$[Zn(NH_2OH)_2]^{++}$ is the most complex which exists in the solutions under investigation here. The finding that this ion is capable of existence is in agreement with the reports of the formulas for the solid coördination compounds and with the previous report of the existence of this ion in aqueous solution.

PULLMAN, WASHINGTON

# NOTES

## Determination of *n*- or *p*-Type Conductivity by the Effect Produced by Hydrogen Adsorption on Electrical Conductivity

BY LOUIS F. HECKELSBERG, GRANT C. BAILEY AND ALFRED CLARK

RECEIVED JULY 6, 1954

**Introduction.**—In the investigation of the electrical and catalytic properties of semi-conductors the determination of the mode of conduction—whether it is *n*-type or *p*-type—is of interest. At the present time the mode of conduction is determined quantitatively by measuring the Hall effect or qualitatively by the thermoelectric effect. As a result of observations made during an investigation of the electrical and catalytic properties of powdered metal oxides and sulfides, we have found another method which can be used for the qualitative determination of the mode of conduction of these materials.

This method involves the effect produced by adsorbed hydrogen on the electrical conductivity of these materials. We have observed in the case of the *p*-type semi-conductor chromium sesquioxide that its conductivity is drastically reduced as rapidly as hydrogen can come in contact with it. The converse effect was observed for the *n*-type semiconductor zinc oxide where the conductivity was drastically increased when hydrogen came into contact with it. As a result of these observations it was decided to check several additional semiconductors to see if this effect was of a general nature.

**Experimental Details.**—As an example of this method we shall describe the procedure followed for nickel oxide. The sample of nickel oxide was pretreated with oxygen at 500° for 12 hours in an apparatus previously described by the authors.[1] With prepurified nitrogen flowing over the nickel oxide its conductivity was measured as a function of temperature. At 300° hydrogen was introduced over the nickel oxide. This resulted in a rapid decrease in the conductivity of the nickel oxide of the order of about $10^{-3}$. After approximately one minute the conductivity began to increase as the nickel oxide was being reduced. This may mean that the nickel oxide on contact with hydrogen underwent a transition from *p*-type to *n*-type and ultimately to a metallic conductor. In the case of chromium sesquioxide where hydrogen does not materially reduce the oxide at 500° the conductivity decreases and remains extremely low.

**Results.**—The results for semi-conductors which we have tested or were tested by others and that exhibit this behavior are as follows: nickel oxide, chromium sesquioxide, stannous sulfide and chromia–alumina were classified as *p*-type semiconductors while titanium dioxide, zinc oxide, zinc sulfide, calcium oxide and tungsten sulfide were classified as *n*-type semi-conductors. The change produced by hydrogen on conductivity has been reported previously for stannous sulfide,[2] chromia–alumina[3] and for zinc oxide.[4] These results agree with the classification of these materials by Hall effect as reported in the literature.

In the case of insulators such as silica this effect was not observed.

The magnitude of change observed was found to vary from a ten-thousand-fold change for titanium dioxide to a threefold change for zinc sulfide.

The effect produced by hydrogen was found to be reversible. After the hydrogen contacted the semi-conductor the material's original conductivity could be restored by flushing the hydrogen out with nitrogen. The change produced on the electrical conductivity by the nitrogen flushing was much slower than the change produced when hydrogen contacted the semi-conductor.

### Discussion

Pretreatment of *n*-type semi-conductors, such as zinc oxide, with hydrogen results in an increase of electrical conductivity caused by an increase in lattice defect concentration. These defects are formed by the oxygen or sulfur combining chemically with the hydrogen leaving a cation-excess material. The increase observed by reduction with hydrogen is slow compared to the rate of increase observed when hydrogen is adsorbed on a semiconductor in an inert atmosphere.

A plausible explanation of the mechanism involved in reducing the current flow in *p*-type semiconductors is as follows. When the hydrogen comes into contact with a *p*-type semi-conductor it dissociates and ionizes. The protons are adsorbed on the surface while the electrons enter the lattice and combine with positive holes. Filling the positive holes—which are considered to be the current carriers in *p*-type semi-conductors—reduces the current flow.

The mechanism involved in the increase in current flow observed when hydrogen comes into con-

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(1) Heckelsberg, Clark and Bailey, "A Correlation between Lattice Defects and Catalytic Activity of Zinc Oxide" presented before a Symposium on Mechanisms of Homogeneous and Heterogeneous Hydrocarbon Reactions at the Kansas City Meeting of the American Chemical Society, March 29 to April 1, 1954.

(2) J. S. Anderson and M. C. Morton, *Proc. Royal Soc. London*, **184A** 83 (1945).

(3) P. B. Weisz, C. D. Prater and K. D. Rittenhouse, *J. Chem. Phys.*, **21**, 2236 (1953).

(4) F. Stockmann, *Z. Physik*, **127**, 563 (1950).

tact with *n*-type semi-conductors may be explained as follows. When the hydrogen comes into contact with an *n*-type semi-conductor it dissociates and ionizes as in the mechanism previously described. The protons are adsorbed on the surface and the electrons enter the solid. The electrons may enter the conduction band allowing more electrons to flow which result in the observed conductivity increased.

The magnitude of the change observed is probably a function of both the surface area of the semiconductor and—in the case of *p*-type semiconductors—the number of positive holes present.

This method for the determination of the mode of conduction has a distinct advantage in its applicability to powdered semi-conductors. The difficulties encountered in making Hall effect or thermoelectric measurements on powdered materials are well known.

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## Thermodynamics of Ionization of 2,2'-Bipyridine and Analogs in Water and in 50% Aqueous Dioxane

BY THOMAS R. HARKINS AND HENRY FREISER

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The acid dissociation constants of a number of substituted pyridine compounds were determined potentiometrically in a 50% by volume dioxane-water mixture. These measurements are of interest in attempting to correlate acid strength and the nature of the solvent.

### Experimental

2-(2-Pyridyl)-benzimidazole was prepared from α-picolinic acid and *o*-phenylenediamine. 2-(2-Pyridyl)-imidazoline was prepared from α-picolinic acid and ethylenediamine. 2-(2-Pyridyl)-benzoxazole was prepared from α-picolinic acid and *o*-aminophenol. The above preparations have been described in detail elsewhere.[1]

C.P. 2,2'-bipyridine was obtained from the Fisher Scientific Company. It melted at 69.0–69.5° after recrystallization from petroleum ether (literature m.p. 69.5°).

Potentiometric measurements of *p*H were made using the Beckman Model G *p*H meter equipped with a glass-saturated calomel electrode pair. The preparation of standard acid and base, purification of 1,4-dioxane, and a description of the titration apparatus and procedure have been given elsewhere.[2]

**Calculations.**—Correction factors for the *p*H readings at each temperature, determined in a manner previously described,[3] were used to convert *p*H readings to hydrogen ion concentrations (not activities).

The acid dissociation constants listed are for the typical reaction

$$BH^+ \rightleftarrows B + H^+$$

where $BH^+$ is the conjugate acid of the base B.

The thermodynamic quantities given pertain to the reverse (association) reaction and have been calculated in the usual manner.

**Results.**—The acid dissociation constants of the various compounds in 50% by volume dioxane are given in Table I.

TABLE I

ACID DISSOCIATION CONSTANTS OF VARIOUS REAGENTS IN 50% BY VOLUME DIOXANE AT 25°

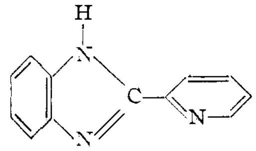
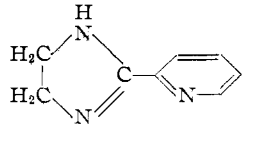
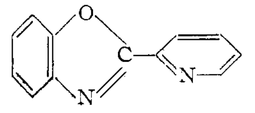
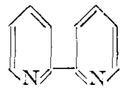
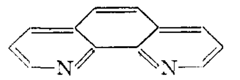
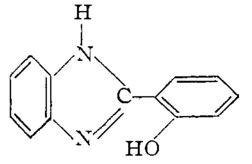
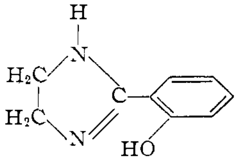
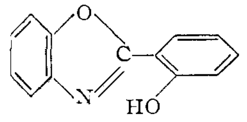
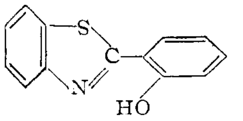
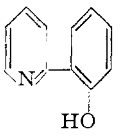
| Compound | Structure | $pK_a$ |
|---|---|---|
| (I) 2-(2-Pyridyl)-benzimidazole |  | 3.44 |
| (II) 2-(2-Pyridyl)-imidazoline |  | 8.54 |
| (III) 2-(2-Pyridyl)-benzoxazole |  | <2 |
| (IV) 2,2'-Bipyridine |  | 3.33 |
| (V) *o*-Phenanthroline |  | 4.96[4] |
| (VI) 2-(*o*-Hydroxyphenyl)-benzimidazole |  | 4.28[3] |
| (VII) 2-(*o*-Hydroxyphenyl)-imidazoline |  | 6.81[3] |
| (VIII) 2-(*o*-Hydroxyphenyl)-benzoxazole |  | <2[5] |
| (IX) 2-(*o*-Hydroxyphenyl)-benzothiazole |  | <2[5] |
| (X) 2-(*o*-Hydroxyphenyl)-pyridine |  | 2.69[3] |

Table II is a summary of the various quantities determined.

The constants as reported herein are not true thermodynamic constants since no activity coef-

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[1] J. L. Walter and H. Freiser, *Anal. Chem.*, **26**, 217 (1954).

[2] H. Freiser, R. G. Charles and W. D. Johnston, THIS JOURNAL, **74**, 1383 (1952).

[3] W. D. Johnston and H. Freiser, *Anal. Chim. Acta*, **11**, 201 (1954).

[4] T. S. Lee, I. M. Kolthoff and D. L. Leussing, THIS JOURNAL, **70**, 2348 (1948).

[5] R. G. Charles, Ph.D. Thesis, University of Pittsburgh, 1952.