

be stable with respect to the first. Since the molecular geometry is similar, both electronic structures may contribute, with the second predominating. Burg's results support a high predominance of the second structure.

Furthermore, the bridge model is capable of including the borine-complex theory of the base reactions of B_2H_6 . A molecule with unshared pair, $:R$, ($:NH_3$, $:N(CH_3)_3$ ethers, etc.) may attack B_2H_6 from the back side of one of the bridge

bonds, leading to $H-\overset{H}{\underset{H}{|}}{B}-\overset{H}{\underset{R}{|}}{B}-H$ (I). If $:R$ con-

tains an acidic hydrogen, (I) may be quickly converted to $H-\overset{H}{\underset{H}{|}}{B}-R'-\overset{H}{\underset{H}{|}}{B}-H$ ($R' + H^+ = :R$) plus

$(H:R)^+$. (This appears to happen with NH_3 but not with $N(CH_3)_3$.) If R does not lose a proton readily, then I may be attacked by another $:R$,

leading to $H-\overset{H}{\underset{H}{|}}{B}-R$.

The proposed attack of B_2H_6 by $:R$ resembles the attack in a Walden inversion, but activation energies should be much lower, rates much higher, since the serious repulsive terms in Walden inversion arise from completed electron shells. A tetrahedral configuration about boron is not objectionable in the above process. It would appear that the bridge model is as satisfactory as any proposed for the interpretation of the reactions B_2H_6 with ammonia and amines.

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R. E. RUNDLE

RECEIVED MAY 9, 1947

ENRICHMENT OF C^{13} AND O^{18} BY A COUNTER-CURRENT GASEOUS EXCHANGE PROCESS USING THERMAL DIFFUSION

Sir:

Using the exchange reaction $C^{13}O + C^{12}O_2 = C^{12}O + C^{13}O_2$ in conjunction with a thermal diffusion column, an enrichment of both C^{13} and O^{18} has been effected. This system is unique in that the thermal diffusion column establishes a counter-current flow of the two gases between which the exchange takes place. The hot element produces the thermal diffusion and also serves as a catalytic surface for the exchange.²

The column consisted of a 1.0-cm. diameter water-jacketed tube 110 cm. long, at the top of which was connected a 20-liter reservoir of carbon dioxide at atmospheric pressure. Platinum filaments were found more satisfactory than either nichrome or tungsten. A hot zinc converter and a thermal conductivity cell at the bottom of the

(1) See Urey and Greiff, *THIS JOURNAL*, **57**, 321 (1935), and Brandner and Urey, *J. Chem. Phys.*, **13**, 351 (1945).

(2) Clusius and Dickel, *Z. physik. Chem.*, **B44**, 397 (1939).

column had a total volume of about 200 cc. Total reflux was obtained by recirculating the carbon dioxide through the converter. The thermal conductivity cell indicated that practically complete conversion to carbon monoxide took place, thus establishing the condition of total reflux. By measuring the buildup rate of carbon monoxide in the reservoir, its transport up the column was found to be approximately 1.0 cc./minute. The carbon monoxide rising up the column undergoes isotopic exchange with descending carbon dioxide. Since the exchange reaction favors the transfer of C^{13} and O^{18} to carbon dioxide, the heavy carbon and oxygen concentrate at the bottom of the column.

The data for three of the experiments are summarized in Table I. The enrichments were measured with a Nier type mass spectrometer to ± 1.0 in the percentage enrichment.

TABLE I

Expt.	Filament	Current, amps.	T, °C. (approx.)	Time, days	% Enrich. C^{13} , O^{18}
1	Nichrome	2.75	700	2.0	4.0 ..
				3.0	6.5 ..
				4.0	9.5 ..
				5.0	10.5 ..
				7.0	14.0 ..
2	Platinum	3.2	800	1.0	9.0 9.0
				2.0	9.0 ..
3	Pt + H_2O	3.2	800	1.2	14.0 ..
				2.2	23.5 18.0

Since water and hydrogen have been shown¹ to be effective catalysts for the exchange, a small supply of water was introduced at the bottom of the column in experiment 3. The results show a higher isotope enrichment.

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T. I. TAYLOR
R. B. BERNSTEIN

RECEIVED JUNE 23, 1947

SPECTROPHOTOMETRIC INVESTIGATION OF THE INTERACTION BETWEEN IONS OF DIFFERENT OXIDATION STATES OF AN ELEMENT

Sir:

It has often been remarked that systems containing an element in two different oxidation states or in a "mixed" oxidation state sometimes manifest abnormally deep and intense coloration.¹

The concentration dependence of this phenomenon has been investigated with a Beckmann spectrophotometer for mixed solutions of tri- and pentavalent antimony in concentrated hydrochloric acid; in addition, the hitherto unreported occurrence of such an "interaction absorption" for mixed stannous-stannic solutions in concentrated hydrochloric acid has been observed.

The figure illustrates the absorption spectra of such mixed solutions and of the components. The optical density of interaction color in the antimony solutions is proportional to the product

(1) E. g., Biltz, *Z. anorg. allgem. Chem.*, **127**, 169 (1923).

of the concentrations of Sb(III) and Sb(V). The table exhibits some of the data supporting this statement. Formally this implies that the

ABSORPTION OF $\lambda = 470 \text{ m}\mu$ BY MIXED Sb(III), Sb(V) SOLUTIONS

C(Sb(III))	0.217	0.157	0.0678	0.251	0.102	0.399
C(Sb(V))	.0868	.143	.227	.250	.399	.109
D/C _{III} C _V	7.70	7.83	7.15	8.23	8.06	7.57

absorbing species is a dimeric complex containing one Sb(III) and one Sb(V), and not a monomeric complex of Sb(IV). This result is in agreement with the known properties of crystals, such as Rb_2SbCl_6 , containing "tetravalent antimony," in which equivalent SbX_6 octahedra of average charge -2 mutually interact in such a way as to give a diamagnetic crystal.² That the concentration of such a dimeric complex in solution is small is suggested by the comparison of the weak color of the mixed solutions with the intense black color of crystals like Rb_2SbCl_6 .

Further investigations of this phenomenon for other oxidation couples and other coordinating

(2) Jensen, *Z. anorg. allgem. Chem.*, **252**, 317 (1944).

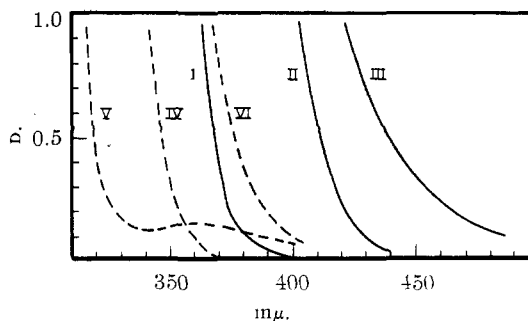


Fig. 1.—Absorption spectra of: I, 0.30 *f* SbCl_3 , II, 0.28 *f* SbCl_3 , III, 0.15 *f* SbCl_3 , 0.14 *f* SbCl_5 , IV, 0.84 *f* SnCl_2 ; I-IV in 11.3 *f* HCl ; V, 0.84 *f* SnCl_2 in 10.9 *f* HCl ; VI, 0.42 *f* SnCl_2 , 0.42 *f* SnCl_4 in 11.2 *f* HCl .

anions, and studies of the radioactive exchange properties of such systems are in progress.

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RECEIVED JULY 3, 1947

NEW BOOK

Vitamins and Hormones. Advances in Research and Applications. Volumes III and IV. Edited by ROBERT S. HARRIS and KENNETH V. THIMANN, Massachusetts Institute of Technology and Harvard University, Cambridge, Mass. Academic Press, Inc., 125 East 23rd Street, New York, N. Y., 1945 and 1946. Vol. III, xv + 420 pp. Illustrated. 15.5 × 23.5 cm. Price, \$6.50. Vol. IV, xvii + 406 pp. Illustrated. 15.5 × 23.5 cm. Price, \$6.80.

Volume III of *Vitamins and Hormones* contains nine reviews which were written by fourteen investigators. Nine of the authors live in the United States, three in England and two in Palestine. The editors are to be congratulated, and more than the usual appreciation is due the authors for the efforts required to prepare these papers during the war period.

The articles on vitamins are reports of progress in work with a large number of vitamins studied under a wide range of conditions. The first four are "The Interrelation of Vitamins," by T. Moore, "The Synthesis of B Vitamins by Intestinal Bacteria," by V. A. Najjar and R. Barrett, "Sulfonamides and Vitamin Deficiencies," by F. S. Daft and W. H. Sebrell, and "Manifestations of Prenatal Nutritional Deficiency" by J. Warkany. For those in the field of growth and nutrition, the reviews should be a welcome compilation of the results which have been published in many journals and in several countries. These reviews assemble the many advances, not only with the references to the literature, but with a closely joined report and discussion of the work. The article by B. C. J. G. Knight on "Growth Factors in Microbiology—Some Wider Aspects of Nutritional Studies with Micro-organisms" is the most extensive, and although the subject matter is divided into fourteen independent sections, the reader's interest is sustained throughout.

E. C. Dodds in a report entitled "Possibilities in the Realm of Synthetic Estrogens" warns against too great optimism those who would like to hasten advances in the field of pharmacology made possible by the strong tool of organic chemistry. Diethylstilbestrol is the outstanding example of what can be done to simplify a natural estrogen; however, before a new start is made to do likewise with another hormone, the short essay by Dr. Dodds should be read.

The subject of "Chemistry of Anti-pernicious Anemia Substances of Liver" is well reviewed by Y. SubbaRow, A. B. Hastings and M. Elkin. The high hopes of 1926-1927 have been tempered. However, the authors state "the amount of material needed by the patient per day has decreased from 400 g. to less than 1 mg. Such progress makes it reasonable to expect the isolation and identification of the active material to be an attainable objective."

What is known of "The Mechanism of Action and Metabolism of Gonadotropic Hormones in the Organism" has been presented by B. Zondek and F. Sulman. Several questions are left unanswered, and it probably will require more investigation before the final chapter can be written.

The last in order of the reviews is "The Role of Acetylcholine in the Mechanism of Nerve Activity" by D. Nachmansohn. From the meager beginning, when traces of acetylcholine were first separated from the surviving heart, a hypothesis has been suggested for the explanation of the mechanism of the nerve impulse. Regardless of what must be added or taken away before the final revision of the subject, the author has marshaled the pertinent facts and creates in the reader the desire to know more about the formation, hydrolysis and pharmacologic action of acetylcholine.

Seven of the nine reviews in volume IV were prepared by investigators who live in the United States; one was