\mu = 7.2$, $a = 0.442$ mm. Full-line curve α calculated from equation (5a), dotted curve α calculated from equation (7) with $\varepsilon_l - \varepsilon_0 = 3.4\cdot10^{-6}$; ○ ○ ○ — α_{obs}.

a sufficiently large radius the retarding action of even a large charge must vanish. It was pointed out in the paper of Frumkin and Levich ([8]) that the theory which brings to equation (5) is strictly applicable only in so far as the variation of the charge caused by the tangential motion is small compared to the initial charge. As is shown in the paper cited, under these conditions the potential difference $\Delta\Phi$ between the front and rear ends of the drop is

$$\Delta\Phi = \frac{2}{3}\frac{(\rho - \rho')\, g a^2 \varepsilon}{\varkappa}\,\frac{1}{2\mu + 3\mu' + \frac{\varepsilon^2}{\varkappa}} \sim \frac{2}{3}\frac{(\rho - \rho')\, g a^2}{\varepsilon} \qquad (8)$$

where the approximate value corresponds to a large charge which is the case we are interested in. The quantity $\Delta\Phi$ increases with a; it is evident, however, that this increase cannot be unlimited. In a certain range of values of a equation (8) will no longer give the exact value of $\Delta\Phi$; it will nevertheless be correct in order of magnitude.

The quantity $\Delta\Phi$ corresponds to some value $\Delta\sigma$ of the difference between the interfacial tension at the front and rear ends of the drop; approximately

$$\Delta\sigma \sim \varepsilon\Delta\Phi \sim \frac{2}{3}(\rho - \rho')\, g a^2 \qquad (9)$$

The quantity $\Delta\sigma$ cannot exceed a given limit either, since the interfacial tension at the front end of the drop will reach its maximum value, owing to decrease in the charge density with increasing velocity of fall, whereas at the rear end the accumulation of charge will at last give rise

to some process of electrolysis (*e. g.* in the case of a positive drop to the transfer of mercury ions to the solution), which will cut short the growth of $\Delta\Phi$ and $\Delta\sigma$. When such a limiting value of $\Delta\sigma_{max}$ is reached, a further increase of the retarding action of the surface forces becomes impossible and the drop returns to the «liquid» regime of fall. The critical value of a corresponding to this transition is, according to equation (9)

$$a \sim \frac{\left(\frac{3}{2}\Delta\sigma_{max}\right)^{1/2}}{(\rho-\rho')^{1/2}\, g^{1/2}} \qquad (10)$$

If one bears in mind that $\Delta\sigma_{max}$, the maximum possible lowering of the mercury-solution interfacial tension, comprises about $^1/_3-^1/_5$ of the value of the total interfacial tension σ, then the criterion (10) practically coincides with that of Bond and Newton, although it has been deduced on entirely different considerations. A closer analysis of equation (8) leads to the conclusion that the theory is strictly applicable only on condition that

$$\varkappa > \frac{3}{2} u_s C$$

where C is the capacity of the double layer; so the theory at $u_s \sim 1$ can only be checked on solutions for which $\varkappa > 10^{-5}$.

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