

Measurements of Decomposition Voltage of $\text{Na}_2\text{O-SiO}_2$ System at Elevated Temperature by Commutator Technique

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Decomposition voltages of Na_2O (30~50 mole %)- SiO_2 binary system were estimated at the temperature range of 700~1200°C by commutator technique. As the experimental procedure, relations between electrolytic current and resulting polarization potential without ohmic loss were observed by 20 cps mechanical commutator, using $\text{Pt}|\text{Na}_2\text{O-SiO}_2|\text{Pt}$ electrochemical system. Experimental decomposition voltages determined from above relationship were the value of 1.5~2.0 V at the temperature beyond about 800°C with comparatively less reproducibility. Further investigations on the decomposition reaction mechanisms were made in reference to both a series of reversible decomposition voltages derived from thermodynamic calculations on the several proposed decomposition reactions and chemical equilibrium in vitreous silicates.

§ 1. Introduction

Several electrolytic and crystallographic investigations have established that ordinary silicate glasses are predominantly ionic substances^{1)~3)}. Although at the ordinary temperature these glasses reveal adequate electrical insulating and dielectric properties, at elevated temperature their melts behave as fairly good ionic, especially cationic, conductor. This means that ordinary silicate glasses may act like "electrolyte" or "fused salt" at higher temperature. In the electrochemical studies of fused salts as well as aqueous solutions, decomposition voltages are often experimentally determined as a pilot value for practice of electrolysis on a given electrochemical system⁴⁾. Experimental decomposition voltage determined by the ordinary methods is explicitly defined as a minimum voltage above which electrode reaction can be actually proceeds, although in the case of irreversible electrode process this value may have less physical meaning. On the other side, several reversible decomposition voltages may be theoretically estimated from the Gibbs free energy changes in the series of the possible electrolytic reactions. Another theoretical value may be experimentally obtained from the emf measurement of reversible cell constructed with the possible components of the electrolyte and electrodes, but this method is not yet available

to the present work because of certain difficulty in utilizing metal electrode such as sodium metal or its alloy at higher temperature. Comparison between these experimental and theoretical values may be available to assume the intrinsic constitutions of the glasses and to explain that electrochemical characteristics, especially, ionic species which participate electrode process and concentration polarization phenomenon. Unfortunately there have been little investigations on the decomposition voltage of the silicate glass melt. Sakai and Seiyama⁵⁾ studied on $\text{Na}_2\text{CO}_3\text{-SiO}_2$ binary system containing less than 50 mole % of SiO_2 at both 950 and 1160°C, using mechanical commutator. From the thermodynamic considerations, they concluded that two successive values of 1.2~1.4 and 1.7~1.9 volts at 1160°C corresponded respectively to the decomposition of Na_2O and SiO_2 in fused salt solution. The present paper contains results of experiment carried out using mechanical commutator and further consideration from thermodynamic stand point on $\text{Na}_2\text{O-SiO}_2$ binary system containing less than 50 mole % of Na_2O at the temperature range of 700~1200°C.

§ 2. Experimental procedure

a) **Sample glasses used** The glass was prepared by melting in a platinum (Pt) crucible an uniform mixture of dry sodium carbonate (chemical reagent grade) and silica (99.9 %

purity) in a silicon carbide furnace at 1200°C or little more and quenching in air the resulting melt to a solid glass on the stainless steel plate. After crushing the glass to the cullet form, each sample was stored in an ordinary glass bottles until remelting for experimental use. Five kinds of sample glasses, that is, 30, 35, 40, 45 and 50 mole % of Na_2O were prepared.

b) Apparatus and procedure In Fig. 1 is

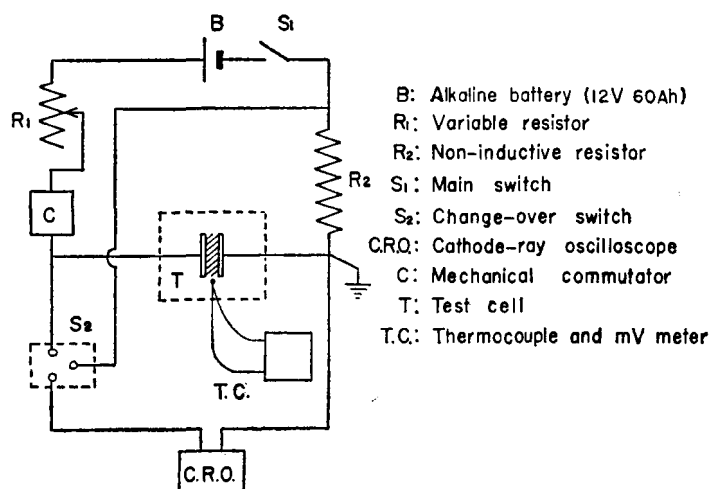


Fig. 1. Circuit diagram of measuring apparatus

shown the schematic arrangement of the main components in the measuring apparatus. In the figure, B represents alkaline storage battery (12 V, 60 Ah capacity) for electrolyzing the experimental cell. R_1 is a variable resistor for controlling electrolytic current and R_2 is a non-inductive resistor (10 Ohm) for measuring electrolytic current by means of cathode ray oscilloscope (C. R. O.). S_1 is a main switch for electrolytic circuit and S_2 is a manual change-over switch for observing alternately both the electrolytic current come from the potential difference across R_2 and resulting polarization potential of the cell. C represents mechanical commutator for making the electrolytic current intermittently. Commutating function is to be revealed by the intermittent electrical contact between phosphor bronze armature and curved small plate fixed on the plastic cylinder which is rotated through a string belt by a c. c. series motor. Pulse width and its interval were adjusted to about 0.02 and 0.05 sec respectively. C. R. O. represents cathode ray dc-ac synchroscope, having the maximum sensibility of 100 mV/cm in vertical axis, for the purpose of observing the each wave from which electrolytic current and

resulting polarization potentials can be estimated respectively. T represents test cell which is constructed from the sample glass as electrolyte and two noble metal electrodes *i. e.* platinum crucible anode and platinum wire cathode of 0.3 mm in diameter and located in a silicon carbide furnace. T. C. is a thermometer comprising Pt-Pt•Rh thermocouple and precise millivolt meter. The order of experimental procedure is

as follows: In the first place Pt crucible containing the cullet is heated in the furnace to $1000\sim 1200^\circ\text{C}$ where no volatilization substantially occurs, followed by inserting Pt wire vertically into the melt to the fixed depth through the ceramic tube attached to the furnace. Then the components are electrically connected each other in a manner similar to that shown in Fig. 1. After the cell is allowed to cool to a chosen temperature, setting R_1 as comparatively higher value and then closing S_1 in a short time and operating C continuously,

both figures on the Braun tube are observed promptly and simultaneously by the manual change of S_2 . From each patterns, whose general forms are schematically shown in Fig. 2, are obtained stationary electrolytic current I and extrapolated polarization potential E as shown in the figure. With the stepwise decrease of R_1 , these manipulations successively repeated in the same manner. Thus a series of polarization potentials corresponding to various electrolytic current can be given at a chosen temperature. If, over a fairly wide range of electrolytic cur-

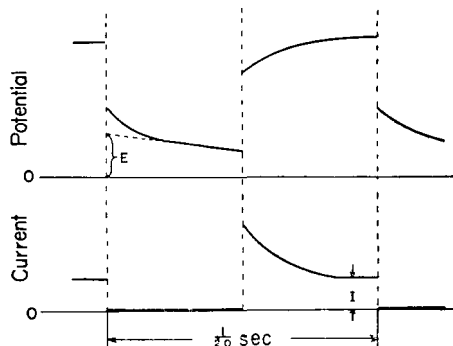


Fig. 2. Transients of electrolytic current and resulting polarization potential

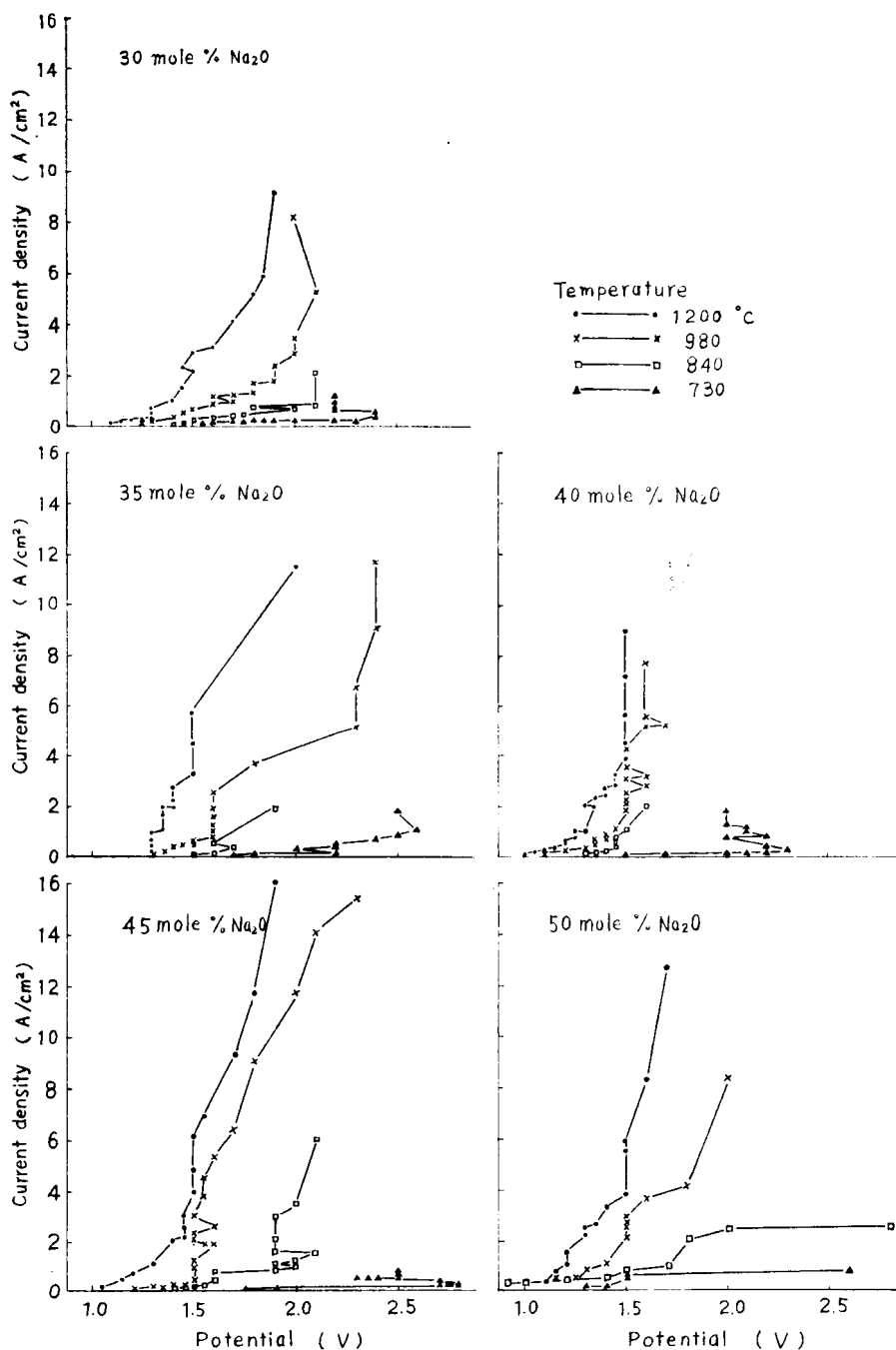


Fig. 3. Relation between stationary electrolytic current and extrapolated value of resulting polarization potential

rent density, one or more of nearly constant values of polarization potentials may be observed, these characteristic values are to be recognized as experimental decomposition voltage of the concerned sample at a chosen temperature.

§ 3. Experimental results

In Fig. 3 and Table 1 are shown relationships

of polarization potentials *versus* electrolytic current densities for cathode and resulting approximate decomposition voltages for five samples at the temperature of 730, 840, 980 and 1200°C respectively. In each measurements at a comparatively lower temperature, reasonable establishment of a certain fixed decomposition voltages was fairly difficult because of both

Table 1. Experimental decomposition voltage of Na₂O-SiO₂ system

Na ₂ O content (mole %)	Temperature (°C)	Approximate decomposition voltage (V)	
30	1200	1.5,	1.9
	980	1.6,	2.0
	840	1.9,	2.1
	730	2.2	
35	1200	1.5	
	980	1.6,	2.3
	840	1.6	
	730	2.1,	2.5
40	1200	1.5	
	980	1.5	
	840	1.5	
	730	2.0	
45	1200	1.5,	(1.9)*
	980	1.5,	2.0
	840	1.6,	1.9
	730	2.5	
50	1200	1.5,	(1.7)*
	980	1.5,	(2.0)*
	840	(1.5)*,	(1.9)*
	730	(1.5)*	

* Figures in parentheses have some uncertainty.

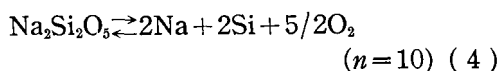
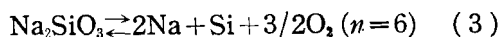
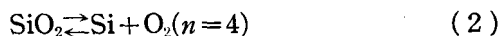
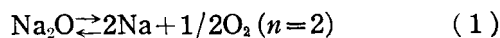
retarding in the reproducibility due to the high increase in the viscosity of the electrolyte and the shortage in boosting electrolysis by outer electric sources. In the course of the experiment, on the cathode Pt wire which was subjected to be highly polarized was there found the deposition of dark greyish substances and innermost electrolyte layer adjacent to the cathode was also fairly contaminated in foggy state. As formerly predicted by Sakai and Seiyama⁹⁾, these deposits, whose isolation from the electrolyte was difficult, were to be recognized as metallic silicon or further formation of Pt-Si alloy from the fact of no weight loss in concentrated hydrofluoric acid. From these experimental evidence, each experiments were carried out using fresh Pt wire cathode and recleaned crucible anode.

§ 4. Discussion

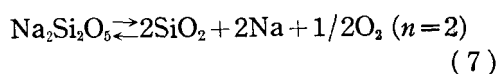
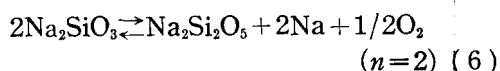
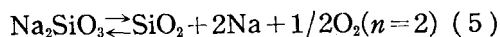
Evaluation of experimental decomposition voltage in reference to corresponding theoretical values: As shown in Fig. 2, polarization potentials, which are observed during rest

period of the intermittent electrolysis, showed decay phenomenon. This shows that experimental decomposition voltages determined from polarization potentials contain intrinsically any irreversible electrode process such as concentration polarization of ions or molecular species which participate electrode reaction. On the contrary, corresponding reversible decomposition voltage, derived from the free energy changes in a given decomposition reaction, is to be defined as the minimum voltage required for the electrolytic decomposition. So several standard decomposition voltages for the possible decomposition reactions were tentatively calculated from thermodynamic data in Table 2 and phase diagram of Na₂O-SiO₂ system⁶⁾, like previous workers⁹⁾.

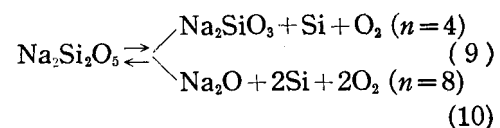
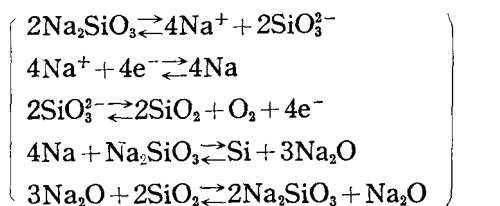
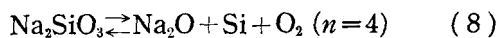
- 1 Direct decomposition of Na₂O, SiO₂, Na₂SiO₃ and Na₂Si₂O₅ to their elements



- 2 Decomposition of Na₂O to its elements in Na₂SiO₃ or Na₂Si₂O₅



- 3 Indirect decomposition of SiO₂ to its elements in Na₂SiO₃ or Na₂Si₂O₅ with consecutive chemical reactions between pre-deposited Na and Na₂SiO₃ or Na₂Si₂O₅



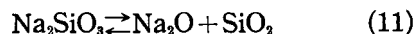
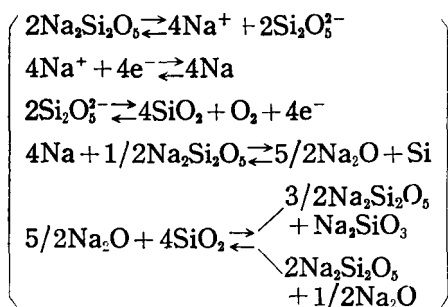
(10)

Table 2. Thermodynamic data in related substances and reactions

Substances		$\Delta H^\circ_{298} \times 10^{-3}$ ^{*2}	S_{298} ^{*2}	C_p ^{*2}
Formula	Description State ^{*1}	(cal/mole)	(cal/deg/mole)	
O ₂	g	0	49.0	$8.27 + 2.58 \times 10^{-4}T - 1.877 \times 10^5/T^2$
Na	c	0	12.2	6.6
Na	l		14.0	7.5
Na	g	25.98	36.72	4.97
Si	c	0	4.47	$5.78 + 6.17 \times 10^{-4}T - 1.01 \times 10^4/T^2$
Na ₂ O	c	-99.4	17.4	$21.4 + 2.10 \times 10^{-3}T - 5.6 \times 10^4/T^2$
SiO ₂	viscous glassy	-202.5	11.2	$12.80 + 4.47 \times 10^{-3}T - 3.02 \times 10^5/T^2$
Na ₂ SiO ₃	c	-363	27.2	$31.14 + 9.6 \times 10^{-3}T - 6.47 \times 10^5/T^2$
Na ₂ SiO ₃	viscous glassy	-360		42.8

Na(l)=Na(c)	$\Delta H_f = 286 - 0.9T$
Na(g)=Na(l)	$\Delta H_v = 26120 - 2.53T$
	$\Delta F_v^\circ = 0$ (at 1153°K)
$\Delta F^\circ \times 10^{-3}$ (cal/mole of each reacting SiO ₄ group ^{*2})	
reaction	800°K 1100°K 1500°K
Na ₂ O + SiO ₂ = Na ₂ SiO ₃	-56.7 -57.1 -58.9
Na ₂ SiO ₃ + SiO ₂ = Na ₂ Si ₂ O ₅	- 2.9 - 3.2 - 3.5

- *1 physical state *2 ΔH°_{298} : standard heat of formation of the given substance from its elements at 298°K
 c: crystalline S_{298} : entropy of the given substance in its thermodynamic state at 298°K
 g: gas C_p : heat capacity at T°K
 e: liquid ΔF° : standard free energy change in formation reaction



Here n represents the number of electrons involved in electrode process. In Fig. 4 is shown each standard decomposition voltages at a given temperature *i. e.* the value of each standard free energy changes in above ten decomposition reactions divided by respective nF (F : Faraday constant). In Fig. 4 each reversible decomposition voltages of pure Na₂O, SiO₂, Na₂SiO₃ and Na₂Si₂O₅ are appreciable values to experimental one. Accordingly, direct decomposition reaction of pure constituents having activities in unity would be probable. But reaction formula No. 1 *i. e.* direct decomposition of pure Na₂O is unlikely to occur because of extremely low equilibrium constant of $10^{-12} \sim 10^{-8}$ at 730~1200°C in the dissociation reaction,

Furthermore, reaction formula No. 2 *i. e.* direct decomposition of pure SiO₂ may be practically impossible. From the same reasons, reaction formula No. 3 and 4 *i. e.* mixed decomposition of Na₂O and SiO₂ may also not be available. As a result, decomposition reaction of Na₂O or SiO₂ in Na₂SiO₃ or Na₂Si₂O₅ such as reaction formula(5)~(10) would be probable.

Relation between decomposition voltage and micro-inhomogeneity of vitreous silicates: Tanaka^{7),8)} predicted that vitreous silicates would have the micro-inhomogeneous structure containing different types of building units and estimated thermodynamically each equilibrium constants for various possible chemical reactions among those building units. If estimated equilibrium constant is unity, standard changes in free energy for the reaction should be equal to zero. Therefore both decomposition voltages of the building units on the left and right sides of the chemical formula are the same. On the contrary, for the large or small equilibrium constants compared with unity large difference is to be expected between decomposition voltages

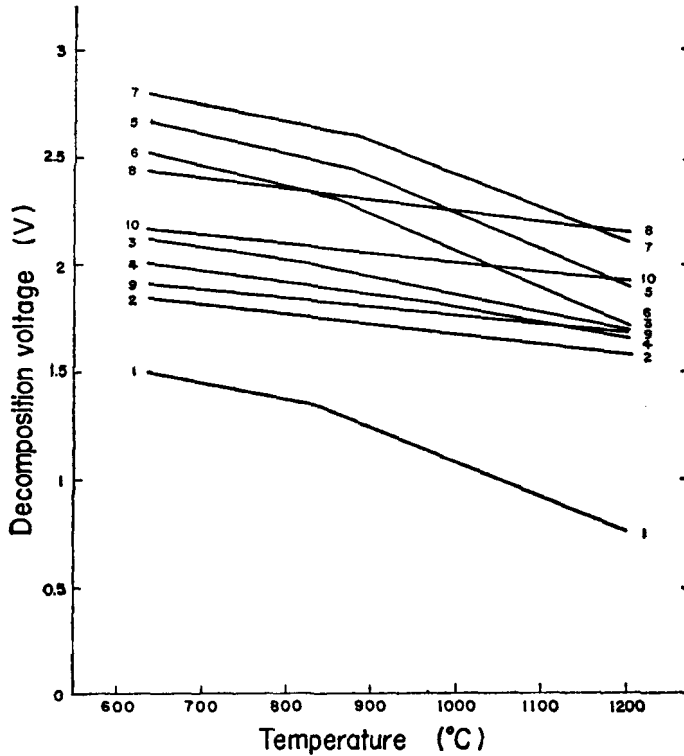


Fig. 4. Standard decomposition voltage at 700~1200°C
Number attached to each solid line indicates corresponding number of reaction formula in the paper.

of the building units on the left and right sides of reaction formula. From these reasons, criteria of micro-inhomogeneity may be available to investigate relation between decomposition voltage and chemical equilibrium.

Acknowledgment

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References

1) *Progress in Ceramic Science*. Vol. 3. Pergamon press, Oxford (1963)

- 2) *Glass-Kogaku Handbook*, Asakura Pub., Tokyo (1963)
- 3) L. PAULING: *The Nature of the Chemical Bond*, 3rd Ed., Cornell University press, N. Y. (1960)
- 4) *Physico-Chemical Constants of Fused Salts*, Kagaku-Dojin, Kyoto (1963)
- 5) W. SAKAI and T. SEIYAMA: *J. Electrochem. Soc. Japan*, 21 (1953) 373, 422, 516.
- 6) E. M. LEVIN, H. F. MCMURDIE and F. P. HALL: *Phase Diagrams for Ceramists*, The American Ceramic Society, Inc., N. Y. (1956)
- 7) M. TANAKA: *J. Ceram. Soc. Japan*, 68 (1960) 205, 72 (1964) 95.
- 8) M. TANAKA: *Bull. Univ. Osaka Pref., Series A*, 13 (1964) No. 2 45.