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Thermodynamics of Vitreous Silicates

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This is the combined article of the first and second papers (M. Tanaka, *J. Ceram. Assoc. Japan*, **68**, 204 (1960); **72**, 35 (1964)) concerning the Thermodynamic Approach to the Structure of Silicate Glasses. A semi-empirical method is presented for estimating the entropies per mole of SiO_4 group for the fundamental building units of crystalline and/or vitreous silicates. These entropies may be estimated by means of dividing the "molar" entropy of each building unit, which is expressed in the form of rational formula, by the number of SiO_4 groups contained in the unit. The method for calculations is shown to obtain free energy changes and equilibrium constants for reactions resulting in silicate building unit from the combination of other types of silicate building units including silica. By applying the present method, the free energy calculations were made for fundamental reactions at temperatures of 298° to 1500°K. between different types of silicate building units including silica to form metasilicate building units, and the thermodynamic expectations were given for the micro-inhomogeneity of vitreous metasilicates.

1. Introduction

Extensive studies have been made by a number of investigators on the structure of vitreous silicates. Theoretical evidences have been meager, however, concerning the possibility that vitreous silicates would have the "micro-inhomogeneous structure" containing different types of building units[1][2]. Thermodynamic studies may be valuable in the field of this kind, for which little specific information is readily available. In these studies, the equilibrium state cannot be correctly evaluated if one is not aware of side reactions[3]. Thus, the equilibria of possible reactions likely to be involved by different types of building units must be considered for making the correct prediction concerning the possibility of the above micro-inhomogeneity of vitreous silicates in the internal equilibrium state.

It may be possible to estimate the reaction equilibria by the method of calculating free energy changes per "mole" of each reacting SiO_4 group for the vitreous silicate formation when the reacting components are expressed by using the rational formulas. The main purpose of this article is to present the method of calculation and to show its application to predict the micro-inhomogeneity of vitreous metasilicates, assuming that basically the same fundamental building units are retained in the vitreous state as in the crystalline.

2. Computation of Standard Entropy

In silica, where the ratio N_{Si} of the number of silicon atoms to the number of oxygen atoms is 0.500, each silicon stom is at the center of a tetrahedron of oxygen atoms, and

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each oxygen is shared by two silicons[4]−[6]. Each silicon atom in vitreous silicates ($N_{Si} <$ 0.500) of alkali and/or alkali-earth metals is also surrounded by four oxygen atoms in the same manner, but each oxygen can no longer be bounded to two silicon atoms, due to the ionic nature of the metal atoms[7][8]. It has been definitely accepted from informations which have been accumulated regarding the structure of vitreous silicates that each silicon atom in vitreous silicates is surrounded tetrahedrally by four oxygen atoms and SiO_4 group is formed[9]−[13].

Therefore, the entropies per "mole" of SiO_4 group for the fundamental building units of vitreous silicates may be approximated by means of dividing the "molar" entropy of each building unit, which is expressed in the form of rational formula, by the number of SiO_4 groups contained in the unit, when the entropy of the unit is determined from the entropy of silicate compound.

The method is illustrated by an example: suppose that the entropy of the building unit of sodium disilicate in the standard state is desired. The experimental value of 39.4 (cal./deg./mole)has been obtained as the molar entropy of sodium disilicate compound $Na_2O \cdot 2SiO_2$(crystal) in the standard state. This datum was taken from reference 14. According to the theory of glass structure[7]−[13] the sodium disilicate may be represented by the rational formula $(2nNa^+)(Si_{2n}O_{5n}^{2n-})$, where n is an integer. The entropy of n mole-$Na_2O \cdot 2SiO_2$ is, then, equal to the "molar" entropy of $(2nNa^+)(Si_{2n}O_{5n}^{2n-})$. The number of SiO_4 groups contained in this rational formula is $2n$. Thus, the entropy per mole of SiO_4 group for the building unit of sodium disilicate may be approximated as follows:

$$39.4n/2n = 19.7 \text{ (cal./deg./mole of } SiO_4 \text{ group)}$$

If a reaction between silicates including silica to form other silicate, in which the molar entropies of the reactants and product are experimentally determined, is visualized by using rational formulas of their fundamental building units, the standrd change in entropy per mole of each reacting SiO_4 group for the reaction may be readily calculated as illustrated by an example in the following section 4.

However, the experimentally determined entropy data are not abundant for silicate compounds as shown in Table 1. The data in this table were taken from reference 14. In estimating the entropies of solid silicates, which have not been experimentally determined, a method of considerable use was found by Kelley[15]; summarizing the method in the form of a rule, Knapp and Van Vorst[16] presented that "the entropy of a solid silicate may be obtained by adding the entropies of the solid oxides from which the silicate may be considered to be obtained". This rule is restricted to the standard state at 298°K. This method may be available for the computation of molar entropy of silicate compounds desired in the foregoing paragraph.

The implications of Kelley's rule show that the standard change in entropy is relatively small for reactions of forming silicates from the combination of their constituent oxides. It was found, however, for the molar entropies of silicate compounds that the maximum deviation of the experimental values shown in Table 1 from the values estimated by Kelley's rule were $\pm 6\%$. In the case of free energy calculation, the effect of this kind of deviation on the free energy change can be evaluated by including the appropriate value of the deviation into the additively estimated values of entropy.

Table 1. Heat of Formation and Entropy at 298°K. (25°C.)

Substance			$\Delta H°_{298}$ * $\times 10^{-3}$	$S°_{298}$ **
Formula	Description	State†	(cal./mole)	(cal./deg./mole)
SiO_2	quartz	c(α)	−205.4	10.00
	crystobalite	c(α)	−205.0	10.19
	tridymite	c(α)	−204.8	10.36
	vitreous	gls	−202.5	11.2
Na_2O		c	− 99.4	17.4
Na_2SiO_3		c	−363	27.2
		gls	−360	—
$Na_2Si_2O_5$		c	—	39.4
Na_4SiO_4		c	—	46.8
CaO		c	−151.9	9.5
$CaSiO_3$	pseudowollastonite	c(α)	−377.4	20.9
	wollastonite	c(β)	−378.6	19.6
Ca_2SiO_4		c(β)	−538.0	—
		c(γ)	−539.0	—
Ca_3SiO_5		c	−688.4	—
MgO		c	−143.84	6.4
$MgSiO_3$		c	−357.9	16.2
Mg_2SiO_4	forsterite	c	−488.2	22.7

† Physical state: c=crystalline; gls = glassy

* Standard heat of formation of the given substance from its elements at 298°K.

** Entropy of the given substance in its thermodynamic standard state, at 298°K.

The data in the columns of $\Delta H°_{298}$ and $S°_{298}$ were taken from reference 14.

3. Computation of Standard Change in Enthalpy

The molar energy of formation E of a crystalline or vitreous oxide M_mO_n from the simple gaseous ions is related to the values Q of molar heats of formation according to equation (1)[17].

$$E[M_mO_n, \text{ crystal}] = Q[M_mO_n, \text{ crystal}] - mQ[M^{(2n/m)+}, \text{ gas}]$$
$$-nQ[O^{2-}, \text{ gas}] - (m+n)RT \qquad \ldots\ldots\ldots\ldots(1)$$

where R is the universal gas constant and T is an absolute temperature. The sign of E was so chosen as to make E greater, the greater the stability of the substance.

Huggins and Sun[17] presented that the additive assumption† could be expressed for a glass or compound of formula $M_mM'_{m'}M''_{m''}\cdots O_n$, as follows;

$$E = \sum_M m_M \varepsilon_M \qquad \ldots\ldots\ldots\ldots(2)$$

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† It was pointed out in their paper that most instances of significant departures from the additive relationship can be attributed to differences between the numbers or arrangements of closest neighbors.

They also showed that the experimental values of ε_{Si} varying with the silicon-oxygen ratio N_{Si} in the glass are fairly well represented by equation (3).

$$\varepsilon_{Si} = (3172 - 123\,N_{Si}) \times 10^3 \text{ (cal.)} \qquad \ldots\ldots\ldots\ldots(3)$$

The additional remark was given by them that this equation would not be expected to hold for compounds which contain more than one kind of ion of large charge (>2). The data used for the computation of E was the values Q at 291°K., which were collected by Bichowsky and Rossini[18].

Now, consider both reactions at 291°K. among each definite amount of simple gaseous ions of sodium, silicon and oxygen to form a solid silicate S_I, and to form a solid mixture of silicates S_{II} (containing higher % Na_2O than that of S_I) and S_{III} (containing lower % Na_2O than that of S_I). Then, it is seen from equations (1) and (2) that the value ΔE_{291} of [(energy of formation for S_I) – (energy of formation for the mixture of S_{II} and S_{III})] is equal to the value ΔQ_{291} of [(heat of formation for S_I) – (heat of formation for the mixture of S_{II} and S_{III})]. Since the standard chagnge in enthalpy ($\Delta H^°_{291}$) is equal precisely to the negative of the above heat of formation ΔQ_{291},

$$\Delta H^°_{291} = -\Delta E_{291} \qquad \ldots\ldots\ldots\ldots(4)$$

By the method established in thermochemistry, the standard change in enthalpy of the system at 298°K. ($\Delta H^°_{298}$) is expressed by equation (5), as follows:

$$\Delta H^°_{298} = \Delta H^°_{291} + [\Delta H \text{ of products above 291°K.}]\,(\alpha)$$
$$-[\Delta H \text{ of reactants above 291°K.}]\,(\beta) \qquad \ldots\ldots\ldots\ldots(5)$$

However, term ($\alpha-\beta$) is negligible and has been dropped:

$$\Delta H^°_{298} = -\Delta E_{291} \qquad \ldots\ldots\ldots\ldots(6)$$

4. Determination of Equilibrium Constant at Room Temperature

There are two fundamental expressions for the standard change in free energy of a reaction

$$\Delta G^°_T = \Delta H^°_T - T\Delta S^°_T \qquad \ldots\ldots\ldots\ldots(7)$$

and

$$\Delta G^°_T = -RT \ln K \qquad \ldots\ldots\ldots\ldots(8)$$

where $\Delta G^°$ is a standard change in Gibbs free energy of the system, $\Delta H^°$ is a standard change in enthalpy of the system, $\Delta S^°$ is a standard change in entropy of the system, T is an absolute temperature at which the reaction takes place, R is the universal gas constant and K is an equilibrium constant.

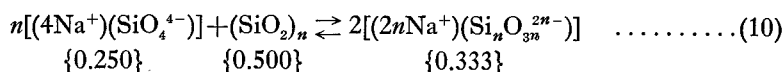For the general reaction $lL + mM + nN \rightleftarrows xX + yY + zZ$

$$K = [(a_X)^x (a_Y)^y (a_Z)^z / (a_L)^l (a_M)^m (a_N)^n] \qquad \ldots\ldots\ldots\ldots(9)$$

wher a is an activity of the individual component.

Now, equilibrium constant K for the reaction at room temperature between funda-
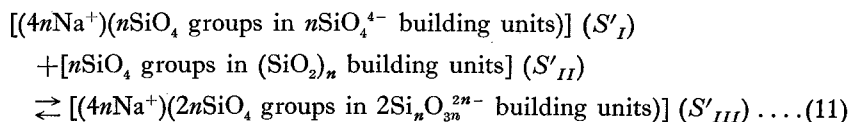
mental building units of silicates including silica to form other type of fundamental build-ing unit may be readily calculated from equations (7) and (8), when the values of $\Delta H°_{298}$ and $\Delta S°_{298}$ for the reaction are computed as described in sections 2 and 3.

As an illustration of the method, consider the following reaction in the standard state at room temperature, in which the fundamental building unit of sodium metasilicate is resulted from the combination of the building unit of sodium orthosilicate with that of silica:

$$n[(4Na^+)(SiO_4^{4-})]+(SiO_2)_n \rightleftarrows 2[(2nNa^+)(Si_nO_{3n}^{2n-})] \quad \cdots\cdots\cdots(10)$$
$$\{0.250\} \quad\quad \{0.500\} \quad\quad\quad \{0.333\}$$

where the value shown within the braces { } is N_{Si} ratio.

Since the numbers of SiO_4 groups in the reactants $n[(4Na^+)(SiO_4^{4-})]$ and $(SiO_2)_n$, and in the product $2[(2nNa^+)(Si_nO_{3n}^{2n-})$ are n, n, and $2n$, respectively,

$$[(4nNa^+)(nSiO_4 \text{ groups in } nSiO_4^{4-} \text{ building units})] \ (S'_I)$$
$$+[nSiO_4 \text{ groups in } (SiO_2)_n \text{ building units}] \ (S'_{II})$$
$$\rightleftarrows [(4nNa^+)(2nSiO_4 \text{ groups in } 2Si_nO_{3n}^{2n-} \text{ building units})] \ (S'_{III}) \cdots(11)$$

For the energies of formation of the reactants and product from the simple gaseous ions, equations (2) and (3) give,

$$\text{Energy of Formation of } S'_I = 4n\varepsilon_{Na}+3141n\times10^3$$
$$\text{Energy of Formation of } S'_{II} = 3111n\times10^3$$
$$\text{Energy of Formation of } S'_{III} = 4n\varepsilon_{Na}+6262n\times10^3$$

Then,

$$\Delta E_{291} = 10n\times10^3/2n$$
$$= 5\times10^3 \text{ (cal./mole of each reacting } SiO_4 \text{ group)}$$

From equations (4) and (6)

$$\Delta H°_{298} = -5\times10^3 \text{ (cal./mole of each reacting } SiO_4 \text{ group)}$$

The entropies $S°_{298}$ of the reactants and product of reaction (10) or (11) are as follows:

$$\text{Entropy of } S'_I = 46.8n$$
$$\text{Entropy of } S'_{II} = 10.0n$$
$$\text{Entropy of } S'_{III} = 54.4n$$

The entropy data for silicate compounds were taken from Table 1. Then, the standard change in entropy for the reaction is:

$$\Delta S°_{298} = -2.4n/2n$$
$$= -1.2 \text{ (cal./deg./mole of each reacting } SiO_4 \text{ group)}$$

Thus, from equation (7)

$$\Delta G°_{298} = -4.6\times10^3 \text{ (cal./mole of each reacting } SiO_4 \text{ group)}$$

and from equation (8)

$$\ln K = (4.6 \times 10^3) / (1.988 \times 298)$$

or

$$K = 2.3 \times 10^3$$

One may be able to determine the equilibrium composition of an elementary reaction, when the equilibrium constant is known.

5. Determination of Equilibrium Constant at Elevated Temperatures

The enthalpy- and entropy-increases as the temperature changes from T_1 to T_2 are respectively related to the heat capacity at constant pressure p:

$$H_{T_2} - H_{T_1} = \int_{T_1}^{T_2} C_p dT \qquad \dots\dots\dots\dots(12)$$

and

$$S_{T_2} - S_{T_1} = \int_{T_1}^{T_2} \frac{C_p dT}{T} \qquad \dots\dots\dots\dots(13)$$

where H is an enthalpy, S is an entropy, and C_p is an heat capacity at constant pressure.

If heat capacity data are available, the changes in enthalpy and entropy for heating at constant pressure may be calculated by equations (12) and (13), respectively. Then, the value of ΔG°_T at an elevated temperature T (°K) may be obtained by the method well established in thermochemistry, as follows:

$$
\begin{aligned}
\Delta G^\circ_T = \Delta H^\circ_{298} & \\
& + [(H_T - H_{298})_{\text{Product}} - \Sigma (H_T - H_{298})_{\text{reactants}}] \\
& - T \Delta S^\circ_{298} \\
& - T [(S_T - S_{298})_{\text{Product}} - \Sigma (S_T - S_{298})_{\text{reactants}}] \qquad \dots\dots\dots\dots(14)
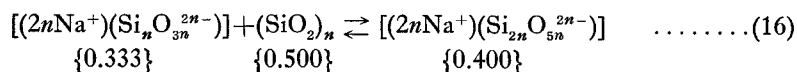\end{aligned}
$$

When heat capacity data are not available, the following estimate of free energy changes of a reaction at elevated temperatures may be possible, if the change in heat capacity is negligible for the initial and final states of the reaction:

$$\Delta G^\circ_T = \Delta H^\circ_{298} - T \Delta S^\circ_{298} \qquad \dots\dots\dots\dots(15)$$

The difference between values of the expression $(H_T - H_{298}) - T(S_T - S_{298})$ for any compound, and for the sum of its component oxides, is equal to the deviation which would arise in the value of ΔG°_T if it were calculated on the assumption that the heat capacities are additive. Richardson et al[19] have emphasized that these differences for silicates formed from oxides are less than 1 kcal., and considerably less than the differences between the corresponding enthalpy and entropy terms.
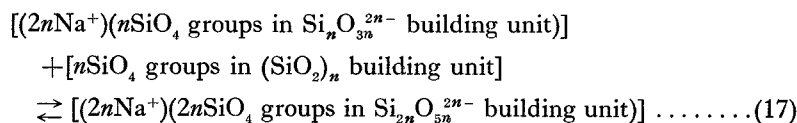
The approximation expressed by equation (15) may be also applied to the computation of values of ΔG°_T for reactions at elevated temperatures between fundamental building units of silicates including silica to form other type of silicate building unit.

This applicability may be illustrated by the following example: calculate the equilibrium constant for reaction (16) in the standard state at elevated temperatures between the building units of sodium metasilicate and of silica to form the building unit of sodium disilicate,

$$[(2n Na^+)(Si_n O_{3n}^{2n-})]+(SiO_2)_n \rightleftarrows [(2n Na^+)(Si_{2n} O_{5n}^{2n-})] \quad \dots\dots\dots(16)$$
$$\{0.333\} \qquad \{0.500\} \qquad \{0.400\}$$

where the value shown in the braces { } is N_{Si} ratio.

This reaction may be written as follows:

$$[(2n Na^+)(n SiO_4 \text{ groups in } Si_n O_{3n}^{2n-} \text{ building unit})]$$
$$+[n SiO_4 \text{ groups in } (SiO_2)_n \text{ building unit}]$$
$$\rightleftarrows [(2n Na^+)(2n SiO_4 \text{ groups in } Si_{2n} O_{5n}^{2n-} \text{ building unit})] \dots\dots\dots(17)$$

By using the procedures decribed in sections 2 and 3,

$$\Delta H^{\circ}_{298} = -2.0 \times 10^3 \text{ (cal./mole of each reacting } SiO_4 \text{ group)}$$

and

$$\Delta S^{\circ}_{298} = 1.1 \text{ (cal./deg./mole of each reacting } SiO_4 \text{ group)}$$

The molar entropy data of the compounds used in the foregoing computation of ΔS°_{298} were taken from Table 1.

Table 2. Free energy changes and equilibrium constants for the reaction (16) at elevated temperatures resulting in the building unit of sodium disilicate from the combination of the building unit of sodium metasilicate with that of silica.

	A		B			
T (°K.)	ΔG°_T (estd)[†] $\times 10^{-3}$ (cal./mole of each reacting SiO_4 group)	K[††]	$[(H_T-H_{298})_{Product} -\Sigma(H_T-H_{298})_{reactants}] \times 10^{-3}$ (cal./mole of each reacting SiO_4 group)	$[(S_T-S_{298})_{Product} -\Sigma(S_T-S_{298})_{reactants}]$ (cal./deg./mole of each reacting SiO_4 group)	ΔG°_T (calcd)* $\times 10^{-3}$ (cal./mole of each reacting SiO_4 group)	K**
298	−2.3	4.8×10	0	0	−2.3	4.8×10
400	−2.4	2.0×10	0.01	0.04	−2.4	2.0×10
500	−2.6	1.3×10	0.05	0.13	−2.6	1.3×10
600	−2.7	9.6	0.11	0.24	−2.7	9.6
700	−2.8	7.4	0.20	0.38	−2.9	8.0
800	−2.9	6.1	0.31	0.53	−3.0	6.5
900	−3.0	5.3	0.45	0.69	−3.2	5.9
1000	−3.1	4.7	0.62	0.86	−3.3	5.2
1100	−3.2	4.3	0.80	1.04	−3.5	4.9

† Estimated from equation (15).
†† Determined from ΔG°_T(estd).
* Calculated from equation (14) by using thermal data at elevated temperatures.
** Determined from ΔG°_T (calcd).

Then, approximate values of $\Delta G°_T$ at elevated temperatures may be readily computed from equation (15), and equilibrium constants at those temperatures may be determined from equation (8) as shown in the column "A" of Table 2.

On the other hand, heat capacities at elevated temperatures have been investigated for SiO_2, $Na_2Si_2O_5$ and Na_2SiO_3[20)21)]. From these thermal data, both values of $[(H_T-H_{298})_{Product} - \Sigma(H_T-H_{298})_{reactants}]$ and $[(S_T-S_{298})_{Product} - \Sigma(S_T-S_{298})_{reactants}]$ for reaction (16) were obtained as a function of absolute temperature as follows:

$$(H_T-H_{298})_{Product} - \Sigma(H_T-H_{298})_{reactants}$$
$$= [-1.5T+0.00252T^2-(10,600/T)+272]/2 \text{ (cal./mole of each reacting } SiO_4$$
$$\text{group) } (298–1147°K.)$$

and

$$(S_T-S_{298})_{Product} - \Sigma(S_T-S_{298})_{reactants}$$
$$= [-3.546 \log_{10}T+0.00504T-(5,300/T^2)+7.331]/2 \text{ (cal./deg./mole of each}$$
$$\text{reacting } SiO_4 \text{ group) } (298-1147°K.)$$

Thus, the value of $\Delta G°_T$ for reaction (16) at any temperature between 298° and 1147°K. calculated form equation (14), and then the equilibrium constant at the temperature is determined from equation (8). These results were shown in the column "B" of Table 2.

As realized from the results shown in Table 2, it is a very useful approximation, when heat capacity data at elevated temperatures are lacking, to determine the equilibrium constants at the temperatures by using equation (15) together with equation (8) for reactions resulting in silicate building unit from the combination of other types of building units of silicates including silica.

6. Application to Vitreous Metasilicate Formation

The data shown in Table 1 may not be directly available to make the free energy claculation for the reactions resulting in metasilicate building units of sodium, calcium and magnesium from the combination of other types of silicate building units including silica. Therefore, the calculations of free energy changes and equilibrium constants for the above types of reactions were made by applying the method presented in the previous sections.

(1) Reactions at Room Temperature

The values of $S°_{298}$ and ε_{Si} are shown in Table 3 for silicates including silica. By using the ε_{Si} and $S°_{298}$ shown in this table, standard changes in enthalpy $\Delta H°_{298}$, entropy $\Delta S°_{298}$ and free energy $\Delta G°_{298}$, and equilibrium constant K were determined for the reactions (Na-1-2) - (Na-1-10), (Na-1-3') - (Na-1-6'), (Ca-1-2) - (Ca-1-10) and (Mg-1-2) - (Mg-1-10), which were shown in Table 4. These results are shown in Tables 5 and 6, in which the equilibrium constants are shown as $\log_{10}K$.

The co-ordination number of O^{2-} ions around Na^+ ion may not be equal in Na_2O reactant and Na_2SiO_3 product for reaction (Na-1-1) shown by using the empirical formulas

Table 3.

Stoichiometric composition	Formula	Mole% M_xO	$S°_{298}$(estd) † (cal./deg./mole)			Silicate anion ††	N_{Si}*	$\varepsilon_{Si} \times 10^{-3}$ ** $\left[\begin{array}{c}\text{cal./mole} \\ \text{of SiO}_4 \\ \text{group}\end{array}\right]$
			$M = \text{Na}$ $x = 2$	$M = \text{Ca}$ $x = 1$	$M = \text{Mg}$ $x = 1$			
M_xO	M_xO	100	17.4 (obsd)	9.5 (obsd)	6.4 (obsd)	—	0	—
$2M_xO \cdot SiO_2$	$M_{2x}SiO_4$	66	46.8 (obsd)	29.0 ± 1.8	22.7 (obsd)	SiO_4^{4-}	0.250	3141
$3M_xO \cdot 2SiO_2$	$M_{3x}Si_2O_7$	60	72.2 ± 4.4	48.5 ± 3.0	39.2 ± 2.4	$Si_2O_7^{6-}$	0.286	3137
$4M_xO \cdot 3SiO_2$	$M_{4x}Si_3O_{10}$	57	99.6 ± 6.0	68.0 ± 4.1	55.6 ± 3.4	$Si_3O_{10}^{8-}$	0.300	3135
$5M_xO \cdot 4SiO_2$	$M_{5x}Si_4O_{13}$	55	127.0 ± 7.7	87.5 ± 5.3	72.0 ± 4.4	$Si_4O_{13}^{10-}$	0.308	3134
$7M_xO \cdot 6SiO_2$	$M_{7x}Si_6O_{19}$	54	181.8 ± 11.0	126.5 ± 7.6	104.8 ± 6.3	$Si_6O_{19}^{14-}$	0.316	3133
$M_xO \cdot SiO_2$	M_xSiO_3	50	27.2 (obsd)	19.6 (obsd)	16.2 (obsd)	$Si_nO_{3n}^{2n-}$	0.333	3131
$M_xO \cdot 2SiO_2$	$M_xSi_2O_5$	33	39.4 (obsd)	29.5 ± 1.8	26.4 ± 1.6	$Si_{2n}O_{5n}^{2n-}$	0.400	3123
$M_xO \cdot 3SiO_2$	$M_xSi_3O_7$	25	47.4 ± 2.9	39.5 ± 2.4	36.4 ± 2.2	$Si_{3n}O_{7n}^{2n-}$	0.429	3119
$M_xO \cdot 4SiO_2$	$M_xSi_4O_9$	20	57.4 ± 3.5	49.5 ± 3.0	46.4 ± 2.8	$Si_{4n}O_{9n}^{2n-}$	0.444	3117
$M_xO \cdot 5SiO_2$	$M_xSi_5O_{11}$	16.7	67.4 ± 4.1	59.5 ± 3.6	56.4 ± 3.4	$Si_{5n}O_{11n}^{2n-}$	0.455	3116
$M_xO \cdot 6SiO_2$	$M_xSi_6O_{13}$	14.3	77.4 ± 4.7	69.5 ± 4.2	66.4 ± 4.0	$Si_{6n}O_{13n}^{2n-}$	0.462	3115
$M_xO \cdot 8SiO_2$	$M_xSi_8O_{17}$	11	97.4 ± 5.9	89.5 ± 5.4	86.4 ± 5.2	$Si_{8n}O_{17n}^{2n-}$	0.471	3114
SiO_2	SiO_2	0	10.0 (obsd)	10.0 (obsd)	10.0 (obsd)	—	0.500	3111

† Entropy of the given substance in its thermodynamic standard state, at 298°K. : (estd) denotes the value estimated by using Kelley's Additive Law of Entropy; (obsd) is the experimentally observed value of Table 1. The deviations of the observed values from the estimated values were within ± 6 % for six kinds of alkali and alkali-earth silicates in Table 1; so the maximum deviation (± 6%) was included here in each of the estimated values; the values observed for silicates of the compositions $2M_xO \cdot SiO_2$, $M_xO \cdot SiO_2$ and $M_xO \cdot 2SiO_2$ were used as references in the later equilibrium calculations.

†† In this column, n of silicate anion formulas denotes an integer.

* Silicon-oxygen ratio.

** A measure of the decrease in energy when one gram-atom of the silicon ion (Si^{4+}) and the equivalent number of oxide ions (O^{2-}) are transferred at room temperature from the gaseous state to an oxide in the solid state: the experimental values are in fairly good agreement with the calculated values for $2Na_2O \cdot SiO_2$, $Na_2O \cdot SiO_2$ and SiO_2 (maximum deviation; about ± 6 × 10^{-2}%)[17].

in Table 4: the co-ordination number is 4 for the crystalline Na_2O with the structure of anti-fluorite type[22], and is reported to be about 6 for glasses of the system Na_2O-SiO_2[7)8)23)24)]. The co-ordination number of O^{2-} ions around M^{2+} ion (that is, Ca^{2+} and/or Mg^{2+}) may not stay the same in MO reactant[25] and $MSiO_3$ product[24)26)] for both reactions (Ca-1-1) and (Mg-1-1) shown in Table 4. Therefore, it is not adequate for reactions (Na-1-1), (Ca-1-1) and (Mg-1-1), as seen from the marginal note of section 3, to estimate the value of $\Delta G°_{298}$ by applying the present procedures. The values of $\Delta G°_{298}$ for the above three reactions were taken from the data by Richardson *et al*[19].

The reactions shown in Table 4 can be divided into four groups (Na-1-1) - (Na-1-10), (Na-1-3') - (Na-1-6'), (Ca-1-1) - (Ca-1-10) and (Mg-1-1) - (Mg-1-10). In each group, the silicon-oxygen ratio N_{Si} of reactants approaches to that of product (0.333) in the order shown in the table, and the N_{Si} ratios of reactants do not change in the three reactions of (Na-1-1), (Ca-1-1) and (Mg-1-1), in the three of (Na-1-2), (Ca-1-2) and (Mg-1-2),...... and in the three of (Na-1-10), (Ca-1-10) and (Mg-1-10). Now, the following evidences are suggested from the comparison of $\log_{10}K$ for reactions shown in Tables 5 and 6: the differences of the equilibrium constants K are not small among the reactions at 298°K.

Table 4. Chemical reactions used for the present thermodynamic calculations.†

Chemical reaction					Reaction no.
Na_2O {0.000}	+	SiO_2 {0.500}	⇄	Na_2SiO_3* {0.333}	(Na-1-1)
$n[(4Na^+)(SiO_4^{4-})]$ {0.250}	+	$(SiO_2)_n$ {0.500}	⇄	$2[(2nNa^+)(Si_nO_{3n}^{2n-})]$ {0.333}	(Na-1-2)
$7n[(4Na^+)(SiO_4^{4-})]$ {0.250}	+	$[(2nNa^+)(Si_{8n}O_{17n}^{2n-})]$ {0.471}	⇄	$15[(2nNa^+)(Si_nO_{3n}^{2n-})]$ {0.333}	(Na-1-3)
$3n[(4Na^+)(SiO_4^{4-})]$ {0.250}	+	$[(2nNa^+)(Si_{4n}O_{9n}^{2n-})]$ {0.444}	⇄	$7[(2nNa^+)(Si_nO_{3n}^{2n-})]$ {0.333}	(Na-1-4)
$2n[(4Na^+)(SiO_4^{4-})]$ {0.250}	+	$[(2nNa^+)(Si_{3n}O_{7n}^{2n-})]$ {0.429}	⇄	$5[(2nNa^+)(Si_nO_{3n}^{2n-})]$ {0.333}	(Na-1-5)
$n[(4Na^+)(SiO_4^{4-})]$ {0.250}	+	$[(2nNa^+)(Si_{2n}O_{5n}^{2n-})]$ {0.400}	⇄	$3[(2nNa^+)(Si_nO_{3n}^{2n-})]$ {0.333}	(Na-1-6)
$n[(6Na^+)(Si_2O_7^{6-})]$ {0.286}	+	$[(2nNa^+)(Si_{2n}O_{5n}^{2n-})]$ {0.400}	⇄	$4[(2nNa^+)(Si_nO_{2n}^{2n-})]$ {0.333}	(Na-1-7)
$n[(8Na^+)(Si_3O_{10}^{8-})]$ {0.300}	+	$[(2nNa^+)(Si_{2n}O_{5n}^{2n-})]$ {0.400}	⇄	$5[(2nNa^+)(Si_nO_{3n}^{2n-})]$ {0.333}	(Na-1-8)
$n[(10Na^+)(Si_4O_{13}^{10-})]$ {0.308}	+	$[(2nNa^+)(Si_{2n}O_{5n}^{2n-})]$ {0.400}	⇄	$6[(2nNa^+)(Si_nO_{3n}^{2n-})]$ {0.333}	(Na-1-9)
$n[(14Na^+)(Si_6O_{19}^{14-})]$ {0.316}	+	$[(2nNa^+)(Si_{2n}O_{5n}^{2n-})]$ {0.400}	⇄	$8[(2nNa^+)(Si_nO_{3n}^{2n-})]$ {0.333}	(Na-1-10)
$n[(6Na^+)(Si_2O_7^{6-})]$ {0.286}	+	$(SiO_2)_n$ {0.500}	⇄	$3[(2nNa^+)(Si_nO_{3n}^{2n-})]$ {0.333}	(Na-1-3')
$n[(8Na^+)(Si_3O_{10}^{8-})]$ {0.300}	+	$(SiO_2)_n$ {0.500}	⇄	$4[(2nNa^+)(Si_nO_{3n}^{2n-})]$ {0.333}	(Na-1-4')
$n[(10Na^+)(Si_4O_{13}^{10-})]$ {0.308}	+	$(SiO_2)_n$ {0.500}	⇄	$5[(2nNa^+)(Si_nO_{3n}^{2n-})]$ {0.333}	(Na-1-5')
$n[(14Na^+)(Si_6O_{19}^{14-})]$ {0.316}	+	$(SiO_2)_n$ {0.500}	⇄	$7[(2nNa^+)(Si_nO_{3n}^{2n-})]$ {0.333}	(Na-1-6')

Chemical reaction					$M=Ca$	$M=Mg$
MO {0.000}	+	SiO_2 {0,500}	⇄	$MSiO_3$* {0.333}	(Ca-1-1)	(Mg-1-1)
$n[(2M^{2+})(SiO_4^{4-})]$ {0.250}	+	$(SiO_2)_n$ {0.500}	⇄	$2[(nM^{2+})(Si_nO_{3n}^{2n-})]$ {0.333}	(Ca-1-2)	(Mg-1-2)
$7n[(2M^{2+})(SiO_4^{4-})]$ {0.250}	+	$[(nM^{2+})(Si_{8n}O_{17n}^{2n-})]$ {0.471}	⇄	$15[(nM^{2+})(Si_nO_{3n}^{2n-})]$ {0.333}	(Ca-1-3)	(Mg-1-3)
$3n[(2M^{2+})(SiO_4^{4-})]$ {0.250}	+	$[(nM^{2+})(Si_{4n}O_{9n}^{2n-})]$ {0.444}	⇄	$7[(nM^{2+})(Si_nO_{3n}^{2n-})]$ {0.333}	(Ca-1-4)	(Mg-1-4)
$2n[(2M^{2+})(SiO_4^{4-})]$ {0.250}	+	$[(nM^{2+})(Si_{3n}O_{7n}^{2n-})]$ {0.429}	⇄	$5[(nM^{2+})(Si_nO_{3n}^{2n-})]$ {0.333}	(Ca-1-5)	(Mg-1-5)
$n[(2M^{2+})(SiO_4^{4-})]$ {2.250}	+	$[(nM^{2+})(Si_{2n}O_{5n}^{2n-})]$ {0.400}	⇄	$3[(nM^{2+})(Si_nO_{3n}^{2n-})]$ {0.333}	(Ca-1-6)	(Mg-1-6)
$n[(3M^{2+})(Si_2O_7^{6-})]$ {0.286}	+	$[(nM^{2+})(Si_{2n}O_{5n}^{2n-})]$ {0.400}	⇄	$4[(nM^{2+})(Si_nO_{3n}^{2n-})]$ {0.333}	(Ca-1-7)	(Mg-1-7)
$n[(4M^{2+})(Si_3O_{10}^{8-})]$ {0.300}	+	$[(nM^{2+})(Si_{2n}O_{5n}^{2n-})]$ {0.400}	⇄	$5[(nM^{2+})(Si_nO_{3n}^{2n-})]$ {0.333}	(Ca-1-8)	(Mg-1-8)
$n[(5M^{2+})(Si_4O_{13}^{10-})]$ {0.308}	+	$[(nM^{2+})(Si_{2n}O_{5n}^{2n-})]$ {0.400}	⇄	$6[(nM^{2+})(Si_nO_{3n}^{2n-})]$ {0.333}	(Ca-1-9)	(Mg-1-9)
$n[(7M^{2+})(Si_6O_{19}^{14-})]$ {0.316}	+	$[(nM^{2+})(Si_{2n}O_{5n}^{2n-})]$ {0.400}	⇄	$8[(nM^{2+})(Si_nO_{3n}^{2n-})]$ {0.333}	(Ca-1-10)	(Mg-1-10)

† In this table, n in chemical equations denotes an integer, and the silicon-oxygen ratios N_{Si} for the reactants and resultants are shown within the braces { } following the chemical formulas for each reaction.

* Thermodynamic calculations were made by Richardson et al[19].

Table 5. Standard changes in enthalpy, entropy and free energy, and equilibrium constant for reactions resulting in sodium metasilicate building units at 298°K. (25°C.)

Group	Reaction no. [†]	$\Delta H^{\circ}_{298} \times 10^{-3}$ [††] (cal./mole of each reacting SiO_4 group)	ΔS°_{298} [†††] (cal./deg./mole of each reacting SiO_4 group)	$\Delta G^{\circ}_{298} \times 10^{-3}$ [*] (cal./mole of each reacting SiO_4 group)	$\log_{10} K$ [**]
	(Na-1-1)	—	—	-56.0 ± 10[***]	41.05 ± 7.33
	(Na-1-2)	− 5.0	− 1.2	− 4.6	3.37
	(Na-1-3)	− 4.4	-1.1 ± 0.4	-4.1 ± 0.2	3.01 ± 0.15
	(Na-1-4)	− 3.7	-1.1 ± 0.5	-3.4 ± 0.2	2.49 ± 0.15
A	(Na-1-5)	− 3.2	-1.0 ± 0.6	-2.9 ± 0.2	2.13 ± 0.15
	(Na-1-6)	− 2.0	− 1.5	− 1.6	1.17
	(Na-1-7)	− 1.0	-0.7 ± 1.1	-0.8 ± 0.4	0.59 ± 0.30
	(Na-1-8)	− 0.8	-0.6 ± 1.2	-0.6 ± 0.4	0.44 ± 0.29
	(Na-1-9)	− 0.7	-0.5 ± 1.3	-0.6 ± 0.4	0.44 ± 0.29
	(Na-1-10)	− 0.5	-0.5 ± 1.4	-0.4 ± 0.5	0.29 ± 0.37
	(Na-1-2)	− 5.0	− 1.2	− 4.6	3.37
	(Na-1-3')	− 2.7	-0.2 ± 1.5	-2.6 ± 0.5	1.91 ± 0.37
B	(Na-1-4')	− 2.0	-0.2 ± 1.5	-1.9 ± 0.5	1.39 ± 0.37
	(Na-1-5')	− 1.6	-0.2 ± 1.6	-1.5 ± 0.5	1.10 ± 0.37
	(Na-1-6')	− 1.1	-0.2 ± 1.6	-1.0 ± 0.5	0.73 ± 0.37

[†] The chemical reaction corresponding to each reaction no. was shown in Table 4.
[††] Standard change in enthalpy at 298°K.
[†††] Standard change in entropy at 298°K.
[*] Standard change in Gibbs free energy at 298°K.
[**] Logarithm of base 10 of the equilibrium constant at 298°K.
[***] Taken from the data of reference 19.

resulting in Na_2SiO_3, $CaSiO_3$ and $MgSiO_3$ from the combination of their component oxides; on the other hand, the differences of K are almost within the suggested range of deviations among the reactions at 298°K. resulting in the metasilicate building units of sodium, calcium and magnesium from the combination of other types of building units of silicates including silica, when the N_{Si} ratio of each of the reacting silicate building units are kept constant in the reactions concerned.

(2) Reactions at Elevated Temperatures

The values of ΔG°_T at temperatures of 400° to 1500°K. for reactions in Tables 5 and 6 are estimated by using equation (15), as shown in Table 7.

The equilibrium constants K for the above reactions were determined from the values of ΔG°_T shown in Table 7 by using equation (8). These results are shown in Figs. 1 to 4 together with values of $\log_{10} K$ at 298°K. listed in Tables 5 and 6: Fig. 1 shows the equilibrium constant as a function of temperature for reactions resulting in metasilicates of sodium, calcium and magnesium from the combination of their component oxides; Figs. 2, 3 and 4 show the equilibrium constant as a function of temperature for reactions among different types of silicate building units including silica to form the building units of metasilicates of sodium, calcium and magnesium, respectively. The curves in Fig. 1

Table 6. Standard changes in enthalpy, entropy and free energy, and equilibrium constant for reactions resulting in the building units of calcium- and magnesium-metasilicates at 298°K. (25°C.)

Reaction no. [†]	$\Delta H°_{298} \times 10^{-3}$ [††]	$\Delta S°_{298}$ [†††]	$\Delta G°_{298} \times 10^{-3}$ [*]	$\log_{10} K$ [**]
	(cal./mole of each reacting SiO$_4$ group)	(cal./deg./mole of each reacting SiO$_4$ group)	(cal./mole of each reacting SiO$_4$ group)	
(Ca-1-1)	—	—	-21.3 ± 1 [***]	15.61 ± 0.74
(Mg-1-1)	—	—	$- 8.6 \pm 1$ [***]	6.30 ± 0.74
(Ca-1-2)	$- 5.0$	0.1 ± 0.9	$- 5.0 \pm 0.3$	3.67 ± 0.22
(Mg-1-2)	$- 5.0$	$- 0.2$	$- 4.9$	3.59
(Ca-1-3)	$- 4.4$	0.1 ± 1.0	$- 4.4 \pm 0.3$	3.23 ± 0.22
(Mg-1-3)	$- 4.4$	-0.2 ± 0.4	$- 4.3 \pm 0.2$	3.15 ± 0.15
(Ca-1-4)	$- 3.7$	0.1 ± 0.9	$- 3.7 \pm 0.3$	2.71 ± 0.22
(Mg-1-4)	$- 3.7$	-0.2 ± 0.7	$- 3.6 \pm 0.3$	2.64 ± 0.22
(Ca-1-5)	$- 3.2$	0.1 ± 0.9	$- 3.2 \pm 0.3$	2.35 ± 0.22
(Mg-1-5)	$- 3.2$	-0.2 ± 0.5	$- 3.1 \pm 0.2$	2.27 ± 0.15
(Ca-1-6)	$- 2.0$	0.1 ± 0.9	$- 2.0 \pm 0.3$	1.47 ± 0.22
(Mg-1-6)	$- 2.0$	-0.2 ± 0.6	$- 1.9 \pm 0.2$	1.39 ± 0.15
(Ca-1-7)	$- 1.0$	0.1 ± 0.9	$- 1.0 \pm 0.3$	0.73 ± 0.22
(Mg-1-7)	$- 1.0$	-0.2 ± 0.8	$- 0.9 \pm 0.3$	0.66 ± 0.22
(Ca-1-8)	$- 0.8$	0.1 ± 0.9	$- 0.8 \pm 0.3$	0.59 ± 0.22
(Mg-1-8)	$- 0.8$	-0.2 ± 0.8	$- 0.7 \pm 0.3$	0.51 ± 0.22
(Ca-1-9)	$- 0.7$	0.1 ± 1.0	$- 0.7 \pm 0.3$	0.51 ± 0.22
(Mg-1-9)	$- 0.7$	-0.2 ± 1.2	$- 0.6 \pm 0.4$	0.44 ± 0.29
(Ca-1-10)	$- 0.5$	0.1 ± 1.0	$- 0.5 \pm 0.3$	0.37 ± 0.22
(Mg-1-10)	$- 0.5$	-0.2 ± 0.9	$- 0.4 \pm 0.3$	0.29 ± 0.22

The notations †, ††, †††, *, ** and *** used in this table are the same as used in Table 5.

were plotted by using the data of Richardson et al[19]. The diameter of each open circle in Figs. 2 to 4 represents the range of suggested deviation of equilibrium constant at the temperature corresponding to the center of the circle. The reaction corresponding to each reaction no. in Figs. 1 to 4 was shown in Table 4.

It is realized from the equilibrium constant vs. temperature curves shown in Fig. 1 that the differences of the equilibrium constants K are not small among the reactions at an elevated temperature resulting in Na$_2$SiO$_3$, CaSiO$_3$ and MgSiO$_3$ from the combination of their component oxides.

Figs. 2 to 4 show that the differences of K are almost within the suggested range of deviations among the reactions at an elevated temperature resulting in the building units of metasilicates of sodium, calcium and magnesium from the combination of other types of building units of silicates including silica, when each N_{Si} ratio of the reacting silicate building units is kept constant among the reactions concerned. As realized from the procedures of computing both values of $\Delta H°_{298}$ and $\Delta S°_{298}$, the former value is not affected, whereas the latter is additively affected, by replacing Na$^+$ ion by Ca^{2+} and/or Mg^{2+}

Table 7. Standard change in free energy for reactions resulting in the building units of sodium-, calcium- and magnesium-metasilicates at elevated temperatures.

Reaction no. [†]	$\Delta G_T^o \times 10^{-3}$ * (cal./mole of each reacting SiO_4 group)				
	$T = 400°$K.	$T = 600°$K.	$T = 800°$K.	$T = 1100°$K.	$T = 1500°$K.
(Na-1-1)**	-56.1 ± 10	-56.4 ± 10	-56.7 ± 10	-57.1 ± 10	-58.9 ± 10
(Ca-1-1)**	-21.3 ± 1	-21.2 ± 1	-21.2 ± 1	-21.2 ± 1	-21.1 ± 1
(Mg-1-1)**	-8.5 ± 1	-8.2 ± 1	-8.0 ± 1	-7.7 ± 1	-7.3 ± 1
(Na-1-2)	-4.5	-4.3	-4.0	-3.7	-3.2
(Ca-1-2)	-5.0 ± 0.4	-5.1 ± 0.6	-5.1 ± 0.8	-5.1 ± 1.0	-5.2 ± 1.4
(Mg-1-2)	-4.9	-4.9	-4.8	-4.8	-4.7
(Na-1-3)	-4.0 ± 0.2	-3.7 ± 0.3	-3.5 ± 0.4	-3.2 ± 0.5	-2.7 ± 0.6
(Ca-1-3)	-4.4 ± 0.4	-4.5 ± 0.6	-4.5 ± 0.8	-4.5 ± 1.1	-4.6 ± 1.6
(Mg-1-3)	-4.3 ± 0.2	-4.3 ± 0.3	-4.2 ± 0.4	-4.2 ± 0.5	-4.1 ± 0.6
(Na-1-4)	-3.3 ± 0.2	-3.0 ± 0.3	-2.8 ± 0.4	-2.5 ± 0.6	-2.0 ± 0.8
(Ca-1-4)	-3.7 ± 0.4	-3.8 ± 0.6	-3.8 ± 0.8	-3.8 ± 1.0	-3.9 ± 1.4
(Mg-1-4)	-3.6 ± 0.3	-3.6 ± 0.5	-3.5 ± 0.6	-3.5 ± 0.8	-3.4 ± 1.1
(Na-1-5)	-2.8 ± 0.3	-2.6 ± 0.4	-2.4 ± 0.5	-2.1 ± 0.7	-1.7 ± 0.9
(Ca-1-5)	-3.2 ± 0.4	-3.3 ± 0.6	-3.3 ± 0.8	-3.3 ± 1.0	-3.4 ± 1.4
(Mg-1-5)	-3.1 ± 0.2	-3.1 ± 0.3	-3.0 ± 0.4	-3.0 ± 0.6	-2.9 ± 0.8
(Na-1-6)	-1.4	-1.1	-0.8	-0.3	$+0.3$
(Ca-1-6)	-2.0 ± 0.4	-2.1 ± 0.6	-2.1 ± 0.8	-2.1 ± 1.0	-2.2 ± 1.4
(Mg-1-6)	-1.9 ± 0.3	-1.9 ± 0.4	-1.8 ± 0.5	-1.8 ± 0.7	-1.7 ± 0.9
(Na-1-7)	-0.7 ± 0.5	-0.6 ± 0.7	-0.4 ± 0.9	-0.2 ± 1.3	$+0.1 \pm 1.7$
(Ca-1-7)	-1.0 ± 0.4	-1.1 ± 0.6	-1.1 ± 0.8	-1.1 ± 1.0	-1.2 ± 1.4
(Mg-1-7)	-0.9 ± 0.4	-0.9 ± 0.5	-0.8 ± 0.7	-0.8 ± 0.9	-0.7 ± 1.2
(Na-1-8)	-0.6 ± 0.5	-0.4 ± 0.8	-0.3 ± 1.0	-0.1 ± 1.4	$+0.1 \pm 1.8$
(Ca-1-8)	-0.8 ± 0.4	-0.9 ± 0.6	-0.9 ± 0.8	-0.9 ± 1.0	-1.0 ± 1.4
(Mg-1-8)	-0.7 ± 0.4	-0.7 ± 0.5	-0.6 ± 0.7	-0.6 ± 0.9	-0.5 ± 1.2
(Na-1-9)	-0.5 ± 0.6	-0.4 ± 0.8	-0.3 ± 1.1	-0.1 ± 1.5	$+0.1 \pm 2.0$
(Ca-1-9)	-0.7 ± 0.4	-0.8 ± 0.6	-0.8 ± 0.8	-0.8 ± 1.1	-0.9 ± 1.6
(Mg-1-9)	-0.6 ± 0.5	-0.6 ± 0.8	-0.5 ± 1.0	-0.5 ± 1.4	-0.4 ± 1.8
(Na-1-10)	-0.3 ± 0.6	-0.2 ± 0.9	-0.1 ± 1.2	$+0.1 \pm 1.6$	$+0.3 \pm 2.2$
(Ca-1-10)	-0.5 ± 0.4	-0.6 ± 0.6	-0.6 ± 0.8	-0.6 ± 1.1	-0.7 ± 1.6
(Mg-1-10)	-0.4 ± 0.4	-0.4 ± 0.6	-0.3 ± 0.8	-0.3 ± 1.0	-0.2 ± 1.4

[†] The chemical reaction corresponding to each reaction no. was shown in Table 4.
* Standard change in Gibbs free energy at $T°$K.
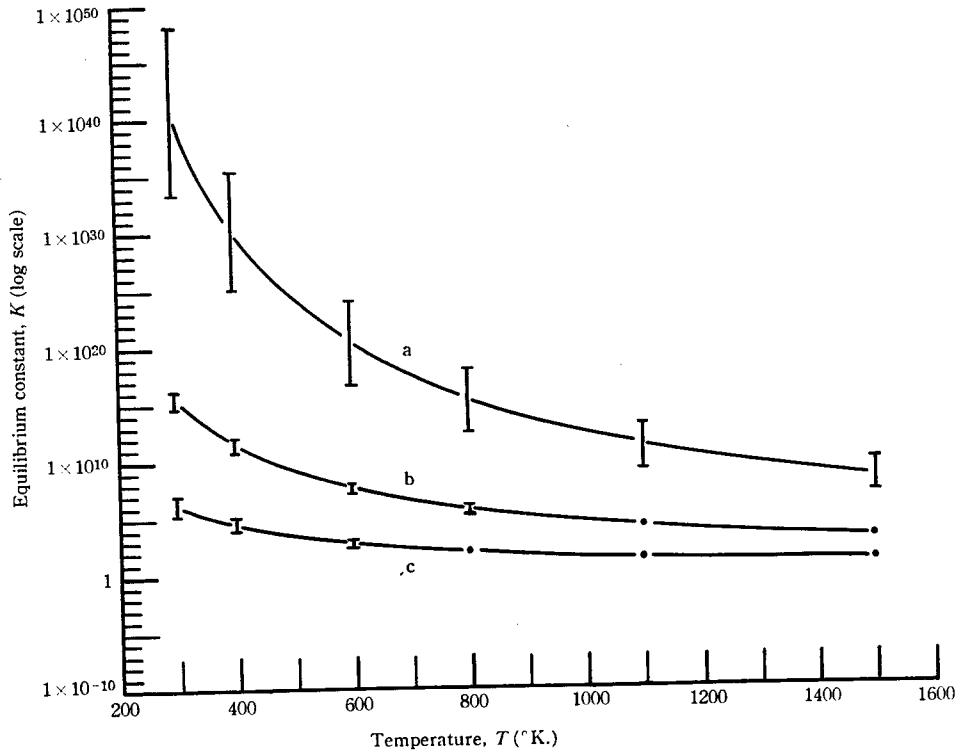** Taken from the data of reference 19.

Fig 1. Equilibrium constant as a function of temperature for reactions resulting in metasilicates of sodium, calcium and magnesium from the combination of their component oxides: a, (Na-1-1); b, (Ca-1-1); c, (Mg-1-1).   The curves in this figure were plotted by using the data of reference 19.
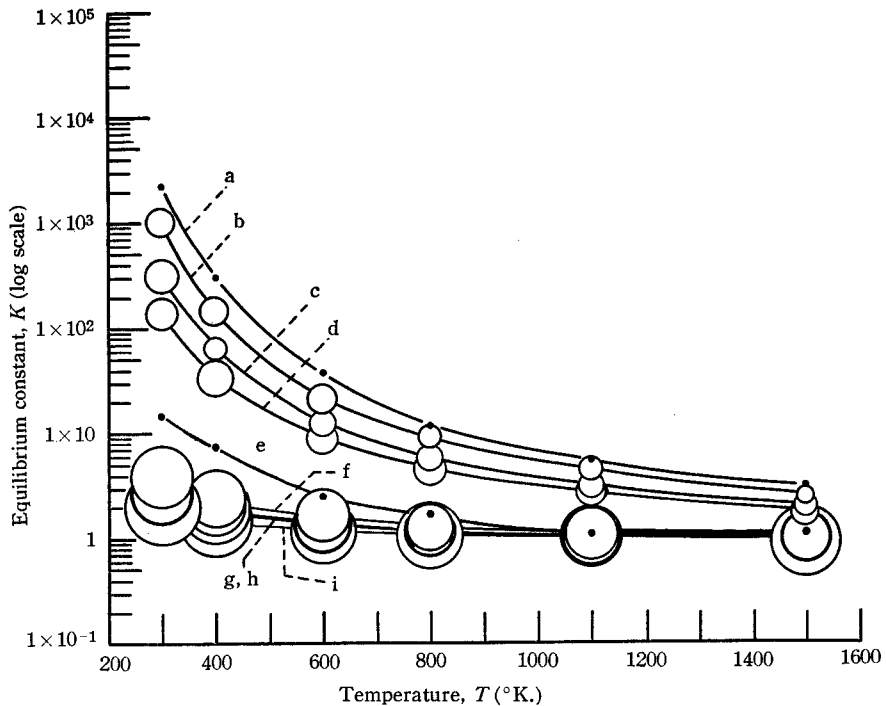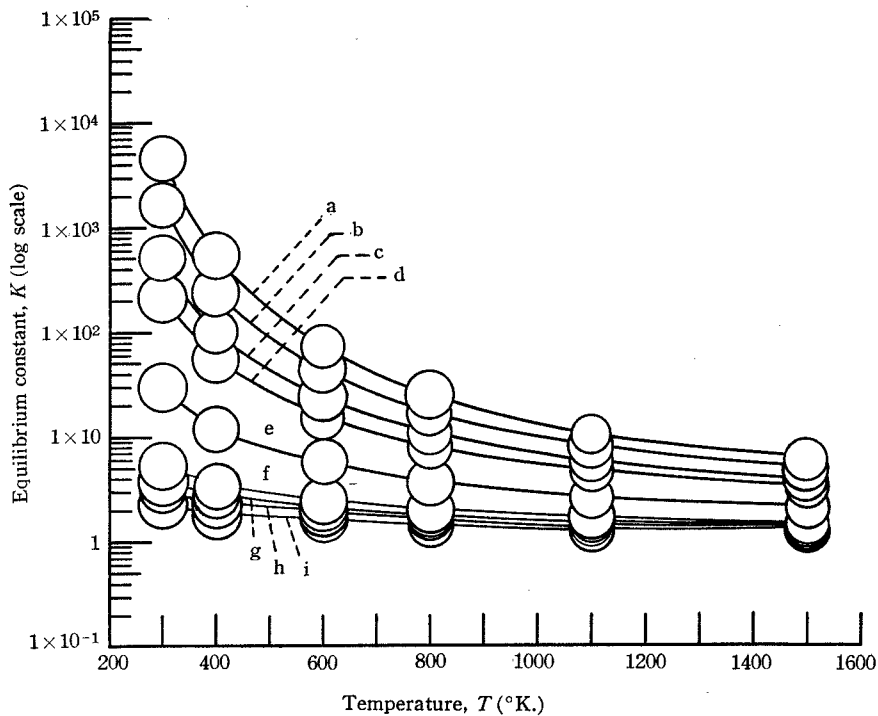

Fig. 2.   Equilibrium constant as a function of temperature for reactions between different types of sodium silicate building units including silica to form sodium metasilicate building unit: a, (Na-1-2); b, (Na-1-3); c, (Na-1-4); d, (Na-1-5); e, (Na-1-6); f, (Na-1-7); g, (Na-1-8); h, (Na-1-9); i, (Na-1-10).

Fig. 3. Equilibrium constant as a function of temperature for reactions between different types of calcium silicate building units including silica to form calcium metasilicate building unit: a, (Ca-1-2); b, (Ca-1-3); c, (Ca-1-4); d, (Ca-1-5); e, (Ca-1-6); f, (Ca-1-7); g, (Ca-1-8); h, (Ca-1-9); i, (Ca-1-10).
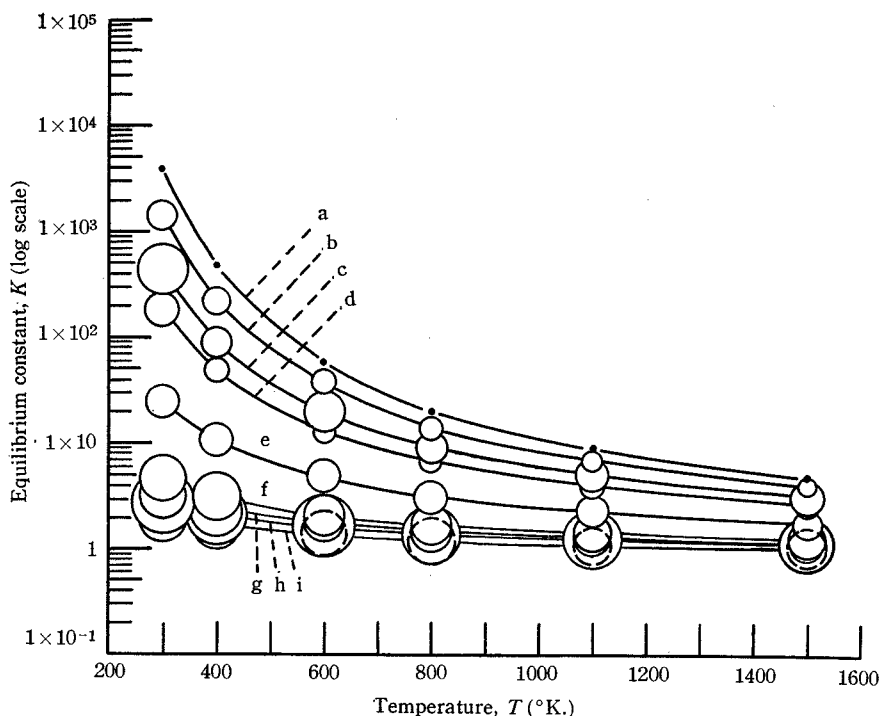

Fig. 4. Equilibrium constant as a function of temperature for reactions between different types of magnesium silicate building units including silica to form magnesium metasilicate building unit: a, (Mg-1-2); b, (Mg-1-3); c, (Mg-1-4); d, (Mg-1-5); e, (Mg-1-6); f, (Mg-1-7); g, (Mg-1-8); h, (Mg-1-9); i, (Mg-1-10).

ions for the above type of reactions resulting in metasilicate building unit. Therefore, the effect of partially or wholly replacing Na^+ ion by Ca^{2+} and/or Mg^{2+} ions on the value of K may be almost within the range of suggested deviations for the reactions concerned.

It is also realized from Figs. 1 to 4 that the value of K for each reaction shown in the figures is decreased with the increase of temperature and is decreased, at a constant temperature, with the decrease in difference between the N_{Si} ratios of each reactant and of the product.

It can be concluded, therefore, that the value of K for the above type of reactions resulting in metasilicate building unit does not depend predominantly on the kind of cations Na^+, Ca^{2+} and Mg^{2+}, but depends mainly on both the temperature at which the reactions occur and the N_{Si} ratios of the reactants.

(3) Ionic Structure in the Internal Equilibrium State

The first part of the problem is concerned on the ionic structure expected for vitreous metasilicates in the internal equilibrium state at room temperature. In Table 5, the value of equilibrium constant K at room temperature for reaction (Na-1-1) is quite large ($\log_{10}K = 41.05 \pm 7.33$), and the value for reactions (Na-1-2) - (Na-1-5) are still large ($\log_{10}K = 3.37$ to 2.13 ± 0.15). The value of $\log_{10}K$ is decreased, however, from 1.91 ± 0.37 to 0.73 ± 0.37 in the order of reactions (Na-1-3') to (Na-1-6'), and from 1.17 to 0.29 ± 0.37 in the order of reactions (Na-1-6) to (Na-1-10). It may be expected, therefore, that the activity of reactants for these reactions in the equilibrium state becomes increasingly appreciable in the order within the respective group of reactions (Na-1-3') to (Na-1-6') and reactions (Na-1-6) to (Na-1-10), in which the linear silicate anions ($Si_2O_7^{6-}$), ($Si_3O_{10}^{8-}$), ($Si_4O_{13}^{10-}$) and ($Si_6O_{19}^{14-}$) are included as reactants.

The ionic structure expected for sodium metasilicate glass in the internal equilibrium state at room temperature can be concluded from the above results, as follows: the glass has the "micro-inhomogeneous structure" containing not only SiO_4 groups of metasilicate building unit but also those of other types of silicate building units, among which one or more types of SiO_4 groups of linear silicate building units may be included; the smaller the difference of the N_{Si} ratio of silicate building unit from 0.333 (N_{Si} ratio of metasilicate building unit), the larger may be the activity of SiO_4 group of the building unit. The same conclusions as above may be reached, by refering the conclusion obtained in the foregoing paragraph (2) of this section, for metasilicate glasses of the composition $(1-m-n)Na_2O \cdot mCaO \cdot nMgO \cdot SiO_2$, where $0 \leq m \leq 1$, $0 \leq n \leq 1$, and $m+n \leq 1$.

The second part of the problem is concerned on the ionic structure expected for metasilicate glasses in the internal equilibrium state at elevated temperatures. As described in paragraph (2), the value of K for each of the reactions shown in Figs. 1 to 4 is decreased with the increase of temperature.

The values of $\log_{10}K$ for reaction (Na-1-1) at elevated temperatures, for example at 1100° and 1500°K., are respectively 11.36 ± 1.99 and 8.60 ± 1.46, and for reaction (Ca-1-1) at 1100° and 1500°K. are respectively 4.22 ± 0.20 and 3.08 ± 0.15. These values are easily determined from the values of $\Delta G°_T$ shown in Table 7 by using equation (8). In the above reaction equilibria, the activity of the reactants may be still negligible.

However, the values of K become smaller for reactions (Na-1-2)-(Na-1-10), (Ca-1-2)-(Ca-1-10) and (Mg-1-2) - (Mg-1-10) at elevated temperatures. As easily determined

by the same way as in the case of the above reactions (Na-1-1) and (Ca-1-1), for example, the values of $\log_{10}K$ for reaction (Na-1-2) at 800°, 1100° and 1500°K. are respectively 1.09, 0.74 and 0.47, for reaction (Na-1-7) at 800°, 1100° and 1500°K. respectively 0.11 $\pm$ 0.25, 0.04 $\pm$ 0.26 and -0.01 $\pm$0.25, and for reaction (Na-1-10) at 800°, 1100° and 1500°K. respectively 0.03 $\pm$ 0.33, 0.02 $\pm$ 0.32 and -0.04 $\pm$0.33. In these reaction equilibria, the activity of reactants may become appreciable, and as shown by the above examples and also by Figs. 2 to 4, the activity of reactants in the equilibrium state may be expected to increase with temperature for reactions (Na-1-2) - (Na-1-10), (Ca-1-2) - (Ca-1-10) and (Mg-1-2) - (Mg-1-10).

It was also suggested in the foregoing paragraph (2) that the value of K for the reactions concerned depended mainly on both the temperature at which the reactions occur and the N_{Si} ratios of the reactants, and the effect on the value of partially or wholly replacing Na$^+$ ion by Ca^{2+} and/or Mg^{2+} ions was almost within the range of suggested deviations.

The micro-inhomogeneity expected for the ionic structure of metasilicate glasses including one or more metals of sodium, calcium and magnesium in the internal equilibrium state above room temperature, can be concluded from the above evidences as follows: the structural micro-inhomogeneity of the glasses is increased with temperature; at a constant temperature, the difference in the structural micro-inhomogeneity may be approximately negligible among the metasilicate glasses concerned.

(4) Change in Ionic Structure with Temperature

When the temperature of metasilicate glasses having internal equilibrium ionic structure at a high temperature is lowered, the structure of the glasses may be changed toward the internal equilibrium state corresponding to the lowered temperature. It is required from the conclusions given in the foregoing paragraph (3) that this structural change involves the process of decreasing the micro-inhomogeneity in ionic structure.

The rate of the structural change is decreased with lowering temperature and, at a temperature below the transformation range, may become extremely slow or almost negligible because of the approach to the near completion of the "frozen-in" state of structure.

It is expected, therefore, that the ionic structure of metasilicate glasses at a temperature below the transformation range may be more micro-inhomogeneous than in the internal equilibrium state corresponding to the temperature, and the micro-inhomogeneity may be increased with increasing the rate of cooling to a temperature below the transformation range.

7. Summary

(1) A semi-empirical method is presented for estimating the entropy per mole of SiO$_4$ group for the fundamental building units of crystalline and/or vitreous silicates.

(2) The method for calculation is shown to obtain the value of free energy changes (cal./mole of SiO$_4$ group) and the equilibrium constants for reactions resulting in silicate building unit from the combination of other types of building units of silicates including silica.

(3) By applying the present method, calculations of free energy changes and equilibrium constants were made for the above type of reactions resulting in the fundamental build-

ing units of metasilicates of sodium, calcium and magnesium at temperatures of 298° to 1500°K. From the results obtained, the following conclusions are expected for the ionic structure of the metasilicate glasses of two- to four-component systems including one or more metals of sodium, calcium and magnesium in the internal equilibrium state: (a) the glasses in the internal equilibrium state at and above room temperature have the "micro-inhomogeneous structure" containing not only SiO_4 groups of metasilicate building unit but also those of other types of silicate building units; (b) the structural micro-inhomo-geneity of the glasses is increased with temperature; (c) at a constant temperature, the difference in structural micro-inhomogeneity may be approximately negligible among the glasses concerned; (d) the ionic structure of the glasses cooled to a temperature below the transformation range may be more micro-inhomogeneous than in the internal equilibri-um state corresponding to the cooled temperature, because of the delay in structural change on cooling and of the approach to the near completion of the "frozen-in" state of structure, and the micro-inhomogeneity may be increased with increasing the rate of cooling.

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