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# DETERMINATION OF THE CHARGE AND THE MAGNITUDE OF COLLOIDAL PARTICLE BY MEANS OF A FLEXIBLE FLOAT.

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The present report is concerned with the determination of the electric charge and the size of the colloidal particle of gold sol by analysing the apparent specific weight of the sol observed by a flexible float, when the gravity of the particles is partially or totally compensated by a vertical electric field.

It has thus been found that a colloidal particle of  $12 \mu\mu$  diameter was loaded with a negative charge effectively less than one elementary charge.

The procedure is based upon the following considerations. Suppose a horizontal parallel plate condenser immersed in a sol of charged, homogeneous particles. When a vertical electric field is applied by charging the condenser the sol will attain a particular sedimentation equilibrium depending upon the field intensity. The resultant force (gravitational and electrical) acting upon a portion of the sol is then,

$$W = W_0 + (mg - \epsilon F)n(h, F), \quad (1)$$

per unit volume, where  $W_0$  is the specific weight of the pure water,  $mg$  the effective weight (true weight minus buoyancy of the medium) of colloidal particles,  $g$  the acceleration of gravity,  $\epsilon$  the effective charge,  $F$  the field intensity and  $n(h, F)$  the concentration of particles at  $F$  and at height  $h$  above the lower plate. Expressing  $n(F, h)$  in the form,

$$n(F, h) = n_0 e^{-\frac{(mg - F\epsilon)h}{kT}}$$

we have

$$W = W_0 + n_0(mg - F\epsilon)e^{-\frac{(mg - F\epsilon)h}{kT}}. \quad (2)$$

where  $n_0$  is the concentration at  $h = 0$ .

$W$  at various  $F$  can be experimentally followed by observing the hydrostatical pressure at the standstill of a flexible float of variable volume

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or bouyancy in the sol, the pressure being calibrated beforehand against the known density of a suitable solution.

The  $n_0$  in the expression, which is not necessarily a constant, depends on the condition of the experiment. In the case when there exists a sufficient amount of a reversible gel at  $h = 0$ ,  $n_0$  will be kept constant at  $n_c$  over a range of the field intensity. We have then according to (2),

$$\frac{\partial W}{\partial F} = \epsilon n_c e^{-\frac{(mg-F\epsilon)h}{kT}} \left\{ \frac{h}{kT} (mg-F\epsilon) - 1 \right\}$$

where  $n_0$  is replaced by a constant  $n_c$ . Putting  $F = 0$  there, we see  $W$  at a definite height  $h$  increases or decreases, when the field is initially applied, according as  $mg h \gtrless kT$ : if  $W$  initially increases, it attains a maximum at the field intensity  $F_m$ , where  $(mg - F_m \epsilon)h = kT$ , and from there on continues to decrease reducing to  $W_0$  at the field intensity  $F_0$ , where,

$$mg = F_0 \epsilon \quad (3)$$

and  $n = n_c$  all over the space.

If one increases  $F$  beyond this point, a steady upward cataphoresis of particles begins forming a reversible gel at the top until that at the bottom is consumed when the sedimentation equilibrium is restored. During the steady cataphoresis, the float is subjected to the upward impact, being possibly kept at standstill by compressing the flexible volume, just as if  $W$  were increased.  $W$  as measured by the float in the presence of the gel would thus seem to reflect back increasing again beyond the point.

In the absence of the gel  $W$  will decrease further below  $W_0$  as readily deduced from Eq. (2), a sedimentation equilibrium being now attained immediately at any time.

This condition enables us experimentally to discriminate which of the cases we are dealing with and to carry out a proper analysis. Along the line of the reasoning developed above, the experimental determination of  $W$  was carried out as follows.

Gold sol was prepared by Bredig's method with conductivity water and used for the experiment after being filtered and left standing for a few days.

The main part of the apparatus used consists, as shown in Fig. 1,

of a flexible float B and of a pair of parallel nickel discs closely fitted to a cylindrical cell of Jena glass. The flexible float is a small closed glass bulb of 6 mm diameter flattened at the top to form a flexible diaphragm and fitted at the bottom with a thin glass thread of about 0.5 mm diameter and 3 cm length.

The cylindrical cell is 20 cm long and 4 cm diameter consisting of two parts fitted to each other by means of a ground joint J. The lower part is connected by a side tube t to a manometer and to a suitable pressure regulator to read and regulate the pressure inside the cell to  $\frac{1}{10}$  mm Hg. The cell is

placed in a Dewar vessel filled with powdered ice to keep the temperature constant at 0°C.

The float is observed by means of a microscope with scale in the field through unsilvered stripes on the wall of the Dewar vessel and through a test tube filled with water inserted between the cell and the inner wall.

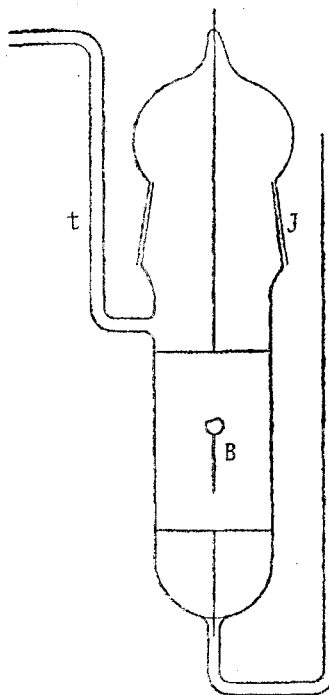
The cell was now thoroughly cleaned, conductivity water introduced up to a level slightly below the side tube t and the ground joint fitted for a preliminary experiment. The pressure was regulated at the standstill of the float at a definite height around the centre of the cell. Repeating the measurement at various field intensity, it was found that the pressure reading  $P$  at the standstill of the float in the pure water was insensitive to the electric field.

The pressure was now calibrated repeating the same measurement without field in potassium chloride solutions of known densities with the result,

$$W = W_0 + 4 \times 10^{-7}(P_{mm} - 461)$$

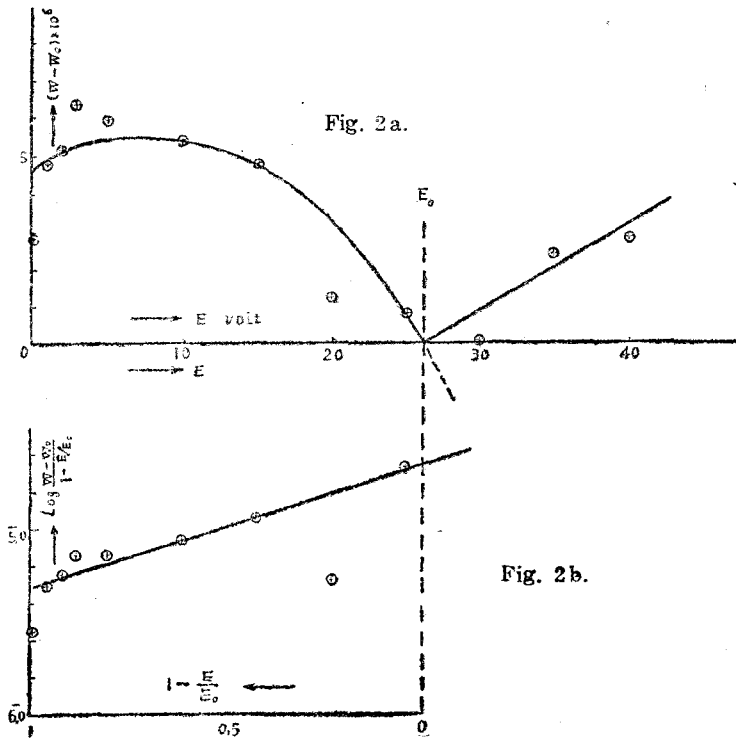
The salt solution was now replaced with the sol, left standing for a few hours and measurements were carried out similarly as above at different potential  $E$  of the condenser.

Fig. 1.



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A typical series of such measurements is shown in Fig. 2a, where  $W - W_0$  is plotted against  $E$ . As seen from the figure  $W - W_0$  increases with increasing  $E$  passes a maximum, decreases from there on until reflected at zero and increases again (this point will be called the "reflection point").



It is not assured that our colloidal particles are homogeneous but the observed rather sharp reflection at  $W = W_0$  is only possible, when the particles, which principally determine  $W$ , have their reversible gel and their  $\epsilon/m$  falls within a sufficiently narrow range.

If these particles are further of homogeneous mass,  $m$ , and accordingly of homogeneous effective charge, the experimental result can be analysed by the relation derived from Eq. (2) putting  $n_0 = n_c$ , that

$$\log \frac{W - W_0}{1 - E/E_0} = \log n_c m g - \frac{mgh}{kT} (1 - E/E_0) \quad (4)$$

where  $mg - \epsilon F$  is replaced by  $mg(1 - F/F_0)$  according to Eq. (3) and  $F/F_0$  in turn by  $E/E_0$  according to the relation,

$$F = E/DL \quad (5)$$

$E_0$  being the potential applied to the condenser at the reflection point,  $D$  the dielectric constant and  $L$  the distance between the condenser plates.

A plot of  $\log \frac{W_1 - W_0}{1 - E/E_0}$  against  $1 - E/E_0$  (Fig. 2b) seems to confirm the linear relation required by Eq. (4) for a sol of homogeneous particles.

Our colloidal particles may well be inhomogeneous even satisfying the condition  $\epsilon/m \approx \text{constant}$ , although not very probable. In such a case  $W - W_0$  is the sum of effects due to different kinds of colloidal particles, i.e.,

$$W - W_0 = \sum_i (W_i - W_0) \quad (6)$$

where  $W_i$  is the gravity acting upon the sol per unit volume when colloidal particles of  $i$ -th class were existing alone in the sol. Expressing individual  $W_i - W_0$  in Eq. (6) as that,

$$W_i - W_0 = n_{c,i} m_i g (1 - E/E_0) e^{-\frac{(1 - E/E_0) m_i g h}{kT}} \quad (7)$$

where  $n_{c,i}$  is the saturation concentration of  $i$ -th colloidal particles, the observed approximate linear relation can be stated as that,

$$\frac{\partial \log \left( \frac{W - W_0}{1 - E/E_0} \right)}{\partial (1 - E/E_0)} = - \frac{gh}{kT} \frac{\sum_i m_i^2 n_i}{\sum_i m_i n_i} \approx \text{const} \quad (8)$$

where

$$n_i = n_{c,i} e^{-\frac{(1 - E/E_0) m_i g h}{kT}} \quad (9)$$

is the number of particles of  $i$ -th class at the specified height.

As seen from Eq. (8) the linear relation is only possible when  $m_i$ 's falls in a sufficiently narrow range.

Granting this we have according to Eqs (4), (3) and (5) with observed

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values,  $E_0 = 26$  Volts,  $h = 4$  cm<sup>(\*)</sup> (measured height of the float's centre above the lower plate),  $L = 6$  cm<sup>(\*\*)</sup> and  $D = 80$ , that,

$$m = 2 \times 10^{-17} \text{ gm}, \quad n_c = 2 \times 10^8, \quad \epsilon = \frac{DLmg}{E_0} = 10^{-10} \text{ e.s.u.}$$

The diameter of a particle is calculated from  $m$  and known densities of gold and water as that,

$$\sigma = \sqrt[3]{\frac{6m}{\pi(19-1)}} = 12 \mu\mu$$

It is remarkable that the effective charge found is less than one elementary charge which may be attributed to some partial screening of positive ions concentrated around the particle originating from some impurity or even from the dissociation of pure water.

The  $\zeta$  potential may be derived from the effective charge by the expression,

$$\zeta = \frac{\epsilon}{Dr} \quad (10)$$

where,  $r$  is the radius of the sphere circumscribed around the colloidal particle and adherent water molecules. The upper limit of  $\zeta$  is obtained

(\*) The present argument is strictly valid if the float has an infinitesimal volume at the specified height since the concentration of particles varies from point to point. Observed increase in  $W$  due to colloidal particles of mass  $m$  is,

$$W' - W_0 = \frac{n_c}{v} \int_0^H (mg - \epsilon F) S e^{\frac{-(mg - \epsilon F)h}{kT}} dh$$

instead of being,  $W - W_0 = n_c(mg - F\epsilon) e^{\frac{-(mg - F\epsilon)h}{kT}}$ , where  $S$  is the sectional area of the float,  $v$  the volume and  $H$  the height of the top end. Assuming a spherical shape for the main part of the float with its centre at height  $h_0$ , the ratio of  $W' - W_0$  to  $W - W_0$  in the absence of electric field, when the largest discrepancy between these quantities is expected is, with the value of  $m$  just found,

$$\frac{W' - W_0}{W - W_0} = \frac{3}{4\epsilon^3} \int_{h_0 - R}^{h_0 + R} \{R^2 - (h - h_0)^2\} e^{\frac{-mg(h - h_0)}{kT}} dh = 1.002$$

where  $R = 0.3$  cm is the radius of the spherical part. We see that deviation due to the finite volume of the float is insignificant compared with the experimental fluctuation.

(\*\*) Measured distance between condenser plates was used without any correction for the stray field with regard to the big dielectric constant of water.

by substituting  $\frac{\sigma}{2}$  for  $r$ , i.e.,

$$\zeta \leq \frac{10^{-10} \times 300}{0.6 \times 10^{-6} \times 80} = 6 \times 10^{-4} \text{ Volt}$$

We have  $\zeta$  on the other hand from the cataphoretic mobility  $v$  and the macroscopic viscosity  $\eta$  according to the expression,

$$\zeta = \frac{6\pi\eta v}{D}$$

which is derivable from Eq. (10) by substituting  $\epsilon/r$  from the relation,  $6\pi\eta r v = \epsilon$ , due to Stokes law.

$\zeta$  thus computed is about hundred times as large as the above result. A possible explanation for the discrepancy is that the screening layer of ions adhering to the particle's surface is effectively thicker in the former than in the latter case, not being teared off by the cataphoretic motion, thus appreciably diminishing  $\epsilon$  as well as  $\zeta$  or alternatively that  $\eta$  in the above expression is not that of ordinary measurements, but that under a strong electric field which if calculated from the present result amounts to 1000 Volt/cm in the direct neighbourhood of the particle.

The question is left open to further investigations.

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