The Review of Physical Chemistry of Japan Vol. 30 No. 1 (1960)

THE REVIEW OF PHYSICAL CHEMISTRY OF JAPAN, VOL. 30, NO. 1, AUG. 1960

STUDIES ON THE YOUNG'S MODULUS OF SILICATE GLASS AS A FUNCTION OF TEMPERATURE

BY JIRO MATSUDA

(*Received June 27, 1960*)

The Young's moduli of soda lime silicate glass were measured by a dynamic method. Variations of these moduli during heating, cooling and successive heating-cooling cycle were measured, and the quenching effect was observed. Variation of the internal friction was also measured in the heating course. Kinetic consideration was applied to the decrease of Young's modulus with time at constant temperature and the structural changes of network former and modifier were interpreted.

Introduction

Variation of Young's modulus of the glass as a function of temperature is closely related to the physical and chemical change of the structure of glass, and particularly the various velocities of the change of its elastic properties are very interesting subjects for the research of glassy structure, because the knowledge of kinetic procedure is available for clearing up the process of physical and chemical changes.

From the dynamic point of view on glassy materials, variations on the elastic properties of glass have frequently been studied by many investigators. The results of these investigations show that Young's moduli of silicate glass generally decreases at elevated temperatures except for the glass of Pyrex type and fused silica. However, most of these investigations have been made by the usual static methods. On the other hand the dynamic methods of measuring the elastic properties of various materials have been used for about twenty years and for the last few years have been applied more widely to other substances than glass1,2). The fact that this method is hardly applied to glass is surprising, for glass is a suitable material for this dynamic method because of its typically isotropic properties. The advantages of these dynamic methods are that the various complex effects of hysteresis or the departures from perfect elasticity don't occur, for the measurement is possible under the condition of minute alternating stresses far below the elastic limit and what is more, the elastic changes at constant temperature as a function of time are easily measured, for repeated measurements can be made on the same sample. For the last few years some investigations have been made on several glassy substances3), but these measurements are limited to various elastic properties as a function of temperature.

From the above mentioned point, the present paper will deal with the elastic change of silicate

---

1) M. Ide, *Rev. Sci. Instr.*, **6**, 296 (1935)
2) J. Zachariasen, *Phys. Rev.*, **44**, 116 (1935)
3) *e.g.* S. Spinner, *J. Am. Cer. Soc.*, **37**, 229 (1954); **39**, 113 (1956)

glass at constant temperature and make the simple kinetic consideration.

Experimentals

Sample of glass Commercial glass rods approximately 6 mm in diameter and 150 mm in length were used as the elastic specimens for this study. Before the measurement, heated for a week in the regulated electric furnace and allowed to at 485°C and cooled gradually to room temperature after the lapse of 100 hours by the clockwork, these glasses were annealed.

The temperature as a function of cooling time about these specimens is shown in Fig. 1. By analytical determination, the ingredients of the glass used are as following list.

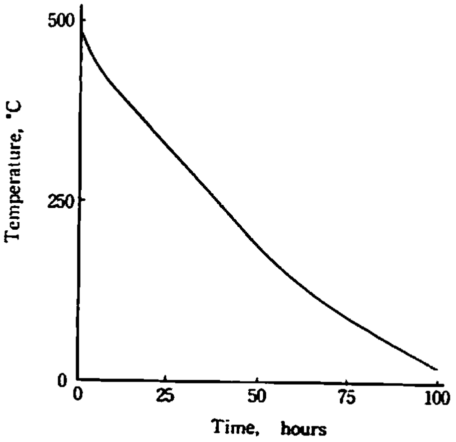

Fig. 1 Cooling curve

Ingredients	Amounts (weight %)
SiO_2	68.68
Na_2O	18.99
K_2O	1.64
CaO	8.45
Al_2O_3	1.91
MgO	trace
BaO	trace
Fe_2O_3	0.29

Apparatus and calculations The block diagram of apparatus for dynamic measurement of Young's modulus is shown in Fig. 2. The audio-oscillator with vernier was several times corrected by a standard crystal oscillator before each measurement. The driver was a magnetic type speaker without a cone. The specimen was suspended horizontally on two fine wires of platinum or iron of 0.3 mm in diameter. One of these wires transmits the excited flexural vibration of the specimen to a crystal pick up. The resulting amplified signal produces a Lissajou pattern on a cathode-ray oscilloscope together with an audio-signal of the same frequency. In the case of flexural vibration, two nodes were located at a distance 0.224 times as long as the specimen length from the ends for the fundamental frequency. In this investigation the supporting wires were not exactly at the ends in order to detect resonant frequencies more easily. In such a case, these wires have slight effects on the vibrating specimen, but this variation is of no importance in the present measurement, for the supported positions are constant during the measurement and the relative changes of Young's moduli are important. The temperature was measured with a thermocouple composed of iron and constantan which was fixed under the middle of the glass. When the supporting wires were even a little slack and sometimes these two wires themselves were in resonance at a certain frequency, it was difficult to detect the resonant

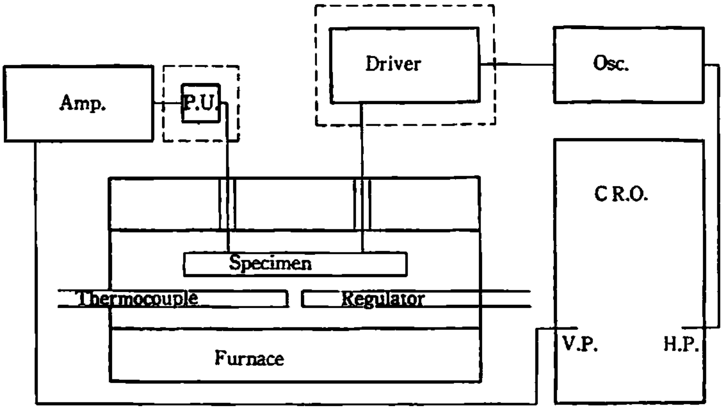

Fig. 2 Apparatus for dynamic measurement of Young's modulus

frequency precisely. This made the measurement very troublesome. In this case such inconvenient resonant frequency of these wires could be taken off by setting plastic cushions around the wires. At high temperatures the amplitude of vibration of specimens decreased and became much less sharp because of increasing internal friction of glass, and in the present investigation the precise measurement was hardly made above 520°C.

Young's moduli, E, can be calculated from the mass and dimensions of the specimen and the resonant frequency of flexural vibration. The equation of this calculation by the dynamic method was given by Pickett[4]. The following equations by Pickett were used in the present investigation

$$E = C_1 W f^2, \tag{1}^*$$

where E : Young's modulus (kilobars)
W : mass of specimen (gm)
f : fundamental flexural frequency
C_1 : $16.0568 \times 10^{-10} d^{-1} (l/d)^3 T_1$,
where l : length of rod (cm)
d : diameter (cm)
T_1 : correction factor by Pickett.

The correction factor, T_1 depends on the shape and Poisson's ratio of the specimen.

On the specimen of glass rod used in the present investigation which was approximately 0.6 cm in diameter, 15 cm in length, T_1 was unit value by Pickett's correction curve, if Poisson's ratio was the value between 1/3 and 0. Poisson's ratio of silicate glass was within the limits of these values and so Pickett's correction curve could be applied to the present investigation. These Young's moduli contained the error of 0.15% which resulted from the graduation of the vernier of the audio-oscillator.

The internal friction Q^{-1} could be obtained as the proportional value to $\Delta f/f$, where f and Δf were the resonant frequency and the peak width respectively. The value of Δf was measured

---

4) G. Pickett, *Am. Soc. Test. Materials. Proc.*, **45**, 846 (1954)

* The dimension of C_1 is (L^{-1}). Consequently E is given dimensionally by the expression, $(E) = (L^{-1}) W f^2 = (M L^{-1} T^{-2})$

as the difference between the two values of frequency at which the amplitude of vibration is half the value of resonance. At high temperatures, the accuracy of these measurements of the peak width was lowered greatly by the increasing internal friction and the energy loss of the supporting wires. Consequently although the temperature at which Q^{-1} showed the peak value and the tendency of the variation of Q^{-1} as the function of elevated temperatures could be observed, its absolute value could not be obtained precisely. But, the observed results gave the values of Q^{-1} of the order between 10^{-2} and 10^{-3}, which are the resonable values of silicate glass.

Thermal expansion was measured by the ordinary optical lever method prepared in this laboratory5).

The heating rate was controlled by the hand-worked trans-former. Prior to the experiment, the relations between the temperatures and the electric currents of the furnace were observed and regulated, repeatedly and a constant heating rate of 3°C per minute could be obtained within the deviation of ±0.2°C.

Thermal expansion Fig. 3 shows the thermal expansion of a rod of the silicate glass used. The temperature increase is 3°C per minute all the time. As shown in Fig. 3, the annealing effect is observed at high temperatures, and the diverging point is about 400°C. The transition temperature* appears at about 500°C. Above this temperature the expansion curve is linear until it reaches the yielding point at about 540°C.

Results

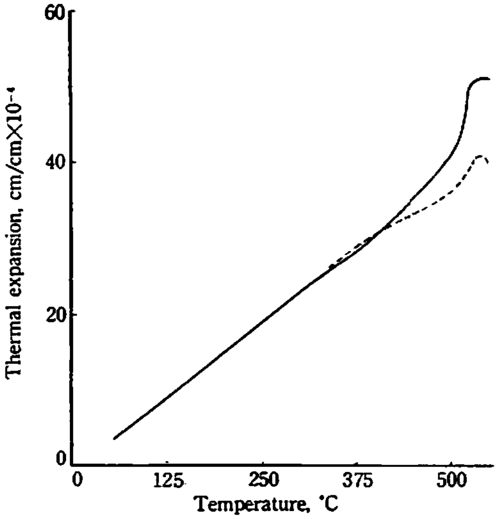

Fig. 3 Thermal expansion

——: annealed glass
⋯⋯: non-annealed glass

---

5) J. Matsuda, *Bull. Chem. Soc. Japan*, **33**, 203 (1960)

* The 'transition' temperature of glass is the one at which the thermal expansion coefficient of the glass begins to show a marked increase with the normal rate of heating during the expansion test. This was defined by Stanworth.

J. E. Stanworth, *Physical properties of glass*, Oxford Univ. Press (1953), p. 176

The coefficients of thermal expansion in various temperature ranges are shown in the following table.

Table 1 Coefficients of thermal expansion (cm/cm/°C × 10^{-6})

Temp. range (C°)	Annealed	Commercial
below 300	7.7	……
300 to 400	9	9
400 to 450	9.4	3.6
450 to 500	10.2	5.4
above 500	28	13.5

The coefficients in the transition temperature range are several times as large as the values in the low temperature range.

As shown evidently from the Equation (1)

$$\frac{E_t}{E_0}=\frac{f_t^2}{f_0^2}\times\frac{1}{(1+\alpha\Delta t)}, \qquad (2)$$

where α : coefficient of thermal expansion

Δt : difference between temperature t and room temperature

E : Young's modulus

f : resonant frequency

t and o express temperature t and room temperature respectively.

The Equation (2) indicates that Young's moduli measured at high temperature must be corrected according to the change of the length.

This correction is of importance in the transition temperature range where the values of α and Δt become great. Naturally α is the adding value of each coefficient in the low temperature ranges.

Young's modulus at elevated temperatures Fig. 4 shows various Young's modulus at elevated temperature on the heating rate of 3°C per minute. These Young's moduli are the values corrected by the Equation (2). The thermal expansion which was used for these corrections is as follow:

Table 2 Thermal expansion (μ/cm)

Temp. (°C)	Annealed	Non-annealed
100	7	7
200	15	15
300	23	23
400	32	32
450	36	34
500	41	36
520	46	38

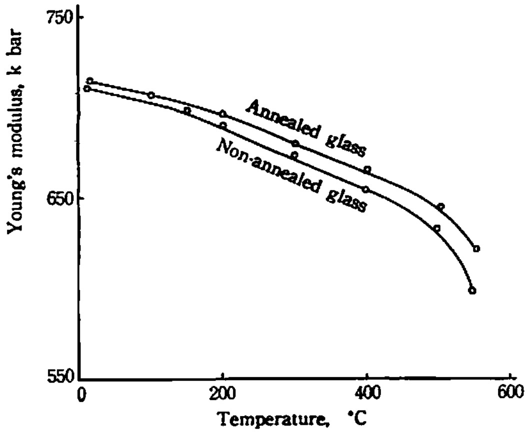

Fig. 4 Young's modulus as a function of temperature

The difference between corrected and uncorrected Young's modulus is within 3 kilobars even at the maximum value at about 500°C. Accordingly the decreases of Young's modulus with the rise of temperature depend on the structural changes themselves. These Young's moduli are, however, the apparent values and not true Young's moduli which are the equilibrium values at each temperature owing to the characteristic properties of the glass; that is, the glass requires some time to reach at the equilibrium structure at that temperature. This subject will be fully discussed later in this paper.

Decrease of Young's modulus at constant temperatures It has long since been shown that the necessary time for the glass kept at constant temperature to be able to arrive at the equilibrium state were a function only of the temperature. Naturally in the low temperature range, the enough to come to equilibrium is long, and may be several decades at room temperature.

According to Naudin's study[6] on the refractive index at a constant temperature, even in the transition region the time required may be several hours. The variation of Young's modulus as a function of time is shown in Fig. 5. These curves were obtained through the following process: each specimen of glass was heated to the requisite temperature at a constant heating rate of 3°C per minute and then held at a constant temperature. The changes of Young's moduli were negligible at constant temperature below 200°C. However, the value of the change of Young's modulus was about 15 kilobars at 500°C. After getting to these constant temperatures, the variation of the length of the specimen was insignificant and didn't affect the calculation of Young's modulus. As the result of this fact, the changes of Young's modulus with time shown in Fig. 5 are caused by the structural changes themselves. These obtained equilibrium Young's moduli are shown in Fig. 6*. The difference between the equilibrium values and the apparant

---

[6] F. Naudin, *Glass Ind.*, 35, 666 (1954)

* These equilibrium values are obtained by kinetic considerations which are illustrated in the section of "discussion" of the present paper.

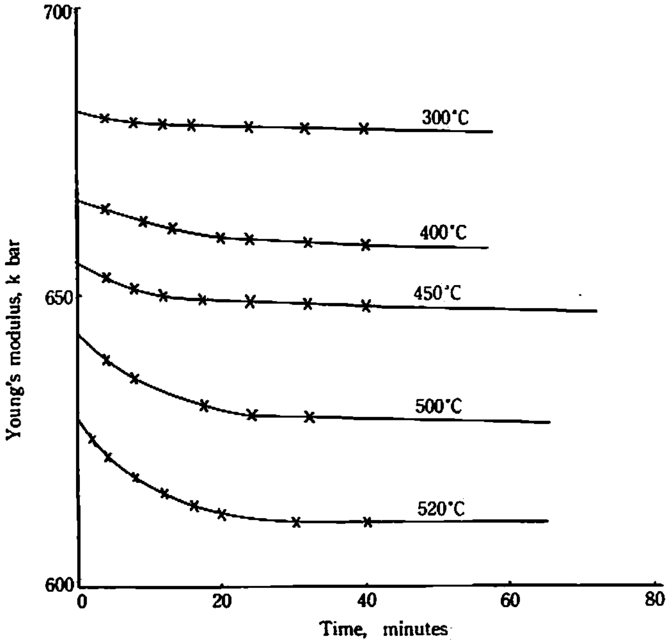

Fig. 5 Young's modulus of various temperature as a function of heating time

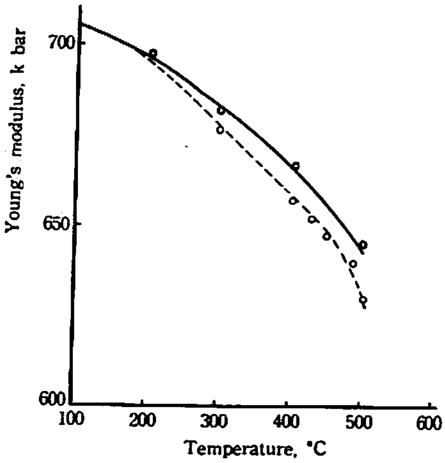

Fig. 6 Difference of apparent and equilibrium Young's modulus

——: apparent values
······: equilibrium values

values which are measured during the rise of temperature, is due to the "delayed structure" of glass. As shown in Figs. 5 and 6, though at high temperatures the decrease of Young's moduli is great, the time it requires to get to the equilibrium state is short compared with the case of the change at low temperature.

The temperature coefficients of Young's modulus are shown in the following table.

Table 3 Temperature coefficients of Young's modulus

Temp. (°C)	dE/dT (kbars/°C × 10^2)
100	− 6
150	−10
250	−15
350	−19
400	−21

These values are plotted in Fig. 7. The temperature coefficients are the linear function with temperatures; that is,

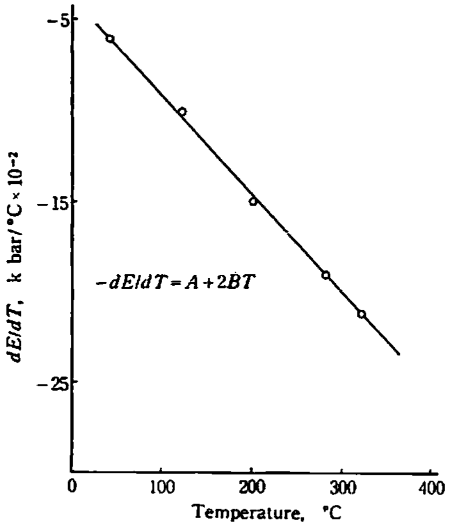

Fig. 7 Temperature coefficient of Young's modulus

$$\frac{dE}{dT} = -A - 2BT$$

$$A \fallingdotseq 4 \text{ (kbars/°C)} \times 10^{-2},$$

$$B \fallingdotseq 0.022 \text{ (kbars/°C/°C)} \times 10^{-2},$$

consequently:
$$E_t = E_0 - AT - BT^2, \tag{3}$$

where E_t : Young's modulus of equilibrium state at temperature t,
E_0 : Young's modulus at room temperature.

Spinner's Equation (3)⁷⁾ can be applied to the present investigation, but it is impossible at the temperature above 450°C. The Equation (3) is only the experimental equation and has no theoretical interpretation, and moreover can be applied only in the temperature range in which

---

7) Reference (3)

glass remains quite elastic.

Apart from the subject of the equilibrium state, the kinetic interpretation of the variation of Young's modulus at constant temperatures is a very interesting subject. However, such investigation is so troublesome that the important experiment to be carried out on the kinetics to interpret the structural change of glasses, is rarely tried. For kinetic considerations, the initial velocity of changes is important rather than the equilibrium state. In view of these facts, the author will study about the kinetics.

Quenching effect on the Young's modulus As stated above, it takes rather long time for glass to settle in the equilibrium state, and such tendency is marked in the low temperature range. Accordingly when glasses held at high temperature are quenched, the structure of these glasses at high temperature will be frozen at low temperature. Taking advantage of this characteristic property of glasses, the properties of glasses heated at high temperature can be investigated at room temperature. As shown in Fig. 4, if annealing is insufficient, Young's moduli are rather small. To study the quenching effects, Young's moduli of several specimens of glass which were quenched in air after having been heated for two hours at the requisite high temperatures were measured at room temperature. The results are shown in Fig. 8. Young's moduli decrease in all the samples, and this tendency is marked at above 500°C of quenching temperature. For reference, the values measured by Stong[8] are plotted above 550°C of quenching temperature.

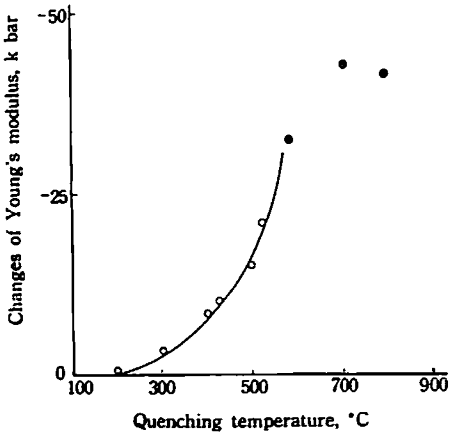

Fig. 8 Quenching effect

○ : author's value
● : Stong's value (soda lime silicate glass)

Internal friction In low temperature range, the glasses have perfect elasticity, but with the increase of temperature, anelastic property improves due to some physical and chemical processes, such as viscous flow, diffusion of alkali ion, thermal conductance etc. The study of the anelasticity of glasses is of great value to interpret various atomic processes which occur in them. The quality can be measured by the internal friction Q^{-1}. $Q^{-1}=0.5773\Delta f/f$, when f and Δf are resonant frequency and peak width respectively. The results are shown in Fig. 9.

---

8) G. Stong, *J. Am. Cer. Soc.*, **20**, 16 (1937). Stong's values were obtained by the static method, about soda lime silicate glass which was not necessary the same as the glass used in this investigation.

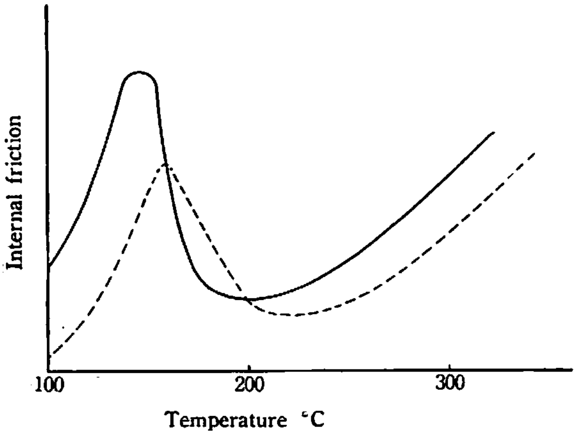

Fig. 9 Internal friction *vs* temperature

——: non-annealed glass
······: annealed glass

The mean values of the three measurements are plotted there. In the annealed glass, the internal friction has the maximum value at about 160°C. The difference between annealed and non-annealed glass is clear; that is, the peak of the former is located at a higher temperature, and smaller in value than that of the latter. Above 250°C, internal friction increases with the rise of temperature.

This result shows that anelastic properties of glass increase with the rise of temperature which controls viscous flow, diffusion of alkali ion and flow of heat.

It is very interesting that glasses have the maximum value of internal friction in the low temperature range, which has been observed by the simple pendulum method[9,10,11]. Forry observed one of the two peaks located between 150° and 250°C in the sodium silicate glasses, and concluded that the peak was most likely responsible for cooperative action of two sodium ions in view of the order of activation energy.

In the glasses under the present investigation, the alkali ions (Na^+, K^+) have the advantage of being much more mobile than the more highly charged ions, and also can produce substitutional disordering even at room temperature. These "order-disorder phenomena" are found more distinctly in glasses containing both Na^+ and K^+ than those containing only one type of alkali ion[12]. Judging from these facts, the author concluded that the peak located at 160°C resulted from the substitutional disordering based on the diffusion of sodium and potassium ions.

Variation of Young's moduli during successive heating-cooling cycles As above stated, the variation of Young's modulus is assumed as an indisputable evidence of the structural change of glass. For the purpose of studying reversible structural changes, variations of Young's modulus were measured with successive heating-cooling cycles repeatedly. Both heating and cooling rates are 3°C per minute all the time, and each maximum temperature in the course

---

[9] J. Fitzgerald, *J. Am. Cer. Soc.*, 34, 314 (1951)

[10] J. McCormick, *ibid.*, 38, 288 (1955)

[11] K. Forry, *ibid.*, 40, 90 (1957)

[12] *e.g.* W. Weyl, *Phase Transformations in Solids*, John Wiley & Sons, Inc., New York (1951), p. 305

of heating is, 100, 300, 400, 450, 475, 500, and 520°C successively at each cycle. Before it was cooled, the glass was heated for two hours at each maximum temperature. It was technically difficult to maintain the constant cooling rate and so variations of Young's modulus in the heating and cooling processes could not be compared precisely as a function of temperature. In spite of such an undesirable handicup, the difference between Young's moduli in these two processes was within the limits of only 2 kilobars below 300°C. These results proved that the glass is a nearly perfect elastic substance in these low temperature ranges.

Even if the glass was heated at the transition temperature about 500°C, the difference could not be over 1 per cent.

These results are different from those of Stong's experiment on the quenched silicate glass[13]. From these results it can be concluded that the glass if fully annealed has rather reversible properties within 1% as for variation of Young's moduli on heating and cooling cycles at the rate of 3°C per minute.

Discussion

As shown in the results of the present investigation, the variation of Young's moduli has negative temperature coefficients, and is surely caused by structural changes of glass. It is difficult to interpret this phenomenon as various type of structural changes are overlapped. Still more the complexity of this problem increases owing to the delayed properties of glass. For instance, during the measurements, delayed and instantaneous changes of the structure of glass affect Young's moduli. But anelastic effects caused by these delayed properties can be suppressed to some extent by the use of the dynamic method.

This is one of the superior points of the method that the static method wants. In view of the facts that the internal frictions don't increase evenly, and Young's moduli greatly decrease above 500°C, there must be at least the two main causes which bring about variation of elastic property as a function of temperature. Accordingly the author attempted to consider about the results on the basis of the kinetics. Up to date, any investigations founded on the kinetics have been hardly applied to the structural change of glass. This is due to the complication of the structure and properties of glass, especially the difficulty of investigation of the transition in solid state. Likewise the author's attempt may be not perfect, and not so accurate as the kinetic study on gaseous or liquidous chemical change. Despite of these defects the results indicate what mechanism the structural change of glass as a function of temperature is. In order to pursue the velocity of the change of Young's modulus under the present experimental condition, the following must be taken into consideration.

Firstly, doesn't the variation of the length of the specimen at a constant temperature affect the apparent Young's moduli? The reason is that resonant frequencies change according to variation of the length of the specimen, even if Young's moduli do not change. For the pur-

---

[13] Reference 8)

pose of this investigation the variation of the length was measured at a constant temperature in the transition range by the optical lever method. This result showed that the variation of length was negligible and would not affect the Young's modulus more than one kilobar in the case of such annealed specimen 15 cm in length and 0.6 cm in diameter.

Secondly, when the temperature is raised to a certain constant temperature by the rate of 3°C per minute, to what extent is the interior of the glass rod heated evenly? In order to study this condition the author considered how long it would take for the center of the glass to have the same temperature as the surface.

In order to simplify the consideration, the effects of the thermal conduction on both ends of the glass rod were neglected. In that case, the following equation of thermal conduction represented by polar co-ordinates could be applied.

$$\frac{\partial T}{\partial t}=k\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right), \tag{4}$$

where r : distance from the center in cross section (cm)

T : temperature (°C)

t : time (sec)

and k : constant decided by the material;

that is, $$k=\frac{K}{S\rho}$$

K: thermal conductivity (cal cm^{-2}. sec^{-1})

S: specific heat (cal per gram per °C)

ρ: density.

Assume $T=R(r)\cdot U(t)$ and $U(t)=Ae^{ct}$,

where A and C are the constants decided by the experimental condition. Then the Equation (4) can be rewritten as

$$\frac{1}{u}\frac{du}{dt}=k\frac{1}{R}\frac{1}{r}\frac{d}{dr}\left(r\frac{dR}{dr}\right)=C$$

or

$$\frac{d^2R}{dr^2}+\frac{1}{r}\frac{dR}{dr}-\frac{C}{k}R=0.$$

If r is written as $$i\sqrt{\frac{k}{c}}\,x$$

$$\frac{d^2R}{dx^2}+\frac{1}{x}\frac{dR}{dx}+R=0.$$

This is exactly Bessel's equation.

Using the solution of the zeroth order* for Bessel's function, the general solution for the Equation (4) is

---

* The solutions except zeroth order are unfit for the present investigation.

$$AJ_0\left(-i\sqrt{\frac{c}{k}}r\right)e^{\prime t}=T(r\cdot t). \qquad (5)$$

From the initial condition, $t=0$, and at the center of glass rod $r=0$, then $A=T(0\cdot 0)$ at room temperature.

It is assumed that the thermocouple shows the temperature of the surface of the glass rod.

To avoid mathematical complexities, the following special case was considered. If the temperature of the surface was raised to $T(r\cdot 0)$°C in a moment from room temperature,

$$J_0\left(-i\sqrt{\frac{c}{k}}r_0\right)=\frac{T(r_0\cdot 0)}{T(0\cdot 0)}, \qquad (6)$$

where r_0 = radius of the glass rod.

When t stands for time necessary for the temperature of the center of the glass rod to be raised to that of the surface,

$$e^{\prime t}=\frac{T(0\cdot t)}{T(0\cdot 0)}, \qquad (7)$$

where $$T(0\cdot t)=T(r_0\cdot 0).$$

When $T(r_0\cdot 0)$ and the room temperature $T(0\cdot 0)$ are 500°C and 10°C respectively, from the Equation (6)

$$J_0\left(-i\sqrt{\frac{c}{k}}r_0\right)=50.$$

From this value of Bessel's function

$$\sqrt{\frac{c}{k}}r_0 \fallingdotseq 7 \qquad (8)$$

If thermal conductivity, specific heat and density of glass are 0.003, 0.3, and 2.5 respectively, k is 0.004, r_0 is 0.3, and c is about 2.2 from the Equation (8). From the Equation (7), $e^{2.2t}=50$, then, $t<2$. Accordingly, the center and the surface of the glass rod have the same temperature within two seconds in this condition.

These results clearly show that the difference of temperature on the cross section of the glass rod is negligiable at the present investigation which was carried out on the heating rate of 3°C perminute.

From these considerations, it is clear that decreases of Young's modulus at a constant temperature were caused by the structural changes of glasses themselves, and these variations are shown in Fig. 5. Fig. 10 shows time coefficients of Young's moduli as a function of the moduli at each time. They were obtained from Fig. 5.

The time coefficient is a linear function of Young's modulus. This can be represented as

$$-\frac{dE}{dt}=k(E-E_e), \qquad (9)$$

where k : rate constant at a certain temperature T
E_e : Young's modulus at equilibrium.

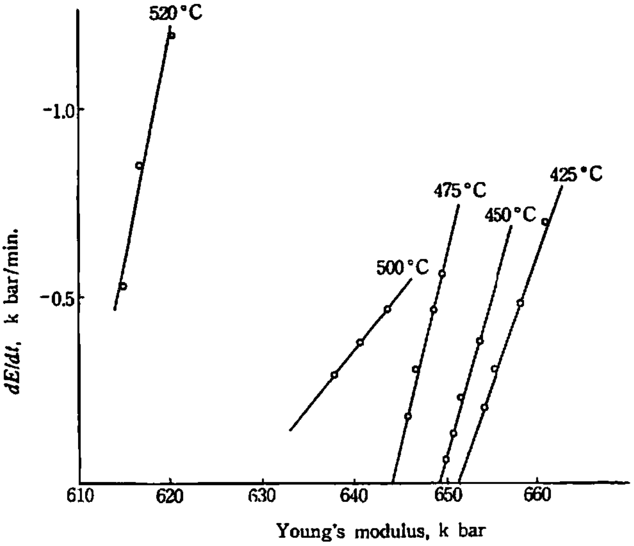

Fig. 10 Velocity of decrease of Young's modulus

As shown in the Equation (9), E_e is Young's modulus at that time when the velocity of variation of Young's moduli is zero; that is, $-dE/dt=0$. This value of E_e can be obtained extrapolating linearly the straight line to the abscissa. Young's moduli plotted in Fig. 6 below 500°C are values of E_e obtained by such an extrapolating method. From the Equation (9) and Fig. 10, it can be also seen that the variation of Young's modulus is the first order as to the Young's modulus. Above 500°C, the calculated velocity $(-dE/dt)$ is rather scattered in the straight line of Fig. 10, and this tendency increases with the lapse of time. Consequently, E_e above 500°C could not be obtained by the extrapolating method.

The slope of each straight line in Fig. 10 represents the value of k at each temperature. These values are shown in the following table.

Table 4 Rate constants at various temperatures

Temp. (°C)	k	$1/Tabs$
425	0.07	1.43×10^{-3}
450	0.09	1.38
475	0.10	1.34
500	0.03	1.29
520	0.11	1.26

This table suggests that the different mechanisms would be approved in the structural change above and below 500°C. The rate constant k is related to the corresponding absolute temperature by Arrhenius' equation $k=Ae^{-B/RT}$ where B is the energy of activation of the rate determining process. The relation between $\log k$ and $1/Tabs$ gives the energy of activation as the slope. As shown in Fig. 11, above 500°C only two points can be plotted, and so these can not be sufficient data.

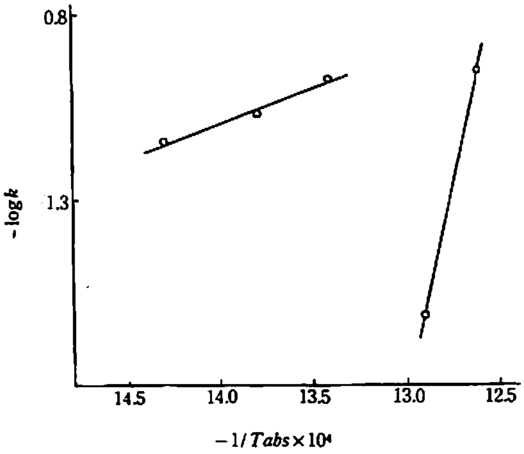

Fig. 11 Relation between log*k* and −1/*Tabs* for the delayed elastic process

But these results show clearly that dissimilar mechanism takes place in the two temperature ranges. The activation energies below and above 500°C are about 10 and 100 kilocalories respectively.

According to these orders of the energies of activation, the following mechanism can be guessed.

Below the transition temperature of 500°C, the delayed elastic properties may be due to the diffusion of alkali ions (Na^+, K^+), for the energy of activation for the diffusion of sodium ion has been known as the order of 10 kilocalories from the investigations of electrocounductivity and internal friction of sodium silicate glass, and this sort of energy of glasses which contain both sodium and potassium ions, may decrease compared with the ones which contain only one type of alkali ion as shown in the example of the "secular rise of zero" of thermometer glasses, and what is more has been known that fused silicate has positive temperature coefficients of Young's modulus[14], and its elastic properties can be theoretically interpreted by the application of Hooke's law to the stretching or compressing of the Si–O–Si units[15]. Consequently the decrease of Young's modulus in the range of temperature below transition point (500°C) may be surely due to the diffusion of alkali ions, and not due to the structural change of Si–O–Si network.

The remarked increase of the energy of activation above 500°C may be due to the viscoelastic flow in glass; that is, delayed elastic properties above this transition temperature may be due to viscous flow in glass.

Taylor and his collaborator[16] found 160 and 140 kilocalories for the energy of activation for delayed elastic distortion and viscous flow process respectively. Wachtman[17] decided that rapid decrease of Young's modulus of poly-crystalline alumina at elevated temperatures was due to grain

---

[14] G. W. Moray, *The Properties of Glass*, Reinhold Publishing Corp., New York (1938), p. 313 and Reference (3)

[15] H. Smith, *J. Am. Cer. Sec.*, 42, 276 (1959)

[16] N. Taylor *et al.*, *J. Soc. Glass Tech. Trans.*, 21, 61 (1947)

[17] J. Wachtman *et al.*, *J. Am. Cer. Soc.*, 42, 254 (1959)

boundary slip and not due to the plastic deformation of individual grain. Both Al_2O_3 and SiO_2 can be formed as network formers in the so-called "Zachariasen's glass structure"[18]. Consequently it is reasonable that the great decrease of Young's modulus of silicate glass is caused by viscous flow. But naturally these different processes can not be divided sharply by the transition temperature of 500°C and these various processes may occur in co-operation at all the temperature ranges. But it may be decided that the delayed elastic properties of glass (decrease of Young's modulus) are caused mainly by the diffusion of alkali ions below transition temperature and mainly by viscous flow above it. At high temperatures, the measurements by the dynamic method used in the present investigation were difficult to make and only a rough estimate could be obtained in these studies. It is desirable hereafter to get more precise interpretation by improving the apparatus of measurement of elastic properties as a function of time at a constans temperature.

Summary

(1) The dynamic method has been applied to the measurement of Young's moduli and internal frictions of annealed silicate glass.

(2) Temperature coefficients of Young's modulus as a function of temperature have been found to be negative, and is represented as $-dE/dT=(A+2BT)$.

(3) Quenching effects have been found to be noticed above the transition temperature.

(4) Internal frictions have maximum peak value at about 160°C, and this peak is shifted to lower temperature and becomes larger in value by quenching glass.

(5) Below 300°C, glass is almost perfectly elastic.

(6) Kinetic consideration has been applied to the decrease of Young's modulus at constant temperature, and this result shows that the decrease of Young's moduli below transition temperature may be caused by the diffusion of alkali ions, and the decrease above that temperature may be caused by viscous flow.

Acknowledgment

The author is greatly indebted to the late Professor R. Kiyama and Professor W. Jono for their interest and many helpful suggestions in connection with this investigation. He also acknowledges the help of Mr. T. Segawa in the Laboratory of Physics, this University for the discussion on thermal conductivity of glass.

Department of Chemistry
Faculty of Science and Literature
Ehime University
Matsuyama, Japan

---

[18] W. Zachariasen, *J. Am. Chem. Soc.*, **54**, 3841 (1932)