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The Influence of the Chemical Nature of Solid Particles on Their Cataphoretic P.D. in Aqueous Solutions

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THE INFLUENCE OF THE CHEMICAL NATURE OF SOLID PARTICLES ON THEIR CATAPHORETIC P.D. IN AQUEOUS SOLUTIONS.

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I.

INTRODUCTION.

In order to arrive at a theory of the action of electrolytes on the formation of a double electrical layer—or, more correctly, on the value of the cataphoretic P.D.—between solid particles and aqueous solutions, it is necessary to know how this action is influenced by the nature of the suspended particle. In former papers by the writer, the effect of electrolytes on the cataphoretic P.D. was studied on proteins[1] and on collodion particles.[2] In this paper experiments on particles of mastic, Acheson's graphite (trade name "Aquadag," Size 5), which I owe to the kindness of Dr. Leonard Waldo, gold (prepared by Bredig's method in solution of N/10,000 HCl), ferric hydroxide, and calcium oxalate are added. To give a more complete picture experiments on collodion and protein are included.

In order to eliminate as much as possible the influence of H and OH ions, the experiments with salts were made in distilled water as near the point of neutrality as was conveniently possible. The distilled water used had a pH of about 5.8, resulting from an equilibrium with the CO_2 of the air of the laboratory. Stock solutions of the salts were prepared with a pH of 5.8 and these were diluted with distilled water of the same pH. Great care was taken to keep the pH of the solutions at 5.8, except in the case of solutions of $ThCl_4$ which were always more acid on account of the hydrolytic

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[1] Loeb, J., *J. Gen. Physiol.*, 1922–23, v, 395.

[2] Loeb, J., *J. Gen. Physiol.*, 1922–23, v, 109; 1923-24, vi, 105.

dissociation of the salt; and of solutions of acid and basic fuchsin, where the pH was not measured.

It was also thought advisable to eliminate impurities as much as possible. Such impurities were contained in some cases in the stock solution of the suspended particles. This error was minimized by using as small a quantity of suspended particles as possible. A few drops of the stock suspension were put into 50 cc. of the salt solution, shaken, and allowed to stand for 20 minutes. When this is done, it is found that the P.D. of the particles in distilled water of pH 5.8 without the presence of salts is generally very small, rarely above 8 millivolts. Only when the particles are themselves electrolytes or when electrolytes are added does the P.D. rise. Statements in the literature that a high cataphoretic P.D. was observed in distilled water without electrolytes suggest the presence of electrolytes in the form of impurities, unless the particle itself was an electrolyte. The value of 26 millivolts for mastic particles in pure water at pH 5.8 in Fig. 2 is too high and unquestionably due to an impurity of some kind. A repetition of the experiments where such errors were excluded gave a much lower P.D., namely about 8 millivolts or less.

Although the P.D. of the particles in water at pH 5.8 is very low in the absence of electrolytes, the sign of charge of the particles at this low P.D. is of the greatest significance for the effect of the salt on the P.D. This effect is entirely different according to whether a particle is positively or negatively charged in pure water near the point of neutrality even if the P.D. be as low as 5 millivolts. We shall therefore designate as negative colloids, such particles which at pH 5.8 are negatively charged in the absence of electrolytes; and as positive colloids, particles which are positively charged at pH 5.8 in the absence of electrolytes.

The method of determining the cataphoretic P.D. was the same as in the preceding papers, namely, the measurement of the rate of migration of isolated particles under the microscope in the way described by Ellis.[3] From the measurements of the velocity of migration the P.D. was calculated with the aid of the Helmholtz-Perrin formula. The apparatus used was that by Ellis as modified by Northrop,[4] with

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[3] Ellis, R., *Z. physik. Chem.*, 1911–12, lxxviii, 321; 1912, lxxx, 597.

[4] Northrop, J. H., *J. Gen. Physiol.*, 1921–22, iv, 629.

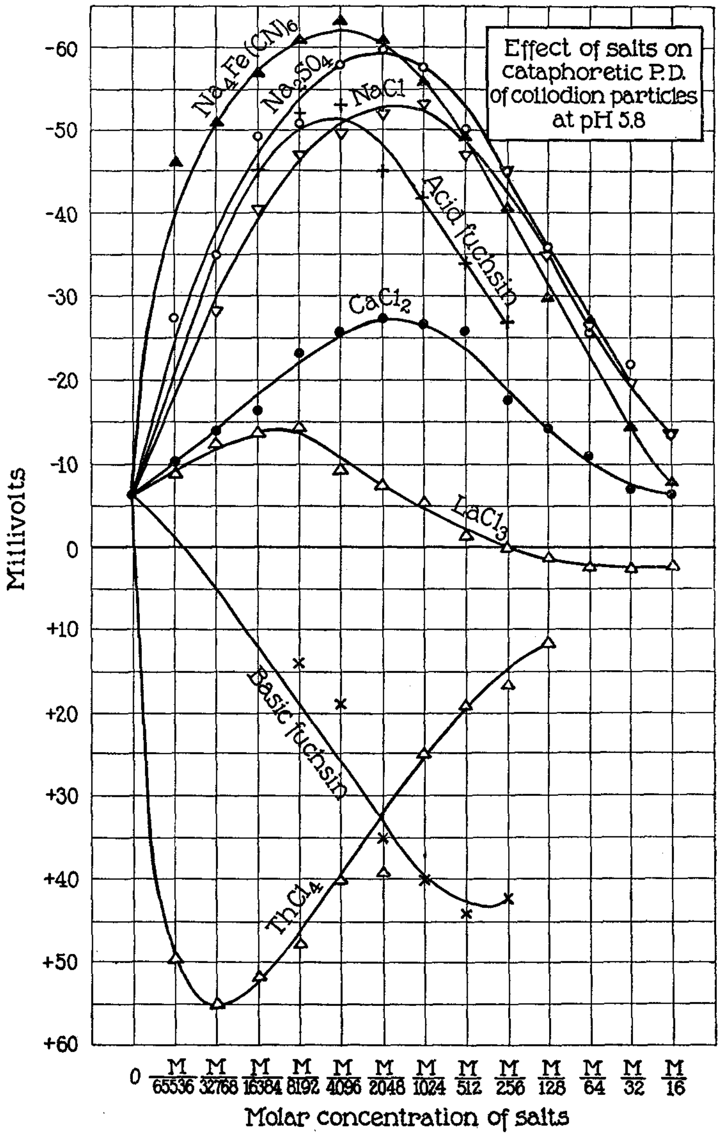

FIG. 1. Influence of salts on the cataphoretic P.D. between collodion particles and aqueous solutions near the point of neutrality, pH 5.8, (with the exception of the solutions of $ThCl_4$ and basic fuchsin). Abscissæ are the molar concentrations of salt solutions, ordinates, the cataphoretic P.D. The signs minus and plus refer to the sign of charge of the particles.

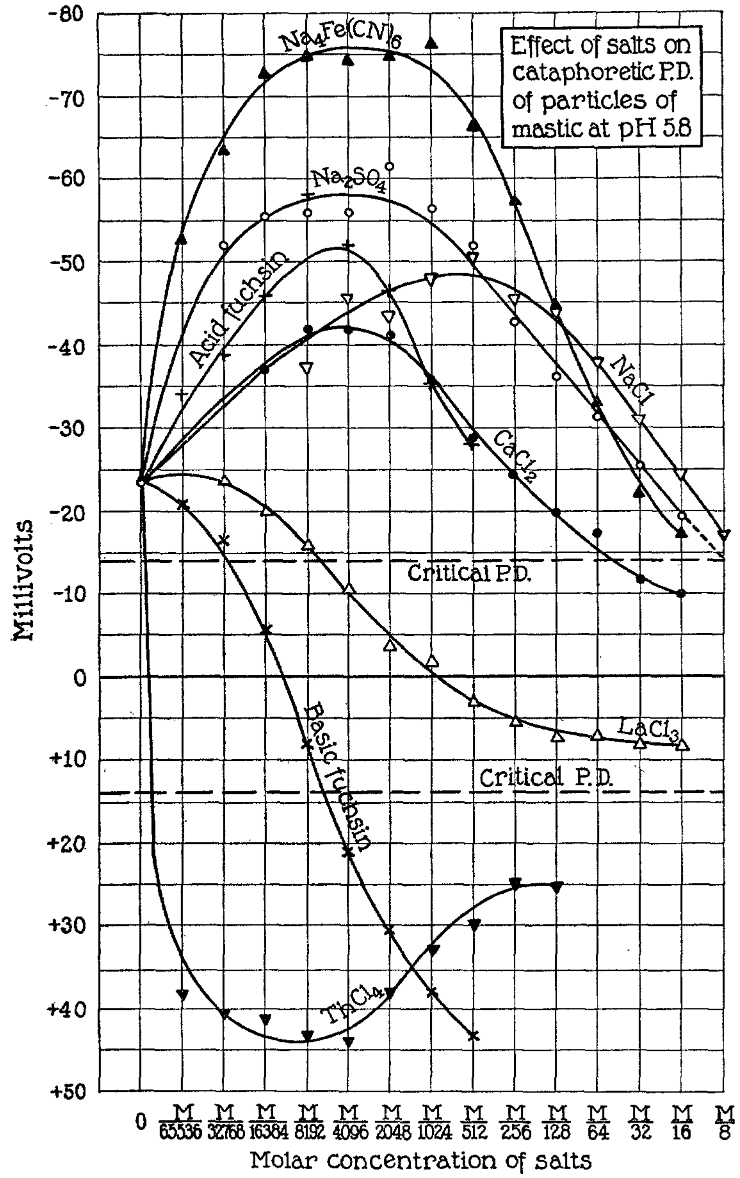

FIG. 2. Influence of salts on the cataphoretic P.D. of mastic particles near neutrality (pH 5.8). The line Critical P.D. indicates the value of P.D. below which the suspension ceases to be stable.

an additional modification introduced by Mr. Kunitz for using dark-field illumination.

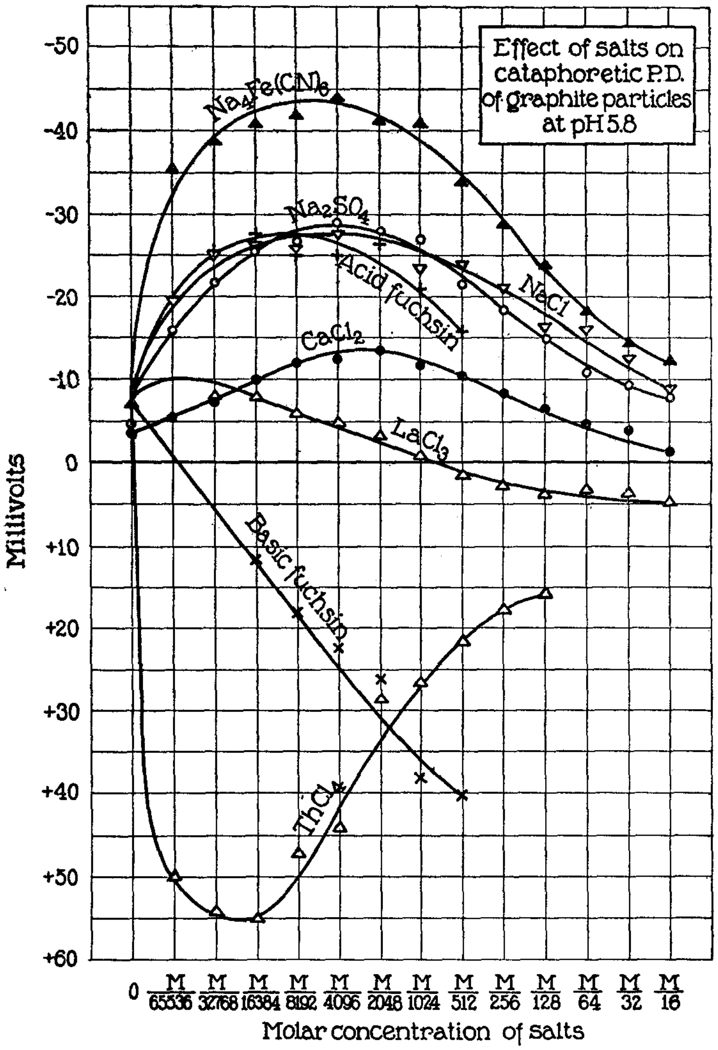

FIG. 3. Influence of salts on the cataphoretic P.D. of particles of Acheson's graphite (trade mark "Aquadag," Size 5) near neutrality, pH 5.8.

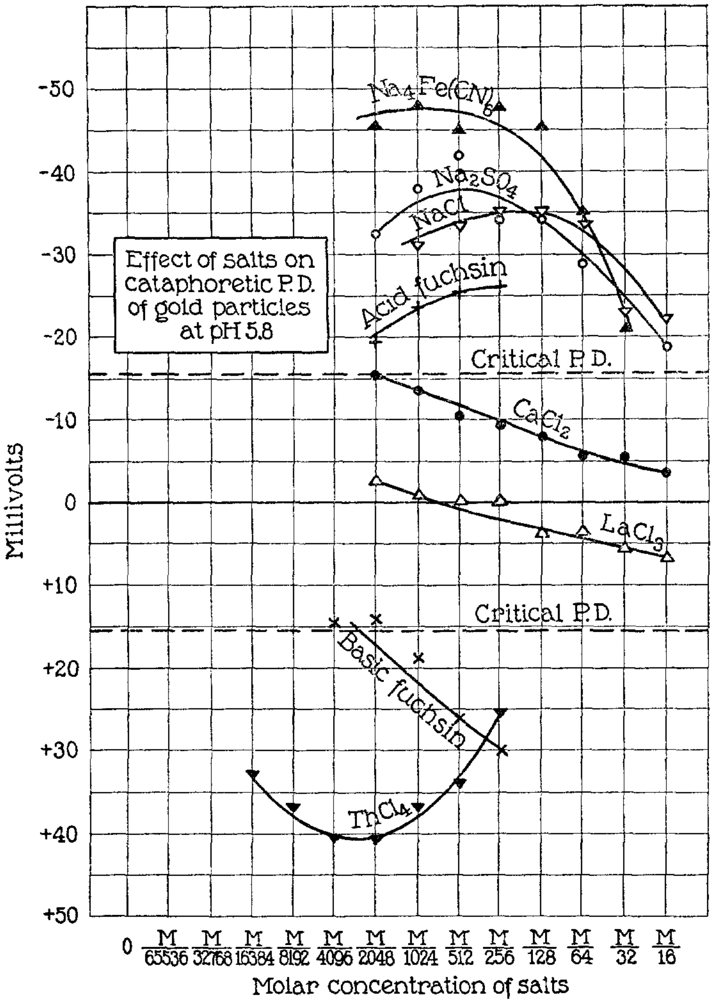

FIG. 4. Influence of salts on the cataphoretic P.D. of particles of gold near neutrality (pH 5.8). Only the effect of concentrations of salts of M/2,048 or above are given.

II.

Experiments on Negatively Charged Particles.

Six types of particles, negatively charged at pH 5.8, were selected for this study, collodion (Fig. 1), mastic (Fig. 2), Acheson's graphite

(Fig. 3), gold (Fig. 4), Na gelatinate (Fig. 5), and crystals of tyrosine. (At pH 5.8 the tyrosine is little if at all dissociated.) In Figs. 1 to 5 the abscissæ are the molar concentrations of the salts while the ordinates are the cataphoretic P.D. in millivolts as calculated from the rate of migration with the aid of the Helmholtz-Perrin formula.[5]

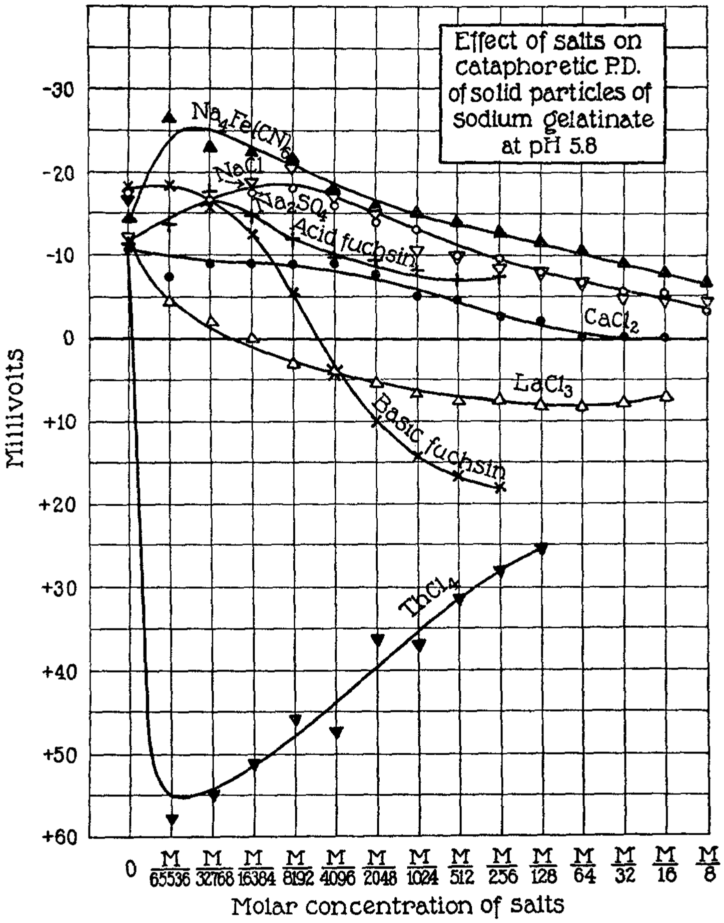

FIG. 5. Influence of salts on the cataphoretic P.D. of solid particles of Na gelatinate near neutrality, pH 5.8.

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[5] Freundlich, H., Kapillarchemie, Leipsic, 2nd edition, 1922, 326 ff. Burton, E. F., The physical properties of colloidal solutions, London, New York, Bombay, Calcutta, and Madras, 2nd edition, 1921, 136 ff.

The sign of the charge is always that of the particle, the negative charges being above the zero line, the positive charges below. In spite of the wide divergence in the chemical nature of the material, the P.D. curves are in all five figures so similar that the following general rules concerning the influence of salts on the P.D. of negative colloids in distilled water of pH 5.8 hold for all of them. For the purpose of discussion, the curves for the collodion particles will be used (Fig. 1). (In expressing these rules, it is more convenient to speak in terms of the charge of the particles instead of the value of the P.D., which is the quantity actually determined.)

In water near the point of neutrality (*i.e.*, at pH 5.8) salts with monovalent cation raise the negative charge of negative colloids with increasing concentration of the salt until a maximum P.D. is reached; this maximum, which never seems to exceed about 70 millivolts,[6] is the higher the higher the valency of the anion, being a little higher for the $Fe(CN)_6$ than for the Cl ion (see Figs. 1, 2, or 3). What is, perhaps, of theoretically greater importance is the fact that the curve for $Na_4Fe(CN)_6$ rises more steeply than that for either Na_2SO_4 or NaCl. When the characteristic maximal P.D. for each salt is reached, a further addition of the same salt causes a fall of the value of the P.D.

Salts of the type of $CaCl_2$, *i.e.*, with bivalent cation and monovalent anion, also raise the negative charge of the particles as long as the concentration is below M/2,048. This is best seen in Fig. 1, representing the effect of the salts on collodion particles. The original P.D. without salt was only about 7 millivolts (in the former papers a P.D. of about 30 millivolts was found in this case, but this was chiefly due to impurities and other imperfections of the technique which have since been remedied). The maximal P.D. in $CaCl_2$ for collodion particles is, however, only about 28 millivolts as against about 53 for NaCl (Fig. 1).

Even a salt like $LaCl_3$ still raises the P.D. (Fig. 1), but only from 7 to about 15 millivolts. The maximal P.D. is reached in $LaCl_3$ at a molar concentration of between M/16,000 and M/8,000. With the addition of more $LaCl_3$ the P.D. is depressed. At a concentration of

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[6] von Hevesy, G., *Kolloid Z.*, 1917, xxi, 129. Lorenz, R., Raumerfüllung und Ionenbeweglichkeit, Leipsic, 1922, 237.

about M/128 the particles become slightly positive, but the P.D. remains at nearly zero even in M/16 $LaCl_3$. In the writer's former experiments the fact that $LaCl_3$ is able to raise the P.D. of collodion particles in very low concentrations was concealed on account of the impurities which had raised the P.D., without the additions of any salt.

No rise occurs, however, in the case of a salt like $ThCl_4$. Extremely low concentrations of this salt make the particles positive, and the P.D. increases with the increase of the concentration, until a maximal P.D. of 55 millivolts is reached at a concentration of $ThCl_4$ between M/30,000 and M/8,000. A further increase in the concentration of the salt depresses the P.D. again (Fig. 1).

TABLE I.

Maximal P.D. *Values in Solutions of* $Na_4Fe(CN)_6$ *at pH 5.8 for Negative Colloids.*

Nature of particles.	P.D.
	millivolts
Mastic	about 75
Collodion	" 62
Acheson's graphite	" 43
Gold	" 47
Crystals of tyrosine	" 45
Na gelatinate	" 25

High positive charges are also produced by basic fuchsin and the P.D. increases with the concentration of the dye until a maximum is reached after which the P.D. drops with further increase in the concentration of the dye.

If we compare the difference in the relative effect of salts on the six negative colloids (Table I) we may use the maximal P.D. values in $Na_4Fe(CN)_6$ as a standard of comparison.

The values for Na_2SO_4 and NaCl vary correspondingly.

III.

Positively Charged Particles.

Figs. 6, 7, and 8 show the effects of salts on positively charged particles; namely, ferric hydroxide, calcium oxalate, and casein chloride. The experiments with ferric hydroxide and calcium oxalate were made at pH 5.8 and care was taken that this pH was not altered by the addition of the salts (with the exception of the dyes). The experiments with casein chloride had to be made on the acid side of the isoelectric point of casein and the pH of 4.0 was selected. The reader will notice that all three positively charged particles are electrolytes while in the case of the negatively charged particles some, *e.g.* Na gelatinate, were electrolytes, while collodion and mastic were apparently non-electrolytes.

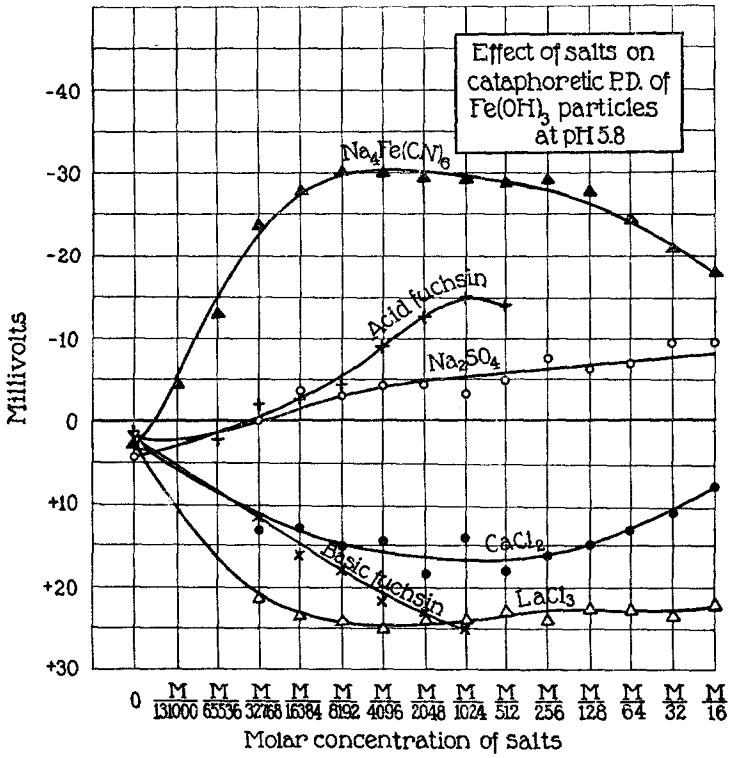

FIG. 6. Influence of salts on the cataphoretic P.D. of particles of $Fe(OH)_3$ near neutrality, pH 5.8.

The curves for the positive colloids differ in an essential respect from those for negative colloids. While in the case of negative colloids the Cl and SO_4 ions had a powerful augmenting effect on the P.D.

these two anions have almost no effect on the positive colloids. Na_2SO_4 makes the positive colloids slightly negative at comparatively high concentrations but the P.D. is very small indeed. Only $Na_4Fe(CN)_6$ and acid dyes make the positive particles negative in rather low molar concentrations, but even here the P.D. remains low (30 millivolts or less).

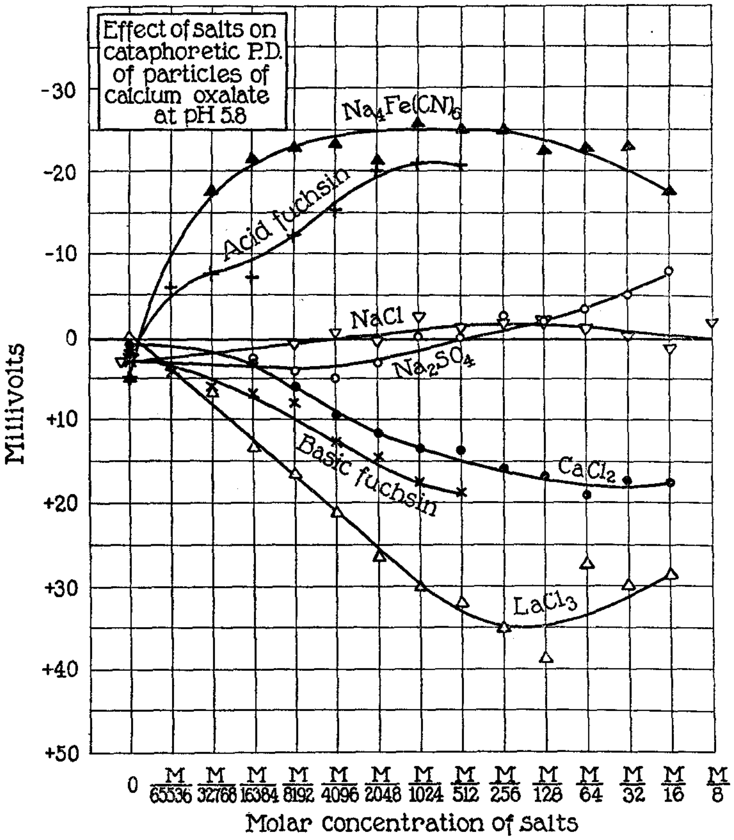

FIG. 7. Influence of salts on the cataphoretic P.D. of particles of calcium oxalate near neutrality, pH 5.8.

Perhaps, it is on account of this lack of efficiency of the Cl ion, that $CaCl_2$ and $LaCl_3$ in low concentrations increase the positive charge of the positive colloids until a maximal P.D. is reached after which a further increase in the concentrations of $CaCl_2$ and $LaCl_3$ will depress the P.D. again.

Basic fuchsin does not act quite as strongly as does $LaCl_3$ on the P.D. of positive colloids but in the same sense.

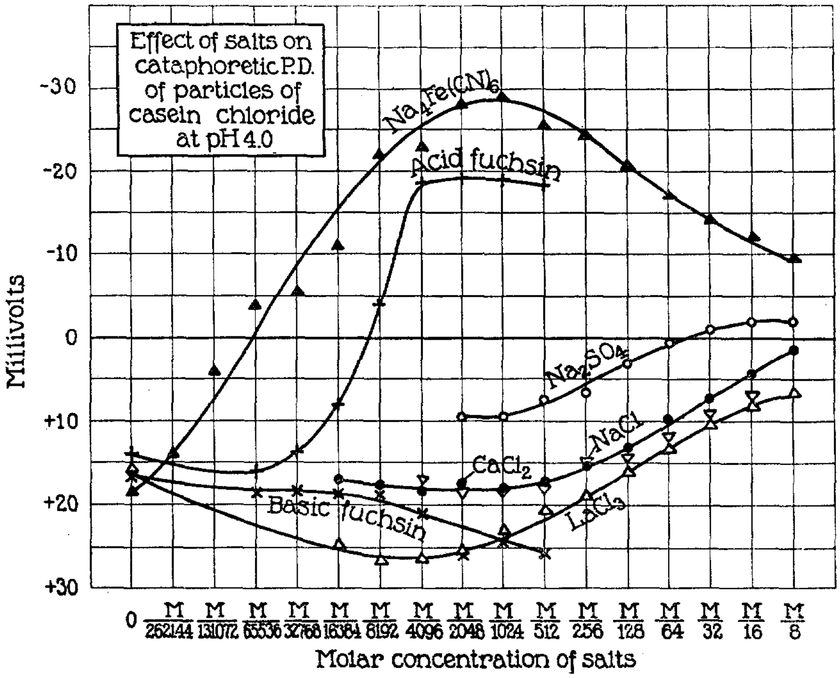

FIG. 8. Influence of salts on the cataphoretic P.D. of particles of casein chloride at pH 4.0.

IV.

The Action of Alkalies and Acids on the Cataphoretic P.D.

The influence of NaOH on the cataphoretic P.D. of different colloidal particles is almost identical with that of $Na_4Fe(CN)_6$. Regardless of whether the colloid is originally negative or positive, NaOH makes the particles always more negative and the P.D. increases until a maximum is reached at about M/4,096 or M/1,024; after which the P.D. drops again upon further increase in the concentration of the alkali (Fig. 9). The OH ion is therefore driven with about the same relative force into the enveloping film as is the Fe(CN)$_6$ ion. Table II gives the maximal values of the P.D. in NaOH solutions.

It might be inferred *a priori* that hydrogen ions act like thorium ions and this would seem to receive support in the statement so often

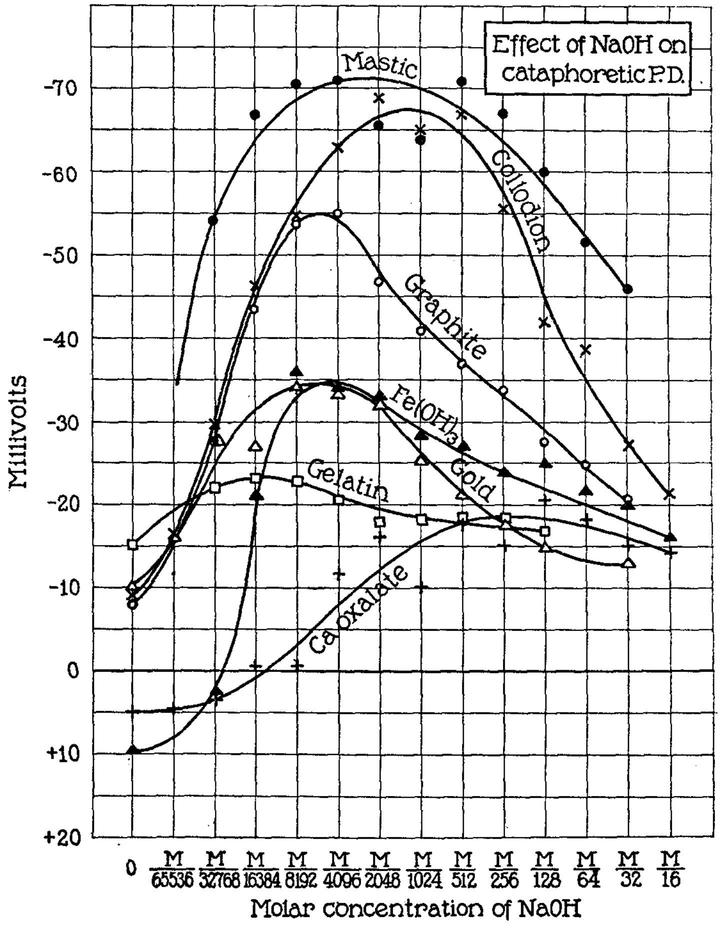

FIG. 9. Influence of NaOH on the cataphoretic P.D. of different kinds of particles.

found in the colloidal literature that hydrogen ions make colloids positive. While this is true for amphoteric electrolytes, Fig. 10 shows that this cannot be generalized. Low concentrations of HCl

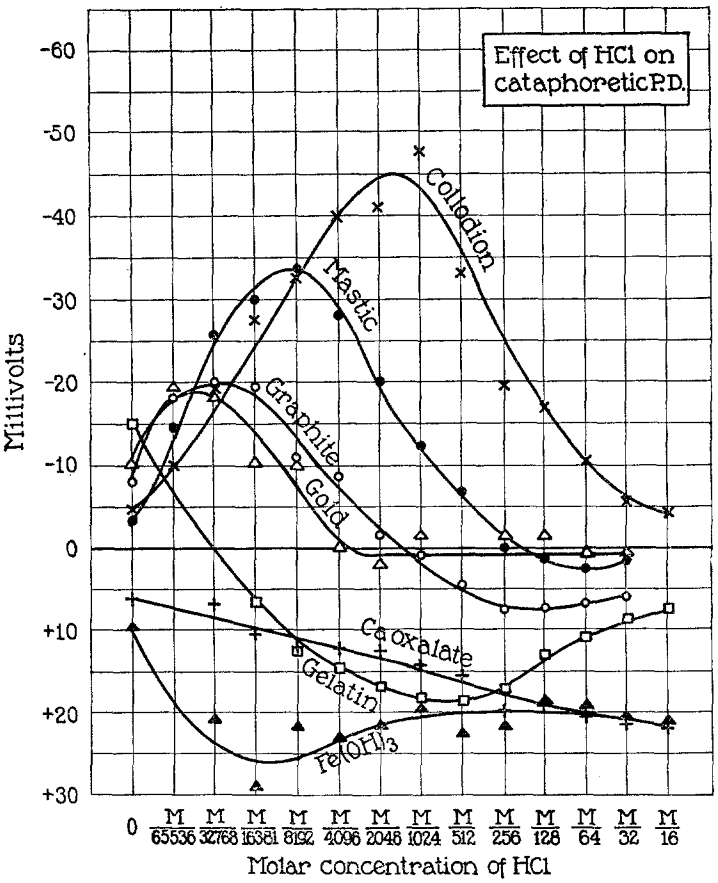

FIG. 10. Influence of HCl on the cataphoretic P.D. of different kinds of particles.

TABLE II.

Maximal P.D. between Different Particles and Solutions of NaOH.

Nature of particles.	P.D.
	millivolts
Mastic	71
Collodion	67
Acheson's graphite	55
Gold	50
$Fe(OH)_3$	35
Na gelatinate	23
Ca oxalate	18

generally increase the negative charge of negative colloids such as collodion, mastic, Acheson's graphite, and gold (Fig. 10) until a maximum is reached, which is quite high in the case of collodion (about 45 millivolts), lower in the case of mastic (about 33 millivolts), graphite, and gold (about 20 millivolts). A further increase in the concentration of the HCl depresses the P.D. (Fig. 10).

In the case of collodion the sign of charge of the particles is not reversed by acid, the collodion particles remaining negative even in M/8 solutions of HCl (Fig. 10). Particles of mastic or of gold may become positive in higher concentrations of HCl, but the P.D. remains very low (2 or 3 millivolts). Graphite becomes slightly more positive in acid, but the P.D. is also low (about 7 millivolts). HCl is therefore even a little less active than $LaCl_3$ which also makes negative colloids positive only at comparatively high concentrations and the P.D. is also never high in this case.

The statement that acids render negative colloids strongly positive seems to be correct only in such cases where the chemical character of the colloid is changed by the acid. Thus amphoteric electrolytes like the proteins are transformed by HCl into protein chlorides where the non-diffusible ion of the particle is a positive protein ion. Particles of Na gelatinate are negatively charged (Fig. 4) but if enough HCl is added the protein is transformed into gelatin chloride where the non-diffusible protein ion is a cation. Gelatin chloride particles may reach a considerable positive P.D. (Fig. 10).

McTaggart[7] states that $Th(NO_3)_4$ makes gas bubbles positive and so does also to a slight extent $LaCl_3$; it would be very important to find out whether or not HCl can produce a considerable positive charge on gas bubbles. The experiments of McTaggart do not seem to give a definite answer to this question. It seems, therefore, that for the present we must discriminate in the effects of HCl on the cataphoretic P.D. between cases where the chemical nature of the particles is changed by the acid and where no such changes occur. In cases of the latter type (presumably collodion particles), solutions of

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[7] McTaggart, H. A., *Phil. Mag., Series 6*, 1914, xxvii, 297; xxviii, 367; 1922, **xliv**, 386.

NaOH and HCl may act like neutral solutions of NaCl on the cataphoretic P.D. as is shown in Fig. 11, the only difference between the three electrolytes being that the OH ion acts a little more strongly than the Cl ion and the H ion slightly more strongly than the Na ion; or, if we use the suggestion of a relative orientation of the ions, along the normal to the interface, OH ions are driven with a slightly greater force into the enveloping film than the Cl ions, and the H ions are driven with a slightly smaller force away from the interface than the Na ions.

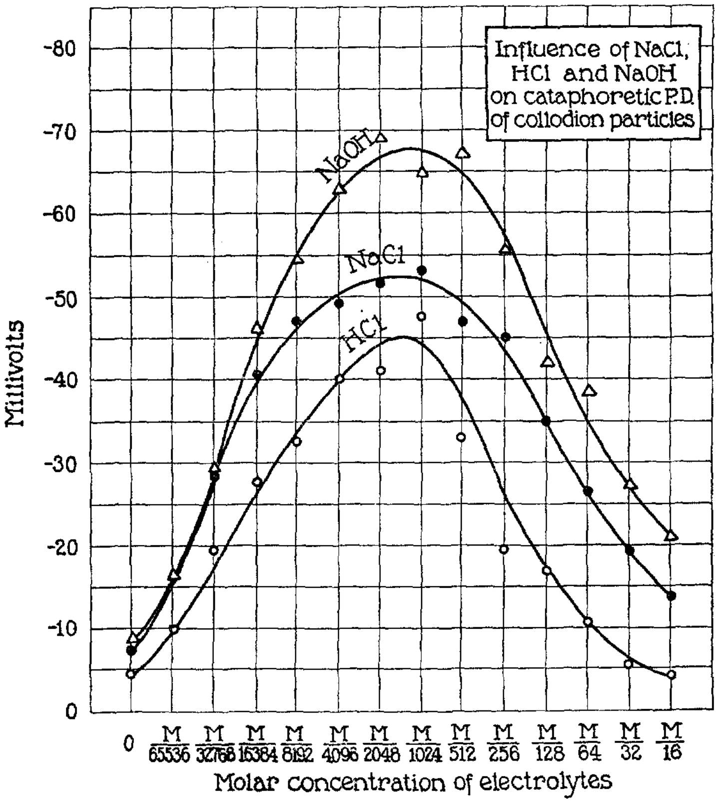

FIG. 11. Comparison of the influence of HCl, NaCl, and NaOH on the cataphoretic P.D. of collodion particles. The curve for NaCl represents the effects of this salt at an approximately neutral reaction, pH 5.8.

V.

Flocculation.

Although it is not an essential part of our problem it may perhaps be of importance to point out that there seems to exist in the case of all of these suspensions a critical P.D. below which they cease to be stable and commence to flocculate. It is rather remarkable that this critical P.D. differs very little with the chemical nature of the suspended particles. The critical P.D. is indicated by lines marked Critical P.D. in Figs. 2 and 4. The suspensions of collodion,[2] mastic, graphite, and gold cease to be stable and flocculation commences when the cataphoretic P.D. falls to a value of between 16 and 13 millivolts. Northrop and De Kruif[8] found a similar value, namely 15 millivolts, for the flocculation of certain bacteria. The values for the flocculation of suspensions of calcium oxalate, denatured casein, and denatured albumin[9] are not very far from this value. The interpretation of this fact seems to be that flocculation can only occur when the average velocity of the particles is high enough to overcome the repelling force due to the P.D. of the double layer. The average velocity of the particles seems to be such that it suffices to overcome the repulsion due to a P.D. of about 14 millivolts or less. Flocculation requires, however, something more than the mere overcoming of the repulsive forces due to the cataphoretic P.D.; namely, the force of cohesion between the particles themselves must be considerably greater than the forces of adhesion between the particles and the water. Particles of gelatin (or of collodion coated with gelatin) will not flocculate even if the P.D. is zero, and the same is true for particles of denatured egg albumin or casein in the presence of gram molecular concentrations of NaCl or $CaCl_2$.[9] In these cases the forces of cohesion of the particles are relatively small compared with the attraction of the particles for water, so that they fail to cohere upon collision even if the cataphoretic P.D. is zero.

It has frequently been stated that the precipitating power of electrolytes increases with the mobility of the active ion.[10] Thus the

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[8] Northrop, J. H., and De Kruif, P. H., *J. Gen. Physiol.*, 1921–22, iv, 639.

[9] Loeb, J., *J. Gen. Physiol.*, 1922–23, v, 479.

[10] Mukherjee, J. N., *Farad. Soc. Rep.*, London, 1921, xx, 103.

precipitating power of the chlorides of alkali metals is said to increase in the order Li < Na < K < Rb < Cs. This cannot be a general rule, since LiCl, NaCl, and KCl influence the P.D. of collodion as well as graphite particles in an identical way. Flocculation is determined by the critical P.D. and since identical concentrations of LiCl, NaCl, and KCl are required to bring about the critical P.D., the flocculating concentrations for these salts should be identical. This was found to be true for suspensions of mastic, graphite, and collodion when care was taken to keep the pH constant. In Tables III, IV, and V are given the flocculating concentrations of different salts at pH 5.8 for suspensions of mastic, Acheson's graphite, and gold. (Only in the case of $ThCl_4$ and basic fuchsin were the pH different.) By flocculation is meant the complete settling of the particles, leaving a completely colorless and clear supernatant liquid; while by suspension is meant that the liquid remains red in the case of gold or gray or opaque in the case of mastic or black in the case of graphite; while no or little settling occurs. The second column of the tables gives the minimal molar concentration required for flocculation, and the third column the highest concentration at which the suspensions remain stable for weeks. In order to get unequivocal results, the values in Columns

TABLE III.

Mastic.

	Flocculation.	Suspension.
LiCl	M/4	M/8
NaCl	M/4	M/8
KCl	M/4	M/8
RbCl	M/2	M/4
CsCl	M/4	M/8
$MgCl_2$	M/32	M/64
$CaCl_2$	M/32	M/64
$SrCl_2$	M/32	M/64
$BaCl_2$	M/32	M/64
$MnCl_2$	M/32	M/64
$LaCl_3$	M/8,192	M/16,000
$ThCl_4$	M/260,000	$\lessgtr$ M/260,000
Basic fuchsin	M/8,000 – M/4,000	>M/4,000 <M/8,000

TABLE IV.

Graphite (Aquadag).

	Flocculation.	Suspension.
LiCl	M/32	M/64
NaCl	M/32	M/64
KCl	M/32	M/64
RbCl	M/32	M/64
CsCl	M/32	M/64
$MgCl_2$	M/512	M/1,024
$CaCl_2$	M/1,024	M/2,048
$SrCl_2$	M/512	M/1,024
$BaCl_2$	M/1,024	M/2,048
$MnCl_2$	M/1,024	M/2,048
$LaCl_3$	M/65,000	M/130,000
$ThCl_4$	M/500,000	$\lessgtr$ M/500,000
Na_2SO_4	M/64	M/128
$Na_4Fe(CN)_6$	M/64	M/256
$MgSO_4$	M/512	M/1,024
Basic fuchsin	M/8,000 and M/16,000	>M/8,000 <M/16,000
HCl	M/2,048	M/4,096

TABLE V.

Gold.

	Flocculation.	Suspension.
LiCl	M/16	M/32
NaCl	M/64	M/128
KCl	M/128	M/256
RbCl	M/16	M/32
CsCl	M/128	M/256
$MgCl_2$	M/16,000	M/32,000
$CaCl_2$	M/4,096	M/8,192
$SrCl_2$	M/8,192	M/16,000
$BaCl_2$	M/16,000	M/32,000
$MnCl_2$	M/8,192	M/16,000
$LaCl_3$	M/260,000	M/500,000
$ThCl_4$	M/500,000	
Na_2SO_4	M/64	M/128

2 and 3 were ascertained after the suspensions had been standing in test-tubes for a week or more at room temperature. Variations occurred only in the case of gold, but they were too irregular and could not be reproduced with any degree of certainty. The writer cannot suppress a suspicion that the variations in the flocculating concentrations of salts in the case of gold particles were the result of traces of impurities introduced accidentally. In Table V only the red suspensions were permanently stable, while those which at the beginning were blue or bluish red had settled.

Odén[11] observed enormous differences in the precipitating power of the salts of the alkali metals on suspensions of colloidal sulfur. Nothing of this kind can be observed in the case of the precipitation of mastic, Acheson's graphite, collodion particles, or even particles of gold.

VI.

Theoretical Remarks.

There are two kinds of forces which can cause an excess of one kind of ions in the enveloping film; namely, forces inherent in the water itself and forces of attraction between the colloidal particles and the ions.

The share which forces inherent in the water have in the orientation of the oppositely charged ions of an electrolyte in the interface can only be ascertained through experiments on the influence of electrolytes on the cataphoretic migration of gas bubbles in aqueous solutions, but experiments of this kind are as yet too incomplete to permit more than the statement that in cataphoresis gas bubbles are generally negatively charged, that their sign of charge is reversed by low concentrations of $Th(NO_3)_4$ and presumably by higher concentrations of $LaCl_3$; and that it is doubtful whether acids alone can cause a noticeable reversal in the sign of charge of gas bubbles (*i.e.* with a P.D. exceeding a few millivolts). If we apply these meager data to the experiments reported in this paper we may say that the effect of $ThCl_4$ or $LaCl_3$ or even of strong acids on dielectrics like collodion or

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[11] Odén, S., Der kolloide Schwefel, *Nova acta regiæ Soc. Sc. Upsaliensis, Series 4*, 1913, iii, No. 4.

mastic are similar to those observed on gas bubbles and that therefore the effects of these three groups of electrolytes on the cataphoretic P.D. of dielectrics may be partly or entirely due to forces inherent in the water itself. Correspondingly it is quite possible that the effect of $Na_4Fe(CN)_6$ which reverses the sign of charge of positive particles may turn out to be due to forces inherent in the water itself. But we cannot yet state with any certainty that the same is true for the effects of ions of lower valency on the cataphoretic P.D. of solid particles.

We can say, however, that where the effects of an electrolyte on the cataphoretic P.D. differ with the nature of the solid particles the forces or conditions inherent in the solid particles must be responsible. The effects of this type of forces and of the forces inherent in the water may be superposed upon each other.

That some particles assume a positive charge in water in the absence of electrolytes can only be due to the chemical nature of the particle, whereby cations (including the hydrogen ions of the water) are more strongly attracted by the particle than the anions. It is noteworthy that the positive colloids mentioned in this paper are all electrolytes. Negative colloids may be electrolytes or non-electrolytes, but since gas bubbles are generally negatively charged, the charge of negative colloids need not be entirely due to a preferential attraction of anions by the solid particle but may be due partly or entirely to the forces inherent in the water as discussed in the preceding papers.[2]

It must be ascribed to forces inherent in the particle that the point of reversal of the sign of charge in the case of proteins coincides with the isoelectric point of the particle.

The considerable variation in the maximal cataphoretic P.D. with the chemical nature of the particle in solutions of $Na_4Fe(CN)_6$ and NaOH (as shown in Tables I and II) must also be ascribed to the influence of the particles themselves.

SUMMARY.

1. The effect of eight salts, NaCl, Na_2SO_4, $Na_4Fe(CN)_6$, $CaCl_2$, $LaCl_3$, $ThCl_4$, and basic and acid fuchsin on the cataphoretic P.D. between solid particles and aqueous solutions was measured near the

point of neutrality of water (pH 5.8). It was found that without the addition of electrolyte the cataphoretic P.D. between particles and water is very minute near the point of neutrality (pH 5.8), often less than 10 millivolts, if care is taken that the solutions are free from impurities. Particles which in the absence of salts have a positive charge in water near the point of neutrality (pH 5.8) are termed positive colloids and particles which have a negative charge under these conditions are termed negative colloids.

2. If care is taken that the addition of the salt does not change the hydrogen ion concentration of the solution (which in these experiments was generally pH 5.8) it can be said in general, that as long as the concentration of salts is not too high, the anions of the salt have the tendency to make the particles more negative (or less positive) and that cations have the opposite effect; and that both effects increase with the increasing valency of the ions. As soon as a maximal P.D. is reached, which varies for each salt and for each type of particles, a further addition of salt depresses the P.D. again. Aside from this general tendency the effects of salts on the P.D. are typically different for positive and negative colloids.

3. Negative colloids (collodion, mastic, Acheson's graphite, gold, and metal proteinates) are rendered more negative by low concentrations of salts with monovalent cation (*e.g.* Na) the higher the valency of the anion, though the difference in the maximal P.D. is slight for the monovalent Cl and the tetravalent $Fe(CN)_6$ ions. Low concentrations of $CaCl_2$ also make negative colloids more negative but the maximal P.D. is less than for NaCl; even $LaCl_3$ increases the P.D. of negative particles slightly in low concentrations. $ThCl_4$ and basic fuchsin, however, seem to make the negative particles positive even in very low concentrations.

4. Positive colloids (ferric hydroxide, calcium oxalate, casein chloride—the latter at pH 4.0) are practically not affected by NaCl, are rendered slightly negative by high concentrations of Na_2SO_4, and are rendered more negative by $Na_4Fe(CN)_6$ and acid dyes. Low concentrations of $CaCl_2$ and $LaCl_3$ increase the positive charge of the particles until a maximum is reached after which the addition of more salt depresses the P.D. again.

5. It is shown that alkalies (NaOH) act on the cataphoretic P.D. of both negative and positive particles as $Na_4Fe(CN)_6$ does at the point of neutrality.

6. Low concentrations of HCl raise the cataphoretic P.D. of particles of collodion, mastic, graphite, and gold until a maximum is reached, after which the P.D. is depressed by a further increase in the concentration of the acid. No reversal in the sign of charge of the particle occurs in the case of collodion, while if a reversal occurs in the case of mastic, gold, and graphite, the P.D. is never more than a few millivolts. When HCl changes the chemical nature of the colloid, *e.g.* when HCl is added to particles of amphoteric electrolytes like sodium gelatinate, a marked reversal will occur, on account of the transformation of the metal proteinate into a protein-acid salt.

7. A real reversal in the sign of charge of positive particles occurs, however, at neutrality if $Na_4Fe(CN)_6$ or an acid dye is added; and in the case of negative colloids when low concentrations of basic dyes or minute traces of $ThCl_4$ are added.

8. Flocculation of the suspensions by salts occurs when the cataphoretic P.D. reaches a critical value which is about 14 millivolts for particles of graphite, gold, or mastic or denatured egg albumin; while for collodion particles it was about 16 millivolts. A critical P.D. of about 15 millivolts was also observed by Northrop and De Kruif for the flocculation of certain bacteria.