

Measurement of High Temperature Thermodynamic Properties of Several Binary Alkali Silicate Glasses*

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The method for continuous measurement of the high temperature heat content, developed by W. Oelsen et al. and applied to the glasses by M. Tashiro, was examined and modified in some points. Relations between the temperature and heat contents referred to the standard temperature 25°C, were determined for the some glasses of R_2O-SiO_2 system, and the specific heats as well as the entropies were calculated. Comparing the results, some views have been obtained relating to the effect of the species and content of alkali ions on the thermodynamic quantities of such glasses.

§ 1. Introduction

Although the general use of glass has not been accustomed to thinking of the specific heat or other thermodynamic properties of it as a criterion which decides the usefulness, these properties certainly provide a fundamental approach to the understanding of the glass structure. At present, however, there exists neither adequate theory for the specific heat of glass nor so many accumulated data concerning with the specific heats and heat contents of glasses¹⁾²⁾³⁾, especially, those as functions of temperature. Therefore, it can be said that much more measurements must be carried out to obtain the enough data and to analyze them before an adequate theory can be developed.

W. Oelsen *et al.*⁴⁾ developed a rapid and accurate method for continuous measurement of the heat content of metals in the range of temperature from 25°C to 1000°C. And M. Tashiro⁵⁾ contributed to make this method more convenient through some modifications, and applied it to several melts of glasses and salts. The authors also have employed this method for the purpose of measuring the heat contents of various glasses adding further examinations and modifications in some points. The present paper involves the data of heat contents, specific heats and derived entropies of several simple binary alkali silicate glasses as well as a descrip-

tion of studies on the instrument and procedure of this method.

§ 2. Outline of Instrument and procedure

The instrument used in the present investigation was composed of three important parts, namely the calorimeter and the specially designed sample container in addition to the heating furnace. In Fig. 1 is shown the schematic representation of principal parts of the instrument.

Except some points which underwent the further modification by the authors, this was essentially the same type that Tashiro described in his paper⁵⁾. In the figure A, fitted under the heating furnace B, is a large Dewar flask and C is a copper cylinder which is closed at the bottom end and contains a sample supporter F, a platinum crucible with nichrome wire spring. The flask A is covered by a cork lid which has three holes for the purpose of inserting the copper cylinder C, a thermistor D and a stirrer E. The sample container G (total weight: 173.2 gm.), of which the shape and size are shown in detail in Fig. 2, is the same as that used by Tashiro. It consists of a platinum crucible (a) with cover (c) and a thermocouple-well (b), a platinum tube closed at the bottom end with eight platinum fins fitted radially to the tube to minimize temperature gradients.

A certain amount (50~70gm.) of sample glass was weighed precisely in the sample container G, and heated up to about 150°C higher than the temperature from which the measurement

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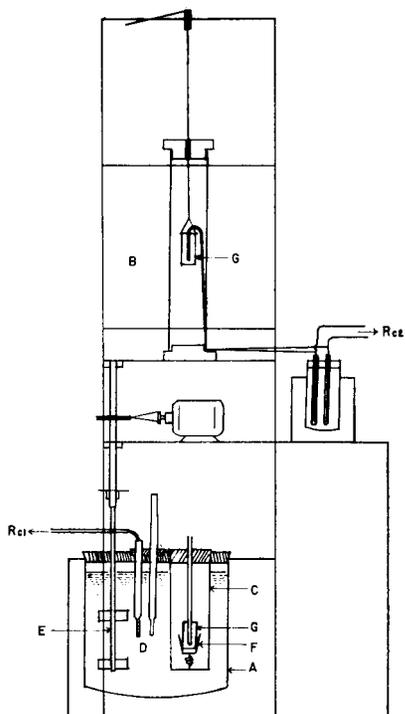


Fig. 1 Schematic representation of the instrument.

- A: Dewar flask, B: Heating furnace,
 C: Copper cylinder, D: Thermistor,
 E: Stirrer, F: Sample supporter,
 G: Sample container

was to be started, and kept at the temperature for about 30 minutes. During this process the glass was remelted and almost satisfactorily refined. In the next step, the sample container was transferred to the supporter F, which soon went down calmly to the bottom of the cylinder C by the help of the nichrome wire spring, due to the addition of weight of sample plus container. After this transferring operation which needed 15~20 seconds, the sample temperature measured by a Pt-Pt·Rh thermocouple (inserted into the thermocouple-well as shown in Fig. 2) and temperature of the bulk water in the calorimeter, measured by thermistor, were recorded simultaneously in successive time lapse until both temperatures reached to congruity. The cooling process required usually about 120 minutes and the cooling rate, needless to say, became progressively slower.

By the operation mentioned above was obtained the calorimeter temperature, being a function of the sample temperature t shown in this paper as T_t . Using this value the heat content of the sample at the temperature $t^\circ\text{C}$ was

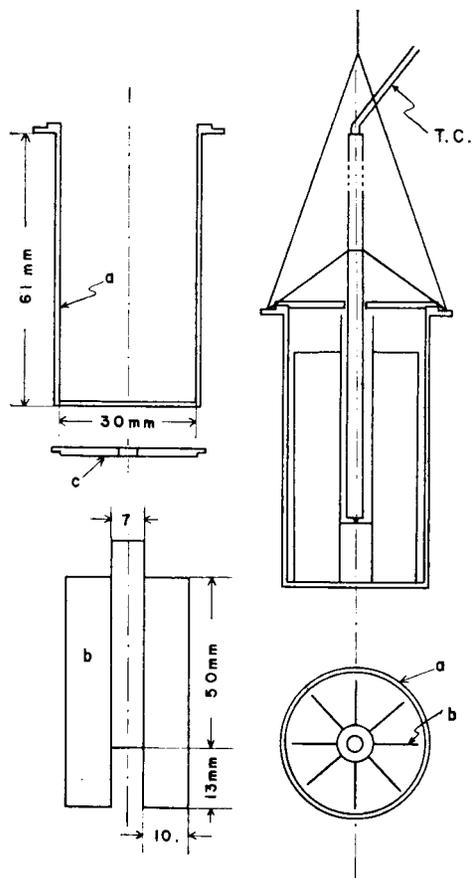


Fig. 2 Detail of the sample container,
 a: Crucible, b: Thermocouple-well, c: Cover,
 T. C.: Thermocouple

calculated by the equation (1) which had been introduced by the previous investigators⁵⁾⁶⁾.

$$H_t^{25} = \frac{W(T_{25} - T_t - \theta_c - \theta_s)}{m} \text{ (cal/gm.)}, \quad (1)$$

H_t^{25} = heat content per gm. of sample at temperature $t^\circ\text{C}$ referred to standard temperature, 25°C .

W = effective heat capacity of calorimeter.

T_{25} = calorimeter temperature when sample temperature is 25°C .

T_t = calorimeter temperature when sample temperature is $t^\circ\text{C}$.

θ_c = correction term for sample container.

θ_s = correction term for thermal loss and mechanical heat of stirring.

m = weight of sample (gm.).

As to the correction terms θ_s , θ_c and the characteristic constant W , examinations in detail will be made in the following sections.

§ 3. Correction term θ_s

θ_s , which corresponds to the mechanical heat of stirring added with the heat leakage from the calorimeter to the surrounding, had to be previously determined by the experiments. Actual observations led the authors to consider that the obtained value of θ_s changed remarkably, depending on the lack of uniformity of the water temperature resulted from the local unbalance between the heat produced by internal friction and the effect of mixing of stirred water in the calorimeter. Therefore, the stirring conditions, namely, design and setting position of the stirrer and its rotation speed, were varied in many ways and examined comparing the temperatures which were measured at the various parts of the calorimeter. Finally the stirrer was determined as shown in Fig. 3A

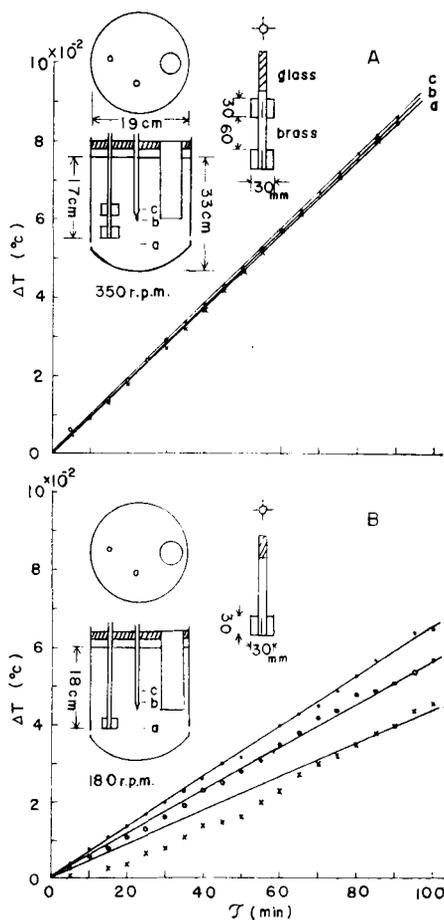


Fig. 3 Changes of the water temperature by stirring time at the three different positions a, b, and c in the calorimeter under the conditions shown in the figures.
A: Condition employed B: Condition not employed

so that the uniform temperature change, produced by heat of stirring, could be realized in the calorimeter as much as possible. The rotation speed of the stirrer was also determined as 350 r.p.m. in the same way.

In Fig. 3 are also shown the relations between the temperature change ΔT and the stirring time τ , at the three different positions in the calorimeter (a, b, c in the figure). The curves correspond to those obtained under the employed condition (Fig. 3A), together with an example of those obtained under the different condition (Fig. 3B). It can be seen that the curves in Fig. 3A show less deviations from the straight lines and better mutual congruity than those in Fig. 3B. This fact means that the employed condition is by far the better. By further examinations it became clear that the rate of change of ΔT , i.e., $d\Delta T/d\tau$, was a function of the average calorimeter temperature T_m , as indicated by the curve in Fig. 4, probably due to the temperature dependency of viscosity of the stirred water. This relation could be formulated as

$$\frac{d\Delta T}{d\tau} = a + bT_m + cT_m^2, \quad (2)$$

where a , b and c were the constants which had to be determined by the experiments. In the present case, the arithmetical mean value of the initial and final calorimeter temperature was used as T_m . After all, the correction term θ_s for the experiment which needed the stirring time τ was given as follows:

$$\theta_s = \int_0^\tau \frac{d\Delta T}{d\tau} d\tau = \int_0^\tau (a + bT_m + cT_m^2) d\tau \text{ (}^\circ\text{C)}. \quad (3)$$

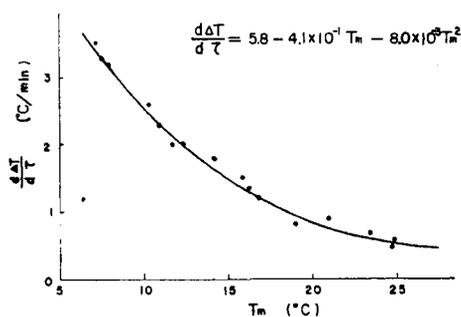


Fig. 4 Relation between the rate of the change of calorimeter temperature by stirring, $d\Delta T/d\tau$ (°C/min), and the average calorimeter temperature, T_m (°C).

§ 4. Correction term θ_c and effective heat capacity of the calorimeter W

The term W which means the total heat capacity of the calorimeter containing 8000 gm. water, was determined by a series of experiments in which a certain amount of heat was, electrically, i. e. by means of a nichrome heater connected to an precise integrating wattmeter, introduced to the calorimeter. The average value of W resulted from twenty-one data was 8417 ± 1.5 (cal/°C). In the other hand, the correction term, θ_c , which corresponds to the heat contents of sample container was calculated from the chemical composition, that is, 80% Pt plus 20% Rh, the total weight and the specific heat data of component metals. The result was indicated, as a function of sample temperature t , by the equation (4),

$$\theta_c = \frac{1}{W} 6.4447 (t - 25) + 0.0007802 (t^2 - 25^2) \text{ (}^\circ\text{C)}, \quad (4)$$

indicating satisfactorily good agreement with the value obtained from tests run on the sample container alone.

§ 5. Measurement and recording of the temperatures

The temperature of the calorimeter and the sample (T_t and t) were measured by a thermistor and a Pt-Pt·Rh thermocouple, respectively, and both temperature were recorded through individual circuits, which are shown as schematic representations in Fig. 5. In the previous

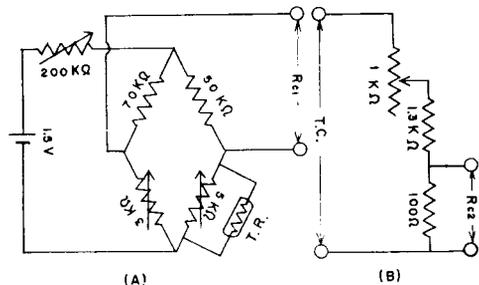


Fig. 5 Circuits used for recording the temperatures.
A: For calorimeter temperature (thermistor T. R.)
B: For sample temperature (thermocouple T. C.)
 R_{c1} , R_{c2} : Recorders

work, a thermometer was used instead of the thermistor. Then, there existed the difficulty in reading successive change of the position of

mercury head moving with considerable rate as the calorimeter temperature increased, especially when the sample temperature, and then the cooling rate, were relatively high. This fact contained the possibility of occurrence of temperature errors which would directly affect the accuracy of results. In the present investigation, however, the anxiety was eliminated by employing the recording system mentioned above.

§ 6. Sample glass

The batches of about 100 gm., prepared using reagent-grade alkali carbonates and highly pure silica sand corresponding to the desired binary glass composition, were melted in a platinum crucible. After the completion of refining, the melt was stirred thoroughly and poured on a stainless steel for the purpose of cooling. Approximately 70 gm. of the glass thus obtained was weighed precisely, in the sample container, and remelted to ready for the measurement. The composition of glasses is listed up in Table 1.

Table 1. Glass samples used

Sample Number	SiO ₂ (mole %)	Composition Alkaline Oxide (R ₂ O mole %)
N 30	70	30 Na ₂ O
N 33.3	66.6	33.3 Na ₂ O
N 35	65	35 Na ₂ O
N 40	60	40 Na ₂ O
N 45	55	45 Na ₂ O
N 50	50	50 Na ₂ O
L 30	70	30 Li ₂ O
L 40	60	40 Li ₂ O
K 30	70	30 K ₂ O
K 40	60	40 K ₂ O

§ 7. Results and Discussion

Heat contents obtained from eqn. (1), H_t^{25} , are expressed by cal/gm. and they can be converted into those in cal/mole, H_t^{25} , by the following equation,

$$H_t^{25} = \{(\text{molecular weight of SiO}_2) \cdot (\text{mole fraction of SiO}_2) + (\text{molecular weight of R}_2\text{O}) \cdot (\text{mole fraction of R}_2\text{O})\} H_t^{25} \quad (5)$$

From the value of H_t^{25} , specific heat, C_p (cal/mole deg.), and entropy referred to the

standard temperature 25°C, S_t^{25} (cal/mole deg.), could be obtained by numerical calculations using the equation (6) and (7),

$$C_p = \frac{dH_t^{25}}{dt}, \quad (6)$$

$$S_t^{25} = \int_{298}^{t+273} \frac{dH_t^{25}}{t+273} = \frac{H_t^{25}}{t+273} + \int_{298}^{t+273} \frac{H_t^{25}}{(t+273)^2} dt. \quad (7)$$

Fig. 6 shows the curve of H_t^{25} of the glass having composition, $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$, together with points that obtained by Tashiro. Both of the results show the fairly excellent agreement.

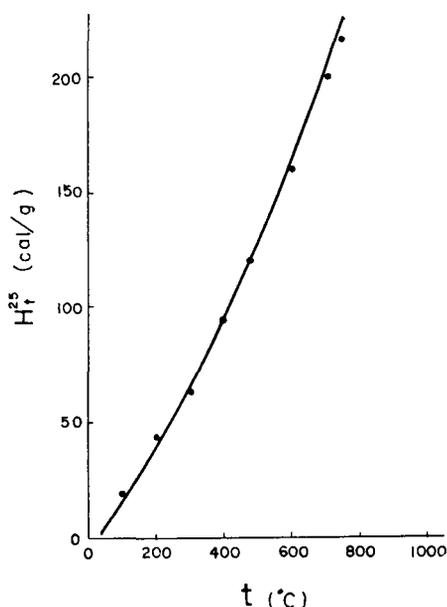


Fig. 6 Heat content H_t^{25} (cal/gm.) of $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ glass. Curve: Value obtained by authors
Points: Value obtained by Tashiro⁵⁾

In Fig. 7A, 7B and 7C are represented the values of H_t^{25} , C_p and S_t^{25} , respectively, for the glasses of $\text{Na}_2\text{O} \cdot \text{SiO}_2$ system, i. e., sample N30~N50. Comparing the curves in these three figures, it can be pointed out that the effect of change of Na_2O concentration does not appear in the temperature range below 350°C, but becomes remarkably beyond this range. From the data of the samples, N30, N35 and N40, which contained 30, 35 and 40 mole % Na_2O , respectively, and gave the glassy phase without any crystal after the experiment, it can be seen that the increase of Na_2O contents brings the increase of these thermodynamic quantities. This fact may be attributed to the increase of

degree of freedom attended upon the increase of alkali ion concentration which gives rise to the decrease of -Si-O- bond energy. Meanwhile, the other two samples which have devitrified remarkably, during the measuring procedure, show the lower values of these quantities being almost equal to each other. For example, their specific heats are about 20% lower than those of the 30 mole % Na_2O glass.

Since the curves of H_t^{25} and S_t^{25} are the values, as already be pointed out, referred to the standard state, i. e., at 25°C and 1 atmosphere pressure, it is necessary to know the absolute values of them at this state to obtain the absolute heat content H_t and entropy S_t of glasses. It should be faced with difficulties, of course, to intend to know the values, at least in the present situation, owing to the lack of such data and methods for precise calculation concerning glasses. The comparison as to the absolute values of the heat content, consequently of the entropy, however, may be possible

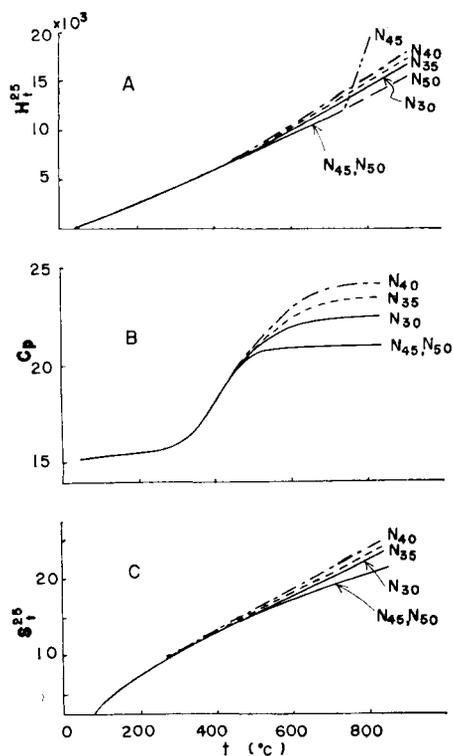


Fig. 7 Molal thermodynamic quantities of glasses of $\text{Na}_2\text{O} \cdot \text{SiO}_2$ system (samples, N30, N35, N40, N45 and N50).

A: Heat contents H_t^{25} (cal/mole)

B: Specific heats C_p (cal/mole deg.)

C: Entropies S_t^{25} (cal/mole deg.)

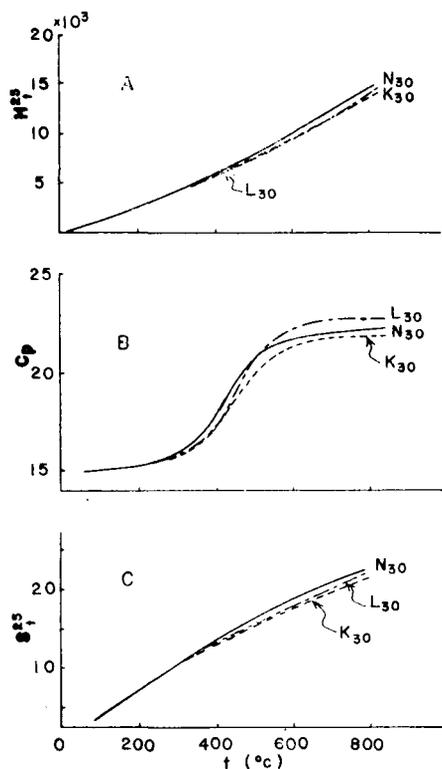


Fig. 8 Molal thermodynamic quantities of $30R_2O \cdot 70SiO_2$ glasses (samples, L 30, N 30 and K 30).
A: H_t^{25} (cal/mole) B: C_p (cal/mole deg.)
C: S_t^{25} (cal/mole deg.)

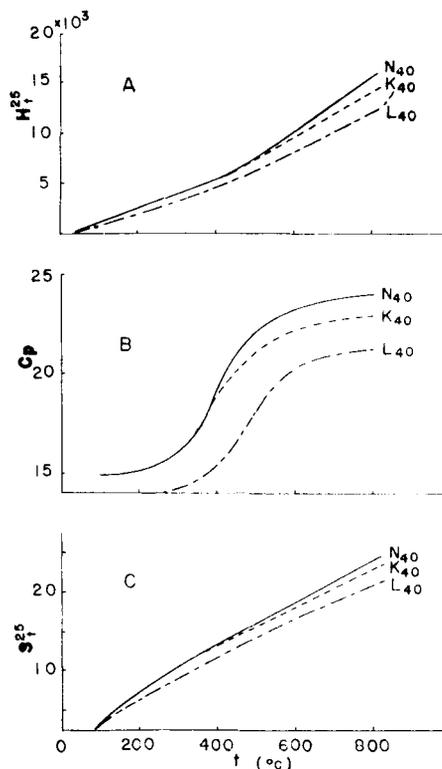


Fig. 9 Molal thermodynamic quantities of $40R_2O \cdot 60SiO_2$ glasses (samples, L 40, N 40 and K 40).
A: H_t^{25} (cal/mole) B: C_p (cal/mole deg.)
C: S_t^{25} (cal/mole deg.)

using some heat data of glasses and crystalline materials at the standard state, for example, heats of solution as were described in the previous paper.

In Fig. 8 and Fig. 9, the thermodynamic quantities of the glasses which contain various alkali ions, that is Li^+ , Na^+ and K^+ , corresponding to the alkali oxide contents of 30 mole % and 40 mole % respectively. Although differences among the heat content curves in Fig. 8A and Fig. 9A, may not be so large that they allow us to believe the sureness in spite of the probable errors, the curves and those of derived quantities indicate, if it can be assumed that they tell the truth, the effects of species of alkali ions, namely, effects of ionic radii and the field strength of electrostatic force around them. Among the glasses which appear in both Fig. 8 and Fig. 9, those in the former did not realize any devitrifications after the experiments, but sample L40 in the latter which contained 40mole % Li_2O devitrified probably because of the high mobility of Li^+ ions of smaller radius. Consequently, the behaviour of

the curves of this glass are markedly different from the others. Generally speaking, it seems that the thermodynamic quantities presented here, except those of Li_2O-SiO_2 system, increase with the decreasing ionic radius of contained alkali ions. This implies that the alkali ions, having higher field strength of the electrostatic force, may bring the more increase of degree of freedom to the glass network through the stronger effect of weakening $-Si-O-Si-$ bond. The somewhat extraordinary behaviour of L30 glass in Fig. 8 may also be explained by the particularly small radius of Li^+ ions, but further investigations are to be carried out to confirm the fact. At all events, relatively small differences among the curves of glasses in Fig. 8 and Fig. 9 suggest the possibility that the glasses, containing different alkali ions but in the same mole fraction, have the similar network structure.

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