tremely clear and gives the impression of having been very carefully prepared. In this regard, the reviewer would have only one suggestion—that greater use might be made of graphical illustrations of the type so convincingly employed in Gurney's book. For example, for the case of hydrogen, a plot of $-1/r+l\ (l+1)/2r^2$ for various values of l, with the radial eigenfunctions superposed on the respective energy levels, renders very plausible the coincidences of these levels in this case and the lack of coincidences if the central field departs in the least from the Coulomb value.

Finally one might remark that the typography of the book is very pleasing and should serve as a model for other American texts. It approaches the English and German books for beauty of format, avoiding the ugly fat radicals, the huge thick integral signs and the black summation signs which so clutter up the pages of most American physics books; and goes far toward making the cuts and equations fit into and become an attractive part of the page instead of standing out like trees in the middle of South Dakota. One even finds (p. 515) an equation pleasantly protruding into the margins, a thing unheard of in American typography. One still finds, however, too much blank space around short equations (*e.g.*, p. 355).

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USES OF CHEMICALS

Uses and Applications of Chemicals and Related Materials. By THOMAS C. GREGORY. vi + 665 pp. New York: Reinhold Publishing Corporation, 1939. $10.00.

TWENTY-FIVE years ago, when we entered the World War, it became necessary for the Secretary of War to commandeer all supplies of various essential chemicals and allocate them according to our war needs. This allocation was made with the assistance and upon the advice of the Chemicals and Raw Materials Division of the War Industries Board. Even in a group of experts of this kind, it was not always possible to find men who were familiar with all the varied uses of a well-known chemical or the proportionate amounts required by various industries. For example, those not specialists had no idea of the quantity of arsenious acid required by the glass manufacturers or of saccharin by the tobacco industry.

Such a book as the one under review would have been very helpful, and it seems to the writer, therefore, that its appearance is opportune, now that we may be facing problems similar to those of 1917–18.

The volume describes, in alphabetical order, the current industrial uses, potential applications and sales possibilities of 5,167 chemicals and related products. It is based upon surveys made over a period of 15 years and published in the *Oil, Paint and Drug Reporter,* under the titles *"Where You Can Sell"* (up to and including the issue of September 9, 1935) and "Industrial Uses of Chemicals and Related Materials" (from the issue of September 16, 1935, onwards). The uses are classified under appropriate sub-headings, synonyms and foreign names are given, and patent references are frequent. At the close of the volume is an extensive "Synonyms and Cross References" index. The book is an encyclopedia of useful information.

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SPECIAL ARTICLES

THE SEMIQUINONE RADICALS OF METHYLENE BLUE AND RELATED DYESTUFFS

THE occurrence of free radicals, designated as semiquinones, as intermediate reduction products of reversibly reducible dyestuffs, was considered as an exceptional case when it was first discovered for pyocyanine and some related phenazin derivatives. Meanwhile, these radicals have been shown to exist for all the more familiar classes of reversible dyestuffs, except for the thiazines and oxazines. Since methylene blue, a thiazine, is the most frequently used dyestuff in biochemical research, the failure of any report about the existence of its semiquinone was somewhat puzzling. This problem is especially important with regard to the hypothesis of compulsory univalent reduction[1] which claims that no oxidation or reduction can proceed with any appreciable speed otherwise than in univalent steps. The faculty of acting as a catalyst for oxidation, especially respiration, should accordingly also be correlated with the faculty of the catalyst to be either a univalent oxidation-reduction system, such as the iron porphyrin compounds; or if it be a bivalent system, to be reducible in two successive, although more or less overlapping steps.

This note is to give a preliminary report on the discovery of the hitherto unknown semiquinones of these dyestuffs.

According to the theory on stability of free radicals, based on the theory of reasonance, the authors came to the conclusion that the radicals of thiazines should be most stable in a very strongly acid solution. This expectation has been verified by experiment. It is easiest to demonstrate the radical of thionin (Lauth's

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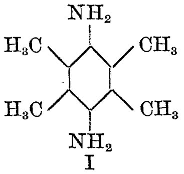
[1] L. Michaelis and C. V. Smythe, *Ann. Review Biochemistry,* 1938.

violet). When a solution of the dye in $20\ NH_2SO_4$ is reduced, say by $TiCl_3$, the free radical appears as intermediate step of reduction. It is yellow and exhibits a series of distinct absorption bands in the blue part of the spectrum, recalling the bands of the triphenylmethyl radical. Analyses of the potentiometric titration curves, obtained by especially adapting the technique to the unusually high acidity of the solutions, showed that this yellow compound is a free radical, not a polymerized compound. The separation of the two steps rapidly diminishes with decreasing acidity but never vanishes entirely. Even in neutral solution an analysis of the potentiometric titration curves reveals that the dye solution in its half-reduced state contains the semiquinone to an extent that may be estimated as between 5 per cent. and 10 per cent. of the total dye. In such solutions the radical can no longer be detected, optically, for two reasons. Firstly, a few per cent. of a light yellow compound escapes optical detection when mixed with the large excess of the deeply colored blue dyestuff itself; secondly, it can be assumed from theoretical arguments that the radical is in a different state of ionization in extremely acid, than in less acid or neutral solution, and that the form existing in neutral solution should exhibit an extremely slight absorption, if any at all, in the visible range of wave-lengths.

The only difference between thionin and methylene blue is that the latter requires still a somewhat higher acidity than thionin in order to obtain the same degree of separation of the two steps of oxidation. The absorption spectrum of the methylene blue radical is quite similar to that of thionin.

Then, these dyestuffs, after all, fit very well into the theory of compulsory univalent oxidation. Any bivalent oxidation reduction system must be capable of forming a semiquinone radical to a measurable extent in order to behave as a reversible system; and any organic dyestuff can act as a catalyst for sluggish oxidations only by intermediation of the radical.

Another experiment should be mentioned with regard to the assertion that the catalytic action of a dye depends on its faculty to form a semiquinone radical. It has been shown recently,[2] that the first oxidation product of diamino durene (I) is a free radical, analogous to those designated as Wurster's dyes. It has been shown furthermore that any methylation at the amino groups destroys the faculty of forming this radical. In the latter case, the benzene ring, the two N atoms and all the atoms attached to the two N atoms are prevented from lying in one plane due to steric hindrance of the voluminous side chains. The steric possibility of such a coplanar arrangement is requisite for establishment of resonance. For this reason the methylated compounds can not form a radical. Now, the unmethylated compound increases respiration of erythrocytes to approximately the same extent as does methylene blue, but the methylated compound has no catalytic effect at all.



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[2] L. Michaelis, M. P. Schubert and S. Granick, *Jour. Am. Chem. Soc.*, 61: 1981, 1939.

THE METABOLISM OF GLUTATHIONE[1]

INVESTIGATIONS concerned with the fate of glutathione in the living organism have dealt almost exclusively with the behavior of the tripeptide as an SH-carrier. The methods used have been based on determination of the SH-group.

Little attention has been paid to the possibility that the combination of the three amino acids, glycine, cystine and glutamic acid in this peptide, GSH, has some special significance aside from its function as an SH-carrier. It is striking that these three amino acids are the ones which are found combined with compounds other than amino acids in the mammalian body, *e.g.,* bile acids and the products of detoxication. One of us has previously suggested that GSH may act as an amino acid donor in the formation of those compounds.[2] In support of this conception a decrease in the substances titratable with iodine in human blood was found after intake of phenyl acetic acid which is excreted as phenyl acetyl glutamine.[3]

It is now possible by the use of the isotope technique to follow directly the fate of the amino acids of GSH and to estimate its rate of turnover. Glycine containing 1.18 atom per cent. N^{15} excess was administered to rats. After two hours the concentration of N^{15} in the GSH of the liver and intestine, together with the N^{15} content of the protein glycine and NPN of these organs, was determined. The GSH was isolated as follows: The frozen and ground livers were extracted with metaphosphoric acid. The GSH was precipitated as the cuprous compound and purified by reprecipitation. The method of isolation yields about 16 mg of copper glutathione per rat liver, correspond-

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[1] This work was made possible through a grant from the Friedsam Fund donated to the Division of Child Neurology, Neurological Institute, New York, N. Y.

[2] H. Waelsch, *Arch. exper. Path. u. Pharm.*, 156: 356, 1930.

[3] H. Waelsch and E. Weinberger, *ibid.*, 156: 370, 1930.