is less direct than our own. The magnitude of the divergence, however, and the importance of this quantity in the theory of the subject warrant a more direct determination of the heat of adsorption. This is being attempted in this Laboratory. There are manifest difficulties in the performance of the experiment. It is of interest to record that recent calculations of Eucken[10] of the work necessary to remove a film of adsorbed hydrogen from the surface of charcoal gave a value of 2500 calories, and in the case of other adsorbed gases similar low values were obtained.

Summary

1. Adsorption isotherms of hydrogen on nickel have been determined using nitrogen as reference gas.

2. A definite saturation capacity of nickel for hydrogen exists, dependent upon the temperature.

3. From the variation of the saturation pressure with temperature the heat of adsorption of hydrogen on nickel has been calculated to be approximately 2500 calories. Other methods of calculation give a value of 12,000 calories. A direct determination is being attempted.

4. The effect of using an inert material for catalyst support has been found to increase greatly the adsorptive capacity per gram of nickel and to yield a catalyst that will stand much more severe heat treatment without diminution of its adsorbing power.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE ELECTROMETRIC TITRATION OF MOLYBDENUM WITH A TITANOUS SALT

BY H. H. WILLARD AND FLORENCE FENWICK

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Introduction

The reduction of molybdic acid to a salt of pentavalent molybdenum by means of trivalent titanium was observed by Knecht and Hibbert.[1] They failed in the attempt to base a volumetric method for the determination of molybdenum upon this fact because of the lack of a suitable indicator for the end-point. An investigation of the applicability of the electrometric titration showed that the reaction is sufficiently rapid for this to be used. The character of the end-point with the polarized bimetallic electrode system with platinum electrodes is essentially as has been described for other titrations.[2] After enough of the titrating solution has been added

[10] Eucken, *Z. Elektrochem.*, **28**, 1 (1922).

[1] Knecht and Hibbert, "New Reduction Methods in Volumetric Analysis," Longmans, Green and Co., **1918**, p. 99.

[2] Williard and Fenwick, THIS JOURNAL, **44**, 2516 (1922).

for equilibrium to be established, there is practically no further change until within about 0.5 cc. of the end-point. The potential difference increases slightly, decreasing again on the addition of excess titanium. Normally the maximum is perfectly definite when the titration is carried out slowly as the end is approached so that equilibrium may be maintained. Otherwise a transient and irregular decrease in e.m.f. may occur before the reaction is quite complete. It is safest to add several drops more of the titanous solution after the supposed end-point has been reached to insure that the potential decrease is permanent and increasing. The reduction is not ideally fast. For this reason it is probable that a better end-point would be obtained with the usual monometallic electrode system. This point was not investigated.

The acid concentration of the molybdenum solution is an important factor; 5–10% by volume of conc. hydrochloric acid is the most desirable; too high a concentration weakens the reducing power of trivalent titanium appreciably. Sulfuric acid is unsatisfactory. Heat increases the velocity of the reaction but is unnecessary except in special cases.

Titration of Sodium Molybdate with Titanous Sulfate

An approximately 0.017 *M* solution of C. P. sodium molybdate was titrated with titanous sulfate[3] standardized by the method of Thornton and Chapman[4] against ferric sulfate prepared from electrolytic iron of known purity.

TABLE I

TITRATION OF PURE SODIUM MOLYBDATE WITH TITANOUS SULFATE

The solutions contained about 8% by volume of conc. HCl and were heated to about 80°. 0.05 *N* Ti factor against Fe, 1.4002.

0.017 *M* Na_2MoO_4 taken Cc.	0.05 *N* $Ti_2(SO_4)_3$ req. Cc.	0.017 *M* Na_2MoO_4 taken Cc.	0.05 *N* $Ti_2(SO_4)_3$ req. Cc.
5.00	2.17	15.00	5.61
10.00	3.92	20.00	7.42

A finite excess of the titanous solution is required over that theoretically necessary for a reduction to the pentavalent state. This excess must be independent of the total amount of molybdenum present and may be determined by titrating solutions of varying molybdenum content and solving the equation, $n(a-x) = (b-x)$, where a and b are the number of cubic centimeters of the titrating solution required for 2 solutions of known molybdenum content, x is the required excess, and n the ratio of the weight of molybdenum in Solution b to that in Solution a.

Using the given formula, the excess of titanous solution required to give the end-point was determined from the data in Table I. By combining

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[3] Prepared by the electrolytic reduction of titanic sulfate and stored in an atmosphere of hydrogen.

[4] Thornton and Chapman, THIS JOURNAL, **43**, 91 (1921).

Expt. 1 with Expts 2, 3, 4, x was found to be 0.42, 0.45, 0.42 cc., respectively; by combining Expt. 2 with Expts. 3 and 4, x was 0.54 and 0.42 cc.; by combining Expt. 3 with Expt. 4, 0.18 cc. was obtained. The average is 0.40 cc. The value of x is to some extent a function of the electrode system used and the magnitude of the polarizing voltage. For the most accurate results the titanium solution should be standardized against a molybdenum solution of known strength, using a volume of the titrating solution as nearly as possible equal to that required for the unknown. It was concluded from the results of a considerable number of titrations that an accuracy greater than 0.1 cc. of 0.05 N solution, which is the equivalent of 0.48 mg. of molybdenum, cannot be claimed for the method.

Titration of Molybdenum in Ammonium Phosphomolybdate

The titration of the molybdenum in a precipitate of ammonium phosphomolybdate is an excellent method of determining the phosphorus content of steels. No special refinements are necessary in standardizing the titanous solution for this purpose, since 37.11 mg. of molybdenum corresponds to 1 mg. of phosphorus and the effect of any slight error in the titration falls far below the limit of accuracy of the precipitation.

After precipitation of the phosphorus in the usual way[5] the ammonium phosphomolybdate is dissolved in ammonia, filtered to remove any iron, and the acidified solution titrated with titanous sulfate. If the precipitate is very large it tends to reprecipitate upon the addition of acid. This may be prevented by the addition of a few drops of phosphoric acid to the ammoniacal solution, but the character of the end-point is thereby altered. In the cold there is no voltage drop with excess of the titrating solution. Just preceding the end-point the normal rise begins, ceases, then continues with increased velocity just as the equivalent point is passed. If the solution is titrated hot, however, the end-point is perfectly normal and as distinct as in the absence of the phosphoric acid. The separation of titanic

TABLE II

DETERMINATION OF PHOSPHORUS IN STEEL

Steel	Sample G.	H_3PO_4 Sp. gr. 1.7 Cc.	Ti^{+++} req. Cc.	% P from Mo factor	% P from Fe factor	% P Certificate value
0.4 C............	2.000	1	9.37	0.1016	0.1027	0.102
Bessemer.........	2.001	0	9.57	0.1016	0.1028	...
0.1 C............	5.003	1	7.20	0.0312	0.0316	
B. O. H..........	5.002	0	7.22	0.0313	0.0316	0.031
	5.004	0	7.30	0.0316	0.0320	
0.1 C............	2.003	0.5	10.31	0.1116	....	0.112
Bessemer.........	2.001	0.5	10.29	0.1100	....	

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[5] Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Company, 3rd edition, 1922, p. 365.

phosphate sometimes occurs but has no effect upon the sharpness of the end-point.

Three Bureau of Standards steels were analyzed by this method; the results are shown in Table II. The 0.05 *N* factor of the titanium solution against molybdenum was 1.6765; against iron, 1. 6956.

The color of the reduced solution is an extremely intense bluish purple and forms an excellent qualitative test for molybdenum even in amounts less than 1 mg. in the absence of tungsten and vanadium.

Effect of Tungsten

One of the most interesting points in connection with the molybdenum titration is the non-interference of tungsten even when present in large amounts. If anything, the end-point is rendered more distinct. Certainly, results seem to be more uniform. There is greater necessity for proceeding slowly near the completion of the titration than when no tungstic acid is present. Very transient decreases in potential occur near the end-point as the titrating solution is added drop by drop but cease just before the reaction is complete, and the permanent end-point drop is very distinct. The color is as characteristic as that of the complex phosphate, and is due to an intense blue-black, finely divided precipitate or a solution in case phosphoric acid is also present.

Various amounts of tungsten, in the form of a solution of pure sodium tungstate, were added to 15.00cc. samples of sodium molybdate, and the molybdenum was titrated. The molybdate was standardized gravimetrically;[6] the 0.05 *N* factor was 1.0005. The titanous solution was standardized against iron; 0.05 *N* factor, 1.2904. All samples contained about 5% of conc. hydrochloric acid and were titrated cold.

Table III

Effect of Tungsten

0.05 *M* $Na_2WO_4.2H_2O$ added Cc.	0.05 *N* $Ti_2(SO_4)_3$ req. Cc.	0.05 *M* $Na_2WO_4.2H_2O$ added Cc.	0.05 *N* $Ti_2(SO_4)_3$ req. Cc.
0	15.38	5	15.02
1	15.10	15	15.06
2	15.07	75	15.06

If the calculated excess of titanous solution, 0.40 cc. (p. 930), is subtracted from 15.38 cc. it leaves 14.98 cc. The results obtained in the presence of tungsten are in very fair agreement with this theoretical value.

Separation of Molybdenum from Iron

Two methods are in general use for the separation of molybdenum from iron prior to the determination of the former element in steels: (1) precipitation of molybdenum as sulfide from slightly acid solution[7] and (2)

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[6] Weiser, *J. Phys. Chem.*, **20**, 657 (1916).

[7] Johnson, "Chemical Analysis of Special Steels," John Wiley and Sons, 3rd Ed., 1920, p. 156.

precipitation of iron as ferric hydroxide by pouring the acid solution into hot sodium hydroxide solution.[8] An attempt was made to use another method based upon the insolubility of lead molybdate in 2% perchloric acid. This gives a complete separation from chromium and vanadium. If no other strong acids are present precipitation is complete, but iron is always occluded to some extent and must be removed by treatment with sodium hydroxide, thus detracting from the value of the proposed method.

Synthetic steels were prepared from ferric nitrate and a standard solution of sodium molybdate. The calculated amount of 60% perchloric acid to form ferric perchlorate and 9 g. in excess was added to each of the samples and the solutions were evaporated until fumes were evolved. A partial dehydration of the molybdic acid occurs but this presents no difficulties. Chromium, if present, is oxidized and lead chromate, which is much less soluble than the molybdate, will later precipitate. After the evaporated samples were dissolved in water the chromic acid was reduced with a slight excess of ferrous perchlorate. The reduced solutions were heated to boiling and the molybdenum was precipitated by slowly adding to the boiling solution[9] a solution of 10 g. of lead perchlorate.[10] The final volume was 300 cc. After the solutions had stood overnight they were filtered through Gooch crucibles, washed with 2% perchloric acid, then with water, and the precipitates dissolved in sodium hydroxide. The asbestos and ferric hydroxide were filtered off, the filtrates acidified with a 5% excess of hydrochloric acid, and titrated with titanous sulfate.

TABLE IV

DETERMINATION OF MOLYBDENUM IN SYNTHETIC STEELS

In all experiments 1 g. of iron and 0.0720 g. of molybdenum were added. The latter required theoretically 10.00 cc. of titanous solution. This solution was standardized against the standard molybdate solution.

Cr added Mg.	V added Mg.	Ti^{+++} req. Cc.	Error Mg. of Mo
0	0	9.95	−0.36
0	0	9.90	−0.72
20	0	10.00	0.0
20	5	9.98	−0.14
20	5	10.00	0.0

Summary

The reduction of hexavalent molybdenum to the pentavalent state by titanous salts is sufficiently rapid for employment of electrometric titration.

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[8] Ref. 5, p. 314.

[9] Lead molybdate precipitates immediately and completely in the cold in 5% perchloric acid in the absence of iron. The latter interferes in the precipitation. With large samples of steel, 2 g. or over, considerable boiling is required for complete precipitation. No precipitation at all occurs in the cold.

[10] Made by dissolving the theoretical quantity of pure litharge in perchloric acid. The oxide was added slowly to the cold, dilute acid, heated to boiling, cooled and filtered.

This gives a means of determining molybdenum in alkali molybdates accurate to within 0.5 mg. and, indirectly, phosphorus in the precipitate of ammonium phosphomolybdate. Tungstic acid presents no interference and it also eliminates the necessity of applying a correction for the excess titanous solution required to give the end-point.

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THE ELECTROMETRIC TITRATION OF SELENIUM IN THE PRESENCE OF TELLURIUM, IRON AND COPPER

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Introduction

The reduction of selenious acid to metal by titanous chloride was observed by Moser[1] and also by Monnier.[2] Moser attempted to develop a volumetric method for selenium based on this reaction using methylene blue as indicator but the results obtained were invariably too high. This was due to the further reduction of the selenium to hydrogen selenide, a compound which had been shown to exist under similar conditions by Pleischl[3] and Trautmann.[4]

Under the condition imposed by Moser, namely, a hot hydrochloric acid solution, the electrometric end-point is either absent or very poor, but in a cold solution containing 25 to 75% of conc. hydrochloric acid and saturated, or nearly so, with sodium chloride, the end-point with the previously described polarized bimetallic electrode system[5] with platinum electrodes is excellent. The presence of the sodium chloride is important. It insures rapid and uniform coagulation of the selenium hydrosol and increases the sharpness of the change in voltage at the end-point. The use of a cold solution also eliminates the almost inevitable loss of selenium by volatilization.

The character of the end-point for this titration is somewhat difficult to describe but is readily discovered by experiment. After enough of the titrating solution has been added to give a constant potential, there is little change until within a short distance of the end-point. Slight fluctuations in the e.m.f. may be manifested; the resistance of the solution is so low that the galvanometer is extremely sensitive. The characteristic rise occurs, with the fall immediately following. The condition of the solution with respect to acidity and foreign salts determines which of the two pre-

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[1] Moser, *Z. anal. Chem.*, **57**, 277 (1918).

[2] Monnier, *Ann. chim. anal. appl.*, **20**, 1 (1915).

[3] Pleischl, *Kastner Arch.*, **93**, 430.

[4] Trautmann, *Bull. soc. ind. Mülhouse*, **61**, 87(1891).

[5] Willard and Fenwick, THIS JOURNAL, **44**, 2516 (1922).