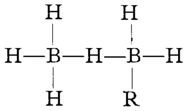
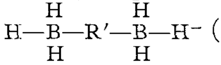
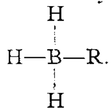
be stable with respect to the first. Since the molecular geometry is similar, both electronic structures may contribute, with the second predominating. Burg's results support a high predominance of the second structure.

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

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.

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA 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[1] $C^{13}O + C^{12}O_2 = C^{12}O + C^{13}O_2$ 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 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}	% Enrich. 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 shown[1] 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.

COLUMBIA UNIVERSITY T. I. TAYLOR
NEW YORK, N. Y. 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] 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).

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