founder in person at its jubilee. To him was presented an illuminated testimonial containing a greeting of appreciation and affection, prepared by order of the society and signed by the president and secretary. There was presented to Miss Natalie P. Fiske, daughter of Professor Fiske, and to the society bronze replicas of a sculptured bas-relief portrait of Professor Fiske, done by the young Philadelphia sculptor, Mr. George John Sklaar, of the faculty of the New Jersey College for Women. A group of mathematicians who had been associated with Professor Fiske in the work of the College Entrance Examination Board presented to the society a portrait of Professor Fiske painted by Mrs. H. E. Ogden Campbell. Professor Fiske spoke in reminiscent vein of interesting events in the early days of the organization.

As a fitting climax to this central event of the celebration, letters addressed to Professor R. G. D. Richardson, secretary of the society, were read from President Franklin D. Roosevelt and Prime Minister W. L. Mackenzie King, of the Dominion of Canada, for the American Mathematical Society extends north of the border. The emphasis reflected in these letters may well be gratifying to all scientists. They are as follows:

From President Franklin D. Roosevelt:

Please extend my greetings to the American Mathematical Society on the occasion of the celebration of its fiftieth anniversary. I trust that genuine satisfaction will come to its members as they contemplate the contribution which the Society has made during the half century of its existence.

It is sometimes difficult to comprehend the values accruing to society from mathematics. It is deeply rooted in social progress as a large part of the technological advance made in recent centuries would have been impossible had it not been for the constant refinement of the essential tool of technology—mathematics. Social sciences also owe a large debt to mathematics. Future advances in the social sciences will be largely dependent upon mathematical treatment of their data.

I congratulate the members of the American Mathematical Society on the important contributions which mathematics has already made. I trust that the years ahead will find mathematicians making significant contributions, as in the past.

From Prime Minister W. L. Mackenzie King:

I shall be pleased if you will extend to the American Mathematical Society, on the celebration of the fiftieth anniversary of its inception, my greetings and warm congratulations upon attaining this significant anniversary.

It is well that we should reflect, on occasions such as this, on the extent to which the learned societies of this continent have contributed to the strength and substance of our national and international life. The work of the American Mathematical Society fills a distinguished place among those academic fellowships which have done so much to keep alive, in our institutions of learning, that integrity of thought which is one of the proudest of our common traditions.

It is my hope that the deliberations of the Society's Jubilee Meeting will be attended by much good fellowship and a lively appreciation of the binding character of the academic fraternity which has so long and so happily prevailed between our two countries.

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SPECIAL ARTICLES

REPULSIVE FORCES BETWEEN CHARGED SURFACES IN WATER, AND THE CAUSE OF THE JONES-RAY EFFECT

CONSIDER a plane surface of potential V which bounds a semi-infinite volume of a dilute salt solution of potential 0. Taking the salt to be of the univalent type, such as KCl and applying the Poisson and Boltzmann equations, the potential distribution must satisfy the equation

$$\frac{d^2V}{dx^2} = 4\pi n_0 (e/D)\,[\exp(Ve/kT) - \exp(-Ve/kT)], \qquad (1)$$

where n_0 is the number of ions (of each sign) per unit volume in the solution in regions where $V = 0$.

Let us put

$$\eta = Ve/kT \qquad (2)$$

and

$$\theta = x/\lambda \qquad (3)$$

where λ, the value of $1/\kappa$ in the Debye-Hückel theory, is given by

$$\lambda^2 = DkT/8\pi e^2 n_0 \qquad (4)$$

Eq. (1) then becomes

$$2d^2\eta/d\theta^2 = \varepsilon^{\eta} - \varepsilon^{-\eta} \qquad (5)$$

In the Debye-Hückel theory it is assumed that η is so small that ε^{η} can be replaced by $1 + \eta$. We wish, however, to apply Eq. (5) to two parallel plates which are separated by the distance b but are so close together and are so highly positively charged that $\eta >> 1$, everywhere between the plates. The Debye-Hückel approximation therefore can not be used, but instead, we can neglect $\varepsilon^{-\eta}$ in Eq. (5), since it is small compared to ε^{η}.

Integration gives

$$\theta = 2\exp(-\eta_M/2)\tan^{-1}[\exp(\eta - \eta_M) - 1]^{1/2} \qquad (6)$$

where η_M is the minimum value of η which occurs at the plane half way between the plates and θ measures the distance from this median plane. If η_1 and θ_1 are the values of η and θ at the surface of the plates and we take the case that the plates are so highly charged that $\eta_1 >> \eta_M$ then Eq. (6) becomes

$$\theta_1 = \pi \exp(-\eta_M/2) - 2\exp(-\eta_1/2) \quad (7)$$

where the term containing η_1 is very small compared to that which contains η_M.

Repulsive Forces Between Plates: The plates are acted upon by forces of two kinds: A pressure nkT due to the negative ions and a negative pressure or pull due to electric field E; the sum of the two must be constant for all values of θ in the space between the plates. At the median plane we see from the symmetry that $E = 0$ and therefore the force acting per unit area on the plates is the pressure $p = n_M kT$ where n_M is the concentration of negative ions at the median plane.

The value of n_M can be calculated from η_M by the Boltzmann equation. To obtain the net pressure between the plates we should subtract the pressure $2n_0kT$ which acts on the other side of each plate, giving

$$p = n_0kT(\exp \eta_M - 2) \quad (8)$$

Since, however, we are taking at present only the case where $\eta_1 >> \eta_M >> 1$ we can neglect the 2 in the parenthesis in Eq. (8) and the last term of Eq. (7) and so from Eqs. (7), (8) and (3), placing $x_1 = b/2$, we obtain

$$p = n_0kT(2\pi\lambda/b)^2 \quad (9)$$

We can now eliminate λ by Eq. (4):

$$p = (\pi/2)D(kT/eb)^2 \quad (10)$$

This gives the repulsive force between two planes with high charges of similar sign when they are separated by a distance which is small compared to 2λ. It is interesting to note that this limiting expression does not contain the potential of the plates, the concentration of the electrolyte or any other adjustable parameter. The force varies inversely as the square of the distance between the plates. To determine its numerical magnitude let us place $D = 81$ (the dielectric constant of water at 20° C), $T = 293°$ K and so obtain

$$p = 8.90 \times 10^{-7}/b^2 \text{ dynes/cm}^2 \quad (11)$$

Thus, when the surfaces are at a distance of 10^{-4} cm (1μ) the repulsive force is 89 dynes cm^{-2}.

This repulsive force, which involves no new mechanism, together with attractive Coulomb forces, is found to be of just the right magnitude to account for the formation of tactoids and unipolar coacervates (which involve the spontaneous separation of certain colloidal solutions into two liquid phases).[1]

Repulsion Between a Plate and an Air-Water Interface: The same pressure p, which acts according to Eq. (10) between two plates separated by the distance b, should also act between a single plate and an air-water interface at a distance $b/2$, for in both cases at a distance $b/2$ from the plate the boundary condition $d\eta/d\theta = 0$ is fulfilled. If then a highly charged (ζ-potential) plate held vertically is partly raised out of a dilute water solution of an electrolyte, the water should drain off until a limiting thickness t is reached, where t will vary with the height h above the water surface. In the liquid of the film when equilibrium has been reached there will be a pressure

$$p = -\rho gh \quad (12)$$

if the pressure at the free horizontal surface is zero. Here ρ is the density and g the acceleration of gravity.

The surface of the water film is acted on by this negative pressure and by the positive outward pressure p given by Eq. (10), and these two forces must be equal. Eliminating p between Eqs. (10) and (12), we find that the film thickness is

$$t = (kT/e)(\pi D/8\rho gh)^{1/2} = 1.52 \times 10^{-5}/h^{1/2} \text{ cm} \quad (13)$$

if we take $D = 81$, $T = 293°$ K, $\rho = 1$, $g = 980$. Thus at a height of 10 cm above the horizontal water surface the film of water should have a thickness of 480 Å.

Experiments are under way to measure the thickness of such films on barium stearate multilayers of critical thickness, which have been made hydrophilic by conditioning in thorium nitrate and sodium silicate. Because of the negative pressure in the water in these films, the vapor pressure of the water must be lowered, but calculation shows that an elevation of temperature of only 0.001° C would decrease t from 480 Å to 165 Å. To obtain data for a quantitative test of Eq. (13) it will be necessary to have good temperature control.

Water Films on the Walls of Capillaries: In a capillary tube of radius r in presence of saturated water vapor, there will also be a water film.

Because of the curvature (one half that of a sphere of equal radius) the surface tension γ exerts a force or pressure γ/r on the surface of the film that acts in the same direction as that given by Eq. (10). Thus in place of Eq. (13) we have

$$\Delta r \doteq (kT/e)[\pi D/8(\rho gh - \gamma/r)]^{1/2} \quad (14)$$

Surface Tensions of Dilute Salt Solutions: Jones and Ray,[2] by developing an extremely accurate differential method for measuring relative surface tensions, have found an extraordinary effect by which very low concentrations of salts appear to *decrease* the surface tension of water. The effect occurs only at molar concentrations (of KCl) below about 8×10^{-4} and the maximum decrease amounts to about 0.015 dyne cm^{-1}.

The theory outlined above which led to Eq. (14) seems to offer a simple explanation of the Jones-Ray effect. A water film on the wall of the capillary has the effect of decreasing the effective radius so that the solution rises to a greater height than if such a

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[1] A paper soon to appear in the *Journal of Chemical Physics*.

[2] Grinnell Jones and W. A. Ray, *Jour. Am. Chem. Soc.*, 59: 187, 1937.

film were not present. The film disappears at higher salt concentrations because the charge (ζ-potential) becomes less (or λ becomes comparable to Δr), and thus the capillary rise h_s decreases and produces an apparent decrease in surface tension.

If we measure the capillary rise in a tube of radius r whose walls are covered by a water film of thickness Δr the surface tension of the water should be calculated by

$$\gamma = \tfrac{1}{2}\rho g h (r - \Delta r). \tag{15}$$

Jones and Ray, however, calculated their surface tension by the equation

$$\gamma_{JR} = \tfrac{1}{2}\rho g h r. \tag{16}$$

The value of Δr can be calculated by Eq. (14) by inserting $\gamma / r = \rho g h / 2$, so that we have

$$\Delta r = (kT/2e)(\pi D/\rho g h)^{1/2} = 2.16 \times 10^{-5}/h^{1/2} \tag{17}$$

According to this interpretation the values of γ_{JR} at low concentrations are higher than the true surface tension of water by an amount:

$$\gamma_{JR} - \gamma = (kT/4e)(\pi D \rho g h)^{1/2} = 0.0107 h^{1/2} \tag{18}$$

Jones and Ray in all their experiments used a single capillary of radius $r = 0.01361$ cm, and the capillary rise was $h = 10.8$ cm. According to Eq. (18) the increment $\gamma_{JR} - \gamma$ should have been 0.035 dyne cm^{-1}. This is of the same order of magnitude as the apparent decrease in surface tension of 0.015 dyne cm^{-1} which they observed at concentrations below 10^{-3} M.

The values of Δr and $\Delta\gamma$ given by Eqs. (17) and (18) have been based on the assumptions that $\Delta r << \lambda$ and $\eta_1 >> \eta_M >> 1$. When these conditions are not fulfilled, Δr and $\Delta\gamma$ will have lower values.

In the following table the values of λ are given for various assumed concentrations between 10^{-3} and 10^{-5} M as calculated from Eq. (4). The next column contains values of $\Delta\gamma$ from a curve plotted from data of Jones and Ray for KCl. From these we can calculate values of Δr which would account for these values of $\Delta\gamma$. The last column gives η_M as calculated from Eq. (8) by inserting $p = \rho g h / 2 = 5300$ dynes cm^{-2}. The values of λ decrease far below the maximum value of Δr (280 Å), but Δr decreases too, so that in all cases the condition $\Delta r << \lambda$ is approximately fulfilled. The reason that Δr never rises as high as 650 Å, which is given by Eq. (17), is that the condition $\eta_1 >> \eta_M$ is not fulfilled at the lowest concentrations.

TABLE I

CALCULATIONS BASED ON THE SURFACE TENSION DATA OF JONES AND RAY FOR KCl

Molar concentration	λ	$\gamma_{JR} - \gamma$ dyne cm^{-1}	Δr obs	η_M
0.0010	97 Å	0.000	..	0.46
.0005	137	.0014	26 Å	0.65
.0003	178	.0065	122	0.82
.0002	217	.009	174	1.01
.0001	307	.012	230	1.36
10^{-5}	970	.015	280	3.15

The ζ-potentials determined by the electric mobility of particles of glass and quartz[3] are negative and are of the order of 50 to 100 millivolts at concentrations of about 10^{-5} to 10^{-6} M and decrease rapidly as the concentration rises from 10^{-4} to 10^{-3} M. The highest values of η_1 calculated by Eq. (2) from these potentials thus range from 2 to 4. The marked decrease in η_M to low values shown in Table I as the concentration increases is probably the cause of the decreases in Δr and $\Delta\gamma$ at higher concentrations.

These rough calculations show that the Jones-Ray effect can be adequately explained on the basis of a water film held on the surface of the capillary tube by electric charges bound by the quartz.

The present paper is merely preliminary. It has been possible to obtain a complete integration of Eq. (5) in terms of elliptic functions. Some calculations have shown that by applying these exact expressions to the experimental data of Jones and Ray it is possible to calculate the potential of the quartz surface at each concentration. These potentials are reasonable and vary with the concentration in the manner shown by mobility experiments.

Further experiments should make it possible to check this suggested theory. For example, we see by Eq. (18) that $\Delta\gamma$, which does not represent a true change in surface tension, should vary in proportion to $h^{1/2}$ or $r^{-1/2}$. The addition of thorium nitrate in concentration of 10^{-6} M brings the ζ-potential of glass to about zero.[3] This should eliminate the Jones-Ray effect. If solutions of proteins are passed through the capillary and this is then carefully washed, the ζ-potential can be made to vary through wide ranges, depending on the choice of protein, and the pH of the solution. This should cause marked variations in the Jones-Ray effect.

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THE EFFECTS OF AGE AND ESTROGEN ON THE STROMA OF VAGINA, CERVIX AND UTERUS IN THE MOUSE[1]

UNDER normal conditions an increase in the amount of collagen in the stroma of vagina, cervix and uterus of mice begins in the first few weeks of life and from then on progresses more definitely in older mice, especially after cessation of the sexually active period. However, on the whole the differences found at different age periods are relatively not great as compared with those experimentally produced through the ad-

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[3] H. A. Abramson, "Electrokinetic Phenomena," Chemical Catalog Company, New York, 1934. See pp. 203–8.

[1] These investigations were carried out with the aid of grants from the International Cancer Research Foundation and from the Committee on Research in Endocrinology of the National Research Council.