diagonal of the unit cube (6.47 Å., calculated from $a_0$ = 3.73Å.) should be equal to the sum of the diameters of one atom of neodymium, 3.65Å.,[3] and one of aluminum, 2.86Å.[4] This check lends further support to the assumption of the cesium chloride type of structure.

The diffraction patterns for the series of compounds CuZn, AgZn and AuZn illustrate very clearly the effect on diffraction data of a large difference in the atomic numbers of the two elements of the compound.[5] CuZn, in which both atomic varieties have about the same diffracting power, produces a body-centered cubic pattern; AgZn produces a simple cubic pattern in which the additional lines characteristic of the simple cubic are very weak; AuZn produces a simple cubic pattern in which all lines approximate their normal intensities. All three compounds have the cesium chloride type of structure characteristic of many β-phase alloys.

It is evident that the cesium chloride type of structure for NdAl is consistent with all available data and the structure is the same as that of β-brass.

It was first pointed out by Hume-Rothery[6] that in all of the β-phases the ratio of valence electrons to atoms is as 3:2. Recently it has been found that the same structure is also common in alloys of the transition elements (FeAl, CoAl, NiAl). It is not surprising, therefore, to find this β-brass structure for NdAl. Westgren has suggested[7] that in order to make these β-phases fit the 3:2 rule, the valence of the transition element must be assumed to be zero. He cites several reasons why this is a legitimate assumption. It is, for example, significant that Ekman[8] prepared the alloys $Co_5Zn_{21}$, $Ni_5Zn_{21}$, $Pt_5Zn_{21}$ and $Pd_5Zn_{21}$, all of which should have the structure of γ-brass, the ratio of valence electrons to atoms being as 21:13 if the valence of the transition element is assumed to be zero. He found the γ-brass structure in every case.

## Summary

The compound NdAl has the cesium chloride type of structure, the structure of β-brass. $a_0$ = 3.73 ± 0.01 Å. As is the case with other β-phase alloys of the transition elements (CoAl, NiAl, FeAl), the ratio of the number of valence electrons to the number of atoms is as 3:2 if the valence of the transition element is assumed to be zero.

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(3) Quill, *Z. anorg. allgem. Chem.*, **208**, 273 (1932).

(4) Wyckoff, "The Structure of Crystals," second edition, The Chemical Catalog Co., New York, 1931, p. 192.

(5) Westgren and Phragmen, *Phil. Mag.*, [6] **50**, 331 (1925).

(6) Hume-Rothery, *J. Inst. Metals*, **35**, 295 (1926).

(7) Westgren, *J. Franklin Inst.*, **212**, 577 (1931).

(8) Ekman, *Z. physik. Chem.*, **B12**, 157 (1931).

URBANA, ILLINOIS RECEIVED SEPTEMBER 5, 1933

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

# Phenanthroline-Ferrous Ion. II. Oxidation Potentials at High Acidities and the Determination of Vanadium[1]

BY GEORGE H. WALDEN, JR., LOUIS P. HAMMETT AND SYLVAN M. EDMONDS

Our investigation of the utility of the new oxidimetric indicator, phenanthroline ferrous ion,[2] has led us by way of a determination of relative oxidation potentials in strong sulfuric acid solutions to oxidimetric methods, both accurate and rapid, for the determination of vanadium and of iron in the presence of each other and of other commonly interfering elements. The present paper deals with the potential measurements and with the determination of vanadium; a subsequent one will describe a direct method, using a silver reductor for the determination of iron in the presence of vanadium and titanium.

Of the numerous methods which have been proposed for the oxidimetric determination of vanadium, those which depend upon a titration of quadrivalent vanadium with an oxidizing agent require the inconvenience of a titration in warm solutions.[3,4] If permanganate is used the presence of chromium renders the end-point fleeting; if ceric sulfate is used, an electrometric titration has been necessary.[4] Those methods which

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(1) This article is based upon part of a dissertation submitted by Sylvan M. Edmonds to the Faculty of Pure Science of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, May, 1933. The material was presented at the Washington meeting of the American Chemical Society, March, 1933.

(2) Walden, Hammett and Chapman, THIS JOURNAL, **53**, 3908 (1931); **55**, 2649 (1933).

(3) U. S. Bureau of Mines Bull. 212 (1923).

(4) Furman, THIS JOURNAL, **50**, 1675 (1928).

depend upon the reverse process, namely, a titration of quinquivalent vanadium with ferrous ion have suffered only from the lack of a satisfactory indicator.[5,6,7,8] The potentials of diphenylamine and of its sulfonic acid are too low for a satisfactory end-point, and the blue color is difficult to see in the presence of much vanadium or chromium.

The potential measurements of Rutter[9] and of Foerster and Böttcher[10] at acidities not higher than 1.5 molar sulfuric acid, and our preliminary experiments agree in showing that the potential of the phenanthroline ferrous indicator is too high for this titration if it is to be carried out at such acidities. Because of the obvious large effect of hydrogen-ion concentration upon an oxidant-reductant system whose reaction is[10]

$$VO_2^+ + 2H^+ + e \rightleftarrows VO^{++} + H_2O$$

we have measured the potentials relative to each other in 1 *m*, 3 *m* and 5 *m* sulfuric acid of the ferric–ferrous system, of the indicator, and of two stages in the vanadate system.

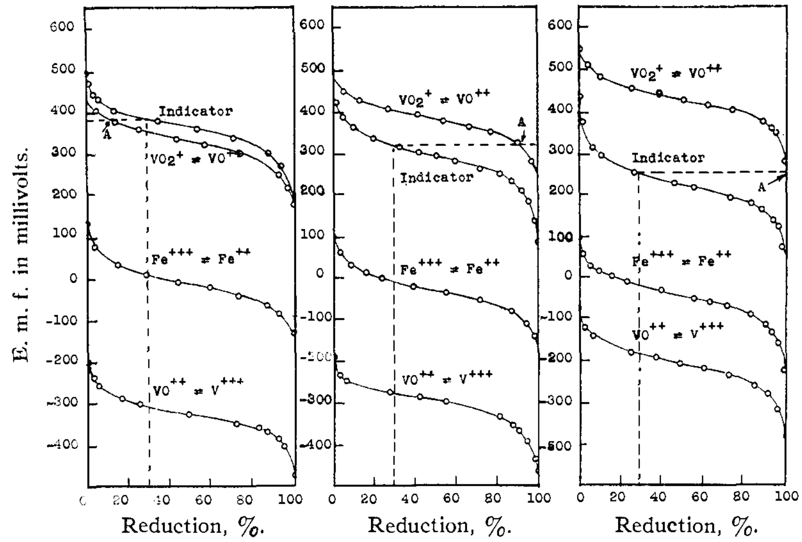

Fig. 1.

## Potential Measurements

These potentials were determined with reference to a quinhydrone electrode in sulfuric acid of the same concentration. For acid concentrations as large as those in question, the convention of reference to a "molar hydrogen electrode" loses all possible meaning because even the most approximate calculation or elimination of the liquid junction potentials necessary would be impossible.[11,12] On the other hand, the large concentration of acid and the relatively low concentrations of the oxidant reductant systems guarantee that values of high precision for the potentials relative to each other of the different systems at any one acid concentration may be obtained.[13] It is only these relative potentials which have any significance for the present or indeed for any other practical purpose.

Potentiometric titrations were made using the experimental set-up and methods described by Walden, Hammett and Chapman,[2] except that in the determinations of the vanadium and of the ferric–ferrous systems platinum electrodes were used and oxygen was excluded by a current of purified nitrogen. The titrations included reductions with titanous chloride of ammonium metavanadate, and of ferric sulfate both separately and in the same solution, and oxidations with ceric sulfate of the phenanthroline ferrous ion. The temperature was 20–25°.

In Fig. 1 the measured potentials in millivolts are plotted against per cent. reduction for each of the systems studied. Table I contains the molar oxidation potentials, all relative to quinhydrone in sulfuric acid of the same concentration. The values obtained from duplicate titration curves checked to within 0.01 volt.

In the first paper of this series,[2] it was shown that for a ferrous sulfate–ceric sulfate titration in a total volume of 200 cc. and using 1 drop of indicator solution, the red color is just visible when 10% of the indicator is reduced. Because of the intensely blue color of the vanadyl ion, however, the indicator must be 30% reduced before its red color can be distinguished in a solution containing 25 cc. of 0.1 *m* vanadyl sulfate and 25 cc. of 0.1 *m* ferrous sulfate in a volume of 200 cc. and with either 1, 3 or 5 *m* sulfuric acid

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(5) Johnson, "Chemical Analysis of Special Steels," 2d ed., John Wiley and Sons, 1914.

(6) Furman, *Science*, **59**, 560 (1924); *Ind. Eng. Chem.*, **17**, 314 (1925).

(7) Willard and Young, *Ind. Eng. Chem.*, **20**, 764 (1928).

(8) Lang and Kurtz, *Z. anal. Chem.*, **86**, 288 (1931).

(9) Rutter, *Z. anorg. allgem. Chem.*, **52**, 368 (1907).

(10) Foerster and Böttcher, *Z. physik. Chem.*, **151**, 321 (1930).

(11) Taylor, *J. Phys. Chem.*, **31**, 1478 (1927).

(12) Guggenheim, *ibid.*, **33**, 842 (1929); **34**, 1540, 1758 (1930).

(13) Brönsted and Pedersen, *Z. physik. Chem.*, **103**, 307 (1922).

present. The potential corresponding to this extent of reduction, the effective oxidation potential of the indicator, is marked by the dotted line A in Fig. 1. If a precision of one part in a thousand is to be obtained in an oxidimetric titration, this effective indicator potential must be separated by 0.18 volt from the molar potential of any of the systems present.

It is only in 5 *m* sulfuric acid, in which the indicator potential is 0.19 volt below the vanadate potential and 0.30 volt above the ferric–ferrous potential, that this condition is satisfied. It follows, therefore, that at this acid concentration, but not at lower ones, precise titrations may be made with this indicator either in the sense of reduction of vanadate to vanadyl or in the sense of oxidation of ferrous to ferric without mutual interference.

**The Determination of Vanadium.**—When a dilute solution of vanadic acid in five molar sulfuric acid is titrated with dilute ferrous sulfate solution in the presence of one drop of 0.025 *M* ferrous phenanthroline indicator solution, there is a pronounced, extremely sharp color change when the vanadium is quantitatively reduced. The change is from greenish-blue to reddish-green and, under the experimental conditions that we have devised, is sufficiently vivid to be easily detected by an analyst inexperienced with the method. Even in the presence of large amounts of iron and chromium the indicator color is sufficiently intense to permit the precise location of the end-point.

### Materials

Two approximately 0.05 *m* ammonium vanadate solutions were prepared from two samples of ammonium metavanadate that had been separately recrystallized four times by solution in warm water and precipitation with ammonium chloride. They were standardized gravimetrically with results shown in Table II by the evaporation and ignition of the residue in platinum and weighing as $V_2O_5$, a procedure which Beans and Parks[14] have shown to be precise. The titer of the ferrous sulfate solution used was based upon comparison with ceric sulfate solutions which had been standardized against sodium oxalate and against potassium dichromate with concordant results by the methods of the first paper.[2] Potassium chrome alum and ammonium molybdate were C. P. salts.

**Titration of Vanadate with Ferrous Ion.**—Twenty-five to 50 cc. of vanadate solution was treated with 100 cc. of 10 *m* sulfuric acid and diluted to 200 cc. After cooling to room temperature, one drop of 0.025 *m* phenanthroline ferrous indicator was added and the mixture titrated with 0.1 *m* ferrous sulfate in 1 *m* sulfuric acid. Table II shows the high precision of this titration.

TABLE I

RELATIVE MOLAR OXIDATION POTENTIALS REFERRED TO QUINHYDRONE AT THE SAME ACIDITY

| $H_2SO_4$ | $E°$ $V^{V}/V^{IV}$ | $E°$ Indicator | $E°$ $Fe^{+++}/Fe^{++}$ | $E°$ $V^{IV}/V^{III}$ |
|---|---|---|---|---|
| 1 M | 0.33 | 0.36 | −0.01 | −0.33 |
| 3 M | .39 | .30 | − .03 | − .29 |
| 5 M | .44 | .23 | − .05 | − .20 |

TABLE II

COMPARISON OF GRAVIMETRIC AND VOLUMETRIC STANDARDIZATION OF AMMONIUM VANADATE SOLUTION

| Soln. | Volumetric obs. | *M*, vol. | Av. dev., pts. 1000 | Grav., obs. | *M* grav. | Av. dev., pts. 1000 |
|---|---|---|---|---|---|---|
| I | 6 | 0.04942 | 1.1 | 4 | 0.04933 | 0.5 |
| II | 4 | .04088 | 0.4 | 8 | .04092 | 1.4 |

TABLE III

DETERMINATION OF SMALL AMOUNTS OF VANADIUM IN THE PRESENCE OF VERY LARGE AMOUNTS OF IRON AND CHROMIUM

| Iron, mg. | Cr, mg. | V (taken), mg. | V (found), mg. | Detn. | Av. dev., pts. 1000 |
|---|---|---|---|---|---|
| 2000 | 40 | 0.000 | 0.012 | 2 | |
| 0 | 0 | 5.207 | 5.196 | 2 | 1.0 |
| 2000 | 0 | 5.207 | 5.202 | 2 | 1.5 |
| 2000 | 20 | 5.207 | 5.190 | 2 | 1.0 |
| 2000 | 40 | 5.207 | 5.224 | 4 | 1.7 |

**Oxidation of Vanadium and Effect of Chromium and Molybdenum.**—We have found the method of Lang and Kurtz[8] very satisfactory for the oxidation of vanadium to the quinquivalent state without simultaneous oxidation of chromium preparatory to its determination by reduction with ferrous ion: 25-cc. portions of vanadate solution II, both alone and in the presence of an equal volume of $^1/_{60}$ *m* chrome alum or of 0.1 *m* ammonium molybdate were reduced with excess ferrous sulfate and then analyzed by the following method.

To 25–50 cc. of the vanadium solution were added 4 cc. of 10 *m* sulfuric acid and then 0.1 *m* permanganate dropwise until a permanent pink persisted for two minutes; 0.5 *m* sodium nitrite solution was then added dropwise until the permanganate color disappeared; 5 grams of urea was added immediately, followed by 100 cc. of 10 *m* sulfuric acid. After dilution to 200 cc. the titration with ferrous sulfate was made as above described. In blank experiments carrying chromium and molybdenum but no vanadium, the first fraction of a drop of ferrous sulfate solution produced the end-point color.

A vanadium determination on Bureau of Standards ferro-vanadium No. 61 was made by this method after solution in a mixture of sulfuric, nitric and hydrofluoric acids, followed by evaporation to sulfuric acid fumes. Three determinations with an average deviation of 1.2 parts per 1000 gave a value of 31.12%, which checks exactly with the certificate value when this is recalculated to the new atomic weight of 51.0 for vanadium.

**Determination of Small Amounts.**—With dilute solutions, an indicator blank becomes necessary, and this is determined most conveniently by measuring the amount of oxidant required to cause complete bleaching of the indicator. Therefore the vanadate solution was treated with a measured excess of 0.01 *m* ferrous sulfate and back-

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(14) Parks, Dissertation, Columbia University, New York, 1930.

titrated with 0.01 *m* ceric sulfate. The color change is from a faintly reddish-yellow to a clear yellow. In the presence of large amounts of iron, as in steel analysis, the addition of phosphoric acid to discharge the iron color becomes necessary. The indicator blank amounts to about 0.15 cc. of 0.01 *m* ceric sulfate in a volume of 200 cc. of 5 *m* sulfuric acid.

Table III contains the results of analyses which show the precision attainable on mixtures comparable to those obtained by solution of commercial steels. We have further analyzed the Bureau of Standards chrome–vanadium steel No. 30 c. A 2-g. sample was dissolved in 20 cc. of 5 *m* sulfuric acid, and after addition of 5 cc. of 8 *m* nitric acid, the solution was evaporated to fumes. After dilution and filtration the insoluble residue was ignited, treated with hydrofluoric and sulfuric acids, and fused with sodium carbonate. The dissolved melt was added to the main solution, and vanadium was then determined by the method given for the determination of small amounts. The results are

| V (found), % | Detn. | Av. dev. pts. per 1000 | V (certificate), % |
|---|---|---|---|
| 0.2377 | 2 | 2.5 | 0.235 (range: 0.225–0.246) |

Two determinations in which the recovery of vanadium from the silica residue was omitted led to values of 0.2349 and 0.2343, so that the amount of vanadium thus carried down is easily detected by this method. It is worthy of note that it is now possible to determine the vanadium content of a steel which carries only 0.2% of that element with a precision of about 3 parts per thousand.

## Summary

Oxidation potentials relative to each other of the ferric–ferrous system, of the phenanthroline–ferrous indicator, and two stages of the vanadate reduction have been measured in 1, 3 and 5 *m* sulfuric acid.

From these the necessary conditions for the separate oxidimetric titration of iron and of vanadium have been predicted.

A rapid and precise method for the determination of vanadium in the presence of iron, chromium and molybdenum has been developed and tested.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

# Determination of Acidity in Ethyl Alcohol by Velocity of Acetal Formation

BY ALDEN J. DEYRUP[1]

The development of the theories of salt effects and general acid catalysis, due mainly to Brönsted, has placed reaction velocity measurement among the accurate methods of determination of acidity in aqueous solution.[2,3] A satisfactory application of the method to non-aqueous solutions depends on the selection of a reaction sufficiently sensitive to hydrogen ion to permit of measurements at low ionic strength. Adkins and Broderick[4] measured the rate of such a reaction, the formation of diethyl acetal from acetaldehyde in alcoholic solution with hydrogen chloride as catalyst. The decrease in velocity constants as the reaction proceeded was attributed to the effect of water produced in the reaction.[5]

This reaction has been investigated as a method of measurement of acidity in absolute ethyl alcoholic solutions. It was found convenient to follow the course of the reaction dilatometrically, the high sensitivity of this method making possible the use of dilute solutions of substrate.

### Materials and Procedure

**Ethyl Alcohol.**—Commercial 95% ethanol was dehydrated by refluxing over several portions of calcium oxide and distilling in an apparatus designed to prevent access of moisture from the air. It was kept in a flask protected with calcium chloride tubes, and its water content was estimated at intervals from density determinations at 25°. The lowest density observed was 0.78505 g./ml., which is in good agreement with the density 0.78506 of Osborne, McKelvy and Bearce.[6] The density was found to vary linearly with the water content from 0 to 1%. The water content was therefore estimated from the density figures for 99 and 100% alcohol in the "International Critical Tables." It was not allowed to exceed 0.02%. No removal of aldehyde was necessary since the acetal formation is first order, and aldehyde increases the density of alcohol as does water.

**Acetaldehyde.**—Commercial acetaldehyde was distilled through a column of calcium chloride, the fraction boiling above 22° being rejected.

**HCl, HBr, HI, $HClO_4$.**—C. P. concentrated acids were used. Since the concentrations of these acids as catalysts did not exceed 0.001 molar, the amount of water introduced with the acid is negligible.

**Picric acid, 2,4-dinitrophenol and oxalic acid** were recrystallized from water, the last being dehydrated at

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(1) National Research Fellow in Chemistry.

(2) Brönsted and Grove, THIS JOURNAL, **52**, 1394 (1930).

(3) Kilpatrick and Chase, *ibid.*, **53**, 1732 (1931).

(4) Adkins and Broderick, *ibid.*, **50**, 178 (1928).

(5) De Leeuw, *Z. physik. Chem.*, **77**, 284 (1911).

(6) Osborne, McKelvy and Bearce, *Bur. Standards Bull.*, 327 (1913).