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The Compressibilities of Certain Molten Alkali Silicates and Borates

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The compressibilities of the systems Na_2O-SiO_2, K_2O-SiO_2 and Li_2O-B_2O_3 have been measured. The measurements lend support to a model of the liquids containing SiO_2 "iceburgs" at low M_2O content and discrete Si or B containing oxy-anions at high M_2O concentrations.

I. Introduction

Compressibility measurements[1] yield structurally informative data for molten silicates, as illustrated by Bloom and Bockris.[2] In this paper, an investigation of the compressibility of certain alkali silicate and borate systems, as a function of composition and temperature, is described.

II. Experimental

Sound velocity measurements were made by the ultrasonic method of Richards, Brauner and Bockris,[1] in a way similar to that described by Bloom and Bockris,[2] whose apparatus was modified as follows.

Current input and element supports were introduced through the bottom plate of the furnace, instead of through the top. This allows the concentricity of furnace tube and radiation shields to be visually controlled, and it is not then necessary to disassemble the furnace after each experiment. The mechanism for the movement of the upper Alundum rod was redesigned. The rod is now fixed in a metal tube with a mechanism which gives a three-point adjustment in two parallel planes perpendicular to the axis of the rod (*cf.*, Bloom and Bockris[2]). The metal tube can rotate in a movable rigid clamp, controlled by a screw movement and rubber brake. The lower Alundum rod supporting the crucible remains stationary during the measurements. Axial radiation shields were mounted on this rod to reduce the temperature gradient below the crucible. Radiation losses upwards were reduced by using shorter crucibles (3" high) and a ceramic plug.

To increase contact pressure between the molybdenum crucible and the bottom of the Alundum rod, the top of the crucible was weighted with a plug of hard-fired Alundum cement, with channels for the upper Alundum rod and thermocouple, and weighing 160 g. or more. Further stabilization of the patterns observed on the oscilloscope was obtained by application of "glue," *i.e.*, $Na_2O \cdot SiO_2$, or, at lower temperatures, B_2O_3 glasses, to the contact area. Excess of the glue was squeezed out at high temperature by applying pressure to the crucible bottom with the upper Alundum rod.

The corrosion of the Alundum rods is rapid at high alkali (particularly Li) contents and causes the positions of the minima on the oscilloscope screen to become indefinite, possibly because of scattering brought about by means of particles introduced into the melt.

Attempts were made to eliminate corrosion by covering the end of the Alundum rod with flat-bottomed, tight-fitting sheaths of molybdenum, 0.006" thick. Corrosion was thereby eliminated, but the loss in strength of the sound wave at the rod–molybdenum interface caused the interference patterns to become too weak to be of use. This position was not improved by the use of high temperature glues. Reduction in contamination of the melts was obtained by using molybdenum thimbles for thermocouple sheaths.

Alundum and mullite rods at temperatures above 1350° will not pass signals which could be measured with the available apparatus. Globar rods absorb too greatly to be of use even at room temperature.

Measurements were made in the system Na_2O-LiO_2, K_2O-SiO_2 and Li_2O-B_2O_3. The mixtures were prepared from A.R. carbonates, ground silica and A.R. HBO_3; the silica sand was 99.9% SiO_2. It was ground, digested with concentrated HCl, washed with distilled water and dried. The mixtures were premelted in a Pt-crucible (electric furnace), poured, broken, remelted (carbon tube furnace) and fired at 1300–1500°, depending on volatility.

Velocity measurements were made at temperature intervals of 20–30°. The constancy of temperature during the readings was usually better than $\pm 2°$ and never worse than $\pm 5°$ 20% Rh/Pt-40%Rh/Pt thermocouples immersed in the melt were used for the measurement of temperature.

III. Results

The numerical results are summarized in Tables I and II and in Figs. 1–6.

IV. Discussion

(1) **General.**—An "iceburg" form of the structure of liquid silicates has been described[3] (see also refs. 4, 5). Increasing addition of "network modifying" oxide (*e.g.*, Na_2O at low concentrations) into the oxygen lattice structure of a network former, *e.g.*, Si, causes the initially random distribution of the modifier cations and the broken bridges to become a microheterogenous type of structure, in which the network modifier cations and broken bridges concentrate into certain regions of the melt to satisfy the maximum coördination requirements of the Na^+ cations. The tendency to form these two different structures (which may be regarded as being the precursors of the macroheterogeneous structure giving rise to immiscibility) increases with increasing field strength of the modifier cation, since this makes greater the energy gained from closer packing, which has to counteract the increase in entropy which would result from the alternative possibility of random distribution of modifier cation and broken bridges. With increase of temperature, an increase of tendency towards the random distribution type of structure should occur, and, as a limit at high temperatures, the classical random network model[6,7] of the silicate lattice is probably approached. As the ratio M_2O/SiO_2 is increased, the microheterogenous structure becomes gradually one of "discrete anions"[8] interconnected by network modifying cations.

(2) **Compressibility of the Alkali Silicates.**—For pure vitreous silica, $d\beta_s/dT$ is negative[7] up to 800°. In a continuous network structure having short-range order only (*e.g.*, that in fused silica), the factors affecting compressibility are: (i): decrease of interatomic distance, without configura-

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[1] N. E. Richards, E. J. Brauner and J. O'M. Bockris, *Brit. J. Applied Physics*, **VI**, 207 (1955).

[2] H. Bloom and J. O'M. Bockris, *J. Phys. Chem.*, **61**, 515 (1957).

[3] J. O'M. Bockris, J. W. Tomlinson and J. L. White, *Trans. Faraday Soc.*, **52**, 999 (1956).

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[7] B. Warren and J. Biscoe, *J. Am. Ceram. Soc.*, **21**, 49, 259 (1938).

[8] J. O'M. Bockris, J. D. Mackenzie and J. A. Kitchener, *Trans. Faraday Soc.*, **51**, 1734 (1955).

TABLE I

SOUND VELOCITIES (v) AT 1 MC FREQUENCY

System Na_2O-SiO_2: Mole % Na_2O

16.1		20.5		25.0		25.0		33.3	
t, °C.	v m/s	t	v	t	v	t	v	t	v
				Mole % Na_2O					
1302	2536	1195	2557	1106	2590	1112	2559	1003	2776
1341	2517	1295	2529	1205	2522	1205	2576	1109	2693
				1290	2532	1298	2565	1199	2615
								1288	2603

42.9		50.0		55.5		60.0	
t	v	t	v	t	v	t	v
1154	2739	1108	2801	1040	2741	1200	2540
1251	2681	1193	2754	1153	2670		
1348	2646	1303	2679	1255	2622		

System K_2O-SiO_2: Mole % K_2O

20.0		25.0		33.3		40.0		44.4		50	
t, °C.	v m/s	t	v	t	v	t	v	t	v	t	v
1207	2434	1201	2357	1094	2334	1054	2342	1005	2298	990	2503
1278	2374	1247	2317	1202	2242	1131	2286	1081	2247	1063	1989
1335	2348	1291	2285	1270	2202	1193	2299	1157	2193	1143	1936
		1359	2256	1347	2147	1276	2207	1233	2157	1221	1895
						1315	2168	1285	2111	1299	1836

System Li_2O-B_2O_3: Mole % Li_2O

0		9.1		16.7		20.0		25.0		33.3		50.0	
t, °C.	v m/s	t	v	t	v	t	v	t	v	t	v	t	v
		794	1332	746	1650	806	1809	787	1952	935	2029	883	2452
896	958 ± 50	903	1319	821	1619	908	1741	849	1910	1013	1991	943	2422
981	1002	992	1301	895	1594	1018	1682	890	1017	1083	1956	1011	2403
1062	1010	1094	1305	963	1572	1115	1639	937	1862	1153	1944	1094	2373
1142	1042	1200	1301	1040	1548	1206	1602	1034	1798				
1218	1051			1135	1524								
				1206	1500								

TABLE II

ISOTHERMAL DATA BY INTERPOLATION

System Na_2O-SiO_2

Mole % Na_2O	16.1	20.0	25.0	33.3	42.9	50.0	55.5	60.0
1200°								
Velocity, m/s[a]		2555	2560	2630	2710	2750	2655	2540
Density, g./cm.^{3}		2.242	2.247	2.249	2.250	2.250	2.240	2.230
Adiab. compress. cm.^{2}/dyne		6.83	6.80	6.43	6.05	5.88	6.33	6.95×10^{-12}
1300°								
Velocity	2563	2525	2550	2555	2660	1680	2600	..
Density[a]	2.228	2.232	2.232	2.227	2.224	2.220	2.209	..
Adiab. compress.	6.98	7.03	6.90	6.88	6.35	6.28	6.70×10^{-12}	

System K_2O-SiO_2

Mole % K_2O	20.0	25.0	33.3	40.0	44.4	50.0
1200°						
Velocity, m/s[a]	2435	2355	2255	2245	2170	1905
Density, g./cm.^{3a}	2.215	2.209	2.207	2.198	2.185	2.164
Adiab. compress., cm.^{2}/dyne	7.62	8.17	7.91	9.03	9.72	12.7×10^{-12}
1300°						
Velocity	2370	2285	2180	2180	2100	1835
Density[a]	2.199	2.188	2.179	2.166	2.150	2.126
Adiab. compress.	8.10	8.75	9.66	9.72	10.55	14.0×10^{-12}

System Li_2O-B_2O_3

Mole % Li_2O	0	9.1	16.7	20.0	25.0	33.3	50.0
900°							
Velocity, m/s	975	1319	1595	1745	1890	2045	2445
Density, g./cm.^{3b}	1.521	1.720	1.862	1.905	1.957	1.98(6)	1.905
Adiab. compress., cm.^{2}/dyne	69.2	33.4	21.1	17.2	14.3	12.05	8.80×10^{-12}
1000°							
Velocity	1000	1311	1560	1690	1830	2000	2405

Density[b]	1.510	1.690	1.821	1.860	1.910	1.93(6)	1.864
Adiab. compress.	65.8	34.4	22.6	18.8	15.7	12.9	9.30 × 10^{-12}
$d\beta_{ad.}/dt$ cm.²/dyn. deg.	− 25	+ 7.3	+ 13	+ 14	+ 13	+ 9.5	+ 5.0 × 10^{-15}

[a] J. O'M. Bockris, J. W. Tomlinson and J. L. White, *Trans. Faraday Soc.*, **52**, 299 (1956). [b] L. Shartsis, W. Capps and S. Spinner, *J. Am. Ceram. Soc.*, **36**, 35 (1953).

tional changes; (ii): a high-low type structural rearrangement, involving bending of the Si–O–Si bonds and giving rise to a compacting of the lattice; (iii): at high pressures, more radical structural changes can be expected, and a collapse of the network, giving a permanent decrease in volume at low temperatures, as is indeed observed.[7] Since vitreous silica is closely related in structure to high-cristobalite, the high-low rearrangement will be obtained under compression but will not affect the thermal expansion. Conversely, the suggested rearrangement under pressure would become increasingly difficult with increasing temperature. Hence, the compressibility of vitreous silica has a negative temperature coefficient.

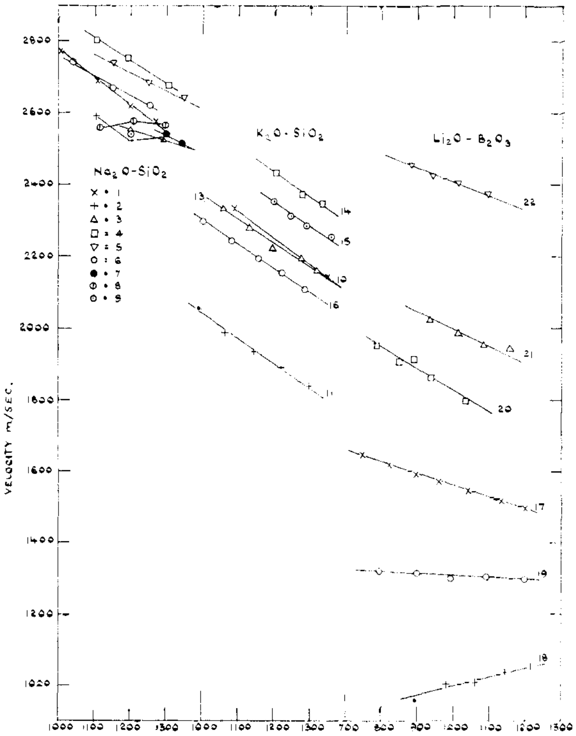

Fig. 1.—Velocity of sound in m. sec.$^{-1}$ Na_2O–SiO_2: 1 = 16.1; 2 = 20.5; 3 = 25.0; 4 = 25.0; 5 = 33.3; 6 = 42.9; 7 = 50.0; 8 = 55.5; 9 = 60.0 mole % Na_2O. K_2O–SiO_2: 10 = 20.0; 11 = 25.0; 14 = 40.0; 15 = 44.4; 16 = 50.0 mole %. Li_2O–B_2O_3: 17 = 0; 18 = 9.1; 19 = 16.7; 20 = 20.0; 21 = 25.0; 22 = 33.3 mole %.

A shift in the mutual orientation of the silicate tetrahedra which must result from compression demands the coöperation of numerous Si–O–Si bonds. In a *random* structure, compression would therefore become easier with introduction of the more flexible broken bonds caused by addition to SiO_2 of M_2O. However, an effect in the opposite direction also arises from such additions, for the M cations at least partly fit into the interstices of the structure and hence restrict its compaction. The net effect may be the small increase in compressibility observed at low M_2O content, with increasing M (Fig. 2).

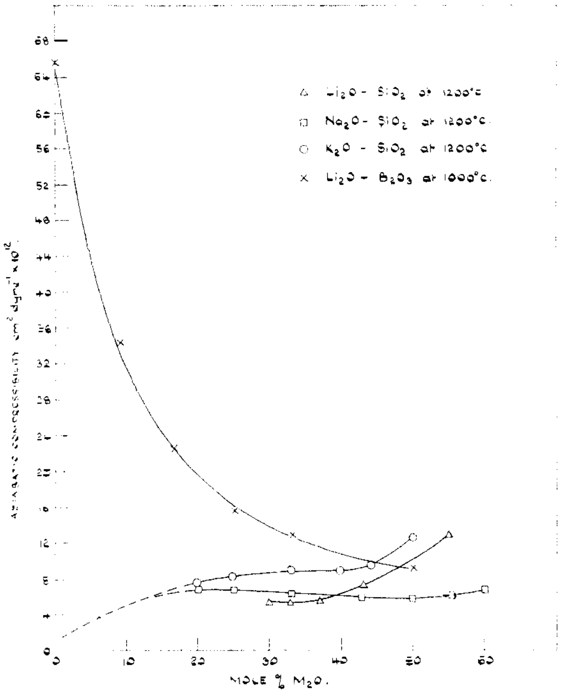

Fig. 2.—Adiabatic compressibility at 1200° as a function of M_2O composition.

In the composition region in which the structure is microheterogenous,[8] the compressibility will reflect the net effect of the compressibility of the silica-rich and alkali-rich regions. Upon increase of the M_2O/SiO_2 ratio, the compressibilities of the silica-rich and metal-rich regions would be expected to remain nearly constant, respectively, the effect of composition being primarily to change the size of the "iceburg," or silica rich, regions. Thus, little change of dv_0/dp with composition would be expected over the relevant composition range in which the structure is microheterogeneous according to the iceburg model (about 10–33 mole % M_2O) and change observed would be expected to be roughly linear with M_2O. The present experimental results are consistent with these expectations (Fig. 2 and 5). On the silica side of the dv_0/dp–composition plot, an inflection would be expected at a composition at which the two structural components become individually compressible, and another inflection after the region of relatively small variation of dv_0/dp with composition to indicate the end to the independence of the silica-rich iceburgs (which now form part of the discrete anion structure). The first of these inflections occurs at about 10–15% M_2O (theory, 10%) and the second between 33 and 45% and at an average composition of 40% M_2O (theory, 33%).

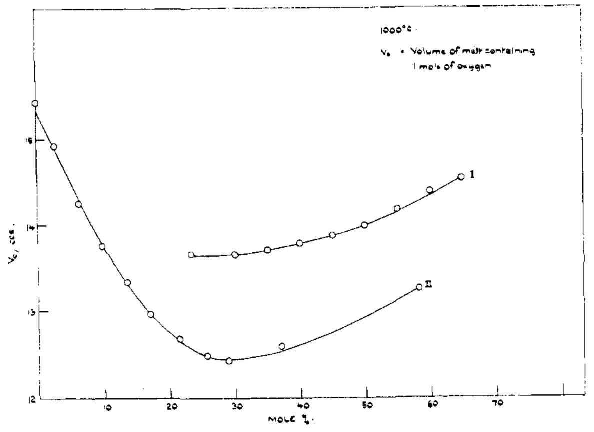

Fig. 3.—Volume, v_0, of melt containing 1 mole of oxygen as a function of composition. (I = O in alkali silicate; II = O in alkali borate).

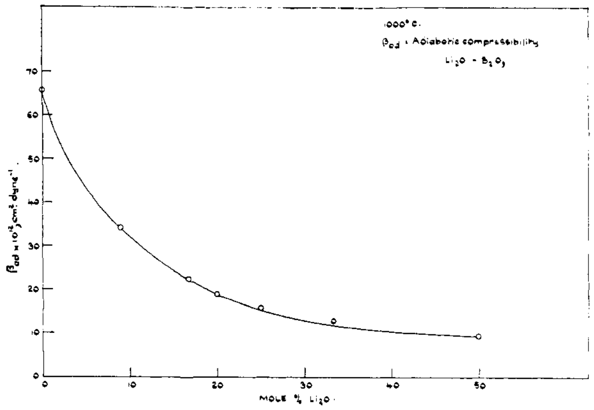

Fig. 4.—Adiabatic compressibility at 1000° of Li_2O–B_2O_3 as a function of composition.

With increase of M_2O/SiO_2 above $^1/_2$, the discrete anions decrease in size.[3,8] Hence, the number of ions per cc. (and per mole of M_2O) increases and the compressibility of the liquid can be regarded more in terms of the (increasing) number and size of the vacancies, which make the principal contribution to the compressibility of simple molten salts,[9] and less in terms of intramolecular lattice properties. The compressibility associated with simple molten salts,[9] however, is much greater than that of largely molecular (*i.e.*, high SiO_2) structures. The increase in β_s at composition of $M_2O/SiO_2 = {}^1/_2$ is therefore consistent with the suggested change in constitution to that of discrete ions at a composition above that of the disilicate.

The size and peripheral field strength of the modifying cation will, according to the model discussed, cause characteristic differences in the compressibility of its corresponding melt for a given M_2O/SiO_2. Up to the disilicate composition, $\beta_{s,Li} < \beta_{s,Na} < \beta_{s,K}$, as expected simply from decreasing field strength of the cations in this series. At high alkali contents, the relationship of β_s–composition curves for Li and K-containing melts can still be understood on the same basis, but the behavior of the Na system differs from that of the Li and K systems. The extended flat section of the dv_0/dp-composition relation for Na_2O–SiO_2 (Fig. 5) may suggest an essentially planar structure for the network fragments at the composition corresponding to the beginning of the microheterogeneous structure. Thus, the compression of such fragments would be mainly in the direction of the normal to the "planes" and their continued breakdown would still leave a planar type arrangement until they become so small that reorientation is possible, and compressibility can increase with increase of M_2O/SiO_2. The strict coördination requirements of the Li-ion and the structural strain caused by the introduction of large K-ions would both be better allowed for in a more random structure.

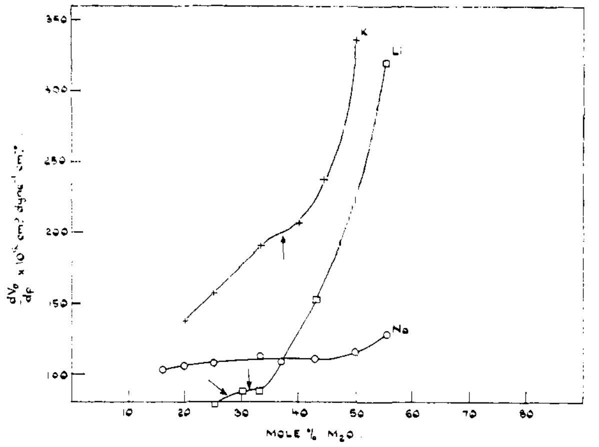

Fig. 5.—Pressure coefficient of v_0 as a function of composition.

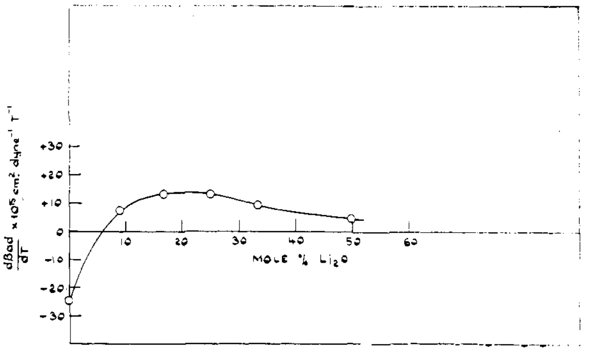

Fig. 6.—Temperature coefficient of adiabatic compressibility as a function of composition for Li_2O–B_2O_3

(3) **Compressibility of the Lithium Borates.**—The behavior of this system is anomalous in the following respects: (i) the adiabatic compressibility of pure B_2O_3 has a negative temperature coefficient (Fig. 6; *cf.* the analogous behavior of SiO_2. However, here, there is no "high-low" type structural arrangement upon the basis of which an interpretation may be made); (ii) the compressibility of M_2O–B_2O_3 *decreases* with increase of M_2O up to 50% M_2O, whereas in the analogous silicate case, it increases.

These striking differences may be compared with the qualitative similarities which exists between, *e.g.*, electric conductance, in the two systems.[10]

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(9) J. O'M. Bockris and N. E. Richards, *Proc. Roy. Soc.* (*London*), **241**, 44 (1957).

(10) J. O'M. Bockris and G. W. Mellors, *J. Phys. Chem.*, **60**, 1321 (1956).

The most fundamental difference between B_2O_3 and SiO_2 and their liquid systems with M_2O lies in the coördination numbers of B and Si. Classically, this has been considered to be three, with an increasing degree of four coördination upon addition of M_2O. Conversely, Grojtheim and Krogh-Moe[11] and Berger[12] concluded that vitreous B_2O_3 was predominantly four coördinated, in equilibrium with the three coördinated form; whereas Fajans and Barber[13] suggested a molecular structure. More recently, the classical structure has been supported by X-ray and electron diffraction measurements of Silver and Bray.[14] Despuljols[15] and Milberg and Meller.[16] The latter authors have concluded that some degree of four coördination is not inconsistent with their measurements. In support of an increase of four coördination on addition of O ions to liquid B_2O_3, Bockris and Mellors[10] observed a decrease of the molar volume of $PbO–B_2O_3$ on addition of PbO to B_2O_3.

Were B_2O_3 entirely three coördinated in the liquid, the effect of temperature would be predominantly to expand the liquid lattice and hence to *increase* the compressibility with increase of temperature. The negative temperature coefficient indicates a temperature-dependent structural change upon compression. Let it be supposed that liquid B_2O_3 contains a significant amount of four-coördinated B.[16] Under pressure, an increase of the four-coördinated structural component would be favored because of the large compacting effect which would follow the formation of the four-coördinated form. Such a transition is consistent with the fact that the compressibility for B_2O_3 is about 10^2 times that for SiO_2 at the lowest temperature at which measurements are here recorded. With increase of temperature, the increasing thermal motion resists a tendency for the coördination to change from three to four upon compression, and hence the compressibility decreases with temperature increases. Such an effect, and the magnitude of the associated negative temperature coefficient of compressibility, will become less upon addition of Li_2O, because this causes an increasing quantity of three-coördinated B to become four-coördinated, so that less of the former material is present for the compacting effect of pressure supposed.

The decrease of β_s with the initial increase of Li_2O content (*cf.* Fig. 4) is consistent with increasing four coördination (*i.e.* the melt is becoming more compact, *cf.* the decrease of molar volume observed upon addition of PbO to B_2O_3[10]). However, this explanation is only consistent with the model of discrete borate ions[10] (or "icebergs"[17]) commencing at about 10% M_2O, up to this composition, or after that until the composition at which the change to four coördination upon addition of Li_2O is complete (33%). Fig. 4 shows a measurement for $Li_2O \cdot SiO_2$ which (therefore anomalously) indicates a β_s value less than that at 33%. Above the 1:1 composition, the structure of the borate melt would be analogous to that of the corresponding silicate, *e.g.*, both have one "single-bonded" O per network-forming cation. With increase of M_2O above 50 mole %, the compressibility would be expected to increase by a mechanism similar to that suggested in section 2.

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[Contribution from The Johns Hopkins University, Baltimore, Maryland]

The Activity of Raney Nickel as a Function of Hydrogen Content

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The surface area of Raney nickel and its activity for ethylene hydrogenation and parahydrogen conversion were studied as a function of hydrogen content. These data were interpreted on the assumption that Raney nickel is a substitutional solid solution of nickel, aluminum and hydrogen promoted with alumina. It was tentatively concluded on the basis of comparison of these results with those reported for the copper-nickel system that the number of valence electrons per unit cell added by dissolved hydrogen, copper or other alloying components is an important consideration in comparison of such alloy systems. The activity of nickel at first decreases and then increases with an increase in the number of added electrons per unit cell.

It has been recognized for some time that Raney nickel catalysts which are prepared by leaching a nickel-aluminum alloy with alkali[1] usually contain not only nickel but also free aluminum and some alumina.[2] Moreover, the catalyst contains sufficient hydrogen[3] to lead some investigators to suggest that it is a compound of nickel and hydrogen.[4] It has also been shown that the activity of these catalysts for the hydrogenation of benzene is a function of the hydrogen content.[3] The role this hydrogen plays in catalysis is not clear, but recent evidence[5] suggests that the metallic phase of the catalyst is an atomic, substitutional, nickel-aluminum-hydrogen alloy wherein the hydrogen func-

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