per liter at 25°. On combining this with Harned's E° value for silver chloride and our E° for silver azide at 25°, the solubility of silver azide is found to be 5.1×10^{-5} mole per liter at 25°.

Summary

The preparation of a stable reproducible form of the silver–silver azide electrode is described.

The standard potential of the silver–silver azide electrode has been determined at 10° intervals from 5 to 45°.

The solubility of silver azide has been estimated to be 5.1×10^{-5} mole per liter at 25°.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF THE UNIVERSITY OF IDAHO]

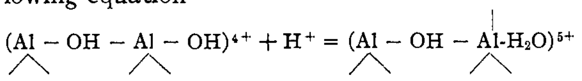
Zirconate Sol Formation—its Dependence upon the Displacing Power of Anions[1]

BY HARRY S. OWENS AND JOHN L. TORGESEN[2]

Thomas and his co-workers[3] have developed a theory of the formation of oxide micelles based on Werner's theory. The growth of the micelles and many other physical and chemical properties can be explained on the basis of a polynuclear complex formed as a result of hydrolysis followed by olation and oxolation.

To elucidate the reactions taking place during peptization, we may assume that the hydrated oxide used as a starting material is a polynuclear complex in which we have ol and oxo groups joining metallic atoms. Thomas and Vartanian[4] have studied the peptization of hydrated aluminum oxide from this point of view. They found that the peptizing ability of various acids was the reverse of the displacing power of the anions involved in the acids. Thus citric acid proved to be a poor peptizer while hydrochloric was a good peptizer.

The micelles produced in their series of peptizations possessed a positive charge, indicating that the reaction controlling the sign of the charge was a reversal of simple hydrolysis and olation by hydrogen ion. The reaction is illustrated in the following equation



$$(\mathrm{Al} - \mathrm{OH} - \mathrm{Al} - \mathrm{OH})^{4+} + \mathrm{H}^+ = (\mathrm{Al} - \mathrm{OH} - \mathrm{Al}\text{-}\mathrm{H_2O})^{5+}$$

The conversion of a hydroxo or *ol* group to an aquo group raises the positive charge on the complex by one unit.

To increase the negative charge on an oxide micelle requires that the anion displace aquo groups. An example of what happens in this event is illustrated with zirconium chloride and potassium tartrate.

$$\mathrm{Zr(H_2O)_8Cl_4} + 3\mathrm{K_2C_4H_4O_4} = \mathrm{K_2[Zr(C_4H_4O_4)_3]} + 4\mathrm{KCl} + 8\mathrm{H_2O}$$

Although this ideal is not in accord with facts, basic tartaro zirconates are formed both in the crystalloidal[5] and the colloidal[6] state. Anions most effective in causing this displacement of aquo groups should be most effective peptizers of hydrated zirconium oxide to produce negative micelles.

Materials and Procedure.—Zirconyl chloride crystallized several times from concentrated hydrochloric acid was precipitated with pure ammonium hydroxide, and washed by centrifugal decantations to the absence of chloride ion. The hydrated oxide was air-dried for various lengths of time and pulverized to pass a 60-mesh sieve. Weighed amounts were then introduced into 500-ml. Pyrex flasks connected through a ground glass joint to a Pyrex reflux condenser. Other samples were taken for analysis of the zirconium content. Peptizations were carried out at the boiling point or about 95°.

The above procedure could not be used for the six-hour sample and in that series the zirconium was weighed as zirconyl chloride, precipitated, dried and equal portions placed in the flasks.

The peptization time was twenty-four hours in every case since time–peptization determinations had shown that the amount peptized after seventeen hours was very nearly constant. Other information pertinent to the procedure is given in Table I.

The method of analysis used for the determination of the zirconium oxide content of the sols was essentially the same as that used by Thomas and Vartanian[4] for total aluminum oxide.

The determination of liminal values was carried out in a manner similar to that used by Thomas and Miller[3]

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[1] Presented before the Colloid Division, Rochester meeting of the American Chemical Society, Sept. 6–10, 1937.

[2] Now at Columbia University.

[3] Thomas and Miller, THIS JOURNAL, **58**, 2526 (1936). This article has references to earlier work.

[4] Thomas and Vartanian, *ibid.*, **57**, 4 (1935).

[5] (a) De Boer, *Z. anorg. allgem. Chem.*, **165**, 1 (1927); (b) de Boer and Emmens, *Rec. trav. chim.*, **49**, 955 (1930); (c) Kremann, Lorber and Maas, *Monatsh.*, **35**, 581 (1914); (d) Rosenheim and Frank, *Ber.*, **40**, 803 (1907); (e) Rimbach and Schneider, *Z. physik. Chem.*, **44**, 482 (1903).

[6] Thomas and Owens, THIS JOURNAL, **57**, 2131 (1935).

except that the mixed sol and electrolyte were allowed to stand for eighteen hours to allow the precipitate to settle.

TABLE I

DATA ON PEPTIZATION METHOD

Sol series	A	B	C
G. of ZrO_2	2.5	3.0	5.25
Ml. of acid	500	500	500
N of acid	0.05	0.05	0.033
Sols centrifuged, min.	60	30	30
Speed of centrifuge, r. p. m.	1200	1600	1600

Results

It is possible to measure the displacement order of anions for aquo groups indirectly by determining the liminal values of salts of the corresponding anions.[3] This follows since the penetration of anions causes a gradual decrease in the charge on the positive oxide micelles until it is zero or nearly so and the sol precipitates. Table II shows a typical series of liminal values obtained with a basic zirconium chloride sol.

TABLE II

LIMINAL VALUE DETERMINATIONS

Potassium salt	Liminal value m. e./liter
Tartrate	5.8
Citrate	6.6
Succinate	6.7
Malate	6.8
Oxalate	7.0
Glycolate	7.0
Lactate	9.5

The relative ability of acids corresponding to the salts in Table II to peptize hydrated zirconium oxide is shown in Table III. Series A, B and C differ from each other by the length of time the oxide was dried being six, thirty and forty-four hours, respectively. Of the acids given, succinic and glycolic seem to be out of order. The reason for the anomaly with succinic acid follows from Mandl's[7] work in which he found that no soluble complex could be formed between zirconium and salts of succinic acid. This is further borne out by electrophoresis experiments which show that the micelles formed with succinic acid are positive while all others are negative. No satisfactory reason for the poor peptizing ability of glycolic acid has yet been found.

TABLE III

RESULTS OF PEPTIZATIONS

Acid	ZrO_2 peptized, mg. per cent. Series A	Series B	Series C
Tartaric	288	148	30
Citric	241	94	16
Malic	...	75	14
Oxalic	207	71	10
Glycolic	...	5	5
Lactic	...	6	4
Succinic	18	...	..

Table III shows further that the longer zirconium oxide is dried the more resistant it is to the action of acids. As a matter of fact the ignited oxide could not be peptized in oxalic acid of the concentration used in these experiments. This change in reactivity can be explained on the basis of more complete oxolation and further agglomeration of the oxide.

There was a striking difference between hydroxy substituted acids and unsubstituted acids in the way the hydrogen ion activity changed during the peptization. Table IV illustrates this difference.

TABLE IV

VARIATIONS IN *p*H VALUES

Acid	Initial	Final
	Series A	
Tartaric	2.4	2.1
Oxalic	1.8	4.2
	Series B	
Tartaric	2.4	2.4
Oxalic	1.8	4.1
	Series C	
Tartaric	2.6	3.2
Oxalic	1.9	4.1

Thus it is seen that the tartaric acid resisted any change in hydrogen ion activity, in fact, the greater the amount of oxide peptized the more acid the medium became. Other hydroxy acids acted in the same way, while other unsubstituted acids acted like oxalic acid. This difference can be explained on the basis of chelation, which would allow a hydrogen ion to split off from the alpha hydroxy group.

Summary

First, the aquo displacing order is so much like the peptizing order in zirconate sol formation to make it more than coincidental and indicates that the Thomas theory of colloidal oxides can be used to predict negative sol formation nearly as well as positive sol formation. Second, aging the oxide makes it more refractory. Third, the alpha hydroxy anions seem to chelate yielding hydrogen ions in the colloidal solution.

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(7) Mandl, *Z. anorg. Chem.*, **37**, 252 (1903).