haps mercury) are thereby introduced into the resulting product, and partly because of the difficulty of obtaining really pure granulated zinc, we made a practical study of the electrolytic reduction method for obtaining an uncontaminated solution of titanous sulfate. In this study the two-compartment type of electrolytic cell was used. The catholyte was a solution of titanic sulfate acidified with sulfuric acid, and the anolyte consisted of dilute sulfuric acid alone, diffusion being prevented by means of a porous partition.

The reduction apparatus which was finally adopted as being most satisfactory is shown in Fig. 1. The Jena glass cylinder C (height, 27 cm.; diameter, 14.5 cm.; capacity, 4.5 liters), with a fritted-glass bottom D (thickness, 0.5 cm.), contains the solution to be reduced.[9] The Pyrex jar J holds the sulfuric acid solution which surrounds the cylinder C. The platinum-sheet electrodes E (3.7 × 3.6 cm.) and F (6.4 × 6.2 cm.) are sealed into glass tubes, each of which confines a small amount of mercury to provide contact between the platinum wire of the electrode and the copper wire of the external circuit. The copper bath B serves to keep the liquids cool during an electrolysis. Cooling water enters at I and leaves at either the upper or lower outlet (O′ or O), depending upon the volume of titanium solution with which one is working. The glass stirrer S mixes the cathode liquid throughout a reduction. The watch glass G, which is sealed to S, and the glass cover resting on top of the jar serve the double purpose of preventing acid spray from reaching the metal parts of the pulley and of keeping extraneous matter from falling into the solutions below. A rheostat R, an ammeter A and a knife switch T are included in the electrical circuit.

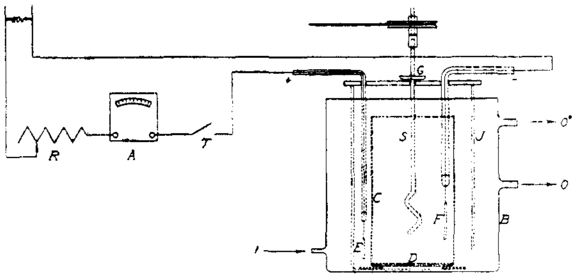

Fig. 1.

In an actual experiment with this apparatus, 2300 cc. of a 0.1 N titanic sulfate solution (prepared as previously outlined, the fifth product of crystallization from the above-named "Purified Powder" being used) was charged into the cup of Jena glass, which in turn was surrounded by 2700 cc. of pure sulfuric acid (1:15). Electrolysis was allowed to proceed for approximately twenty-eight hours, the average current being 7.5 amperes. At the conclusion of the run the liquid in the porous cup was stored in an atmosphere of hydrogen.[10]

The solution resulting from the above experiment was found to be 0.082 N with respect to titanous ion.

A colorimetric test showed that 50 cc. of this titanous sulfate solution contained considerably less than 0.00005 g. of iron.

Summary

The purification of the double oxalate of titanium and potassium and the preparation therefrom of solutions of titanic sulfate and titanous sulfate for use in refined analysis are described.

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[9] In early experiments a Coors cup of unglazed earthenware which was employed as the porous vessel, was found to be a serious source of iron. Accordingly, we looked for a container which would be inert toward all ordinary chemical reagents and which would, in addition, retain liquids poured into it and yet not offer too much resistance to the electric current. It was found that a Jena glass cylinder with a fritted-glass bottom of porosity "G4" fulfilled these requirements. Several cylinders of this type (C, D, *Fig.* 1) were made to order for us by the Jenaer Glaswerk Schott & Gen., Jena (Germany).

[10] The storage apparatus was similar to the one employed by Thornton and Chapman, THIS JOURNAL, **43**, 91 (1921).

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NOTES

The Preparation of Diphenylbenzidine and its Use as an Oxidation–Reduction Indicator

BY L. A. SARVER AND J. H. JOHNSON

The value of diphenylbenzidine as an oxidation–reduction indicator has been pointed out in previous papers.[1] In the present communication a method is reported for the preparation of this substance in quantity.

To a mixture of 1 liter of concentrated sulfuric acid, 2 liters of glacial acetic acid, and 12 liters of water is added, slowly and with stirring, a solution of 50 g. of diphenylamine in 500 cc. of acetic acid. Should any diphenylamine separate during the process, it may be redissolved by warming to not higher than 50°. To the resulting solution at 15–25° is added slowly and with vigorous stirring a solution of 22 g. of potassium dichromate in 500 cc. of water; after five minutes the excess dichromate is reduced with a solution of 10 g. of sodium bisulfite. The colloidal precipitate is collected on the filter with the aid of a filter medium. The greenish-black product is placed, while still wet, in a warm concentrated solution of sodium bisulfite; when light brown, it is filtered off, washed with hot water, thoroughly dried, pulverized, and extracted with 1250 cc. of boiling xylene. The residue is extracted again with the

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[1] I. M. Kolthoff and L. A. Sarver, *Z. Elektrochem.*, **36**, 139 (1930); THIS JOURNAL, **52**, 4179 (1930); L. A. Sarver and I. M. Kolthoff, *ibid.*, **53**, 2906 (1931).

same solvent. The pure diphenylbenzidine separates on cooling; after filtering off and washing with alcohol until the washings fail to yield a white cloud upon dilution with water, the product is dried at 110°. The yield is 60–65%,[2] m. p. 244–245° (uncorr.).

About 10% of the crude product is insoluble in boiling xylene, and 25–30% remains in solution in the cold mother liquor. This more soluble product probably consists largely of 2,2'-dianilinodiphenyl. One liter of xylene dissolves 0.3 g. of diphenylbenzidine at 25°.

The indicator may be employed satisfactorily by mixing 1 drop of a 0.1% solution in sulfuric acid with 10 cc. of a mixture of equal parts of glacial acetic acid and sirupy phosphoric acid. By the use of such a solution, good end-points are obtained with 0.01 N standard solutions, provided stirring has been continuous and thorough.

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(2) This method has been repeated by Dr. R. E. Montonna and Mr. L. T. Jilk, of this Laboratory, who have obtained a yield of 50% when working on a ten times larger scale.

SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINN.
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Heat of Vaporization of a Pure Substance from the Measurement of the Temperature at Two Points and the Vertical Distance between Them

BY S. C. COLLINS

Consider a vertical tube containing a small quantity of the pure liquid and its saturated vapor. Sufficient heat is applied to the liquid to maintain the desired temperature. Since the insulation is not perfect, the walls of the tube are kept moist by condensation of the vapor. The temperature at A, a point near the lower end, will be slightly higher than that at B, a point near the upper end, because the pressure is higher. Let the difference in temperature, dT, be measured with a differential thermocouple. Denoting the difference of pressure by dp, $dp = gh/V'$, where V' is the specific volume of the saturated vapor, g the acceleration of gravity and h the vertical distance between the points A and B.

Substituting for dp in Clapeyron's equation

$$L = \frac{dp}{dT}\, T(V' - V) \qquad (1)$$

its value, gh/V', one obtains the relation

$$L = \frac{T}{dT}\, gh \left(1 - \frac{V}{V'}\right) \qquad (2)$$

At temperatures not too near the critical point V' may now be calculated with sufficient precision by means of the equation of state for ideal gases. The value of V, the specific volume of the liquid need be known only roughly.

In the case of water vapor at 100° the calculated value of V' is incorrect to the extent of 1.6%. The error in the latent heat, L, resulting from the use of the calculated value of V' in equation (1) is 1.6%, whereas the same value used in equation (2) produces an error of only 0.001%.

To illustrate the order of magnitude of the quantities to be measured the following table is prepared. The length of the tube is assumed to be 20 meters. The values of dT were calculated from existing data.

Substance	Temp., °C.	dT
H_2O	50	0.0265
	100	.0324
CCl_4	50	.304
	65	.343

It is anticipated that difficulties in preparing samples of sufficient purity and in measuring dT with the required precision may prove serious but not insurmountable.

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RESEARCH LABORATORY OF PHYSICAL CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
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x-Ray Diffraction Studies of Built-up Films of Long-Chain Compounds

BY G. L. CLARK, R. R. STERRETT AND P. W. LEPPLA

The technique developed by Blodgett and Langmuir[1] for transferring monomolecular films of long-chain compounds from a water surface to a glass surface and the opportunity thus afforded to apply a known number of layers of molecules, one on top of the other, has proved to be exceedingly valuable in x-ray diffraction studies of long-chain compounds. For a number of years studies have been made on films of these compounds produced by melting the substances into a thin film on a suitable backing or by evaporating a solution of the substance in a suitable solvent. The unknown factor has been the actual number of molecular layers in the oriented film. With a little practice, we have now found it possible to build up successive monomolecular films of vari-

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(1) THIS JOURNAL, **56**, 495 (1934); *J. Franklin Inst.*, **218**, 143 (1934).