With an excess of phosphorus trichloride over the stoicheiometry of the above equation, two phases are observed—one phase consisting of phosphorus trichloride, the other, of HCl dissolved in pyrophosphorous acid. Orthophosphorous, pyrophosphorous, and hydrochloric acids appear to be miscible, so that only one phase is found when five or more moles of $(HO)_2HPO$ are used per mole of PCl_3. To the precision of 1 per cent of the total phosphorus by N.M.R., phosphorus trichloride and ortho-phosphorous acid react completely, when these substances are combined. No study has been made of the possibility of detecting an equilibrium when a small amount of pyrophosphorous acid is dissolved in a large excess of anhydrous hydrochloric acid under pressure.

AUGER's experiments were repeated at 35° and 100°C using both phosphorus tribromide and phosphorus trichloride. When the stoicheiometry of equation (1) was followed, pyrophosphorous acid was formed in at least 99 per cent purity. Pyrophosphorous acid containing only traces of HCl can also be obtained by opening the sealed tube corresponding to the stoicheiometry of equation (1) at acetone–dry ice temperatures and allowing the HCl to escape upon warming to room temperature. We have found the melting point of pyrophosphorous acid to be 36°C.

Due to indirect spin–spin splitting the of phosphorus by hydrogen, two sharp resonance peaks of equal intensity are seen in the N.M.R. spectrum at -21 p.p.m. and $+28$ p.p.m. of the magnetic field (as referenced to 85 per cent orthophosphoric acid at 25°C). This demonstrates that the pyrophosphorous acid is a symmetrical molecule; and the fact that the observed resonances exhibit the same chemical shifts as do the resonance peaks for sodium pyrophosphite made by careful dehydration of monosodium orthophosphite proves the structure. The P-H indirect spin–spin splitting equals 0·40 Gauss, which is the same as the splitting observed in the N.M.R. pattern of orthophosphorous acid. Moreover, the N.M.R. chemical shift from the ortho- to the pyrophosphorous acids is 11 p.p.m.—a value which is about equal to the chemical shift when going from ortho- to pyro-phosphoric acids.

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Physico-chemical studies on mercurous molybdate

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THE precipitation of metal molybdates is affected by a number of factors, e.g. concentration of MoO_3, age, formation of polymers and hydrolysis. Therefore simple gravimetric and titrimetric methods fail to indicate the correct composition of the precipitated salt. Hence the present investigation was initiated.

Experimental

Solutions of A.R. Na_2MoO_4 and $Hg_2(NO_3)_2$ were prepared in conductivity water. The former were standardized as the quinoline complex(1) $MoO_2(C_9H_6ON)_2$; $Hg_2(NO_3)_2$ was standardized against NaCl potentiometrically. Conductivities were measured with a Kohlrausch Universal Bridge, using a headphone, and were corrected for the dilution effect.(2) Titrations were performed in both forward and reverse directions in aqueous and aqueous alcoholic media. Potentiometric titrations were performed with a bright platinum foil electrode in conjunction with a S.C.E. and Cambridge pH-meter. For amperometric titrations a 'Manual Polarograph' was used; measurements were made using a moving coil galvanometer and a dropping mercury electrode as cathode. Current values obtained after each successive addition of the titrant to the electrolysis cell were corrected for the dilution effect.(3) To suppress maxima in the C-V curves, 0·1 per cent gelatine was used, and to eliminate the migration component of the limiting current 1 M KNO_3 was used as the supporting electrolyte.

As the nature of the molybdate ion is a function of H^+ concentration, precipitation of molybdate is mainly governed by the pH of the solution, and it is interesting to study the conditions necessary

(1) R. NIERICKER and W. D. TREADWELL, *Helv. Chim. Acta* **29**, 470 (1946).
(2) G. CHARLOT and D. BEZIER, *Quantitative Inorganic Analysis* p. 293. John Wiley, New York (1957).
(3) I. M. KOLTHOFF and J. J. LINGANE, *Polarography* (2nd Ed.) p. 890. Interscience, New York (1952).

for precipitation of mercurous molybdate. Dilute solutions of mercurous nitrate free from mercuric ion are prepared in water only, as the presence of free nitric acid leads to the formation of polymolybdate ion. Following KUAN PAN *et al.*(4), and BEVAN(5) we have also, studied the titration curves for mineral acid and Na_2MoO_4 and have found that at pH 4–6 trimolybdate ion predominates over other species. We have obtained normal mercurous molybdate $Hg_2O{\cdot}MoO_3$ in this pH-range; as this is a highly insoluble compound, a small concentration of molybdate ion is sufficient to precipitate the normal salt. Our observations are in accord with the views of REMY(6) that usually normal molybdates are precipitated when polymolybdates might be expected.

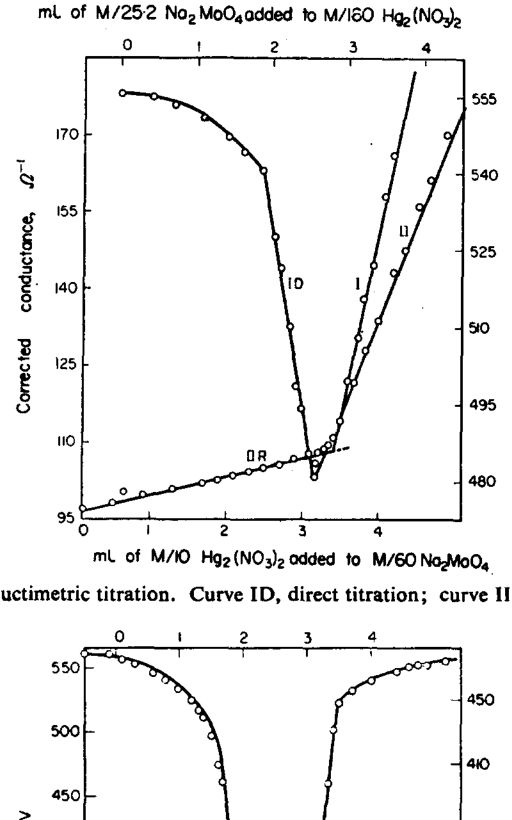

FIG. 1.—Conductimetric titration. Curve ID, direct titration; curve IIR, reverse titration.

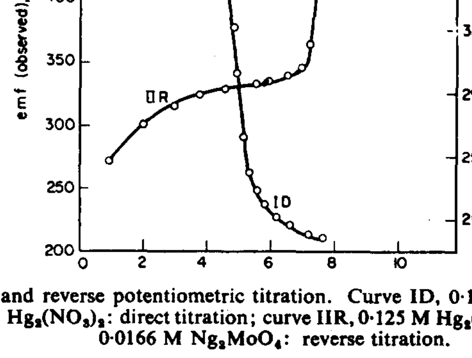

FIG. 2.—Direct and reverse potentiometric titration. Curve ID, 0·1M Na_2MoO_4 added to 20 cc of 0·025 M $Hg_2(NO_3)_2$: direct titration; curve IIR, 0·125 M $Hg_2(NO_3)_2$ added to 20 cc of 0·0166 M Ng_2MoO_4: reverse titration.

(4) KUAN PAN and T. M. HSEU, *Chem. Soc. Japan* **26**, 126 (1953).

(5) BEVAN, *Ann. Rep. Chem. Soc.* **53**, 53 (1943).

(6) H. REMY, *Treatise on Inorganic Chemistry* p. 168. Elsevier, London (1956).

Fig. 1 (curves I and II) shows that the reaction between $Hg_2(NO_3)_2$ and Na_2MoO_4 may be followed conductimetrically. Both direct (I) and reverse conductivity curves (II) consist of two rectilinear branches with a sharp intersection at a point corresponding to the formation of mercurous molybdate Hg_2MoO_4, according to the following reaction

$$Hg_2(NO_3)_2 + Na_2MoO_4 \rightarrow Hg_2O{\cdot}MoO_3 + 2NaNO_3$$

The angle between the branches of the titration curves is very sharp. The changes in conductance can be explained on the basis of ionic mobilities. In alcohol, the results are improved slightly.

From Fig. 2 it may be seen that the reaction may also be successfully investigated with either of the reactants as the titrant. The equivalence point obtained from the maximum value of dE/dV and from the point of inflection in the curve occurs at a point corresponding to the formation of $Hg_2O{\cdot}MoO_3$.

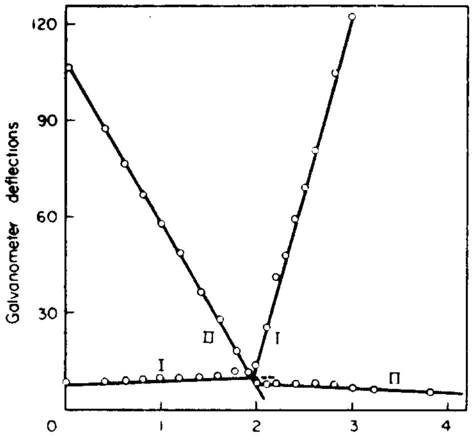

Fig. 3.—Amperometric titration. Curve I, ml of 0·05 M $Hg_2(NO_3)_2$ added to 5 ml Na_2MoO_4: reverse titration; curve II, ml of 0·05 M Na_2MoO_4 added to 10 ml $Hg_2(NO_3)_2$.

In direct titration (curve I), a precipitate initially separates but at the end-point, a sol appears to be formed. In reverse titration (curve II), the e.m.f. is slow to reach a steady value; the precipitate finally settles at the end-point, suggesting that the equivalence point has been reached. Alcohol and electrolytes such as KNO_3 and NH_4NO_3 have no effect on the end-point, nor on the nature of the curves.

Fig. 3 shows that the reaction can also be studied by amperometric titration, since one of the reacting substances shows a "polarographic diffusion current". At zero applied potential only the Hg_2^{++} ion, gives well-defined polarographic waves. In direct titration (curve II) the diffusion current decreases and reaches a minimum at the equivalence point, whereas in the reverse titration (curve I) no diffusion current is observed in the beginning; as the equivalence point is approached, the diffusion current increases linearly from almost zero. The results obtained by conductimetric, potentiometric and amperometric titrations are in concordance.

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A laboratory scale preparation of N_2F_4(1)

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Dinitrogentetrafluoride has been reported as a product of a reaction between NF_3 and certain solid metals.(2) When copper is used, temperatures near 375° and residence times in the order of 13

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(2) C. B. Colburn and A. Kennedy, *J. Amer. Chem. Soc.* **80**, 5004 (1958).