Chemistry. — *"Electric charge and limit value of Colloids"*. By Dr. H. R. Kruyt. (Communicated by Prof. Ernst Cohen).

(Communicated in the meeting of June 27, 1914).

1. The present conception as to the relative stability of the suspensoid system and the way in which it may be suspended has been developed according to the following train of thoughts.

Hardy [1]) and afterwards Burton [2]) have undoubtedly established the fact that this relative stability falls and stands with the electric charge of the suspended particle. Indeed, the permanently suspended particle that exhibits a vivid Brown's motion, has a cataphoretic mobility of the order 2—4 μ per second and per $\frac{\text{Volt}}{\text{c.M.}}$; if by addition of an electrolyte one diminishes the relative stability, this velocity also decreases and therefore, the electric charge of the particle has evidently decreased also. The "iso-electric" point, where that charge seems to have become zero, coincides with the moment of the smallest stability. Since the research of Whitney and Ober [3]) we know moreover, that with the repeal of the stability (the coagulation) is coupled a combination of the coagulating ion with the particles, and by Freundlich's [4]) researches we arrived at the knowledge that these phenomena are described quantitatively by the equation of the adsorption-isotherm.

From these elements is built up the theory that the particle owes its charge to the selective ion-absorption in its boundary layer and loses it by the selective adsorption of the oppositely charged ion of the coagulating electrolyte. As specific properties of the adsorbent are usually of but very subordinate influence on the order of the characterizing quantities in the adsorption, the action of diverse electrolytes on all capillary-electric phenomena ought to exhibit the same order, which the researches as to the electro-endosmotic phenomena compared with those of the coagulation of colloids have indeed confirmed.

It now occurs to me that the researches on the current potentials, particularly those which have been communicated in the preceding paper, are capable of furnishing us not only with a new proof of that equality of order, but also demonstrate that the influence which

[1]) Z. f. physik. Chem. **33**, 385 (1900).
[2]) Phil. Mag. [6] **11**, 425; **12**, 472 (1906) and **17**, 583 (1909).
[3]) Z. f. physik. Chem. **39**, 630 (1902).
[4]) Zeitschr. f. physik. Chem. **73**, 385 (1910) and **85**, 641 (1913).

electrolytes exert on the charge of a glass capillary is *quantitatively* the same as that exerted on the colloidal particle during the coagulation.

2, As regards the order of the ion-actions, it has been pointed out in the previous paper that the ions discharge more strongly, when their valency is higher and that the heavy metals exert more influence than the light ones of equal valency. It is well-known that the limit values for the coagulation of suspensoids just exhibit the same peculiarities.

3. In order to make a quantitative comparison it should be first observed that the limit values for KCl and $BaCl_2$ in the same sol. are generally in the proportion of about 60 : 1. In contact with either of these solutions the charge of the particle thus gets equally diminished. We may, therefore also expect that the charge of a glass capillary will be lowered by a solution of KCl to the same extent as by the sixty times weaker $BaCl_2$ solution. Hence, when from the tables in the preceding paper we calculate the charge in concentrations of KCl and $BaCl_2$ in the said proportion, those should be equal if the idea as to the limit value just revealed is a correct one.

The calculation of the charge is possible according to the theory developed by HELMHOLTZ [1]). The current potential is sequel to the electric double layer formed at the wall of the capillary and is related to the electric moment M as follows.

$$E = M \frac{\omega}{\eta} P \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which ω represents the specific resistance and η the constant of the internal friction whilst P represents the pressure employed. For comparison purposes we can consider the electric moment of the double layer just as well as the charge ε per unit of section, as it is in inverse proportion therewith.

We write equation (1):

$$M = \frac{E}{P} \frac{\eta}{\omega}.$$

If now we indicate the quantities relating to a $BaCl_2$- solution with the index b, those relating to the 60 times more concentrated solution of KCl with the index k, then on the strength of the above considerations we must get

$$\left(\frac{E}{P}\right)_b \frac{\eta_b}{\omega_b} = \left(\frac{E}{P}\right)_k \frac{\eta_k}{\omega_k}.$$

([1] Wied. Am. 7, 337 (1879).

As we only have in view very dilute solutions, we may put $\eta_b = \eta_k$ (namely $= \eta_{H_2O}$). From this follows

$$\frac{\left(\dfrac{E}{P}\right)_b}{\left(\dfrac{E}{P}\right)_k} = \frac{\omega_k}{\omega_b} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

or in words: *the relation of the current potentials of two electrolyte solutions whose concentrations are related as in the limit values of colloids are inversely proportional to the specific resistances of those solutions.*

Meanwhile attention should be called to the fact that by limit values in this connexion we must not understand the concentration γ of the electrolyte added. From this a part is withdrawn by adsorption and hence, to the setting in end-condition appertains a lower concentration, which we will call χ. In the experiments as to the current potentials we may probably identify the total concentrations with the equilibrium concentrations as the adsorbing surface (the glass walls) is so small: only in the case of the exceedingly weak $AlCl_3$ solutions a doubt may arise. But in the colloid systems that difference may not be neglected. These χ-values themselves
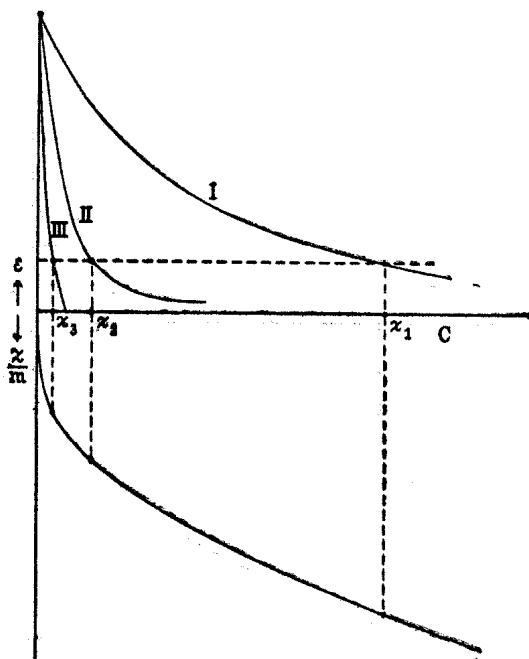

Fig. 1.[1]

---

[1]) In Fig. 1 on the axis of coordinates should be read $\dfrac{x}{m}$ in stead of $\dfrac{\chi}{m}$.

have been determined only for As_2S_3 [1] and HgS_2 [2] and for electrolytes not used here.

The proportions are :

$$\text{With } As_2S_3 \quad \chi_{NH_4Cl} : \chi_{UO_2(NO_3)_2} = 82$$
$$\text{,, } Hg_2S \quad \chi_{NH_4Cl} : \chi_{BaBr_2} = 29.$$

The proportion chosen $60 : 1$ is, therefore, a rough approximation, but a comparison with γ-values of other sols (Pt, Au etc.) renders it probable that it represents the average.

The relations between charge, adsorption and limit value are elucidated schematically in the above figure. In the upper half of the figure is drawn the charge ε of the capillary in dependence on the concentration of the traversing liquid, so that I, II, and III stand for uni-, di- and trivalent cations respectively. In the lower half is given, with the same concentration axis, the correlated adsorption of the electrolyte as a downward directed ordinate. If now χ_1, χ_2 and χ_3 indicate the relation of the limit values for uni-, di- and trivalent cations, respectively the correlated downward directed ordinates must show the proportion $1 : 1\frac{1}{2} : 3$ and the upward directed ones *equal* values.

4. For verification of this relation appeared suitable :

(a) 10 μMol $BaCl_2$ — 600 μMol KCl.

b) 25 μMol $BaCl_2$ — 1500 μMol KCl.

It would not do to simply take the specific conductivity powers as being proportional to the concentrations because in the so strongly diluted $BaCl_2$ solutions the conductivity power of water could not be neglected. Hence, I have made a direct measurement of the relation of the specific resistances by filling in WHEATSTONE's bridge a vessel of arbitrary but fixed capacity with the liquids used.

The relation of these resistances was in the pair (a)

$$\frac{\omega_b}{\omega_k} = \frac{4630}{247} = 19$$

and in the pair (b)

$$\frac{\omega_b}{\omega_k} = \frac{2770}{99.9} = 28$$

The values of $\frac{E}{P}$ are obtained from the research communicated in the preceding paper.

[1] FREUNDLICH, Zeitschr. f. physik. Chem. **73**, 385 (1910).
[2] FREUNDLICH en SCHUCHT, ibidem **85**, 641 (1913).

As the relation of the potentials for (a) we obtain $\frac{13.9}{10}$ or **14**; as the relation of the resistances : **19**.

From the combination (b) we obtain for the potentials $\frac{7.9}{3}$ or **26**, for the resistance **28**.

This agreement undoubtedly tells much in favour of the above mentioned theory. With concentrations somewhat larger than 60 the agreement might be better still.

5. The material of RIÉTY [1]) is only once suitable for testing the relation (2).

For so far his measurements have been executed with solutions of salts other than chlorides his measuring electrodes were non-reversable ones and his results are therefore useless for quantitative verification. I have only been able to find one combination of chlorides where concentrations have been measured which are comparable with limit values : they are KCl and HCl. For As_2S_3-sol these limit values have been determined to 50 and 31 mMol p. L. respectively [2]).

Now from his experiments RIÉTY has calculated the potential at the capillary wall in certain units for 0.01 n. KCl as **3.1**. We can use this figure again for comparison purposes at it is directly proportional to the charge.

In the case of HCl he determined for 0.005 n : 3.39, for 0.010 n : 2.8. For the comparison with 0.01 n HCl we must know the potential at the concentration $\frac{31}{50} \times 0.01 = 0.0062$. This, I have interpolated by assuming that the logarithms of the potentials are directly proportional to those of the concentrations, after I had first convinced myself that this interpolation [3]) formula was quite satisfactory in the longer series stated in RIÉTY's paper. We then find **3.2** which is again a splendid agreement.

6. Quantitative comparisons with the trivalent cation are difficult to draw, because the χ-values thereof are either not known or uncertain. From the treatises cited on p. 648 we, however, get the impression that the χ-values diverge very little from zero, as is also expected from Table IV of the preceding communication, because a complete discharge takes place already at a concentration of 0.8 μ mol.

7. A no less striking parallelism between charge and limit value

[1]) Ann. de chim. et de phys. [8], **30**, 1 (1913).

[2]) FREUNDLICH, Kapillarchemie (Leipzig 1909) Table 81. True, those are γ- and not χ-values, but with these univalent ions, this cannot have any serious influence.

[3]) To this formula should only be attached the significance of an interpolation formula.

41

is furnished by the shape of the curve found for the current potential with AlCl$_3$ solutions. This line is absolutely connected with the so-called *irregular series*.

From what is stated in § 3 in connection with Table IV (fig. 3, respectively) of the preceding paper it follows that the concentration at which the battery shows an exchange of poles, is also that of the zero-charge of the capillary, whilst its positive charge goes up to about 3μ mol. and thence lowers without however reaching zero again. An AlCl$_3$ solution will consequently have first a discharging and therefore a coagulating effect on a negative sol.; at higher concentrations it will render it a positive sol and only at a much higher concentration it will again reverse the charge and cause coagulation. But therewith are described exactly the phenomena which, for instance, have been observed by BUXTON and TAEGUE[1]), when they coagulated mastix with AlCl$_3$ and indigo or Pt with FeCl$_3$. The lower non-coalescent, the lower coalescent zone, the upper non- and coalescent zones, they can so to say be read off from the figures of the preceding communication.

One is accustomed to attribute the phenomenon of the irregular series to a special action of the hydrolytically resolved hydroxides of the coagulating ion. In connection with the preceding arises a doubt whether to Al(OH)$_3$ ought really to be attributed a preponderating significance. For it does not seem probable that the AlCl$_3$ which is present in such a small concentration, can cause a reversal of charge in the capillary. Much more acceptable seems the following idea. A strongly discharging cation unloads the capillary at *such* a small concentration that the small anion-concentration cannot prevent a complete reversal of charge. Of this the anion-concentrations are capable in the case of Ba$\cdot\cdot$ and K$\cdot$ because there the charge gets nearer the zero value only at so much larger concentrations.

Hence, the afterzone phenomenon will occur, as soon as the discharge by the cation is already very large at small concentrations and is favoured by a feeble action of the anions. This strongly discharging action of the cation may arise from its higher valency or from its strong adsorbability. The fact that irregular series were observed, for instance, also with strychnine nitrate, new fuchsin, brilliant-green, auramine and silver nitrate[2]) is quite in harmony with this argument. For here we are dealing with strongly adsorbable cations and because they are univalent the equivalent anion

---

[1]) Z. f. physik. Chem. **57**, 64 (1907.

[2]) FREUNDLICH, l. c.

concentration present is still proportionately three times less than with $AlCl_3$.

A start has already been made with investigations to get a proper insight, particularly in this question of the irregular series.

8. Finally it should be pointed out that the previous considerations also give an explanation of the fact often stated by us that in the case of Al-salts we can determine the limit value much more accurately than with salts of uni- or bivalent metals. Two tubes with As_2S_3 sol. which contain Al in concentrations situated $1^o/_o$ above and below the limit value, respectively exhibit after shaking a quite clear and a turbid fluid respectively. In the case of bivalent cations we must, so as to make quite sure, take the difference somewhat larger and very much so for a univalent ion. It is self-evident that the cause lies in the fact that $\dfrac{d\varepsilon}{dc}$ (ε charge, c concentration of coalescing ion) for $Al^{\cdots}$ is $>$ for $Ba^{\cdots}$ and this again $>$ for $K^{\cdot}$.

Utrecht. June 1914.   VAN 'T HOFF-*Laboratory.*

(November 7, 1914).