the alkali, yielding the following figures for its 0.1 N factor: (1) 1.0039, 1.0045; (2) 1.0031, 1.0030; (3) 1.0037, 1.0033; (4) 1.0039, 1.0037; (5) 1.0035, 1.0033; average, 1.0036.

The results of standardizing the alkali by these various methods may be exhibited most clearly in tabular form:

Method.	0.1 N alkali factor.
I. Benzoic acid	1.0040
II. Hydrochloric acid, factor from constant boiling pressure	1.0039
III. Hydrochloric acid, factor from AgCl determination	1.0037
IV. Arsenic acid	1.0036

Summary.

It has been pointed out that arsenious oxide is a desirable substance for use as a primary standard in volumetric analysis; and it has been shown that it may be employed, without too complicated manipulation, for this purpose in alkalimetry.

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COAGULATION OF ARSENIOUS SULFIDE SOL BY ELECTROLYTES.

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The coagulation of arsenious sulphide sol by electrolytes has been studied by a number of investigators,[1] who observed certain peculiarities which led the present writer to undertake a study of the coagulation phenomenon in detail.

The sols examined were prepared in the way given by Linder and Picton; the water used was obtained by the method described by Jones and Mackay.[2] Two sols were prepared, one containing 32.9 (No. I), the other (No. IV) a very fine one containing 3.54 millimols As_2S_3 per liter; Nos. II and III were made by diluting No. I four times and twenty times, respectively. Series of parallel experiments were made, in which equal depths of liquid contained in similar test tubes were observed and compared; very slight changes in the sol can be detected if comparison is made between the sample under observation and a blank with water added in place of the electrolyte solution.

Influence of the Quality of the Sol.—The changes observed on addition of an electrolyte are that after a certain time, depending on the concentration of the electrolyte, an increased turbidity is perceptible; this turbidity increases until the sol becomes almost, or even completely, opaque. The maximum opacity depends upon the quality of the original

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[1] Schulze, *J. prakt. Chem.*, 25, 431; Linder and Picton, *J. Chem. Soc.*, 61, 114, 172 (1892); 67, 63 (1895); Freundlich, *Z. physik. Chem.*, 44, 129 (1903); 73, 385 (1910); 83, 97 (1913); 86, 458 (1914).

[2] *Z. physik. Chem.*, 14, 317 (1894).

sol. There then appears a net-like formation throughout the sol which, if left undisturbed, becomes more and more coarse; this portion of the change can be followed with the microscope when the sol is dilute, but the later stages can be observed directly. A heterogeneous structure, attended by a diminution in opacity, is noticeable; the time when this maximum opacity is reached gives an idea of the progress of the process of coalition.

The next characteristic change observable is that this net-like structure begins to settle as a clot. This is accompanied by the appearance at the topmost layers of a visible net or membrane-like structure, separating a clear layer of liquid at the upper part from the turbid layers. The depth of this layer increases with time, and finally the whole settles to the bottom. The settling of the clot is irregular. It sometimes sticks to the side of the tube but on mere shaking, breaks up into flocks coarse enough to settle in a short time or even instantaneously. The time for its complete settling is not characteristic of the rate of coagulation; but that required for the appearance of perceptible change or for the attainment of the maximum opacity or for the beginning of the settling yields a definite idea of the rate of the change.

With concentrated sols the above changes are somewhat masked, especially the appearance of the maximum opacity. This is because such sols soon become opaque and further change cannot be followed; moreover there is then no perfect clearance but the upper layers remain slightly turbid. Such behavior is due to the fact that the process of coalition, even when far from complete, advances sufficiently to produce, with such sols, formations which have a visible rate of settling. The upper, paler layers look quite clear in transmitted light; the *process of coagulation of this remaining portion of the sol begins anew, and thus the coagulation goes on in stages until finally we have the complete separation of the colloid.* With fairly dilute sols the above phenomenon is not so marked; since in such cases formation of clots settling at a visible rate would require almost the completion of the process of coalition. However, with dilutions of electrolytes such that the rate of coalition is very slow the above phenomenon occurs even with dilute sols. Here the maximum of opacity is to be looked for at the lower parts of the tube. The settling or sedimentation plays an extremely small part in the coagulation of colloidal arsenious sulfide.

The series of Sols I, II and III show that the concentration of electrolyte required to produce any change in a given time increases with the dilution of the sol. For equal concentrations of electrolyte the time for complete separation of the colloid may vary from a few minutes to about a month, according to the dilution of the sol. Thus with $N/16$ NaCl, As_2S_3 begins to separate from Sol I in 10 minutes, from Sol II after more than a day, and from Sol III not unless full 10 days have elapsed.

How rapidly the time for visible change, or the beginning of the separation of the colloid, changes with concentration of electrolyte, will be clear from the following example: With Sol III a concentration of $N/10$ NaCl produces visible change in a few seconds but with $N/16$ NaCl the change is not noticeable after six hours, and with $N/22$ NaCl noticeable change takes place only after four days. The variation of the concentration of added electrolyte has a much more marked effect on the stability of the sol than the variation of the concentration of the sol. The influence of the fineness of the sol in determining its stability is apparent when comparison is made between Sol IV and Sol I or Sol II. Sol IV contains less As_2S_3 than Sol II, but is not more stable to electrolytes than Sol I. Another peculiarity that strikes one on comparing Sol I and Sol IV, is that, whereas at lower dilutions of the electrolyte both sols show nearly equal stability, at higher dilutions Sol I increases in stability at a remarkably greater rate than Sol IV. Freundlich[1] found, contrary to what has been recorded above, that with decreasing concentration of the sol the concentration of electrolyte required to coagulate it decreases in a regular way; he refers this difference in the concentration of the electrolyte to increased adsorption in the more concentrated sol, due to the increased surface. Woudstra,[2] Reissig[3] and others have, however, observed that the greater the concentration of the colloid the less the amount of the electrolytic required to coagulate it.

On the other hand it appears that the increase of stability with dilution of the sol is what should be expected. The facility for the coalition of the colloidal particles certainly decreases with increasing mutual distance between them resulting from dilution. With increasing fineness of a sol, the concentration of the colloid remaining the same, the distance between individual particles decreases and hence the facility for the coalition increases. The increased Brownian movement also facilitates encounters between the particles. The progress and the visibility of the change in the colloid certainly depend on the above factors. It may be here added that the rapidity with which sols become stable with increasing dilutions of electrolyte points to the fact that at a certain dilution of the electrolyte the sol is no longer affected.

The Method of Addition of the Electrolyte to the Sol.—The process of coagulation being irreversible with this sol, the addition of small quantities of an electrolyte of much higher concentration cannot fail to produce immediate changes, which the final concentration of electrolyte attained after the mixture is of itself not able to effect. This is more objectionable if the quantity of electrolyte is added in a small volume, as with increase

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[1] *Z. physik. Chem.*, 44, 129 (1903).

[2] *Ibid.*, 61, 607 (1908).

[3] *Ann. Physik*, [4] 27, 186 (1908).

in concentration of electrolyte its coagulative power increases very rapidly. Equal volumes of sol and electrolyte were taken and addition was effected in small quantities followed by a thorough mixing, the whole process not taking more than a minute.

It was decided to avoid this method of mixing altogether by actually producing the sol in the electrolyte solution as a medium in place of water. The behavior of sols prepared in this way was compared with that of sols produced in water and subsequently mixed with electrolyte solutions so as to yield the same total concentration of both colloid and electrolyte; differences were observed, but the results are not really comparable because the amount of free H_2S in the two series was not the same.

In order to determine the effect of free H_2S, a quantity of sol containing 6.53 millimoles As_2S_3 was prepared in the usual way, except that one portion of it was not freed from dissolved H_2S by a stream of hydrogen. The effect of addition of a series of concentrations of KCl to these two samples was then examined, and it was found that the two series of sols showed great differences in stability. The sol containing H_2S almost to saturation is remarkably more stable than that freed from H_2S. Thus there can remain no doubt as to the fact that dissolved H_2S increases the stability of As_2S_3 sol. The portion freed from H_2S by a stream of hydrogen was next saturated with H_2S and the original sol containing excess of H_2S freed from it by a stream of hydrogen. These on examination gave the same result, the sol now containing free H_2S being more stable of the two. The difference in stability is as marked as before.

That free arsenious oxide, either in solution or suspension, does not influence the stability of the sol to any noticeable extent was next proved in the following way: A sol of the same As_2S_3 content as Sol III was diluted in one case with equal volume of a freshly prepared As_2O_3 solution, and in another with equal volume of water. The behavior of these two samples did not show any noticeable difference when examined with a series of concentrations of KCl.

This peculiar influence of H_2S is very noteworthy in view of the opinion held by some authors that the presence of electrolyte in many colloids is a necessity. Acids like HCl have a great coagulative power, whereas H_2S has a stabilizing power. To this stabilizing influence of H_2S observed here, is to be attributed the success of previous investigators in preparing metallic sulfide sols of great concentration. Wessinger and Spring[1] prepared sols of metallic sulfides by washing sulfide precipitates with H_2S water. Later Linder and Picton[2] used this method in preparing sols of metal sulfides of great concentration.

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[1] *Bull. soc. chim.*, **49**, 452; **48**, 166.

[2] *Trans. Chem. Soc.*, **1892**, 138.

Relative Coagulative Powers of Different Electrolytes.—A comparison of the coagulative power of different electrolytes was next made. With concentrated sols very low concentrations of polyvalent metallic ions have to be used; to avoid this, the dilute Sol III was used. *It has been observed that the order of the relative coagulative powers of different electrolytes is independent of the quality of the sol.* To define the coagulative power of any given electrolyte, we have first to investigate the factors that determine it. It has been shown that it depends on the concentration, the fineness, and the H_2S content of the sol. Thus the coagulative power of any given electrolyte has not a definite value and varies with the above factors. We can speak of coagulative power with respect to a specific sol. For the same electrolyte the coagulative power is determined by the dilution of the electrolyte which would produce a certain change in the colloid. The general method is to find out the concentration of electrolyte that would instantaneously lead to complete separation of the colloid. But there are also other methods in vogue. The value for the coagulation dilution would thus vary according to the nature and magnitude of the change in the sol in terms of which the coagulative power of any electrolyte is measured, and also on the method used. As a result, comparison between the coagulative power of any electrolyte by different methods is not possible. The present worker has observed that the order of the relative coagulative powers of different electrolytes is independent of the quality of the sol used. But the different methods do not even give the same order of the coagulative power, as will be made clear from a comparison of the data obtainable on As_2S_3 sol.

TABLE I.—ORDER OF THE COAGULATIVE POWER OF VARIOUS ELECTROLYTES AS DETERMINED BY DIFFERENT METHODS.

	Linder and Picton.[1]	Freundlich.[1]	As observed in the course of this investigation.
Trivalent	$Al_2(SO_4)_3$	$AlCl_3$	$Al_2(SO_4)_3$
	$AlCl_3$		
			$Ba(ClO_3)_2$
Divalent	$BaCl_2$	$SrCl_2$	$BaCl_2$
	$SrCl_2$	$BaCl_2$	$SrCl_2$
	$MgSO_4$	$MgSO_4$	$MgSO_4$
Monovalent	HCl	HCl	HCl
	NH_4Cl	NH_4Cl	NH_4Cl
	KCl	KI	KCl
	KBr	KCl	KNO_3
	KI	KNO_3	KBr
	$NaCl$	$NaCl$	$NaCl$
	KNO_3	$LiCl$	KI
	$NaNO_3$		$NaNO_3$
			$LiCl$

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[1] *Loc. cit.*

The difference comes out quite markedly if comparison is made of the actual figures for relative coagulative powers of the electrolytes. Very little doubt can exist as to the accuracy of the data given in the third column. Whetham's Law[1] is not in agreement with the measurements made by Freundlich or by the present author, though Linder's and Picton's data seems to support it fairly.

In the opinion of the author this discrepancy is due to certain defects inherent in the methods used. The method of titration of the sol with electrolyte used by Linder and Picton[2] and others has been repeated, and it has been observed that if use be made of different concentrations of the same electrolyte for titration of the same preparation of sol, the quantities of electrolyte required are not in inverse ratio of the concentration of the electrolyte—in other words, different final concentrations are required to produce the same effect. With such methods the comparison of coagulative powers is liable to be inaccurate. Moreover the end point of coagulation is not easy to follow and varies with the rate of shaking and the time allowed for titration. Evidence in support of these statements is afforded by Table II, in which a series of results obtained with Sol III are brought together.

Electric conductivity of mixtures of sols and electrolytes was measured. It was hoped that if adsorption of the electrolyte occurred to any extent it would be evident from the diminution of the conductivity. The results, however, prove that if adsorption takes place at all, it is very slight. As controls throughout this part of the work two series of solutions were examined. In one series a definite volume of As_2S_3 sol was mixed with a definite volume of an electrolyte of a certain concentration. In the other the same volume of conductivity water as that of As_2S_3 sol taken was mixed with the same volume of the electrolyte of the same concentration taken in the other series. The two samples were kept side by side in an asbestos box and the temperature during the measurement of conductivity was noted. Whenever difference in temperature between the two samples of more than 0.1° was observed, the data were rejected. In some cases the results were controlled for either samples by a second or even a third repetition. The values for the conductivity were found to be always constant in all such cases. The observed conductivity of the sol and electrolyte is always greater than that of the electrolyte itself. If, however, the conductivity of an equal volume of the sol diluted with the same volume of water as that of the electrolyte used, be added to the conductivity of the electrolyte we get the same value for the conductivity as that observed. This shows that the conductivity of the electrolyte changes little if at all. From an examination of various dilutions of the following

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[1] *Phil. Mag.*, 48, 474 (1899).

[2] *Loc. cit.*

TABLE II.—OBSERVATIONS ON THE EFFECT OF ADDITION OF VARIOUS SALT SOLUTIONS ON THE BEHAVIOR OF SOL III.

Dilution of added salt.	Time required for perceptible change.	Approx. time for maximum opacity.	Dilution of added salt.	Time required for perceptible change.	Approx. time for maximum opacity.
	$Al_2(SO_4)_3$			HCl	
20000	9 min.	17 hrs.	20	A few secs.	$>$15 min.
10000	$<$1 min.	31 min.	18	Inst.	9 min.
9000	A few secs.	20 min.	16	Inst.	3 min.
8000	Instantaneous	10 min.	15	Inst.	1 min.
7000	Instantaneous	4 min.	14	Inst.	Inst.
2000	Instantaneous	Inst.		KNO_3	
	$Ba(ClO_3)_2$		14	25 min.	34 hrs.
700	10 min.	....	13	8 min.	22 hrs.
600	A few secs.	4 min.	12	3 min.	13 hrs.
500	Inst.	2 min.	10	A few secs.	24 min.
400	Inst.	Inst.	9	Inst.	2 min.
	$BaCl_2$		8	Inst.	Inst.
700	15 min.	....		KBr	
600	A few secs.	8 min.	14	20 min.	30 hrs.
500	Inst.	4 min.	13	8 min.	18 hrs.
400	Inst.	1 min.	12	4 min.	10 hrs.
360	Inst.	Inst.	11	A few secs.	5 hrs.
			10	Inst.	32 min.
	$SrCl_2$			KI	
700	7 min.	55 min.	13	20 min.	26 hrs.
600	3 min.	24 min.	12	9 min.	...
500	A few secs.	13 min.	11	5 min.	10 hrs.
400	Inst.	6 min.	10	2 min.	5.5 hrs.
300	Inst.	2 min.	9	Inst.	7 min.
	$MgSO_4$			$NaNO_3$	
600	5 min.	38 min.	12	21 min.	25 hrs.
500	1 min.	20 min.	10	8 min.	10 hrs.
400	A few secs.	11 min.	9	3 min.	1.2 hrs.
200	Inst.	Inst.	8	A few secs.	8 min.
			7	Inst.	3 min.
			6	Inst.	1 min.
				LiCl	
			10	7 min.	15 hrs.
			9	5 min.	12 hrs.
			8	3 min.	6 hrs.
			7	A few secs.	$<$3 hrs.
			6	Inst.	1 min.

electrolytes—KCl, HCl, $BaCl_2$, $SrCl_2$ and $Al_2(SO_4)_3$ it was observed that the conductivity agrees with the sum of conductivities whether complete or partial separation of the colloid has taken place or not. This is also true for great dilutions of the electrolyte. Deviations from the additive rule were within the limits of experimental error. This shows that the conductivity of the sol is to be attributed not to the particles of the colloid, but to dissolved H_2S or As_2O_3 or anything else. The conductivity of the colloidal granules thus seems to be very small. Different sols were examined, but the nature of the results obtained was the same. From Dumansky's data[1] on conductivity measurements of colloidal $Fe(OH)_3$ in presence of electrolytes, Wo. Ostwald[2] calculated the amount of adsorption by the colloid of those electrolytes which have a coagulating action on it. But, as we have seen, absolutely no change in conductivity is observed with As_2S_3 sols.

From data given by Linder and Picton it would appear that adsorption of barium takes place to a marked degree with liberation of an equivalent quantity of HCl. This adsorption with consequent liberation of HCl has been confirmed by Whitney[3] and Duclaux.[4] The author has also been able to confirm this, but it has been found that on washing carefully the precipitated As_2S_3, the amount of barium in it is very small and scarcely capable of quantitative measurement. However, from a large quantity of precipitated As_2S_3 an amount of barium was obtained which gave a slight turbidity with H_2SO_4, but was too small for quantitative estimation. This quantity might as well have been adsorbed by the coagulated sol or due to chemical interaction with As_2S_3 as Duclaux supposes.

Summary and Conclusion.

(1) With dilution of sols of As_2S_3 the stability increases.

(2) Fine sols are less stable than coarse sols of the same arsenious sulfide content.

(3) Coagulation of colloidal arsenious sulfide with electrolytes is mainly a process of coalition of the colloidal particles. Coalition takes place all through the substance of the sol with formations of definite clot-like structures. Sedimentation plays an extremely minor part in coagulation. The rate of coalition is determined by the concentration and nature of the electrolyte. With concentrated sols and relatively dilute electrolytes the coagulation goes on in stages till the complete separation of the colloid takes place.

(4) Dissolved hydrogen sulfide has the interesting effect of markedly stabilizing arsenious sulfide sols against electrolytes.

(5) Adsorption of electrolytes by the colloid does not take place to any marked extent as is proved from conductivity measurements and analysis.

(6) The order of the relative coagulative powers of various electrolytes is different as determined by different methods.

My best thanks are due to Profs. Rây and Bhaduri.

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[1] *Z. Chem. Ind. Koll.*, 1, 281 (1906).

[2] *Gedenkboek Bemmelen*, **1910**, 267.

[3] THIS JOURNAL, **23**, 842 (1901).

[4] *J. chim. phys.*, **6**, 592 (1908).