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.

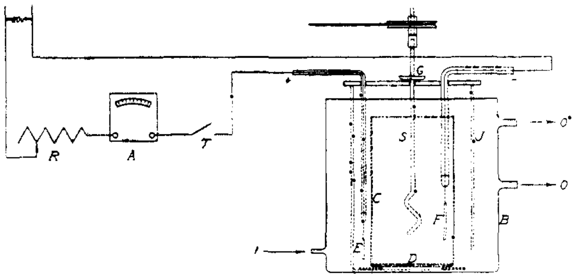

Fig. 1.

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).

BALTIMORE, MD. RECEIVED DECEMBER 19, 1934

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.

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RECEIVED OCTOBER 22, 1934

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.

CONTRIBUTION NO. 343
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RECEIVED DECEMBER 11, 1934

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).

ous substances, not only on glass but on several plane and curved metal surfaces. With the latter type of backing, of course, the necessity for oscillation of the specimen during the x-ray exposure is removed.

We have now made diffraction patterns for stearic acid from one up to 187 layers, and for several other acids and derivatives. Blodgett and Langmuir found that a trace of calcium ion in the water upon which the monomolecular films were produced, was very highly advantageous in the successful transference of the film from the water to glass. A calcium-ion concentration corresponding to a saturated solution of calcium carbonate is, indeed, very helpful in this process.

The question then arises as to whether the film is actually stearic acid or calcium stearate. From very careful measurements the long spacing for these built-up layers transferred from water containing calcium ion is found to be 47.55 Å., which evidently corresponds to the thickness of two monomolecular films turned in opposite directions (the methyl group end of the molecule turns in when the plate is pushed into the film trough, and the carboxyl end oriented down in the water, turns in, when the plate is pulled out). The long spacing for a film of pure synthesized calcium stearate studied by the older methods is found to be 47.53 Å., for the length of two molecules. It is clear, therefore, that soap formation has actually taken place on the water surface. In order to test this conclusion further it was possible, after numerous trials and by forming new films for each step, to take up stearic acid films from the surface of purest distilled water. The spacing for this specimen is 46.05 Å., which is still appreciably greater than the value for a film from molten stearic acid, namely, 39.62 Å. Palmitic acid on water containing calcium ion gives the principal spacing of 43.50 Å., again corresponding to the soap, and myristic acid a spacing of 39.55 Å.

Aside from the fact that this method permits the study of reactions of this type and also makes possible the preparation of films in the ideal condition since each layer is distinctly monomolecular, it follows that very interesting data with respect to intensities of diffraction interferences in various orders can be obtained. A few of these are presented here as typical examples. The values are given relative to a standard intensity of 10 for the first order of the long spacing for 61 layers of stearic acid (or actually calcium stearate) on polished cadmium. The temperature in all cases was 25° and the pH of the solution containing Ca^{++} was 8.7.

INTENSITY DATA

Stearic acid (on water containing Ca^{++}) transferred to cadmium

Layers	Intensity of orders of diffraction for long spacing 1	2	3	4	5
45	7	2	3.5	0	1
61	10	2	4.5	0	0
85	12	3	5.9	0	2.5
121	15	3	7.1	0.5	2.0
187	20	5	10	1.5	3.1
Palmitic acid (on water containing Ca^{++}) transferred to brass					
55	Incompletely resolved	1.2	4	0	1.1
85		3.5	8	0.5	3
151	23	4.5	10	.5	4
Stearic acid on pure water transferred to brass					
71	7	0.5	2.5	0	0
125	12	3	4.7	0	1

The sharpness of the interferences depends upon the number of layers in the film. For 25 layers of calcium stearate, the first order interference is so sharp that it appears as a spot, while for increasing number of layers the spot lengthens gradually into an arc indicative of less perfect orientation. Faint but perfectly definite patterns are obtained with 9 layers. Further work with prolonged time is under way to ascertain the minimum number of layers required to produce any diffraction effects.

It is quite clear from these preliminary investigations that this new technique will be of very great value both in studies of the theory of diffraction from these films of long chain compounds and for practical applications of diffraction information to the lengths, structures and properties, such as lubrication, residing in these long molecules. However, there is an even wider scope of possibilities as illustrated by the following experiment. A solution of ferric chloride in petroleum ether is spread on water containing ammonium hydroxide. A film of ferric hydroxide is formed which can be transferred as easily to glass as stearic acid. The film can be formed upside down by floating a benzene solution of ammonia on an aqueous solution of ferric chloride.

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RECEIVED DECEMBER 24, 1934

Reading Device for Burets

By Walter P. White

Some burets having the graduations run halfway around the tube proved quite satisfactory in the easy avoidance of parallax error, but the large amount of white marking or some other cause rendered the meniscus very hard to distinguish. A very bright background, used by some observers, made the meniscus clear, but gave an uncomfortable glare, while the graduations in front of the meniscus were invisible, which was troublesome, even if not seriously so. With a moderately bright background a vertical black surface just below and behind the meniscus showed it up clearly, but left its apparent position variable with the height of the black surface, while the graduations in front of the meniscus were still invisible. Every difficulty was avoided by the following arrangement. A split perforated cork 5 cm. in diameter was clamped or pinned together around the buret, with its upper surface darkened. To this was tacked a card or piece of white celluloid, extending back at an angle of 45°, and partly above the cork. The whole was illuminated by light from the side. Then the meniscus showed very clear against the not too bright card, while, reflecting as it did a *horizontal* surface, its position did not change perceptibly with moderate movement of the cork. All the graduations were very distinctly visible, except, of course, that part of them directly behind the meniscus. Reasonably bright illumination of the room was quite sufficient, and seemed much better than any concentrated light, unless this was just right, in position and intensity.

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RECEIVED DECEMBER 24, 1934

The Thermal Dissociation of Lithium Hydride

By Charles B. Hurd and George A. Moore, Jr.

The thermal dissociation of lithium hydride has been studied in this Laboratory for about two years. The method used has been that of Hurd and Walker [THIS JOURNAL, **53**, 1681 (1931)]. Great difficulty has been experienced in keeping the lithium inside the metal cylinder from passing through the metal and attacking the quartz tube. In only one run have we been successful. The results for that run are given here, since it has become necessary to discontinue work on the problem. The lithium was loaded into a nickel cylinder which then received a thin but smooth coating of cobalt by electrodeposition.

The pressures of hydrogen obtained were

Temp., °K.	782	870	871.5	922	926	953
p_{H_2}, cm.	0.010	0.185	0.175	0.730	0.780	2.67

The last figure is given by Guntz [*Compt. rend.*, **122**, 244 (1896); **123**, 694 (1896)] and falls slightly above our curve.

By plotting log p against reciprocal T, we have obtained a value of ΔH from the slope. If the reaction is assumed to be

$$2\text{LiH} = 2\text{Li} + \text{H}_2$$
$$\Delta H = 44{,}000 \pm 2000 \text{ cal.}$$

It is interesting to compare this value with the value obtained calorimetrically by Guntz and Benoit [*Ann. chim.*, **20**, 5 (1923)] of 43,600 calories.

The agreement between the values of ΔH obtained from our dissociation pressures and the calorimetric value of Guntz and Benoit would suggest that the dissociation proceeds as indicated.

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RECEIVED DECEMBER 31, 1934