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On the Phenomena of Wetting and the Adhesion of Bubbles.

II. The mechanism of the adhesion of bubbles to a mercury surface

By *A. Frumkin* and *A. Gorodetzkaja*

The experiments described in the present paper were carried out in 1935; the discussion of the experimental data was, however, for various reasons greatly delayed.

With reference to the considerations outlined in the first part of this work, it was interesting to trace the kinetics of the adhesion of bubbles to a mercury surface in an electrolyte solution at different polarizations, inasmuch as the dependence of the equilibrium contact angle upon polarization and the composition of the solution for these systems had already previously been subjected to a careful examination [1].

Experimental part

With the help of a set-up which is described in detail in the Russian version of this paper [2], a hydrogen bubble under a glass holder could be pressed against a clean cathodically polarized mercury surface in the same solution. Special precautions were taken to avoid vibration of the mercury.

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[1] A. Frumkin, A. Gorodetzkaja, B. Kabanow a. N. Nekrassow, Sow. Phys., 1, 255 (1932), B. Kabanow a. V. Ivanishenko, Acta Physicochimica URSS, 8, 701 (1937).

[2] A. Frumkin a. A. Gorodetzkaja, J. Phys. Chem. (Russ.) (1938), in print.

The study of the adhesion process was accomplished by means of direct observation of the changes occurring in the liquid layer between the mercury and the bubble at the moment of the adhesion of the latter.

Observations were made and photographs were taken in reflected light (the lamp was placed behind the apparatus, somewhat above the mercury surface) through an inclined horizontal microscope (magnification in photographing ca. 30-fold).

Prior to starting the experiments, the solution was saturated with hydrogen during 12—16 hours. It is only after such a prolonged bubbling of hydrogen that the solution is completely freed from oxygen, so that the mercury surface fails to become oxidized in course of the experiments and the results obtained are sufficiently well reproducible. Before each run the mercury surface was renewed.

Observations were carried out in Na_2SO_4 solutions of various concentrations and in twice distilled conductivity water.

It was found that the presence of every particle of dust in the solution is liable to distort the whole picture of adhesion (cf. below), for which reason special measures were taken to reduce the amount of dust both in the water and in the added salt.

Before use the water was allowed to stand in a closed vessel for several days; Na_2SO_4 was recrystallized from conductivity water in a closed vessel; the whole experimental set-up was also carefully covered in order to be protected against dust.

To ensure better observation of the adhesion process, the bubble was pressed out of the holder as slowly as possible until a brown spot visible under the microscope made its appearance between the bubble and mercury (contact area). Then the pressing out of the bubble was stopped, and adhesion occurred spontaneously. After a certain lapse of time the contact area at first exhibits concentric circles of interference fringes, then loses its colour and at last breaks up, giving a finite contact angle. The change of the contact area from the coloured to the colourless phase is the best sign of adhesion.

As indicated above, the presence of dust particles on mercury, distorts the picture of adhesion. In the case of a hydrophobic particle, the break of the film begins in its neighbourhood (the whole area being colourless and thick while round the dust particle con-

centric circles of interference fringes are observable). On the contrary, in the case of a hydrophilic particle there remains a colourless spot around the particle, while the rest of the area is already coloured.

Sometimes it is possible to judge of the contamination of the mercury surface by the appearance of separate water spots of irregular shape remaining in the film after the adhesion of the bubble.

Concerning the kinetics of adhesion the following observations are in the first place worth making: The closer the bubble is pressed to the mercury surface, the slower its adhesion is liable to proceed.

We carried out several measurements of the kinetics of adhesion of identical bubbles as a function of the diameter of the (coloured) contact area visible in the microscope. The diameter of the bubble was equal to 2,6 mm. in all experiments (Table 1).

Table 1

1 *N* Na_2SO_4 Polarization 1,2 V (against a normal calomel half-cell)

Diameter of contact area in mm.	Interval of time between appearance of contact area and moment of film break (adhesion), in sec.
0,08	3—4
0,2	7
0,4	20
0,9	over 20 — partial adhesion (see below)

Observation showed that when the bubble was strongly pressed against the mercury, the water had no time to get away from under the bubble and remained under it, retarding the adhesion [3].

On account of this, in all our further experiments the approach of the bubble to the mercury was effected as slowly as possible and was stopped as soon as the contact area became visible in the microscope (at that moment its diameter was ca. 0,08 mm.).

The results of the experiments in solutions of Na_2SO_4 of various concentrations and in conductivity water are given in Table 2.

[3] The phenomenon of the adhesion slowing down if the approach of the bubble is carried out too quickly is analyzed in detail in a paper by B. Derjaguin a. M. Kussakow, published after the termination of the present experiments (Bull. Acad. Sci. URSS, Série Chim., 1132, 1937).

Table 2

Kinetics of the adhesion of an H_2-bubble to mercury as a function of the degree of polarization and concentration of the solution

Polariz. (Volts)	1 N	$10^{-2}N$	$10^{-3}N$	$10^{-4}N$	Conductivity water
—0,2	15—20 sec.				
—0,1			a few sec.		
0,0	1 sec.	fractions of a sec.	fractions of a sec.		
0,2	instant.				
0,4	„				
0,6	„	instant.	instant.	fractions of a sec.	0,5—2 sec. (potential close to maximum of electrocapillary curve)
0,8	„		„		
1,0	„		„	fractions of sec.	
1,2	5 sec.			1½—2 min.	
1,4	15 sec.		5 min.	No adhesion observed in the course of a few min.	
1,6	30—40 sec. (partial adhesion)	2 min. (partial adhesion)	11 min. (partial adhesion)		
1,8	No adhesion	No adhesion	No adhesion		

In all solutions of Na_2SO_4 with polarizations close to the maximum of the electrocapillary curve (0,5 V), adhesion occurs so quickly that there is no possibility to see coloured contact area at all.

The break of the film takes place at a single point — in the middle of the contact area — and spreads instantaneously towards the edges.

Table 2 illustrates the fact that with an increase in the charge of the mercury surface (with increasing distance from the electrocapillary maximum towards either the cathodic or the anodic side) the process of film rupture is gradually slowed down.

With a polarization of 1,6 V, only „partial adhesion" takes place. This consists in the film breaking in one place only, which is apparently due to the presence of impurities. In the course of this process, a spot of irregular shape is formed covered with several lenses of water; but this spot, even during a long period of time (1 hour), fails to spread over the remaining area which keeps on being so thick as to be unable to show interference colours. If we now try to tear the bubble off the mercury, it will be found to adhere to mercury just along the perimeter of the spot formed.

With a further increase in polarization (1,8 V) the bubble will no longer adhere to mercury, even after prolonged contact (half an hour).

As shown in Table 2, a decrease in the concentration of the electrolyte has an effect similar to an increase in the charge of the surface, since it appreciably slows down the kinetics of adhesion.

Thus, with a polarization of 0,6 V in normal solution and up to 10^{-3} N, the adhesion occurs instantaneously, in 10^{-4} N solution after fractions of a second, and finally in conductivity water after 0,5—1 sec.

With a polarization of 1,6 V partial adhesion in normal solution occurs after 30—40 sec., while in a $10^{-3}N$ solution occurs only after 11 min.

In Na_2SO_4-solutions of higher concentration the surface under the bubble after adhesion remains perfectly smooth (Fig. 1). On the other hand, in conductivity water soon after adhesion (sometimes after some fractions of a second and sometimes within a few seconds) all the surface appears covered with finest water lenses. With time, these lenses grow larger, ultimately reaching quite con-

siderable dimensions. The gradual growth of the lenses with time is illustrated in photographs 2—7 (Fig. 1, s. Plate 3), where one and the same surface is shown after increasing intervals of time. (The latest photograph was taken two days after the adhesion of the bubble).

The appearance of lenses was also observed in dilute solutions of Na_2SO_4 (below $10^{-3}N$), but in this solution the lenses did not increase with time, retaining their original size for a period of 12 hours.

Discussion

The most strongly pronounced effect observed in the course of our experiments is the slowing down of adhesion with increasing distance from the maximum of the electrocapillary curve, to which, as this follows from our preceding work, there also corresponds a maximum of contact angle. In this case there accordingly exists full parallelism between the influence of the surface charge on the contact angle and the influence exerted upon the resistance to rupture of the layer between the bubble and the surface upon which factor the kinetics of adhesion depend, as is likely to be expected under the simplest conditions according to part I. Things are different in regard to the effect of concentration. A decrease of concentration of Na_2SO_4 at a constant potential manifestly retards the adhesion of the bubble, whereas the equilibrium contact angle even increases slightly (except the maximum region where it practically remains unchanged). It will be shown below how this circumstance can be accounted for.

On a non-charged mercury surface, *i. e.*, at the maximum, adhesion occurs instantaneously. A slight delay is noticeable only in the most dilute solutions. From the nature of the dependence of the kinetics of adhesion upon the charge it may be concluded that this delay is connected with a small adsorption potential which may exist even in capillary-inactive Na_2SO_4 and, moreover, that on an entirely non-charged mercury surface the behaviour of a water layer comes very close to the limiting case of very poor wetting as described by curve *2* in Fig. 1 of part 1. In this case even very thick layers of water are labile and break up easily. The stabilization of these layers takes place only through the appearance of an electric double layer on the surface, particularly if the latter has

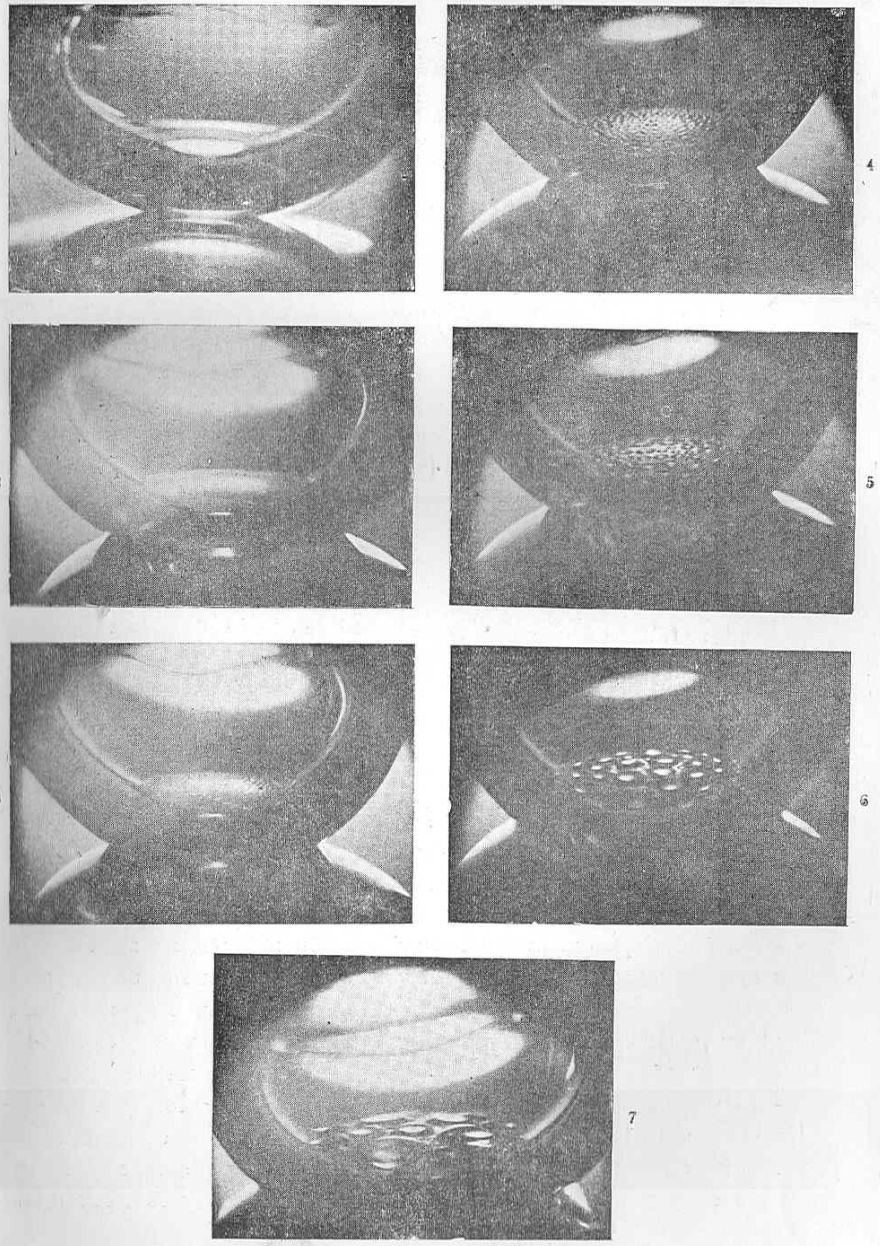

Fig. 1.
1. N Na_2SO_4. 2—7. Conductivity water.

a diffuse structure. In this respect the behaviour of the water layers investigated by us differs markedly from the behaviour of the stable layers of water on hydrophilic of glass and mica, examined by B. Derjaguin and M. Kussakow[4], though in the latter case the presence of an electrolyte in the solution also tends to lower the stability of the film. This effect was, however, noticed only with polyvalent cations ($AlCl_3$, but not with KCl).

We have attempted to give an explanation of the stabilizing effect of a double layer upon water films on a metal surface. Derjaguin and Kussakow have discussed the influence of the interaction between two diffuse ionic layers, connected with the surfaces of a metal and of a bubble, upon the stability of the layer between the metal and the bubble (1. c. p. 1138). In solutions containing no capillary-active electrolytes, however, the charge of the bubble is small and has probably no real influence. Yet, even in the absence of a surface charge on the bubble, a double layer on the metal surface ought to prevent the squeezing out of the film of water by an air bubble, since the ions of the double layers are repelled from the free water surface. If we apply to this case the electrical image method as is done in the theory of negative adsorption of electrolytes on a free water surface[5] and if we further consider the dielectric constant of water as infinitely great relatively to the dielectric constant of the gas, then the interaction between the ions of the double layer and the free surface of water will be exactly the same as if on the other side of the surface there was a mirror image of the double layer[6]. Further, as this follows from the condition of the electroneutrality of the system, at the very surface of the solution the potential gradient in the solution becomes equal to zero. From these two requirements it follows that the forces acting in our system are equal to the forces between two surfaces charged to the same potential and immersed

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[4] B. Derjaguin a. M. Kussakow, Bull. Acad. Sci. URSS, Série Chim., 1136 (1937).

[5] Wagner, Physik. Z., **25**, 474 (1934).

[6] Along the perimeter of the contact area there must exist a potential gradient parallel to the mercury surface. We do not consider the influence of this effect upon the interaction between the bubble and the mercury, which is permitted if the contact area of the bubble is not too small.

into the same solution at a distance equal to the double thickness of the layer. This interaction was calculated by B. Derjaguin[7]. If we denote by φ the potential difference between metal and solution, by D — the dielectric constant of water, by h — the thickness of the water layer on the mercury surface and by K — the thickness of a diffuse double layer at the given concentration according to Gouy-Debay, then the pressure P which has to be applied for pressing the water from the mercury surface to a thickness h, will be equal to

$$P = \frac{D}{8\pi}\frac{\varphi^2}{K^2}\cosh^{-2}\frac{h}{K} \tag{1}$$

which according to B. Derjaguin expresses the repulsion between two surfaces immersed in a solution at a distance $2h$. For the case $h \gg K$ we hence obtain:

$$P = \frac{D}{2\pi}\frac{\varphi^2}{K^2}e^{-\frac{2h}{K}} \tag{1a}$$

Derjaguin's calculation is made with the assumption $\varphi \ll \frac{RT}{F}$ — a case which did not generally take place under the conditions of our experiments; if $\varphi \gg \frac{2RT}{F}$, but simultaneously $h \gg K$, then eq. (1a), (cf. Appendix) should be modified as follows:

$$P = \frac{8D}{\pi}\frac{\left(\frac{RT}{F}\right)^2}{K^2}e^{-\frac{2h}{K}}. \tag{2}$$

The calculation has been made by us upon the assumption, that the layers have the structure of a diffuse layer, *i. e.*, taking no account of the radius of ions. For $\varphi \gg \frac{2RT}{F}$ this assumption will only hold at a sufficient distance from the electrode surface, wherefore we made no attempts to calculate with greater accuracy the magnitude P for the case of $h \ll K$ and a large φ. For a qualitative comparison of the effect of the layer for different values of h, we shall subsequently use eq. (1).

[7] B. Derjaguin, Bull. Acad. Sci. URSS, Sér'e Chim., 1157 (1937).

According to eq. (1) of the first part of the present work, $\sigma - \sigma_0$, *i. e.*, the excess in the tension of a layer with thickness h over the tension of a very thick layer σ_0, equals:

$$\sigma - \sigma_0 = -\int_h^\infty h\,dP = hP + \int_0^\infty P\,dh = \frac{D}{8\pi}\frac{\varphi^2}{K^2}\left[h\cosh^{-2}\frac{h}{K} + K - K\operatorname{tgh}\frac{h}{K}\right] \tag{3}$$

assuming that P is expressed by eq. (1).

If $h \gg K$ then eq. (3) will be transformed into

$$\sigma - \sigma_0 = \frac{D}{2\pi}\frac{\varphi^2}{K^2}h\,e^{-\frac{2h}{K}}, \tag{3a}$$

but if $h \ll K$ then

$$\sigma - \sigma_0 = \frac{D}{8\pi}\frac{\varphi^2}{K}. \tag{3b}$$

The equations obtained express the effect of an electric double layer upon the stability of solution films. As has been stated above, in the absence of a charge on the mercury surface, well-pronounced phenomena of incomplete wetting are observed, and, consequently (see part I), the dependence of the magnitude $\sigma - \sigma_0$ upon the thickness of the layer $\sigma - \sigma_0 = f(h)$ should be expressed by a curve with a maximum and a minimum. Assuming for greater simplicity that in the presence of a double layer the effects computed according to eq. (3) are simply added to $f(h)$, we are able to throw some light on the influence of a double layer upon the wetting of the mercury surface. With an increase in φ, the quantity $\sigma - \sigma_0$ increases for all finite values of h. In conformity with the reasoning contained in the first part of this work, this must necessarily involve a diminution of the contact angle and simultaneously hinder the adhesion process. Let us now suppose that at constant φ, the dilution of the solution increases, *i. e.*, K increases. Then, according to eq. (3a), for large h (*i.* e., small S, see part I) $\sigma - \sigma_0$ increases, and the adhesion consequently becomes more difficult. However, for small h (large S) an increase of K according to eq. (3b) causes a decrease of $\sigma - \sigma_0$, and consequently, along the σ, h-curve which is obtained in summing the right-hand parts

of eq. (3) with $f(h)$, the values corresponding to small h (large S) ought to decrease. In this case, as was explained in the first part of the present work, equilibrium wetting may become impaired, *i. e.*, the contact angle may increase notwithstanding the increase in the stability of the thick layers.

Further, from eq. (3a) it follows that for large values of K, *i. e.*, at low concentrations, the stabilizing effect of the double layer extends over considerable distances even for small φ, since at great distances the magnitude of the effect is determined, in the first place, by the exponential term. Thus, even the small adsorption potentials, which exist at the maximum of the electrocapillary curve may, under these conditions, exercise a certain stabilizing effect on the solution film. From the aforesaid it may be concluded that the relations derived are qualitatively correct in representing the phenomena observed.

We have also carried out a few quantitative calculations using eq. (2). For $c = 0{,}001\ N$ $K = 10^{-6}$ cm.; hence, for $h = 5 \cdot 10^{-6}$ cm. $P = 50$ dynes/cm.^{2} and for $h = 3 \cdot 10^{-6}$ $P = 3200$ dynes/cm.^{2}; the respective values of the increase of surface tension $\sigma - \sigma_0$, equal $2{,}5 \cdot 10^{-4}$ and 10^{-2} dynes/cm. For comparison let us note that according to the data quoted by Derjaguin and Kussakow for water on glass, $P = 4300$ for $h = 5 \cdot 10^{-6}$. The calculated values, however, show a much greater decline with a rise of h than was observed by these authors.

For solutions of higher concentration, eq. (2) gives very low values of P. Thus, at $c = 0{,}1\ N$ ($K = 10^{-7}$ cm.) even for $h = 10^{-6}$ cm. P amounts only to 0,2. But our experiments show that although the stabilizing effect of the double layer is less manifest at high concentrations than at low ones, the dependence upon concentration cannot be so strong, since, even in solutions of normal concentration with sufficient charges, the adhesion of the bubble is hindered. This leads us to believe that the effect of ions upon the properties of the film is not restricted to an electrostatic interaction with the interface. The ions may influence the structure of the water in the film in some way, perhaps as suggested by Bernal and Fowler, thus lowering the free energy of the film.

Finally it is to be remarked that to build up a complete theory of the effect of a double layer upon the kinetics of adhesion it will be necessary, along with the increase in the stability of water layers in the presence of electric charges, to take into account other effects also. When the water is pressed out, there should arise in the film streaming potentials which will impede the motion of water as though they were increasing its viscosity. This effect should also grow with an increase of the total potential difference and dilution of the solution.

When a film breaks, a large number of small lenses are formed in solutions of low concentration. This occurs much in the same way as in the case of the films of fatty acids on water. No lenses are observed at higher concentrations. It may be supposed that, at higher concentrations, owing to the great instability of films, the rupture takes place before the film has time to become sufficiently thin. In this case, as this follows from the considerations stated in the first part, the formation of a great number of lenses will be impossible. The rupture of more stable films obtained at lower concentrations sets in at a much smaller thickness of the film and can cause the formation of small lenses. We have not yet been able to account for the reasons of the gradual growth of lenses after their formation.

Conclusions

In the present work the kinetics of the adhesion of bubbles to a mercury surface in solutions of different concentrations have been studied, and it has been shown that adhesion occurs instantaneously if the surface is not charged and the solution contains electrolytes; it becomes hindered with a decrease of concentration and growth of surface charge. In solutions with concentrations $10^{-3}\ N$ and less, numerous small lenses appear on the mercury surface after the break of the film.

It has been shown that the relations between the kinetics of adhesion and the contact angle after break are in qualitative agreement with the theory of the stability of thin layers as developed in the first part of the present work, assuming that the stabilizing effect of an electric double layer upon a thin layer of water is in the main caused by the electrostatic repulsion of ions from the free surface of water.

Appendix

Calculation of the interaction between two charged surfaces at a distance $2h$ in an electrolyte solution.

We reproduce this calculation here both since it was also made for the case $\varphi > \frac{2RT}{F}$ and because the very course of our derivation differs somewhat from that given by B. Derjaguin in his paper. Let the X-axis pass perpendicularly to our surfaces and let the origin be located midway between them. We denote by φ_x the value of φ at point x (evidently $\varphi_x = \varphi_{-x}$). In the text the quantity φ_h was denoted by φ without any index. Integrating the Poisson equation (ρ density of charge)

$$\frac{\partial^2 \varphi_x}{\partial x^2} = -\frac{4\pi\rho}{D} = \frac{8\pi F c}{D} \sin \text{hyp} \frac{F\varphi_x}{RT}$$

between the limits $x = h$ and $x = 0$, we obtain

$$\left(\frac{\partial \varphi_x}{\partial x}\right)^2_{x=h} = \frac{16\pi cRT}{D}\left(\cos \text{ hyp} \frac{F\varphi_h}{RT} - \cos \text{ hyp} \frac{F\varphi_0}{RT}\right),$$

since

$$\left(\frac{\partial \varphi_x}{\partial x}\right)^2_{x=0} = 0.$$

The pressure acting upon each of the surfaces is equal to the difference between the osmotic pressure of the ions, which are in excess as compared with an equal volume of the solution, and the attraction of electric charges (the solvent is here considered incompressible):

$$P = 2cRT\left(\cos \text{hyp} \frac{F\varphi_h}{RT} - 1\right) - \frac{D}{8\pi}\left(\frac{\partial \varphi_x}{\partial x}\right)^2_{x=h} =$$

$$= 2cRT\left(\cos \text{hyp} \frac{F\varphi_0}{RT} - 1\right).$$

Since, according to our assumption, $h \gg K$, $\varphi_0 \ll \frac{RT}{F}$ and consequently

$$P = \frac{cF^2}{RT}\varphi_0^2 = \frac{D}{8\pi}\frac{\varphi_0^2}{K^2}. \qquad (4)$$

For the calculation of φ_0 we shall first find a value φ_{h_1} at a distance h_1 satisfying the following conditions: h_1 is so great that within the interval $h_1 < x < h$ the dependence of φ_x on x is such as if there existed only one charged surface, but, on the other hand, the decrease of φ_x in this interval is already so considerable that for $x = h_1$, $\varphi_{h_1} \ll \frac{2RT}{F}$. According to the equation of the diffuse double layer of Gouy we obtain:

$$\frac{1 + e^{\frac{\varphi_{h_1}}{2RT}}}{1 - e^{\frac{\varphi_{h_1}}{2RT}}} = e^{\frac{h-h_1}{K}} \frac{1 + e^{\frac{\varphi_h F}{2RT}}}{1 - e^{\frac{\varphi_h F}{2RT}}}.$$

According to our conditions the left-hand side reduces to $-\frac{4RT}{\varphi_{h_1} F}$, whence

$$\varphi_{h_1} = -\frac{4RT}{F} e^{-\frac{h-h_1}{K}} \frac{1 + e^{\frac{\varphi_h F}{2RT}}}{1 - e^{\frac{\varphi_h F}{2RT}}}.$$

We shall subsequently confine ourselves to two particular cases. If $\varphi_h \ll \frac{2RT}{F}$ then

$$\varphi_{h_1} = e^{-\frac{h-h_1}{K}} \varphi_h, \qquad (5)$$

but if $\varphi_h \gg \frac{2RT}{F}$, then

$$\varphi_{h_1} = \frac{4RT}{F} e^{-\frac{h-h_1}{K}}. \qquad (5a)$$

In the interval $|x| < h_1$ the solution of B. Derjaguin, according to which

$$\varphi_0 = \varphi_{h_1} \cos \text{hyp}^{-1} \frac{h_1}{K} \sim 2\varphi_1 e^{-\frac{h_1}{K}},$$

can be applied, and with the help of eq. (5) and (4), for small φ_h we obtain: $\varphi_0 = Re^{-\frac{h}{K}} \varphi_h$,

$$P = \frac{D}{2\pi} e^{-\frac{2h}{K}} \frac{\varphi_h^2}{K^2} \qquad (6)$$

and for large φ_h:

$$\varphi_0 = \frac{8RT}{F} e^{-\frac{h}{K}}$$

$$P = \frac{8\left(\frac{RT}{F}\right)^2}{\pi K^2} e^{-\frac{2h}{K}}. \qquad (6a)$$

Eq. (6) with $h \gg K$ is identical with the equation given by B. Derjaguin. From eq. (6a) it follows that within the limits of the applicability of the diffuse layer theory P, does not increase indefinitely with the growth of φ_h, but tends towards a certain limit which would be obtained from eq. (6) by substitution of $\frac{4RT}{F}$ for φ_∞.

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