containing an amyl group and a methyl group.

2. Electric moments have been determined for 2,2-dimethoxyheptane, 2,2-diethoxyheptane, 2,2-dipropoxyheptane, diethoxymethane and dineopentoxymethane.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KENTUCKY]

The Action of Molten Lithium Salts on Glass[1]

BY OLUS J. STEWART AND DAVID W. YOUNG

Burt[2] in describing his attempt to pass lithium ions electrolytically through the wall of a sodium coulometer by operating the instrument in a bath of molten lithium nitrate, wrote: "If the nitrate of lithium, a smaller ion than sodium, is used in place of sodium nitrate, the glass of the bulb in a few minutes closely resembles a white eggshell; it is very weak and will not hold a vacuum."

While repeating Burt's experiment the senior author of this paper shortly observed that a thermometer bulb which dipped into the bath of molten lithium nitrate had dropped off, a second thermometer soon failed to function and a stirring rod, subsequently introduced, quickly turned white. Examination showed that the surface of the immersed glass was covered with a network of nearly microscopic fractures which gave it an etched appearance. This phenomenon differed from that observed by Burt. The former was non-electrolytic, the latter electrolytic. Investigation shows that the phenomenon is a manifestation of a metathetical reaction wherein lithium ions replace sodium ions in glass and the decrease in weight of the glass is a measure of the lithium involved. The superficial fracturing of soda-lime glass in the manner indicated appears to be a phenomenon uniquely effected by molten anhydrous lithium salts and provides a simple means for identifying the element. The reaction is not limited to the surface of the glass but may penetrate the interior.

The Identification of Lithium.—On cautiously and repeatedly passing through a flame a common soda-lime test-tube, rod or microscope slide to which adheres a drop of lithium nitrate solution, the water will evaporate and the anhydrous salt will melt. After slight additional heating, followed by the cooling, washing and drying of the glass, it will be observed that that portion of the glass which has been in contact with a sufficient quantity of melted lithium nitrate is white. Suitable illumination then will show the whitening of the glass is due to a multitude of fractures which are visible to the naked eye, but are more readily observed under a magnifying glass.[3]

If the drop of solution under examination contains as much as 0.00005 g. of lithium, the fractures will be so numerous that the glass will be white or etched, but when working with very dilute solutions careful examination of the glass under a microscope is required to discover the few scattered fractures. The smallest quantity of lithium we have been able to detect in a drop of solution by this micro method is 1×10^{-6} g. which, assuming 20 drops to the ml., represents 0.00002 g. of lithium per ml. The test for lithium may be carried out in the presence of the salts of other elements, but the latter may reduce the effectiveness of the former by dilution, by formation of mixed crystals and by etching or roughening the glass surface. Pyrex glass is not fractured by lithium.

The Estimation of Lithium.—A quantity of standard lithium nitrate solution from a weight buret was evaporated to dryness in a small weighed Pyrex beaker provided with a stirrer. After adding a known quantity of coarsely ground glass wool, sufficient water (2–4 ml.) was introduced to redissolve the salt and permit thorough mixing. Prompt evaporation to dryness was followed by heating for a period of one to two hours at approximately 310°. When the beaker had cooled, water (2–4 ml.) was added for dissolving the sodium nitrate produced in the re-

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(1) A portion of this communication formed the basis of a thesis submitted by David W. Young in partial fulfilment of the requirements for the degree of Master of Science at the University of Kentucky, 1935.

(2) Burt, *J. Opt. Soc. Am.*, **11**, 87 (1925).

(3) The analysis of the Automatic Machine Made test-tubes used in this part of the work was kindly furnished by Kimble Glass Company, Vineland, N. J.: SiO_2 67.7, $Al_2O_3(Fe_2O_3, TiO_2)$ 2.8, CaO 5.5, MgO 3.9, BaO 2.0, Na_2O 14.8, K_2O 1.3, B_2O_3 1.3, Sb_2O_3 0.2, ignition loss 0.2.

action and for transferring the wool to a weighed porous-bottomed porcelain crucible to which suction was applied.

After washing the wool with the minimum quantity of water, the crucible containing the major portion of the wool and the beaker with its stirrer and small residue of wool were dried, cooled and weighed. Since the reaction was solely the substitution of lithium for sodium in the glass, the difference between the weight of the original sodium glass wool and that of the resulting lithium glass wool, corrected for the solvent action of the wash water, was the basis for the calculation of the quantity of lithium involved.

The solubility correction factor was determined for each fresh batch of wool by means of blank analyses which were similar in all details to the lithium analyses except for the fact that lithium nitrate was omitted and sodium nitrate was introduced at the outset. The quantity of sodium nitrate used in a blank was of the order of magnitude of that produced in a regular analysis. The value of the correction factor, expressed as weight of glass dissolved per g. of wool per ml. of wash water, varied from 0.5×10^{-5} g. to 1.7×10^{-5} g. (3.9×10^{-5} g. in analyses b). This fact emphasizes the necessity for similarity in the treatment of the wool in analysis and blank. The value of the correction applied in each analysis can be derived from the data, Table I. The argument for the correction is not entirely convincing because the factor was determined for a sodium glass in the blank and applied to a lithium glass in the analysis.

Table I is an abbreviated but representative list of results. The period of heating was one hour in b, c and g, two hours in all others. The temperature during the heating was 330° in b, 300° in c and 310° in the others. The quantity of wash water was 40 ml. in a, b and c, 30 ml. in d and e, 20 ml. in f and 15 ml. in g. Solutions analyzed in d and e contained, respectively, 0.2 g. of sodium nitrate and 0.2 g. of potassium nitrate in addition to the lithium salt. It will be observed that the weight of wool recovered (uncorr.) in analysis e is greater than the weight of wool taken. When this weight was corrected for a corresponding increase in the weight of the blank, a net loss in weight resulted. Comparative study of the data shows that it is desirable to treat the glass wool in analysis and blank as follows: heat for two hours at 310° and wash with 20 ml. of water.

Two analyses of the standard solution by the Rammelsberg ether–absolute alcohol method, as revised by Palkin, yielded the values 0.467 g. and 0.469 g. of lithium per 100 g. of solution. It is seen therefore that lithium may be determined by the glass wool method either in the presence or absence of sodium nitrate with a precision of approximately 1%, but potassium nitrate interferes seriously.

TABLE I

	Soln., g.	Wool taken, g.	Soln. per g. wool, g.	Wool recov. Uncorr., g.	Wool recov. Corr., g.	Loss, g.	Li per 100 g. soln., g.
a	0.891	3.0131	0.296	3.0017	3.0035	0.0096	0.464
a′	2.541	3.1542	.807	3.1245	3.1265	.0277	.470
b	0.910	2.1310	.427	2.1170	2.1202	.0097	.461
b	0.763	2.8798	.265	2.8674	2.8717	.0081	.459
c	2.010	3.0134	.667	3.0014	3.0032	.0102	.219
d	1.210	4.3900	.276	4.3746	4.3768	.0132	.471
d	1.009	6.3861	.158	6.3719	6.3751	.0110	.471
e	1.002	3.9522	.253	3.9591	3.9432	.0090	.388
f	1.195	2.8692	.416	2.8560	2.8563	.0129	.466
f	1.191	2.6774	.446	2.6642	2.6644	.0130	.471
g	0.288	4.9172	.059	4.9138	4.9142	.0030	.450

The Nature of the Phenomenon.—In his electrolytic experiment Burt[2] recognized the replacement of sodium by lithium. The analytical data of the present paper support the opinion that a similar exchange takes place quantitatively in the non-electrolytic reaction.

In order to make this point more certain the filtrates and washings from several analyses were collected and treated for the recovery of the positive ion as chloride which in turn was converted to sulfate. The chloride had the characteristic crystalline form of sodium chloride and, within reasonable limits of error, the weights of chloride and of sulfate, assumed to be sodium salts, corresponded with the quantity of lithium which had been used. Following this the filtrates and washings from four other analyses were collected and treated for the precipitation of calcium as oxalate. The very slight precipitate required but 0.23 ml. of 0.1 N permanganate for oxidation in acid solution. It is therefore concluded that sodium only is displaced from glass by lithium. Filtrate and washings from one analysis, concentrated to 0.5 ml., gave only faint spectroscopic test for lithium.

The fracturing phenomenon keeps pace with the chemical reaction but the whiteness of the wet glass is never pronounced because the molten liquid smooths out the light-scattering surface discontinuities. The cracks in general are directed at random but at first there frequently appear groups of parallel fractures which probably follow lines of strain originally in the glass.

The depth of normal fracturing is deceptive to the eye. The cracks do not often puncture the glass for no certain case of gaseous diffusion or aqueous electrolysis through fractured glass was observed and a microscope in focus on the cracks of the fractures side of flat glass is out of focus when the sides are reversed. (Gross accidental cracks or breaks in the glass are not referred to here.) It is noteworthy also that, when the fractures occur, all strains appear to be relieved for the depth of fracturing is not further extended by heating, cooling or rough handling. In fact a test-tube which has been subjected to a five-minute treatment is as strong as unfractured glass. Long continued action, however, may carry the process entirely through the glass. The cracks will then be filled with alkali nitrates which will decompose when heated and cause the mass to swell.

The question arises: is the reaction exclusively a surface phenomenon or does lithium penetrate the interior of the glass? This question may be answered by comparing the number of sodium atoms on one sq. cm. of glass surface with the number of sodium atoms actually displaced per sq. cm. The glass wool mentioned in the analytical section of this paper served admirably for the present problem because it was not fractured by lithium and therefore its surface area remained constant.[4]

In calculating the number of sodium atoms on each sq. cm. of surface a spherical glass molecule having the following formula was assumed: $(Na_2O)_5 \cdot B_2O_3 \cdot Al_2O_3 \cdot (SiO_2)_{20}$.[5]

Spherical models of all atoms in the molecule were cast in clay to the scale, Å. = 1 cm., using the following ionic radii: Na 1.00, Al 0.55, B 0.20, Si 0.40, O 1.35 Å.[6] The diameter of the close-packed molecular model was 12.75 cm. Since the cross-sectional area (1.27×10^{-14} sq. cm.) of the corresponding glass molecule accounts for ten sodium atoms it follows that there are, per sq. cm. of glass surface, 7.85×10^{14} sodium atoms which are not more than one molecular diameter below the surface.

The average cylindrical particle of ground glass wool was 2.3×10^{-3} cm. in diameter and 11.4×10^{-3} cm. long. The density of the glass was approximately 2.6. One gram of the wool therefore had a surface area of 740 sq. cm. In this research 2.64×10^{-4} g. lithium was the smallest quantity which reacted with 1 g. of wool (Table I, analysis g). It follows then that 8.75×10^{-4} g. of sodium was displaced on 740 sq. cm. of surface and 3.1×10^{16} sodium atoms reacted for each sq. cm. of surface. This figure is nearly forty times as large as the number of sodium atoms available for displacement on the same surface. Therefore it is concluded that the reaction was not wholly superficial and lithium penetrated the interior. If a similar calculation is carried out for analysis a′ it is found that lithium penetrated the interior 570 molecular diameters (7.28×10^{-5} cm.), which, however, is only 6.3% of the radius of the wool fiber.

Since the reaction between lithium nitrate and glass does not take place appreciably below the melting point of the anhydrous salt, a temperature at which the sodium ions of the glass are presumably in a state of intense kinetic activity, one may hazard the opinion that the fracturing of the glass results from the shrinking of the surface during the readjustment of interionic forces necessitated by the fact that lithium ions (r = 0.70 Å.) cannot fill completely the spaces vacated by sodium ions (r = 1.00 Å.).[6] Once a lithium ion has entered the outer surface of the glass, it holds a strategic position for displacing a sodium ion of the interior. In accord with this explanation of fracturing is the observation that a thermometer whose bulb has been etched by lithium registers temperature too high.[4]

In this research no small ion was found which could duplicate the action of lithium. This was somewhat unexpected especially in the case of the mercurous ion (r = 0.72). The negative results may have been due to the low sublimation temperature of mercury salts though it may bespeak a lack of simplicity for the mercurous particle.

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(4) Thin glass is less easily fractured than thick glass. Our search for fractures on glass wool fibers failed. We conclude that shrinking of the surface of thin glass is accompanied by sufficient distortion to prevent rupture.

(5) The glass wool used in all the work was an Austrian product analyzing: Na_2O 17.9, K_2O 1.9, CaO 0.7, MgO 0.1, Al_2O_3 1.9, Fe_2O_3 0.1, B_2O_3 4.0, SiO_2 73.1%. In deriving the formula Na_2O and K_2O were grouped as Na_2O; CaO, MgO, Fe_2O_3 and Al_2O_3 were grouped as Al_2O_3.

(6) R. W. G. Wyckoff, "The Structure of Crystals," Chemical Catalog Co., New York, 1931, p. 192.

Summary

1. Attention has been called to a non-electrolytic reaction between molten lithium salts and glass wherein sodium ions of the glass are displaced by lithium ions.

2. The reaction has value in analytical chemistry but, from the quantitative standpoint, its application is limited.

3. The nature of the phenomenon was studied in some detail.

LEXINGTON, KENTUCKY RECEIVED MARCH 1, 1935

NOTES

Comparison of Viscosity Data

BY FRANCIS T. MILES[1]

In a recent paper[2] Miss Mary D. Waller calculates for a number of compounds the ratios of the viscosities at the melting and boiling points and correlates the values of this ratio, η_f/η_b, with the molecular symmetry of the compounds. Molecules of high symmetry are found to have low values of η_f/η_b, and *vice versa*. In a preliminary paper[3] the same author states that the melting and boiling points can be used as comparison temperatures. It is well known, however, that the melting point of a compound is influenced by the symmetry of the molecule. Dietz and Andrews[4] have pointed out that in the series, benzene, dihydrobenzene, tetrahydrobenzene, cyclohexane, the melting points of the two symmetrical compounds, benzene and cyclohexane, are 100° higher than those of the unsymmetrical compounds, while the boiling points of all four compounds lie in a range of only 2°. These authors have proposed an explanation for this influence of molecular symmetry on the melting point. If a pair of compounds had the same boiling points and equal viscosities at equal temperatures, the less symmetrical of the two compounds, having the lower melting point, would have a higher viscosity at the melting point and therefore a higher ratio, η_f/η_b. It is interesting to calculate whether the changes of η_f/η_b in a series of similar compounds are due primarily to the variation of viscosity with temperature or merely to the lower melting points of the unsymmetrical compounds.

The variation of viscosity with temperature can be expressed approximately by an equation of the form

$$\log \eta = A + B/T_{\mathrm{Abs.}}$$

and this relation was used by Miss Waller to extrapolate viscosity data to the melting and boiling points. It follows from this equation that

$$\log r = \log \eta_f - \log \eta_b = B(1/T_f - 1/T_b)$$

Thus it is possible to separate log r into two factors of which one, B, represents the variation of viscosity with temperature, and the other, $1/T_f - 1/T_b$, represents the extent of the liquid range and is independent of the viscosity of the liquid, except in so far as this may be a factor in determining the melting and boiling points. Miss Waller tabulates values of $T_b - T_f$ and states that changes in this do not explain the changes in r. In view of the above equation, however, it is interesting to compare log r and $1/T_f - 1/T_b$, and this is done in Tables I and II. The first four columns in each table are taken directly from Miss Waller's paper. In the fifth column are values of log r calculated from these data. Values of $1/T_f - 1/T_b$, calculated from the melting and boiling points, are given in column six, and in the last column values of B are calculated from the relation

$$\log r = B(1/T_f - 1/T_b)$$

TABLE I

	η_f	η_b	r	log r	$(1/T_f - 1/T_b) \times 10^3$	$B \times 10^{-2}$
Benzene	0.0082	0.0034	2.2	0.38	0.76	5.0
Toluene	.055	.0026	21	1.33	2.92	4.5
Ethylbenzene	.059	.0025	24	1.37	3.13	4.4
o-Xylene	.019	.0026	6.6	0.86	1.67	5.2
m-Xylene	.018	.0024	7.5	.88	2.14	4.1
p-Xylene	.00703	.0024	3	.47	1.04	4.6

TABLE II

	η_f	η_b	r	log r	$(1/T_f - 1/T_b) \times 10^3$	$B \times 10^{-2}$
Pentane	0.038	0.0021	18	1.26	3.83	3.3
Hexane	.0194	.0021	9	0.96	2.67	3.6
Heptane	.0279	.0021	13	1.12	2.77	4.05
Octane	.0189	.0021	9	0.96	2.11	4.55
Nonane	.025	.0021	12	1.08	2.14	5.05
Decane	.0232	.0021	11	1.04	1.90	5.5
Undecane	.0295	.0020	16	1.17	1.92	6.1

Table I gives the results for benzene and some of its homologs. Examination of the last two

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[1] Exchange Fellow at the University of Basel from Princeton University under the auspices of the Institute of International Education.

[2] Waller, *Phil. Mag.*, **18**, 579 (1934).

[3] Waller, *ibid.*, **18**, 505 (1934).

[4] Dietz and Andrews, *J. Chem. Phys.*, **1**, 62 (1933).