Summary

1. The oxidation-reduction potential of the system azobenzene-disulfonate–hydrazobenzene–disulfonate has been measured in 0.2 *N* hydrochloric acid. The system is strictly reversible and the usual electrochemical equations are applicable.

2. The rate of *irreversible* reduction of certain azo dyes has been found to be essentially independent of the dilution, indicating that the rate-controlling step is a monomolecular reaction.

3. The reduction of the type of azo dye studied (*ortho*- or *para*-hydroxy-azo compound) involves complete cleavage of the molecule even with very "mild" reducing agents. The potential of the reagent and *not* the specific nature of the reagent determines the speed of this irreversible reduction.

4. The apparent reduction potentials (A. R. P.) of 27 carefully prepared and purified hydroxy-azo dyes have been measured at 23° in 0.2 *N* hydrochloric acid. The nature of the aromatic nucleus carrying the hydroxyl group seems to be the most important factor in determining the A. R. P. No exception to the validity of the electrochemical formulation of *this type of irreversible reduction* has been found.

5. A mechanism has been suggested that is in accord with all the qualitative information available. Certain approximate equations based on this mechanism lead to values for the relative rates of reduction with two reagents that are of the same order of magnitude as those found experimentally.

CAMBRIDGE, MASSACHUSETTS

NOTE

Benzohydrylamine from Benzophenone Oxime.—This year, for at least the fourth time,[1] it was reported that benzophenone oxime may be reduced to benzohydrylamine by sodium and alcohol. The other three accounts in chronological order are given by Noyes,[2] by Konowalow[3] and by Jones and Hurd.[4]

Beilstein fails to mention the preparation of benzohydrylamine by this method. Undoubtedly, therefore, when it is again needed in an investigation, this method of preparation will again be "rediscovered" and reported in the literature. Quite independently about four years ago, the author learned of Professor Noyes' priority. When approached about it at that time, Dr. Noyes graciously waved aside the suggestion that the omission of reference to his article be rectified in a Note. It is now sub-

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[1] Billon, *Compt. rend.*, **182,** 470 (1926).

[2] Noyes, *Am. Chem. J.*, **15,** 545 (1893).

[3] Konowalow, *Chem. Zentr.*, **72,** 1002 (1901).

[4] Jones and Hurd, THIS JOURNAL, **43,** 2438 (1921).

mitted, however, in the hope that others will not continue to make the same error.

Contribution from the Chemical Laboratory
of Northwestern University
Evanston, Illinois

Charles D. Hurd

Received July 21, 1926
Published September 4, 1926

NEW BOOKS

A Condensed Collection of Thermodynamic Formulas. By P. W. Bridgman, Professor of Physics in Harvard University. Harvard University Press, Cambridge, 1925. Humphrey Milford, Oxford University Press, London. 34 pp. 24 × 16 cm. Price $1.50.

The ten quantities commonly employed in thermodynamic argument, namely, p, t, v, s, dQ, dW, E, H, Z and Ψ (defined in Table I), give rise to 720 first derivatives of the type $[\partial x_1/\partial x_2]_{x_3}$, of which any three are independent, and among which more than ten billion relations exist. Any one of these relations could be obtained at once from a table giving each of the 720 derivatives in terms of the same set of three, but a much smaller table will suffice. The smallest would be one of eight entries, giving the total differentials of eight of the quantities with respect to two of them selected as independent variables, but its use would involve algebraic elimination of the ratio of the two independent differentials by means of the equation $dx_3 = 0$. Professor Bridgman's Table II (t and p independent) which is based on the relation $[\partial x_1/\partial x_2]_{x_3} \equiv [\partial x_1/\partial a_1]_{x_3}/[\partial x_2/\partial a_1]_{x_3}$, enables any one of the 720 to be written down at once; it contains 90 entries of which 45 are duplicates, double entry being employed to facilitate reference.

The 65,000 second derivatives can be obtained by purely formal differentiation from the 21 entries of Table III (t and p independent). Table IV gives the first derivatives for systems such as water in equilibrium with steam, where p is a function of t; v and t are here chosen as independent variables. Then come eight "examples of the use of the tables"—problems not at all of the conventional type; and finally a section on the extension of the tables to systems in which pressure is not the only mechanical variable, with examples involving sudden tension of steel, electromotive force and surface tension.

In the Introduction, the method of constructing the tables is made clear; the effect of the whole book on the student should be to convince him that the mathematical relations which take up so much space in conventional textbooks of thermodynamics can all be obtained "in an entirely routine way, without any tricks of manipulation," and that the real thermodynamic difficulties are those involved in clearly understanding what the problem is, and in expressing it in the language of the mathematical theory.

W. Lash Miller