they were completely soluble). After evaporation nearly to dryness concentrated hydrochloric acid was added to facilitate the removal of nitrogen oxides. The evaporation to dryness was repeated and the residue taken up with water containing a small amount of hydrochloric acid. Upon analyzing this solution according to the method described in a previous paper[6] it was found that no weighable amount of metals other than palladium was present. A small amount of platinum was indicated by a slight color reaction with potassium iodide and also with α-furil dioxime, but the latter did not yield a precipitate sufficient to weigh within any degree of accuracy.

It may be thus seen that the presence of the other metals of the group has but slight effect in the removal of the palladium. The percentage error shown is low in comparison with standard procedures used to effect this task. At best the analytical separations of the platinum metals are not usually as conclusive as those available for use with others so widely known. A means, therefore, which can be attained quickly to yield the metal directly is desirable. The selective action of ethylene also adds to this advantage.

Summary

A new and practical method for the determination of palladium, either alone or in mixtures of all of the other metals of the platinum group, is given. By means of the specific action of ethylene gas toward palladium in reducing it to the metallic condition, gravimetric factors need not be used, and the process of reduction of organic derivatives of the metal in hydrogen is not necessary, when the metal is desired as an end-product. In mixtures of the six platinum metals, the error in the recovery of the palladium is only about 0.75%.

[6] Ogburn, THIS JOURNAL, **48**, 2507 (1926).

LEWISBURG, PENNSYLVANIA

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A Study of the Use of the Tungsten–Nickel Electrode System in Neutralizations[1]

BY N. HOWELL FURMAN AND GEORGE W. LOW, JR.

This investigation of the bimetallic electrode system, tungsten–nickel, was made in order to determine the possibilities of the system in neutralizations. Kahlenberg and Krueger[2] were the first to make a comprehensive study of the use of bimetallic systems in neutralizations. They used normal solutions of strong acid and base, and recommended especially tungsten in conjunction with one of the following: copper, nickel, silicon or cobalt. They gave no data for weak acids or bases. In a subsequent paper Holt and Kahlenberg[3] studied various systems in greater detail, using 0.1 N solution of hydrochloric acid, sodium hydroxide, ammonium

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[1] Presented at the Eighty-third meeting of the American Chemical Society, New Orleans, La., 1932.

[2] Kahlenberg and Krueger, *Trans. Electrochem. Soc.*, **56**, 201 (1929).

[3] Holt and Kahlenberg, *ibid.*, **57**, 361 (1930).

hydroxide and various amines. They stated that the nickel electrode is unsatisfactory because it is attacked by acids. In our work this difficulty did not prove to be serious. They added the reagent in increments of 0.2 cc., which makes it difficult to judge whether a particular electrode system is of value for precise work.

Various bimetallic systems have been studied by other investigators. Willard and Fenwick[4] found that the polarized platinum system gave a good indication of the end-point in the titration of a strong acid with a strong base. Brünnich[5] stated that the system platinum-graphite gave satisfactory results in the titration of both weak and strong acids with sodium hydroxide. Fuoss[6] recommended the following pairs of electrodes for neutralizations: Sb-Pb, Bi-Ag, Sb-Cu amalgam, Cu-CuO.

None of these investigators checked the potentials of the two metals repeatedly against a reference half cell as has been done in this work. Closs and Kahlenberg,[7] however, determined end-points with systems composed of a single metal and a calomel electrode. They found tungsten, bismuth, arsenic, antimony and molybdenum to be the best indicator electrodes.

Experimental

Materials and Apparatus.—Tungsten wire 0.635 mm. in diameter, and nickel wire 1.829 mm. in diameter were used. The surfaces of the electrodes were cleaned with emery paper and by treatment with nitric acid. A saturated calomel cell and a Leeds and Northrup students' type potentiometer and accessories were employed. Solutions were stirred with a motor-driven stirrer. The calibration of the volumetric ware was checked and buret corrections were applied.

Approximately 0.5 and 0.1 *N* solutions of the various reagents were prepared and standardized by well-established methods. The alkali solutions were nearly, but not entirely, freed from carbonate and protected by "ascarite" tubes.

During titrations at least three e. m. f. readings were taken after additions of reagent, namely, tungsten-nickel; tungsten-calomel; nickel-calomel. The electrical end-points (maxima of Δ e. m. f./Δ cc.) were compared with the end-points obtained in independent titrations using phenolphthalein or methyl orange indicators. The presence of a small amount of carbonate in the alkali caused two electrical end-points to be found, one at the end of the neutralization of free alkali and conversion of carbonate to bicarbonate, and the other at the end of reaction between bicarbonate and acid.

A summary of typical data is given in Table I.

When alkali was titrated with acid, carbon dioxide was absorbed from the atmosphere, and hence the phenolphthalein end-point was determined either by having the indicator present during the titration, or by independent titrations run under similar conditions.

The titration of a strong acid with a strong base or *vice versa* is satisfactory either in 0.5 *N* or 0.1 *N* solution. A careful study of the e. m. f.-cc. graphs for the individual metals against the calomel electrode made it

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(4) Willard and Fenwick, THIS JOURNAL, **45**, 715 (1923).

(5) Brünnich, *Ind. Eng. Chem.*, **17**, 631 (1925).

(6) Fuoss, *Ind. Eng. Chem., Anal. Ed.*, **1**, 125 (1929).

(7) Closs and Kahlenberg, *Trans. Electrochem. Soc.*, **54**, 369 (1928).

TABLE I

END-POINTS

Solution in beaker (approx. normality)	Size of sample, cc.	Solution added (approx. normality)	Phenolphthalein		Methyl orange	
			Indicator, cc.	Electrical, No. 1	Indicator, cc.	Electrical, No. 2
0.5 *N* NaOH	25.02	0.5 *N* HCl	17.27[a]	17.15	17.62	17.65
	25.02		17.42[a]	17.42	17.62	17.63
	9.97		6.77	6.77	7.07	7.04
	9.97		6.82	6.78	7.02	7.02
	9.97				7.02	7.02
0.1 *N* NaOH	24.93	0.1 *N* HCl	17.26	17.16	18.41	18.48
	9.99		6.93	6.93	7.53	7.46
	9.99		6.98	7.02	7.45	7.45
0.5 *N* HCl	25.03	0.5 *N* NaOH	35.38	35.38	35.28	35.30
	25.03		35.43	35.43	35.33	35.33
	10.03		14.14	14.09	13.99	14.03
	10.03		14.24	14.19	14.14	14.14
0.1 *N* HCl	24.95	0.1 *N* NaOH	33.91	33.86	33.66	33.66
	24.95		33.91	33.96	33.66	33.71
	9.97		13.47	13.42	13.29	13.33
0.2 *N* HAc	20.00	0.5 *N* NaOH	11.10	10.93		
	20.00		11.07	10.91		
	10.00		5.68	5.48		
0.2 *N* HAc	10.00	0.1 *N* NaOH	27.12	25.58		
	5.00		13.53	12.38		
	5.00		13.58	12.48		
0.5 *N* NH_4OH	20.00	0.5 *N* HCl			18.27	18.24
	10.00				9.18	9.14
	10.00				9.53	9.54 (CO_2)
Na_2CO_3	1.4753 g.	0.5 *N* HCl			55.14	55.10
	1.0969				40.96	40.94
	1.0665				39.86	39.82
	0.8995				33.54	33.56
0.5 *M* H_3PO_4	10.00	0.5 *N* NaOH	No results which could be interpreted			

[a] The discrepancy between these values is due to different rates of titration, and very long exposure of the second solution to air. The second end-point is exact.

clear that the electrical end-point at the *P*H at which phenolphthalein changes was due primarily to the change in potential of the tungsten electrode, the nickel–calomel system being relatively insensitive in this region. The latter electrode system shows a large break in potential in the methyl orange region, and the change with reference to the calomel half-cell is in the opposite direction to that undergone by the tungsten (with reference to the calomel cell) in this region.

The titration of ammonia with hydrochloric acid gave excellent results, the break in potential (tungsten–nickel) being sharper than with the usual combination of indicator electrode and reference half-cell, because the rapid changes of the two metals are in opposite directions, as is shown in

Fig. 1 A and B. Study of a number of graphs not reproduced here indicates that the nickel electrode serves as an approximate *P*H indicator in alkaline solutions, for the graphs are nearly parallel to those given by the tungsten electrode. Near the end-point there is an abrupt discontinuity in the behavior of the nickel, and in the acid region the nickel–calomel system shows little tendency to follow *P*H changes in a regular fashion. Holt and Kahlenberg (Ref. 3, Fig. 2) pointed out that nickel and cobalt differed from most of the other metals which they studied in manner of change of potential upon passing from acid to alkaline solution or *vice versa*.

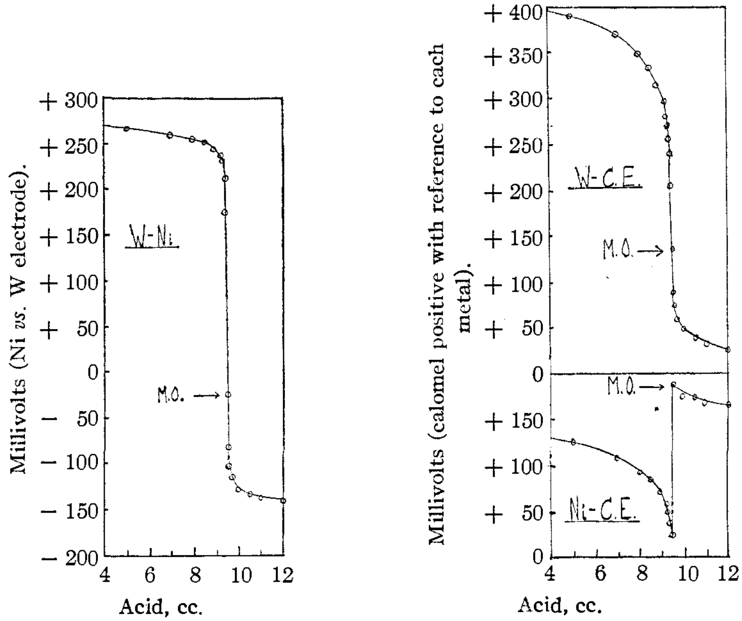

Fig. 1A. Fig. 1B.

Fig. 1.—A. Graph for titration of 10 cc. of approximately 0.5 *N* ammonia with 0.5 *N* hydrochloric acid, using the W-Ni system. B. Showing the behavior of the individual electrodes during the course of the titration represented in A. (M. O. indicates the methyl orange end-point. C. E. denotes the saturated calomel electrode.)

We should expect that the tendency of nickel to undergo a sharp change at a *P*H near the methyl orange transition (4–5), while exceedingly useful in the titration of weak bases, would vitiate the results in the titration of a weak acid with a strong base. This conclusion is amply borne out by the results in the case of acetic acid. As is shown in Fig. 2, A, B, there is an excellent electrical end-point in this titration, but the maximum change is always displaced from the true end-point though rarely or never to the same extent in successive titrations. There is a second small maximum in

Δ e. m. f./Δ cc. at the true end-point in the case shown in Fig. 2, but this maximum does not appear clearly in many of the titrations.

The erratic behavior of the nickel electrode was evident during the progress of titrations of sodium carbonate with hydrochloric acid. In some instances the minor electrical end-point which apparently corresponded to the phenolphthalein end-point was displaced several cc. (10 cc. in one case) from the indicator change. The second and major electrical change, however, coincided quite accurately with the methyl orange end-point.

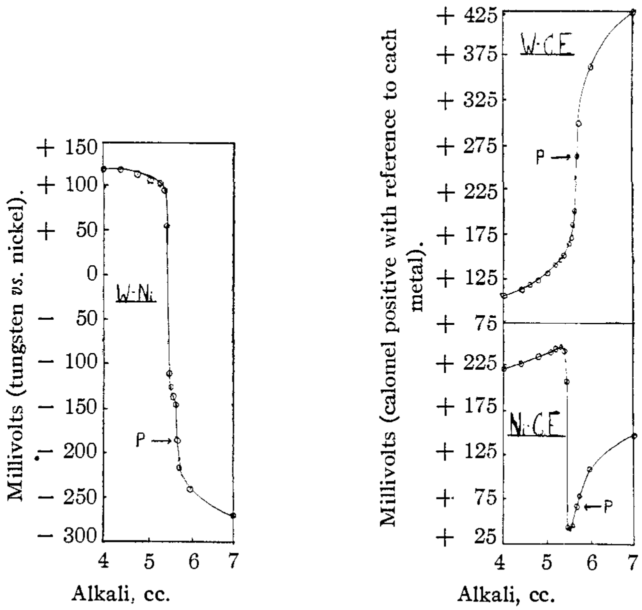

Fig. 2A.

Fig. 2B.

Fig. 2.—A. A graph for titration of 10 cc. of approximately 0.2 *N* acetic acid with 0.5 *N* sodium hydroxide. P indicates the phenolphthalein end-point. B. Shows the behavior of the individual metals during the course of the titration plotted in A. Note the characteristic behavior of the nickel electrode.

It was not possible to interpret the results of the titration of phosphoric acid with alkali. Electrical maxima were obtained, but not at stoichiometric points. The largest jump in potential was observed when phenolphthalein was added after the first end-point, as indicated by the tungsten–calomel system, had been passed. In the presence of this indicator there were erratic potential changes (*nickel electrode*) during the titration of carbonate with acid.

Summary

The tungsten–nickel electrode system has been shown to be of value in the titration of strong acid with strong base, or *vice versa*.

The system appears to be one of the most satisfactory in the titration of weak base with strong acid. In the titration of weak acids or polybasic acids the system appears to be of little use.

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The Dependence of the Ultrafiltrate from a Sol of "Ferric Hydroxide" upon Rate of Ultrafiltration; Donnan Equilibrium and *P*H of Sols

BY JAMES W. MCBAIN AND WINIFRED L. MCCLATCHIE

The unequal distribution of all mobile ions in any system involving a restraint upon certain electrical charges, now commonly known as the Donnan equilibrium,[1] was given quantitative formulation in the subject of electrokinetics by Gouy and Chapman for the diffuse double layer in the neighborhood of surfaces and colloidal particles, then by Donnan in 1911 for membrane equilibria, and very much later by Debye and Hückel in 1923–1924 for the interior of ordinary solutions. Further, although the classical nomenclature of colloids, still frequently employed, took no cognizance thereof, it is well known that all charged colloids in ionizing solvents partake of the nature of salts.[2]

Nevertheless, these matters have been overlooked in assigning to hydrogen ion, or any other ion, definite values of concentration in a sol, although these must vary greatly according to the distance from a colloidal particle. It is intriguing to reflect that the readings of electrode potential of the hydrogen electrode (or other reversible electrode) in different parts of a sol must be identical, although the actual concentrations of any ion yielding the constant electrode potential must vary even as a time average from point to point. A portion of the liquid near a positively charged particle such as that in a sol of "ferric hydroxide"[3] must be less acid than that further away, and although exhibiting the same hydrogen or chloride electrode potential, the actual *P*H and *P*Cl must be different in different parts of the sol. Serious discrepancies must, therefore, appear in the

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(1) For references, including the classical work of Gibbs, see T. R. Bolam, "The Donnan Equilibria," G. Bell and Sons, Ltd., London, 1932.

(2) For the most comprehensive and authoritative monograph, see Wo. Pauli and E. Valkó, "Elektrochemie der Kolloide," Julius Springer, Vienna, 1929.

(3) It should be recalled that a sol of so-called "ferric hydroxide" prepared from ferric chloride is a colloidal complex salt. It contains as essential constituents particles consisting of heavily hydrated oxide or hydroxide with undissociated oxychloride and the positively charged ferric or ferroxy ion, compensated by an electrochemically equal amount of free chlorine ions in the surrounding liquid. There is also a trace of hydrochloric acid in hydrolytic equilibrium. These sols are by no means necessarily dilute, they possess a moderate proper conductivity and definite lowering of freezing point, and they diffuse as rapidly as sucrose.