Fig. 5.—0.1000 molar $(NH_4)_2H_2P_2O_5$–0.1000 molar HCl.

4.3. This fact, moreover, reveals that the third hydrogen for the poly-basic pyrophosphorus acid must be definitely acidic. Furthermore, after the hydration had proceeded for one hundred eighty-seven hours and had reached 92.28% completion the pH value had decreased to 3.77. The solution became more acidic, which may be interpreted to mean that the second hydrogen of orthophosphorous acid is still more acidic than the third hydrogen of the pyrophosphorous acid. These facts are shown graphically in Fig. 3. The final pH value, disclosed by extrapolation,

for the 0.2 M $NH_4H_2PO_3$ formed seems to lie somewhere near 3.7 at 30°.

The characteristics manifested in the hydration of pyrophosphite are similar to those shown in the case of pyrophosphate at pH values below 6.5 only. The pyrophosphate is stable in an alkaline solution. No hydration occurs.[5] Hydration of pyrophosphite does occur in alkaline solution. The rate increases as the pH increases. This is the characteristic difference in behavior of the respective compounds of phosphorus concerning hydration.

Summary

1. A method for the determination of orthophosphites in the presence of pyrophosphites has been developed.

2. Data are presented on the hydration of $(NH_4)_2H_2P_2O_5$ in the following solutions

Solution I,	0.1000 M NaOH	0.1000 M $(NH_4)_2H_2P_2O_5$
Solution II,	.01000 M NaOH	.1000 M $(NH_4)_2H_2P_2O_5$
Solution III,	Distilled water	.1000 M $(NH_4)_2H_2P_2O_5$
Solution IV,	.1000 M $HC_2H_3O_2$	.1000 M $(NH_4)_2H_2P_2O_5$
Solution V,	.1000 M $KHSO_4$	.1000 M $(NH_4)_2H_2P_2O_5$
Solution VI,	.1000 M HCl	.1000 M $(NH_4)_2H_2P_2O_5$

(5) Kiehl and Coats, THIS JOURNAL, **49**, 2180 (1927).

[CONTRIBUTION FROM THE LABORATORY OF PHYSIOLOGY, YALE UNIVERSITY SCHOOL OF MEDICINE]

The Standard Potential of the Silver–Silver Azide Electrode

BY ALICE C. TAYLOR AND LESLIE F. NIMS

The standard potentials of a stable reproducible silver–silver azide electrode, prepared electrolytically, have been obtained from electromotive force measurements of the cell

Ag–AgCl/NaCl(m)/KCl(satd.)/NaN₃(m)/AgN₃–Ag(+)

over the temperature range from 5 to 45°. The electromotive force of such a cell is represented by an equation of the form

$$E = E^0_{AgN_3} - E^0_{AgCl} - \frac{RT}{F} \log \frac{m_{N_3^-} \, \gamma_{N_3^-}}{m_{Cl^-} \, \gamma_{Cl^-}} + E_D \quad (1)$$

At infinite dilution the sum of the diffusion potentials, E_D, would be very small and can be neglected. Consequently, for equal concentrations of azide and chloride, the potential at infinite

dilution is related to the standard potentials of the electrodes in the following manner

$$E^0_{AgN_3} = E_{(inf.\ dil.)} + E^0_{AgCl} \quad (2)$$

Experimental Details

Sodium azide (Eimer and Amend) was twice recrystallized from an aqueous solution saturated at 90° by cooling it to 10° and adding an equal volume of alcohol. A colored impurity was then removed by treatment with charcoal (Norite A) and a third crystallization was effected, this time with an equal volume of acetone. The resulting crystals were well washed with acetone and the product was dried at room temperature. Weighed samples dried at 110° were taken for analysis. These were converted to sodium sulfate and the results indicated that a satisfactory degree of purity of the sodium azide had been obtained. Sodium chloride was twice recrystallized from

water. The potassium chloride used for the salt bridges was Eimer and Amend C. P. salt.

Silver–silver azide electrodes were made as follows: carefully purified silver oxide supported on platinum spirals was decomposed to pure silver at 400°. The silver was then made the anode in an electrolytic cell containing a 0.1 molal sodium azide solution and a current of 5 milliamperes per electrode was passed through the cell for thirty minutes. The electrodes were then soaked in three changes of the solution in which they were to be measured.

The silver–silver chloride electrodes were similar to those designated as Type 2 by Harned.[1]

Stock solutions of the salts used were made up in triplicate. Each solution was analyzed for sodium by conversion to the sulfate and for chloride or azide constituent by electrometric titration with silver nitrate. These stock solutions were diluted in calibrated glassware using the same flask and pipets for corresponding solutions.

Electrode vessels were constructed from test-tubes. A test-tube was fitted with a three-hole rubber stopper carrying duplicate azide or chloride electrodes and a long inverted U-tube which made contact with the bridge solution. The U-tube was tightly stoppered with cotton at the end near the electrodes to prevent disturbance of the boundary at the other end when the cells were placed in position in the thermostat. Another test-tube held a potassium chloride solution plus sufficient solid potassium chloride to keep the bridge solution saturated at all temperatures. The completed cell was formed by dipping the two U-tubes of the electrode vessels into the bridge solution contained in the third test-tube.

The cells were placed in a water thermostat which could be adjusted quickly and easily to any desired temperature. The electromotive force of the cells was determined with a Leeds and Northrup Type K potentiometer and Type R galvanometer. Because of the high resistance of the long columns of solution in the U-tubes, the potentiometric sensitivity was increased by the use of a microvoltmeter.[2] Comparison measurements showed that the introduction of this amplifier into the circuit did not alter the potentiometric readings.

Once equilibrated, the potentials of the cells remained constant for periods as long as three days. The e. m. f. of triplicate cells was obtained at several temperatures. When the cells were brought back to the initial temperature, regardless of the direction of the change, the readings checked the original values within ±0.1 mv. and agreed among themselves to within ±0.2 mv. These facts indicate that the free diffusion type of liquid junction employed was stable and reproducible.

Results

Electrolytic silver–silver azide electrodes prepared in the manner described are as stable and as reproducible as the thoroughly investigated silver–silver chloride electrodes (average deviation ±0.02 mv.).

The observed e. m. f. values of the cell at vari-

(1) Harned, THIS JOURNAL, **51**, 416 (1929).

(2) Burr, Lane and Nims, *Yale J. Biol. Med.*, **9**, 65 (1936).

ous temperatures are listed in Table I. Since there is no apparent trend of the potentials with the concentration, an average of the potentials was taken for each temperature as the potential of the cell at infinite dilution. From these values and the values of E^0 for the silver–silver chloride electrode determined by Harned and Ehlers,[3] the E^0 values given in Table II for the silver–silver azide electrode were calculated by equation (2).

TABLE I

E. M. F. OF THE CELL

Ag–AgCl/NaCl(m)/KCl(satd.)/NaN$_3$(m)/AgN$_3$–Ag($+$)

m	5°	15°	25°	35°	45°
0.1	0.0620	0.0656	0.0694	0.0733	0.0772
.07	....	.0656	.0695	.0733	.0772
.05	.0620	.0657	.0696	.0733	.0772
.03	.0622	.0658	.0696	.0733	.0772
.02	.0620	.0656	.0694	.0733	.0771
.01	.0621	.0658	.0696	.0734	.0773
Averages	.0620	.0657	.0695	.0733	.0772

TABLE II

E^0 OF THE ELECTRODE N$_3$⁻/AgN$_3$–Ag

t, °C.	E^0_{AgCl}	E. m. f.	$E^0_{AgN_3}$
5	0.2339	0.0620	0.2959
15	.2285	.0657	.2942
25	.2224	.0695	.2919
35	.2156	.0733	.2889
45	.2082	.0772	.2854

From these data it is possible to calculate, by means of equation (3), the variation of the standard potential of the silver–silver azide electrode with temperature.

$$E^0_{calcd.} = E^0_{25} - 0.000262(t - 25) - 0.00000313 (t - 25)^2 \quad (3)$$

From this equation and the appropriate thermodynamic formulas ΔF^0, ΔH^0 and ΔS^0 for the reaction
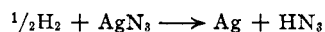
$$^{1}/_{2}H_2 + AgN_3 \longrightarrow Ag + HN_3$$

were calculated and the values appear in Table III.

TABLE III

SOME THERMODYNAMIC PROPERTIES OF THE REACTION

$$^{1}/_{2}H_2 + AgN_3 = Ag + HN_3$$

t. °C.	$E^0_{obsd.}$	$E^0_{calcd.}$	ΔF^0	ΔS^0	ΔH^0
5	0.2959	0.2959	−6828	−3.2	−7700
15	.2942	.2942	−6788	−4.6	−8100
25	.2919	.2919	−6735	−6.0	−8500
35	.2889	.2890	−6668	−7.5	−9000
45	.2854	.2854	−6585	−8.9	−9400

Brown and MacInnes[4] have found that the solubility of silver chloride is 1.314×10^{-5} mole

(3) Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933).

(4) Brown and MacInnes, *ibid.*, **57**, 459 (1935).

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°.

[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

$$(Al - OH - Al - OH)^{4+} + H^+ = (Al - OH - Al\cdot H_2O)^{5+}$$
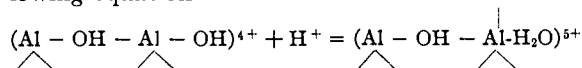
The conversion of a hydroxo or *ol* group to an aquo group raises the positive charge on the complex by one unit.

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.

$$Zr(H_2O)_8Cl_4 + 3K_2C_4H_4O_4 =$$
$$K_2[Zr(C_4H_4O_4)_3] + 4KCl + 8H_2O$$
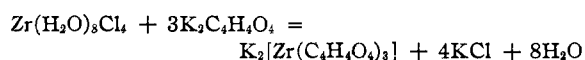
Although this ideal is not in accord with facts, basic tartaro zirconates are formed both in the crystalloidal[5] and the colloidal[6] state. Anions most effective in causing this displacement of aquo groups should be most effective peptizers of hydrated zirconium oxide to produce negative micelles.

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]

(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).