The entropy increment for niobium pentoxide between 51 and 298.16°K. was obtained by Simpson-rule integration of a C_p against log T plot. The extrapolated increment, below 51°K., was calculated using the Debye and Einstein function sum, $D(163/T) + 2E(311/T) + 2E(489/T) + 2E(970/T)$, which fits the experimental heat capacity data over the entire measured range with a maximum deviation of 0.6%. The entropy results appear in Table II.

TABLE II

ENTROPIES AT 298.16°K. (CAL./DEG. MOLE)

	Mn_2O_3	Nb_2O_5
0–51°K. (extrap.)	2.08	2.51
51–298.16°K. (meas.)	24.32	30.30
$S^0_{298.16}$	26.4 ± 0.5	32.8 ± 0.2

The measured portions of the entropy constitute about 92% of the totals at 298.16°K. The limit of error assigned to the manganese sesquioxide value is larger than usual to allow for extra uncertainty in extrapolation below 51°K.

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[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY OF CHEMISTRY AT HARVARD UNIVERSITY]

Electrode Potentials in Molten Silicates

BY ROSTISLAV DIDTSCHENKO[1] AND EUGENE G. ROCHOW

RECEIVED FEBRUARY 12, 1954

A reversible oxygen electrode has been developed for investigating the activity of oxide ion in solutions of metal oxides in molten lead silicate. Operation of the electrode in the system Pt:O_2/standard glass//standard glass + R_xO_y/O_2:Pt provides a series of potentials which vary with the basicity of the oxide R_xO_y as well as with its concentration. The regular dependence of potential upon the size, the charge, and the electronic structure of the dissolved metal ion is considered in terms of the random-network theory of glasses.

The crystallographic investigations of Bragg and Pauling have established that solid silicates are predominantly ionic substances the structures and properties of which are determined by the charges, sizes and proportions of the ionic constituents. It was suggested by Zachariasen[2] that similar factors must be operative in the formation of glasses in general, and of silicate glasses in particular. This assumption was confirmed by the X-ray investigations of Warren and his school,[3] which led to the formulation of the so-called "random-network theory of glasses" in its present form. According to this theory the silicate glasses consist of an irregular network of SiO_4 tetrahedra with short-range crystallographic order. The remaining cations are statistically distributed in the holes of that network in such a way that they are coördinated with an optimum number of single-bonded oxygen ions from the silicate network.

Glasses have always been considered to be undercooled liquids, and hence it seems justifiable to assume that the internal structure of a silicate melt must be very similar to that of the solid glass obtained from it. In such a silicate glass, oxygen ion is a predominant constituent. Furthermore, the activity of oxygen ion in silicate melts is primarily responsible for their acidic or basic behavior. A detailed knowledge of oxygen ion activity therefore is important from the theoretical point of view. Since there is very little general information about the activities of the constituents of silicate melts, we thought it interesting and useful to develop a method of measuring the oxygen ion activity in a simple silicate system, with special emphasis upon the changes of this activity due to the presence of dissolved metal oxides.

The problem is analogous to pH measurements in aqueous solution, and the obvious way of tackling it would be to use an electrode that responds reversibly to oxygen ion activities, as in an oxide concentration cell consisting of molten silicates. It has been shown that the platinum–oxygen electrode at 800–1000° is reversible to oxygen and to oxide ion in molten carbonates,[4] borates[5] and sulfates.[6] Thus we had reason to believe that the platinum–oxygen electrode should also be applicable to molten silicates, if the experimental difficulties could be mastered.

We set out to measure the e.m.f. of the cell type

Pt:O_2/silicate solvent//silicate solvent + M_xO_y/O_2:Pt

where M_xO_y designates an oxide dissolved in a simple silicate. Lead silicate of the composition $PbO{\cdot}SiO_2$ was selected as the solvent because of its advantageous properties such as low melting point and excellent glass-forming ability with other oxides. For obvious reasons, in the future we shall refer to this lead silicate as our "standard glass."

Experimental

The standard glass was prepared by melting in a platinum crucible an intimate mixture of dry lead oxide and silica in an electric muffle furnace under oxygen at 850–900° and quenching the resulting melt to a solid glass. All other glasses were made in the same way by previously adding to the standard glass mixture the exactly weighed amount of an oxide, carbonate or nitrate so as to give a glass having the desired concentration of the oxide under investigation. All substances used were of analytical purity.

The construction of the cell created considerable difficulty. Several designs constructed from alundum and magnesia were tried without success; the alundum was strongly attacked by molten silicates, and the magnesia crucibles available to us had good chemical resistivity but were either too porous or too dense. The construction finally adopted used two identical porous porcelain cups which were fired previously at the sintering temperature (1200°) in a gas furnace. The insides of the cups were lined with platinum

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[1] Natvar Fellow at Harvard University in 1952–1953.

[2] W. H. Zachariasen, THIS JOURNAL, **54**, 3841 (1932).

[3] B. E. Warren, *J. Am. Ceramic Soc.*, **24**, 8 (1941).

[4] E. Bauer and R. Brunner, *Z. Elektrochem.*, **41**, 794 (1935).

[5] P. Csaki and A. Dietzel, *Glastech. Ber.*, **18**, 33 (1940).

[6] H. Flood and T. Forland, *Acta Chem. Scand.*, **6**, 257 (1952).

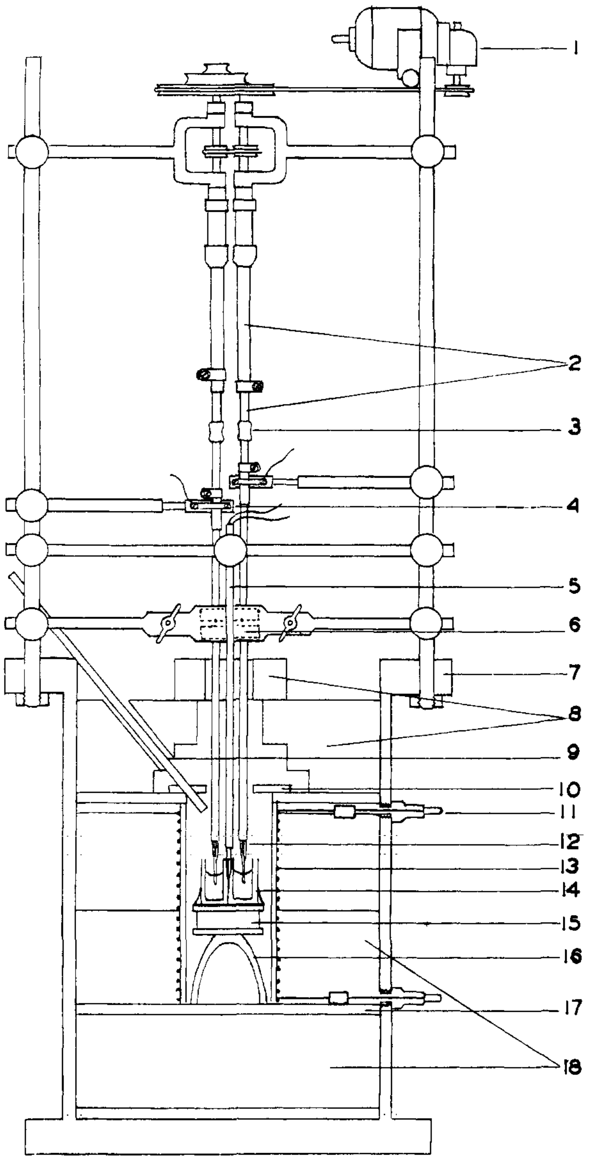

Fig. 1.—Schematic cross-section through furnace and cell: 1, stirring motor; 2, extendable tubes for lifting and lowering of the electrodes; 3, insulating rubber connections; 4, platinum brushes on elastic suspension; 5, platinum–rhodium thermocouple; 6, ball bearings to support the rotating electrodes; 7, furnace casing; 8, cover bricks; 9, ceramic gas inlet tube to sweep the cell with oxygen; 10, cover plate; 11, insulated connections to the power line; 12, platinum electrodes; 13, heating coil (platinum); 14, electromotive cell; 15, insulating plate from fused magnesia; 16, crucible of fused alumina used as support; 17, alundum plate; 18, thermal insulation of silica bricks.

foil, and they were placed in a flat platinum dish. The dish and one of the cups then were filled with finely powdered standard glass while the other cup held the glass containing the dissolved oxide under investigation.

This arrangement permitted the diffusion of the melts through the platinum lining and the walls of the crucible, establishing electrolytic contact with the glass in the platinum dish, which acted as an electrolytic bridge. Although there was some chemical attack on the porcelain cups, the platinum lining prevented contamination of the melts inside the cups to such an extent that potentials remained practically constant for periods of many hours.

The electrodes (see Fig. 1) consisted of thick platinum wires supported by long refractory tubes attached to the rotating mechanism. The rotation of the electrodes in the melt during the measurements proved advantageous because it promoted the establishment of equilibrium at the platinum–melt–oxygen interfaces and counteracted possible concentration polarization. We convinced ourselves that the electrodes were not significantly polarized by measuring the internal resistance of the cell at 60 and at 1000 cycles, and found that the two values were identical.

The cell was placed inside a platinum-wound resistance furnace as shown in Fig. 1. The temperature of the cell was measured with a platinum–rhodium thermocouple, which also was a part of the thermoregulating circuit[7] (see Fig. 2). In this circuit part of the heating current was diverted through a thyratron tube triggered by a photocell. The amount of current passing through the thyratron during each cycle was proportional to the intensity of light falling on the photocell from the light beam of the thermocouple galvanometer moving across a horizontal V-slit in front of the photocell. After a rapid initial heating under manual control, temperatures of 800° to 1000° could be kept constant within ±0.5° by this device.

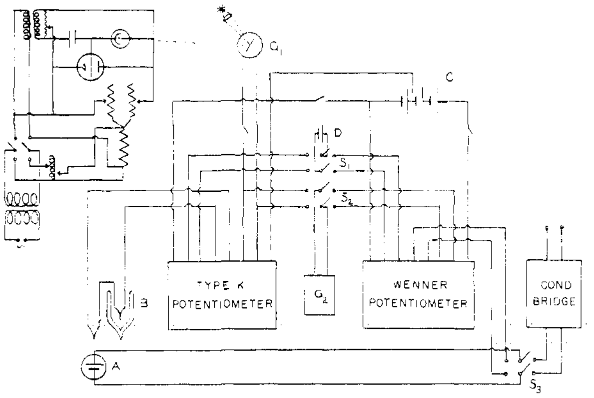

Fig. 2.—Measuring and thermoregulating circuits: A, electromotive cell; B, thermocouple with cold junction; C, 6-volt storage battery; D, standard cell; G_1, mirror reflex galvanometer which operates the thermoregulating circuit in the upper left corner of the diagram; G_2, mirror reflex galvanometer to measure the cell potentials; S_1, S_2, S_3, switches.

The cell e.m.f. was measured with a Wenner potentiometer (Fig. 2) which allowed the determination of potentials to ±0.01 mv. The individual potentials could be indeed measured with such exactness, but the reproducibility of potentials on supposedly equivalent samples was in most cases only ±5 mv. at an observed level of 300 mv.

In order to find whether our electrodes responded to differences in concentration of oxygen ion in the silicate melts, we measured a series of cells of the type

$$-\mathrm{Pt}:\mathrm{O_2}/\text{standard glass} + \mathrm{R_2O}//\text{standard glass}/\mathrm{O_2}:\mathrm{Pt}\ +$$

where R_2O is Li_2O, Na_2O or K_2O at varying concentrations in the range of 0.1–0.5 mole of oxide per mole of standard glass. The polarity of the cells was always as indicated above and the negative potentials increased with increasing concentration of alkali oxides, as shown in Fig. 3. They also became more negative in the order $Li_2O < Na_2O < K_2O$ at any chosen concentration.[8] This result was in complete agreement with our assumption that the electrodes should respond to the oxygen ion activity as function of the concentration and the basicity of the oxides dissolved in the silicate melt.

We also wished to reassure ourselves that the electrode reaction involved oxygen gas. For this purpose, we investigated the response of the cell to changes in partial pressure

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(7) R. M. Zabel and R. R. Hancor, *Rev. Sci. Instr.*, **5**, 29 (1934).

(8) Complete details and original observations are available at Harvard University in the thesis by Rostislav Didtschenko entitled "Electrode Potentials in Molten Silicates."

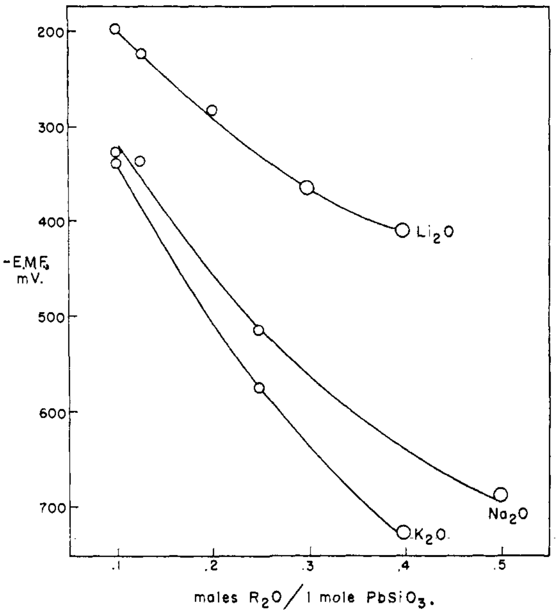

Fig. 3.—Potentials as function of concentration of different alkali oxides.

of oxygen at one of the electrodes. This was done by passing over or bubbling through the melt in one half-cell an inert gas, like nitrogen or helium, containing small amounts of oxygen. In a qualitative way the potentials always changed in the direction expected for an oxygen gas electrode.[8]

~~The major part of the~~ investigation, the systematic investigation of the effect of foreign oxides on the activity of oxygen ion in our standard glass, was then conducted by measuring the e.m.f.'s of the cells

$$\mathrm{Pt:O_2/standard\ glass//standard\ glass} + n\mathrm{R}_x\mathrm{O}_y\mathrm{/O_2:Pt}$$

where n is the number of moles of an oxide R_xO_y such as to give a glass containing 0.2 mole of foreign metal ion per mole of standard glass. We investigated glasses containing oxides of the following metals: all the alkali metals, all alkaline earth metals, thallium, lead, cadmium, zinc, bismuth, boron, aluminum, titanium, silicon and germanium. The cell potentials at 800°, 850° and 900° were observed, although only those at 900° are plotted in Figs. 3, 4 and 5. Readings of the potentials were taken at 5-minute intervals over a period of from 90 to 365 minutes.[8]

Discussion

The potentials obtained are considered to be a measure of the change in oxygen ion activity of the standard glass due to the presence of dissolved oxides. This change must be some function of the attraction exerted upon the negative oxide ions by the cations of the dissolved oxide. After Dietzel[9] we adopted as the measure of this attraction the quantity z/a^2, where z represents the charge of the cation and a is the distance between the centers of the cation and the coördinated oxygen ion. This distance can be calculated from the sum of the atomic radii corrected for the most likely coördination number.[10]

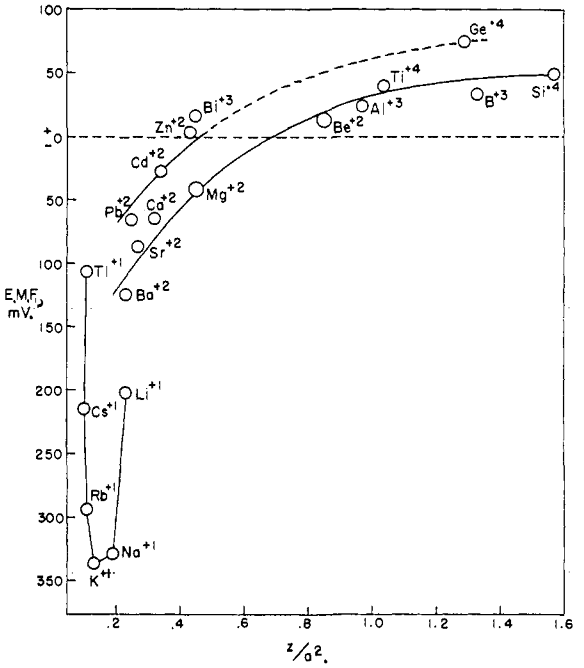

Fig. 4.—Potentials as function of z/a^2 values for different ions at constant concentration and temperature.

When the potentials are plotted against z/a^2 values for the respective oxides, the plot represented in Fig. 4 is obtained. Some conclusions immediately seem evident: (A) potentials related to cations with a completed noble gas shell fall on the hyperbolic curve between Ba^{+2} and Si^{+4}. The typical alkaline earth oxides give negative potentials increasing in the order of basicity of these oxides. The so-called "acid" oxides like beryllium oxide, alumina, boron trioxide, titania and silica give positive potentials increasing in that order. Thus the basic or acidic character of an oxide is due to the increase or decrease of oxygen ion activity in the silicate system in which the oxide is dissolved. For the ions of noble gas type, the change in oxygen ion activity varies with the coulombic fields of these ions as expressed by z/a^2. Titania actually does not belong to this series because the outer shell of Ti^{+4} ion does not have the noble gas configuration.[11] This gives rise to additional polarization forces which increase the attraction between the cation and the oxygen ions, and therefore titania acts as a stronger acid than expected from its z/a^2 value. (B) The latter effect observed for titania is even more pronounced in the case of cations having 18 electrons in their outer shells. The respective cell e.m.f.'s of these ions fall upon a second hyperbolic curve which is displaced toward more positive potentials.[12] One may be tempted to see in this displacement a measure of the polarization forces.

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(9) A. Dietzel, *Z. Elektrochem.*, **48**, 9 (1948).

(10) The ionic radii are from the recent and complete listing by T. Moeller ("Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1952, p. 140) for coördination number 6. The average coördination numbers in glasses are given by B. E. Warren, *J. Am. Ceramic Soc.*, **24**, 8 (1941), and the Moeller radii were corrected to those coördination numbers by use of the equation

$$R_{\mathrm{I}}/R_{\mathrm{II}} = (A_{\mathrm{I}}B_{\mathrm{II}})^{\frac{1}{n-1}}/(A_{\mathrm{II}}B_{\mathrm{I}})$$

where the subscripts denote different coördination numbers, A is the Madelung constant, and B is the repulsion coefficient of the Born equation. The values of the Born exponent n are given in L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1948, p. 339.

(11) W. Colbert, *J. Am. Ceramic Soc.*, **29**, 40 (1946).

(12) The oxides of metals which according to their z/a^2 would fall in the dashed region of the curve (SnO_2, for example) unfortunately did not form homogeneous glasses in this system, and so did not give any measurable potentials.

(C) The potentials for glasses containing alkali oxides do not follow either pattern. They form a parabolic curve, shifted toward more negative potentials, which has a pronounced minimum for potassium oxide. This oxide is therefore the strongest base in our system, since a minimum in the e.m.f. means a maximum in the oxygen ion activity. This behavior can tentatively be explained on the basis of the random network theory by the interaction of two opposing effects: decreasing z/a^2 value, and increasing coördination requirements in the series from lithium to cesium. The increasing coördination (Warren, ref. 10) affects the oxygen ion activity in the opposite direction and leads to the occurrence of a maximum.

Our cells are not amenable to exact thermodynamic treatment since they have liquid junctions and the junction potentials are not known. On the other hand, it has been found that the junction potentials in cells involving molten salts are usually very small and can be neglected for an approximate quantitative treatment.[13] In our case it may be reasoned that the junction potentials are in all probability not larger than the reproducibility of the measurements (5 mv.).

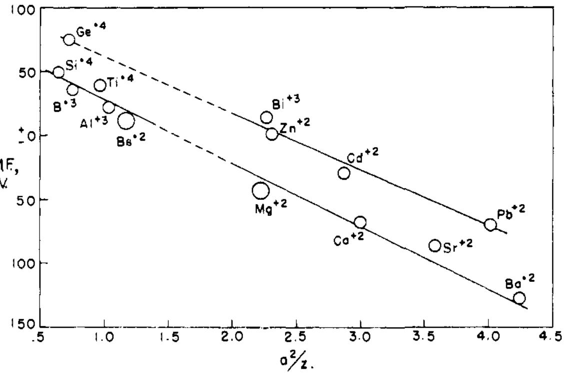

Fig. 5.—Potentials *vs.* a^2/z values.

If we neglect the junction potentials and consider the oxygen ion activity of the standard glass as our "standard state," we can calculate the oxygen ion activity for every solution from the Nernst equation

$$\text{e.m.f.} = -\frac{RT}{nF}\ln O^{-2}_{\text{sol.}}$$

For the glasses whose potentials fall on the main hyperbolic curve, a more general treatment can be attempted. If we plot these potentials against the inverse z/a^2 values we obtain the straight line of Fig. 5, which is expressed by the empirical equation

$$\text{e.m.f.} = 0.050a^2/z + 0.079$$

Combining this with the first equation and calculating the constants, we have

$$\ln O^{-2}_{\text{sol.}} = 0.429\ a^2/z - 0.678$$

Of course, this equation is true only for our particular solvent at 900°. It is interesting to find the Nernst equation applicable here, but in order to obtain any deeper insight into the nature of the constants evaluated above it would be necessary to conduct similar investigations in a series of lead silicates of different $PbO:SiO_2$ ratios and to measure the potentials as a function of temperature.

Acknowledgment.—The authors deeply appreciate the assistance of the Mallinckrodt Fund at Harvard University in obtaining reagents and materials.

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[13] L. Holub, F. Neubert and F. Sauerwald, *Z. physik. Chem.*, **A174**, 161 (1935).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

The Solubilities of Sulfur Hexafluoride in Water and of the Rare Gases, Sulfur Hexafluoride and Osmium Tetroxide in Nitromethane[1]

BY HAROLD L. FRIEDMAN

RECEIVED FEBRUARY 20, 1954

The following gas solubilities (Ostwald coefficients) have been determined at 25° with an accuracy of about 3%: in water, SF_6 = 0.0055; in nitromethane, He = 0.0175, Ne = 0.0245, A = 0.145, Kr = 0.380, Xe = 1.14, SF_6 = 0.377, OsO_4 = 1100. The OsO_4 value was obtained indirectly by studying the partition of OsO_4 in nitromethane–water mixtures. The solubilities of SF_6 also have been measured at lower temperatures. Sulfur hexafluoride exhibits the lowest solubility in water at 25° of any gas known, owing to an abnormally large entropy decrease upon forming the solution. Rough agreement with the regular solution theory is exhibited by these substances in nitromethane. It is found that the 25° solubilities of the rare gases in a variety of solvents, including water, may be correlated by the equation $\log x = a + bg$ where x is the solubility and a and b depend only upon the solvent and g depends only upon the gas. This correlation is accurate to ±5% in the solubility.

In connection with a study of the free energy of transfer of electrolytes from water to nitromethane[2] it seemed of interest to obtain for comparison the free energies of transfer of neutral molecules similar in size and structure to the ions of the electrolytes. Some solubilities which were obtained for this purpose are reported here (Table I).

The solubilities of helium and argon in water were obtained to check the method used here.

Aqueous Solutions of Sulfur Hexafluoride.—It is noteworthy that at 25° SF_6 has the lowest solubility in water reported for any gas. Thus the Ostwald coefficients for some other solutes in water at 25° are: N_2 = 0.016,[3] CH_4 = 0.033,[3] C_2H_6 = 0.045,[3]

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[1] This work was supported by the Atomic Energy Commission.

[2] H. L. Friedman and G. L. Haugen, THIS JOURNAL, **76**, 2060 (1954).

[3] J. H. Hildebrand and R. L. Scott, "The Solubility of Non-Electrolytes," Reinhold Publ. Corp., New York, N. Y., 1950, Chapt. XV.