exact density measurements and additionally the temperature fluctuation was within ±5 mK. In the present study, however, the temperature control was improved within ±2 mK. This also brought higher resolution in the $T_c$ determination with the aid of the exact density determination.

Hejmadi and Powers (*3*) presented their $T_c$ value as 293.054 ± 0.03 K which was determined by using their calorimetric measurements near the critical point. This value of $T_c$ is in good agreement with the present value with a difference of 19 mK, whereas the other previously reported values (*1*, *6*, *8*, *9*) are smaller than the present value by about 0.2 K.

**Acknowledgment**

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**Glossary**

| | |
|---|---|
| $A$, $B$ | coefficients in eq 1 |
| $P$ | pressure in MPa |
| $T$ | temperature in K |
| $\Delta t$ | reduced temperature, $\Delta t = (T - T_c)/T_c$ |
| $\beta$ | exponent describing the coexistence curve |
| $\rho$ | density in kg/m$^3$ |
| $\Delta\rho$ | reduced density, $\Delta\rho = (\rho - \rho_c)/\rho_c$ |

*Subscript*

| | |
|---|---|
| c | at the critical point |

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# Acid Strength of Molten Oxide Mixtures

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**In order to evaluate the relative acid strength of molten oxides, a simple emf method was devised. In reference to the activity of $Na_2O$, an acid strength variation of $P_2O_5 > MoO_3 \approx WO_3 > B_2O_3 > GeO_2 \approx SiO_2$ was found. Variations in the relative basicity (in terms of $Na_2O$ activity) of as much as $10^{15}$ were found among binary melts containing $Na_2O$, when combined with the data of concentration cells of the previous works.**

## 1. Introduction

It is nearly 4 decades since the thermodynamic properties of the oxide mixtures were discussed in terms of the acid–base concept. Lux[1] introduced the relation

$$\text{base} = \text{acid} + O^{2-} \qquad (1)$$

and employed an emf method as early as 1939. Flood and Førland[2] noted further that an acid oxide network reacts with the $O^{2-}$ ion from the basic oxide to give

$$X\text{-}O\text{-}X + O^{2-} = 2X\text{-}O^- \qquad (2)$$

if written in the present notation for the covalent bond. They and their co-workers have given a qualitative series of strength of acid and base oxides. Since then various definitions have been proposed and many experimental methods have been devised. Solubilities of acid gases, equilibrium measurement with metallic phases, use of indicators, and emf methods are the notable examples. Optical basicity,[3] currently under development, will be a promising alternative. These methods except for the emf one are applicable only to a limited range of compositions and are basically qualitative in general nature.

In our laboratory,[4-8] concentration cells were devised in which the electrode reaction and the junction potential are well defined and the cells allow measurement for rather long durations of time. The thermodynamic activity of $Na_2O$ in $Na_2O$ + MO (MO; $P_2O_5$,[4] $B_2O_3$,[5] $GeO_2$,[6] $SiO_2$,[7] and $MoO_3$[8]) of over $10^8$ range has been measured. The results were interpreted in terms of acid-to-base reaction upon mixing the component oxides.

In the present paper, the emf method is extended to cells consisting of two different binary melts where $Na_2O$ is the common constituent and its activity determines the emf value. The experimental results give the relative strength of acid oxides. Quantitative evaluation of acid strengths of various oxides has not been carried out systematically in spite of its technological importance.

## 2. Experimental Section

The cell employed in the present work is of the type[6]

$$O_2(Pt)|Na_2O\text{-}MO_I(\text{reference})||Na_2O\text{-}MO_{II}|O_2(Pt)$$

where $Na_2O\text{-}MO_I$ is the reference and $Na_2O\text{-}MO_{II}$ is the sample melt. The two melts were electrically connected with an alumina rod wetted with the melts. As in our previous works, it can be assumed that $Na^+$ is the sole conductor in the junction. Furthermore, the electrode reaction in an air atmosphere can be shown by

$$^1/_2O_2 + 2e^- = O^{2-} \qquad (3)$$

Therefore, a virtual current of 2 Faradays from the left to the right of the cell corresponds to a transfer of 1 mol of $Na_2O$ from the left to right compartment. Thus the emf is given by

$$2EF = -RT \ln a_{Na_2O}/a^\circ_{Na_2O} \qquad (4)$$

Table I. Experimental Results of Emf's

| sample melt | reference melt | emf equation | temp range/K | $E$/mV at 1300 K |
|---|---|---|---|---|
| $0.67Na_2O\cdot0.33P_2O_5$ | $0.33Na_2O\cdot0.67SiO_2$ | $E/\mathrm{mV} = -(0.17 \pm 0.05)T + 480 \pm 60$ | 1320–1401 | 259 |
| $0.10Na_2O\cdot0.90GeO_2$ | | $E/\mathrm{mV} = (0.17 \pm 0.01)T + 180 \pm 10$ | 1331–1455 | 401 |
| $0.33Na_2O\cdot0.67GeO_2$ | | $E/\mathrm{mV} = -(0.0093 \pm 0.0015)T \pm 5.9 \pm 2.3$ | 1325–1472 | −6 |
| $0.33Na_2O\cdot0.67B_2O_3$ | | $E/\mathrm{mV} = (0.18 \pm 0.02)T - 12 \pm 20$ | 1163–1272 | 222 |
| $0.50Na_2O\cdot0.50P_2O_5$ | $0.10Na_2O\cdot0.90B_2O_3$ | $E/\mathrm{mV} = (0.39 \pm 0.02)\mathrm{T} - 305 \pm 30$ | 1033–1135 | 202 |
| $0.50Na_2O\cdot0.50MoO_3$ | | $E/\mathrm{mV} = (0.16 \pm 0.16)T - 810 \pm 180$ | 1060–1117 | −602 |
| $0.50Na_2O\cdot0.50WO_3$ | | $E/\mathrm{mV} = (0.24 \pm 0.01)T - 890 \pm 10$ | 1054–1163 | −578 |
| $0.10Na_2O\cdot0.90B_2O_3$[a] | $0.33Na_2O\cdot0.67B_2O_3$ | $E/\mathrm{mV} = -0.54T + 1200$ | | 498 |

[a] Quoted from ref 5 in order to evaluate the emf value referred to the common $0.33Na_2O\cdot0.67SiO_2$ melt.

where $a_{Na_2O}$ and $a^{\circ}_{Na_2O}$ are the thermodynamic activities of $Na_2O$ in the sample and reference melts, respectively.

The melts were prepared from the chemical regents of sodium carbonate anhydride, $SiO_2$, $Na_2MoO_4\cdot2H_2O$, $Na_2WO_4\cdot2H_2O$, $H_3BO_3$, $Na_4P_2O_7$, $NaPO_3$, and $GeO_2$ of "Guaranteed Reagent" grade supplied by Wako Pure Chem. Ind., Ltd. Each mixture of nominal composition was melted in the platinum cell crucible and was kept at a high temperature in order that residual $CO_2$ gas could be expelled completely before the emf measurement.

The precision of the emf's is estimated to be ±3 mV in general cases. However, a $Na_2O-P_2O_5$ melt crept up the bridge as well as the crucible wall. Therefore, the time interval allotted for one run of the system containing $Na_2O-P_2O_5$ was not long enough to evaluate the temperature dependence precisely. As for $0.5Na_2O\cdot0.5MoO_3$ vs. $0.1Na_2O\cdot0.9B_2O_3$, the precision was also poor since the $Na_2MoO_4$ melt was found (after the experiment) to correspond to a sharp equivalence point of neutralization in the $Na_2O-MoO_3$ binary system and the emf value is quite sensitive to any contamination from the junction material.

## 3. Results and Discussion

Table I contains a list of the systems, temperature ranges, temperature equations of the emf's, and their values at 1300 K. The reference melt $\{0.33Na_2O\cdot0.67SiO_2\}$ was replaced in some cases by $0.10Na_2O\cdot0.90B_2O_3$ because of its easier handling properties. In such cases the corresponding change in data must be corrected. The concentration dependence of $Na_2O-B_2O_3$ as measured in the previous study[5] and the present datum of $0.33Na_2O\cdot0.67B_2O_3$ vs. $0.33Na_2O\cdot0.67SiO_2$ were used.

These emf's at 1300 K were plotted in Figure 1 (solid circles). The open circle is the reference point. The value of $0.33Na_2O\cdot0.67GeO_2$ was only -6 mV and coincides with the reference point in Figure 1. The emf–composition relations of each binary system have been reported in the previous papers. Each system was measured in reference to the melt of particular composition. Those emf–composition relations were shifted vertically to pass through the present experimental points (lines in Figure 1). The fact that the curve of $Na_2O-GeO_2$ drawn through the point at $0.33Na_2O\cdot0.67GeO_2$ passes also through the point at $0.10Na_2O\cdot0.90GeO_2$ proves that the cells of the present and previous types functioned properly.

As it has been speculated in the previous papers,[5,6] the activity change of $Na_2O$ of many orders of magnitude may be attributed not to the concentration of $Na^+$ but mainly to the concentration of $O^{2-}$ which is determined by reaction 2, whose equilibrium constant is specific to every binary system. It is especially true for the activity change in a small composition interval. Therefore, considering that thermodynamic activity of a molecular entity rather than that of an ion is sounder, we believe the basicity of the melt may be defined to be equal to the activity of $Na_2O$ in the following discussion. Sodium oxide is not a unique choice among basic oxides. Since $Na^+$ is a rather large ion and bears a small charge, $Na^+$ ion may not behave specifically. Moreover many acid oxides mix with $Na_2O$ at relatively low temperatures (cf. CaO).

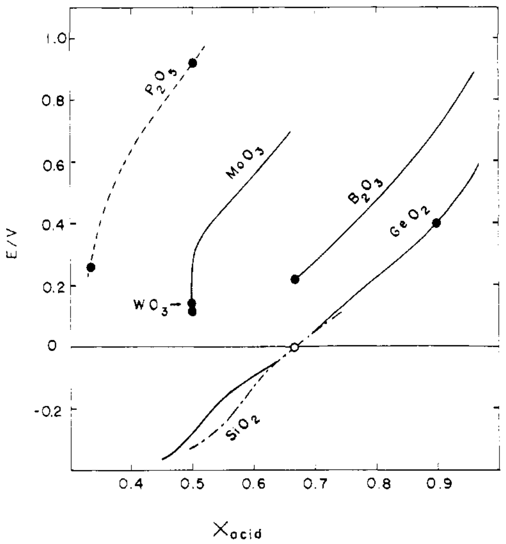

**Figure 1.** The emf's referred to $\{0.33Na_2O\cdot0.67SiO_2\}$ melt plotted against mole fraction of the acid oxide of each system at 1300 K.

Figure 1 indicates that the acid strength decreases in the order $P_2O_5 > MoO_3 \approx WO_3 > B_2O_3 > GeO_2 \approx SiO_2$. To the knowledge of the present authors, Figure 1 is the first presentation of a common and quantitative basicity of various oxide melts containing a common basic oxide. (The sequence of the order of qualitative acid strength has already been found by Flood and Førland 30 years ago.) At the same mole ratio, say at 50 to 50, the acidity of a $Na_2O-P_2O_5$ melt is $10^9$ times as strong as that of a $Na_2O-SiO_2$ melt. In most of the literature concerned with thermodynamic studies on oxide melts, the activity of the component has been discussed with respect mainly to its deviation from Raoult's law or Henry's law. Activities over many orders of magnitude have not been considered in oxide melts in contrast with a field of dilute solutions of oxide ion in a nonoxide solvent like halides or nitrates. Furthermore none of the usual methods like vapor pressure measurement or chemical equilibrium measurement, etc., itself may cover such a wide range of activity as that of $Na_2O$ in the present emf method.

Figure 1 demonstrates not only the acid strength of each acid oxide but also how the basicity of a mixture decreases with $Na_2O$ content. As it is easily understood from previous knowledge on silicates, any acid with a gigantic network seems to function as a polyacid with an infinite series of the equivalence points.[9] This is revealed for $SiO_2$, $GeO_2$, and $B_2O_3$ in Figure 1. On the contrary, $MoO_3$ and possibly $P_2O_5$ show rather sharp inflections at the equivalence points. This kind of information is quite important in understanding the bonding nature in the oxide melts and will find technological application. One may prepare an oxide melt of a desired basicity and of a desired degree of buffer action. Use of mole fraction as the abscissa in Figure 1 is only one of possible choices. Discussions in the future may find an alternative to be better.

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# Cryoscopic Constant, Molar Volumes, Compressibility, and Viscosity in the Systems $CH_3(CH_2)_7COOH-CH_3(CH_2)_7COOM$ (M = Na, K, Rb, Cs) at 30 °C

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**The cryoscopic constant of nonanoic acid is measured and the enthalpy of fusion deduced is compared with the value extrapolated from previous measurements on higher homologues. Density, compressibility, and viscosity of solutions of alkali metal nonanoates in nonanoic acid are reported.**

## Introduction

As a part of our research on fused aliphatic acids, we report the experimental values of some measurements carried out on mixtures of nonanoic acid (pelargonic acid) and alkali metal nonanoates.

## Experimental Section

Pycnometric, viscosimetric, ultrasonic, and cryoscopic experimental methods are described in previous papers (*3–6*). In the pycnometric measurements care was taken to minimize the error due to the adhesion of solutions on the capillaries; e.g., the capillaries were cleaned with a very thin tube of plastic and with cleaning paper rolled around a very thin metallic wire. Notwithstanding, the density and $\varphi_V$ values are obtained at a reliability of 0.7 × $10^{-4}$ g/mL and 1 mL/mol, respectively. The compressibility data, obtained via ultrasonic velocity ($\beta_s = 1/u^2d$) (*9*), and viscosimetric data are given with a reliability of 0.1 × $10^{-6}$ $bar^{-1}$ and 0.1 cP, respectively. The cryoscopic measurements were performed as previously described (*4*), but in this procedure the furnace was substituted by a glass double vessel with circulation of methyl alcohol thermostated in a Lauda ultracryostat. Fluka Puriss nonanoic acid was used without further purification; the melting temperature and some physical properties measured at 30 °C are given in Table I. The alkali metal nonanoates were prepared by complete reaction between stoichiometric amounts of the corresponding carbonates and of a warm alcoholic solution of nonanoic acid. The soap precipitated at room temperature was recrystallized twice from ethyl alcohol and dried under dynamic vacuum at increasing temperature (90 °C maximum). C. Erba RP carbonates were used. Owing to the high cost of $Cs_2CO_3$, the cesium soap prepared was sufficient only for three measurements. The lithium nonanoate is practically insoluble in nonanoic acid and the corresponding system was not studied.

Table I. Some Physical Properties of Nonanoic Acid

| | |
|---|---|
| $d°$, g/mL | $0.8968_4$ |
| $\eta°$, cP | 6.0 |
| $\beta_s°$, $bar^{-1}$ | 65.7 × $10^{-6}$ |
| $T_{fus}$, K | 285.0 |

Table II. Experimental Values of Density, Compressibility, and Viscosity for the Solutions of Alkali Metal Nonanoates in Nonanoic Acid

| nonanoate salt | $C$, mol/L | $d$, g/mL | $10^6\beta_s$, $bar^{-1}$ | $\eta$, cP |
|---|---|---|---|---|
| Na | 0.0400 | $0.8979_7$ | 65.7 | 6.3 |
| | 0.0612 | $0.8986_1$ | 65.6 | 6.5 |
| | 0.1166 | $0.9001_8$ | 65.4 | 7.1 |
| | 0.1767 | $0.9018_8$ | 65.0 | 7.5 |
| | 0.2277 | $0.9033_5$ | 65.2 | 7.9 |
| K | 0.0410 | $0.8986_1$ | 65.4 | 6.4 |
| | 0.0869 | $0.9005_6$ | 65.2 | 6.9 |
| | 0.1229 | $0.9021_1$ | 64.9 | 7.4 |
| | 0.1374 | $0.9027_3$ | 65.0 | 7.5 |
| | 0.1749 | $0.9043_3$ | 64.9 | 8.1 |
| | 0.2298 | $0.9066_0$ | 64.6 | 8.8 |
| Rb | 0.0761 | $0.9031_0$ | 65.3 | 6.8 |
| | 0.1093 | $0.9057_5$ | 65.0 | 7.2 |
| | 0.1474 | $0.9088_7$ | 64.9 | 7.7 |
| | 0.2156 | $0.9143_0$ | 64.4 | 8.6 |
| Cs | 0.0992 | $0.9093_4$ | 65.0 | 7.2 |
| | 0.1225 | $0.9122_8$ | 65.0 | 7.5 |
| | 0.1768 | $0.9190_5$ | 64.6 | 8.3 |

## Results

***Cryoscopy.*** On the basis of previous experiences (*6*), diphenyl is a good cryoscopic solute in aliphatic acids because the corresponding crystallization curves approach the ideal one and formation of mixed crystals is not evident. For this reason diphenyl has been employed in order to determine the cryoscopic constant $(\Delta T/m)°$. The $(\Delta T/m)°$ value is, on the contrary, very low when K or Na soaps are employed as solutes: diphenyl 8.0 K $m^{-1}$; potassium nonanoate 4.6 K $m^{-1}$; sodium nonanoate 5.1 K $m^{-1}$. A value of 8.0 is assumed for the cryoscopic constant and the enthalpy of fusion is calculated following the formula

$$H_f = (RT_0^2M/1000k)$$

where $k$ is the cryoscopic constant. The values $H_f$ = 3.19 kcal/mol, and $S_f$ = 11.2 eu are obtained with a precision of ±2%. These values agree satisfactorily with the equation

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