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The Enthalpy of Vitreous Beryllium Fluoride

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The enthalpy increments of beryllium fluoride were measured by the drop method in the glassy and liquid states from 450 to 914 K. The other thermodynamic functions were also calculated. The estimated configurational entropy of the supercooled liquid showed its temperature dependence to be small compared with those of nearly all other glass-forming liquids. The theory of Adam and Gibbs was applied to explain both the present enthalpy data and the Arrhenius viscosity behaviour over an unusually wide temperature range. The similarity between beryllium fluoride and silicon dioxide was also shown with respect to the heat capacities of the glassy and supercooled liquid states.

Beryllium fluoride has been considered to be the low-temperature model of silicon dioxide. Similarities between them are observed in many respects, for instance, in the crystal structure, the structure of the vitreous state, and the low-temperature heat capacities.

On the other hand, silicon dioxide differs from nearly all other glass-forming liquids, which exhibit marked and rather abrupt increases in their heat capacities from the glassy to the liquid state. Since this glass transition occurs in most liquids at a viscosity of approximately 10^{13} poise, it should be realized around 1430 K for silicon dioxide.[1,2] The best calorimetric data on vitreous silicon dioxide indicate the heat capacity to show a smooth and monotonous temperature dependence in this temperature region.[3,4] As for beryllium fluoride, the glass transition temperature can be expected from the viscosity data to be about 580 K.[5,6] However, the enthalpy increments or the heat capacities of the vitreous beryllium fluoride have not yet been measured in this temperature region because of the spontaneous devitrification.[7,8]

Recently, the rates of crystallization were measured in our laboratory for vitreous samples of beryllium fluoride which had various different thermal histories.[9] The results showed that the glass which has been prepared by quenching, as in the previous calorimetric study described above, certainly crystallizes abruptly, but that when the glass or, more correctly, the supercooled liquid has not been brought to room temperature, it does not crystallize, not even at the most appropriate temperature for crystallization, *i.e.*, 740 K, in the case of beryllium fluoride, within the time scale of the calorimetric experiments (say, one or two hours). This is related to the nucleation process. Therefore the enthalpy of the vitreous sample can be measured in the temperature region that the previous work could not cover. The purpose of the present work is to measure the enthalpy increments and to calculate the other thermodynamic functions of vitreous beryllium fluoride in the temperature range in which the glass transition may be observed. Further, the enthalpies of the glasses at 298.15 K were measured by solution calorimetry in order to detect any effect of the heat treatments. The results of the enthalpy of the vitreous state are compared with those for silicon dioxide and other glass-forming substances.

Experimental

Materials. The beryllium fluoride used for this study was prepared from a commercial beryllium fluoride (Mitsuwa Kagaku Co., Ltd.) which was approximately 99.5 moles per cent pure. The sample was heated at about 380 K, and then the remaining water was removed by gradually raising the temperature to about 900 K over a 2-day period. The above preparation was performed in a nitrogen atmosphere. All the containers were made of platinum tubes 8 mm in diameter, 45 mm in height, and 0.2 mm thick (2 to 2.5 g). Samples of 1.5 to 2.5 g were loaded into the sample containers, after which the tops of the containers were sealed by arc-welding in a glove-box filled with nitrogen.

Drop Calorimetry. The calorimeter used for this study was a high-temperature calorimeter of the Calvet type described previously.[10] The assembly of the apparatus for the present work is identical to that used in the previous work[8] except that the thermostat maintained at 298.15 K is now replaced by an electric furnace and that liquid mercury is used instead of coarse silver powder in the calorimeter cells. The electric furnace is shown in Fig. 1. The samples were held at the A position to be maintained at 903 K and then taken down to the B position to be maintained at the measuring temperature, *T*, in the electric furnace. It took 40 to 70 min for the samples to achieve the thermal equilibrium, and the average cooling rates ranged from 10 to 40 K min^{-1}. Then the samples were dropped into the calorimetric receiver at room temperature. The measureing temperatures ranged from 450 to 914 K. The temperatures were measured with a calibrated chromel–alumel thermocouple in terms of IPTS-68. The energy equivalent of this calorimeter was determined by the drop method, using a calorimetric standard, synthetic sapphire, provided by the National Bureau of Standards. As a preliminary check on the accuracy of the calorimetric systems, the enthalpy increments of gold were measured at several temperatures in the temperature range of the main measurements. The enthalpy results did not deviate more than ±0.6 per cent from the values in Kelley's table, and so the calorimetric system was assumed to be working satisfactorily.

Solution Calorimetry. The calorimeter used was of a CM-502 model micro-calorimeter (LESCA, Ltd.). Two types of glassy samples were used in this solution calorimetry. One was "quenched glass" which had been prepared by heating the sample at various temperatures above the melting point, and by then dropping it into a silver crucible at room temperature for rapid cooling. The other was "slowly cooled glass" which had been cooled slowly from 903 K to several temperatures below the melting point and then quenched in the same manner as in the drop-calorimetry experiment.

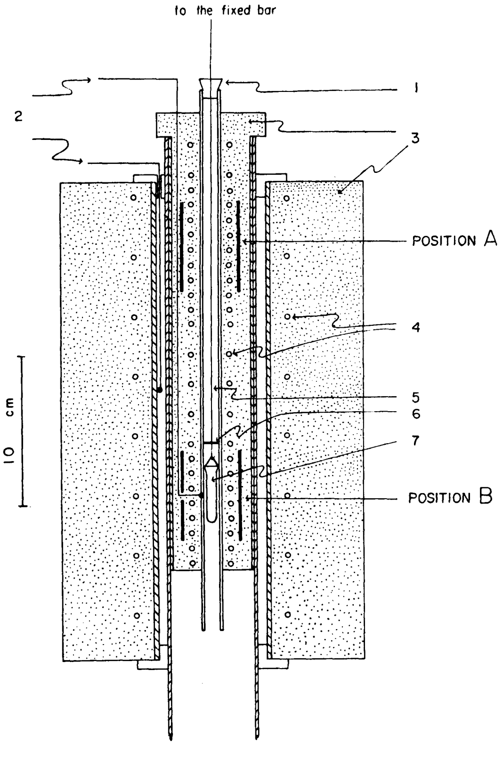

Fig. 1. Furnace assembly.
1: Cap with a pinhole, 2: thermocouples, to the temperature controllers, 3: asbestos, 4: heaters, 5: nichrom wire, 6: radiation shield fixed to nichrom wire, 7: platinum sample container.

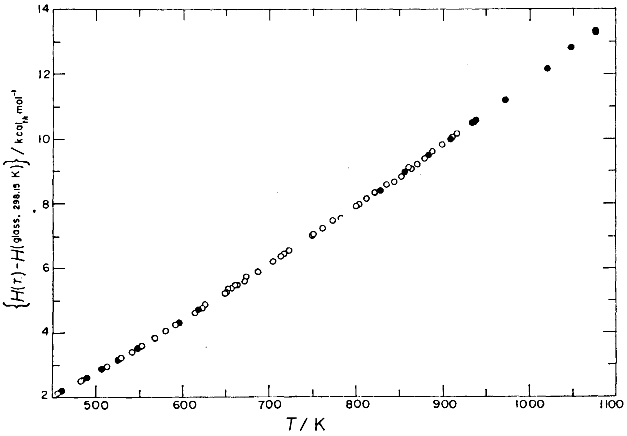

Fig. 2. Enthalpy increments of beryllium fluoride
○: Present work, ●: our previous work (Ref. 8).

These samples (about 0.5 g) were crushed to the grain sizes in order to dissolve them easily in the solvent which contained 47 g of sodium acetate in one liter of 0.1M acetic acid solution. Calorimetric calibration was performed electrically by means of the heater in the calorimeter.

Results

The results obtained by the drop method, including the data of the glass and liquid, are listed in Table 1 and are depicted in part in Fig. 2. These enthalpy increments are referred to the enthalpy of glass at 298.15 K, H (glass, 298.15 K). However, because of their very nature, the enthalpies of the glasses at room temperature might differ from each other according to the temperatures before dropping. This point was not cleared up in the previous work by Taylor and Gardner.[7] The heat of solution measurements were carried out in order to ascertain whether H (glass, 298.15 K) varies from one sample to the other. The results of the measurements are given in Table 2. From the results, the enthalpy differences, H (glass, 298.15 K) $-H$ (α-q-BeF_2, 298.15 K), in all runs appeared to have a nearly constant value, (1070 ± 60) cal$_{th}$ mol^{-1}.* This value is in good agreement with what had been obtained by the transposed-temperature drop calorimetry where the glassy sample was prepared by quenching the melt from 903 K.[8] The investigation by the X-ray diffraction method also did not reveal any difference between the X-ray diffraction halos of glassy samples with different thermal histories. Furthermore, in order to ascertain whether the crystallization was completely prevented and whether a particular experimental value of the enthalpy suffered from the heat effect of premelting or pretransition, the so-called Shomate plot[11] was applied to the enthalpy increments, which included the present results as well as those of the glass below 630 K and the liquid from the melting point to 1083 K obtained previously.[8] The Shomate plot gives a straight line, as is depicted in Fig. 3. No crystallization effect exceeding the experimental error could be detected by this plot. Further, since any glass transition is accompanied by a heat-capacity increase around the glass-transition temperature, this plot will be bent around this temperature. A tentative plot with the increase of 0.4 cal$_{th}$ K^{-1} mol^{-1} at 580 K for this system shows a clearly distinguishable bending at this temperature; this is in contrast with the fact. Therefore, no distinction between glass and supercooled liquid is appreciable in the present system. The least-squares treatment gives the following equation

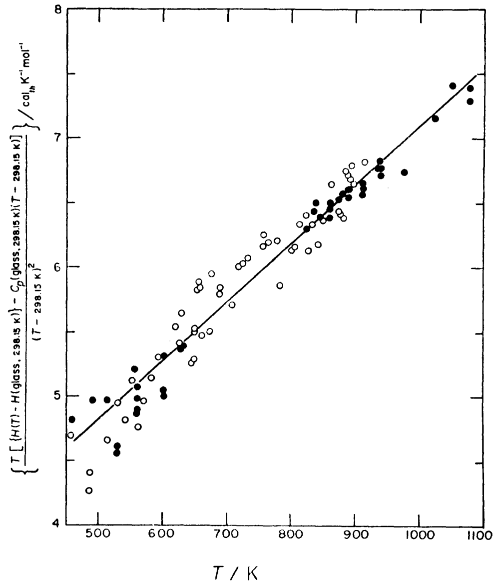

Fig. 3. Shomate plot of enthalpy increments.
○: Present work, ●: our previous work (Ref. 8).
The value of C_p (glass, 298.15 K) is cited from Ref. 7.

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* Throughout this paper cal$_{th}$=4.184 J.

TABLE 1. EXPERIMENTAL VALUES OF $\{H^\circ(T)-H^\circ(298.15\ \mathrm{K})\}$ FOR BERYLLIUM FLUORIDE

Figures in parenthesis after temperature denote the number of measurements and the values in column 3 are those calculated from Eq. (1).

$\delta=\{H^\circ(T)-H^\circ(298.15\ \mathrm{K})\}\ (\mathrm{calc.})-\{H^\circ(T)-H^\circ(298.15\ \mathrm{K})\}\ (\mathrm{expt})$

$\mathrm{cal_{th}}=4.184\ \mathrm{J}$

T/K	$H^\circ(T)-H^\circ$ (glass, 298.15 K)/cal$_{th}$ mol^{-1}		δ/cal$_{th}$ mol^{-1}
	expt	calcd	
455.1	2119.7	2101.2	−18.5
456.6	2151.9	2123.4	−28.5
482.7	2494.1	2513.9	+19.8
484.6	2531.6	2542.7	+11.1
488.3	2631.8	2599.0	−32.8
502.9	2868.0	2823.1	−44.9
510.0	2959.8	2933.1	−26.7
511.0	2970.6	2948.7	−21.9
511.4	2948.2	2954.9	+6.7
526.1	3194.8	3185.1	−9.7
527.0 (3)	3169.4	3199.3	+29.9
528.1	3227.9	3216.7	−11.2
539.8	3391.8	3402.3	+10.5
549.2	3570.5	3552.6	−17.9
553.6	3648.3	3623.4	−24.9
556.3	3675.9	3666.9	−9.0
556.5	3667.2	3670.1	+2.9
557.5	3672.1	3686.3	+14.2
557.7	3671.5	3689.5	+18.0
558.8	3676.0	3707.3	+31.3
567.7	3837.5	3851.7	+14.2
579.7	4048.0	4047.8	−0.2
591.1	4249.9	4235.7	−14.2
599.1 (3)	4335.0	4368.4	+33.5
600.1	4356.1	4385.1	+29.0
600.4	4354.1	4390.1	+36.0
602.1 (2)	4322.7	4418.4	+95.7
602.5	4376.7	4425.1	+48.4
602.8	4350.9	4430.1	+79.2
617.8	4714.1	4681.5	−32.6
624.0	4792.5	4786.1	−6.4
626.1	4866.9	4821.6	−45.3
626.8 (2)	4832.3	4833.5	+1.2
645.1	5102.7	5145.2	+42.5
646.6	5178.2	5170.9	−7.3
647.8	5193.4	5191.5	−1.9
648.3	5150.9	5200.1	+49.2
648.7	5282.7	5207.0	−75.7
649.5	5292.3	5220.7	−71.6
652.8	5349.2	5277.4	−71.8
656.4	5397.9	5339.5	−58.4
660.5 (2)	5428.6	5410.3	−18.3
671.2	5572.3	5595.8	+23.5
672.0	5680.1	5609.8	−70.3
686.1	5883.3	5856.2	−27.1
686.6	5895.5	5864.9	−30.6
705.2	6174.9	6193.1	+18.2
716.4	6439.6	6392.2	−47.4
723.2	6556.6	6513.8	−42.8
728.0	6643.7	6599.8	−43.9
752.2	7112.4	7036.9	−75.5
753.4	7102.9	7058.7	−44.2
761.1	7244.2	7199.0	−45.2
773.5	7458.6	7426.1	−32.5
783.9	7524.0	7617.7	+93.7
793.5	7762.0	7795.3	+33.3
794.1	7809.2	7806.5	−2.7
801.1	7909.7	7936.6	+26.9
803.3	7953.3	7977.5	+24.2
806.0	7972.5	8027.9	+55.4
807.4 (2)	8017.3	8054.0	+36.7
812.1	8164.8	8141.9	−22.9
818.4	8312.5	8260.0	−52.5
821.0	8343.9	8308.8	−35.1
823.0 (3)	8370.5	8346.4	−24.1
823.7	8374.7	8359.6	−15.1
824.2	8355.0	8369.0	+14.0
829.0	8376.3	8459.4	+83.1
832.1	8511.8	8517.9	+6.1
833.5 (2)	8580.0	8544.4	−35.6
836.6 (2)	8633.6	8603.0	−30.6
836.7	8600.4	8604.9	+4.5
836.9	8654.8	8608.7	−46.1
837.4	8632.0	8618.2	−13.8
837.9 (6)	8634.5	8627.7	−6.8
838.6 (2)	8642.1	8640.9	−1.2
839.1 (2)	8643.9	8650.4	+6.5
843.8	8648.0	8739.6	+91.6
846.9 (4)	8790.3	8798.5	+8.2
853.2	8881.0	8918.5	+37.5
859.5 (2)	9020.2	9038.8	+18.6
860.0 (2)	9035.8	9048.4	+12.6
860.3 (2)	9086.5	9054.1	−32.4
860.8	9136.4	9063.7	−72.7
861.3	9131.2	9073.2	−58.0
869.7	9219.3	9234.3	+15.0
871.6	9247.3	9270.9	+23.6
872.9 (8)	9278.2	9295.9	+17.7
873.1 (2)	9276.7	9299.7	+23.0
874.9	9288.2	9334.4	+46.2
878.8 (4)	9399.6	9409.5	+9.9
882.8	9407.2	9486.8	+79.6
883.0	9560.4	9490.6	−69.8
886.8	9616.7	9564.2	−52.5
888.8	9633.5	9602.9	−30.6
890.7 (2)	9641.5	9639.7	−1.8
891.5 (2)	9676.8	9655.2	−21.6
891.7	9648.0	9659.1	+11.1
892.1	9738.1	9666.9	−71.2
892.8	9708.7	9680.5	−28.8
899.3	9803.6	9806.8	+3.2
909.5 (5)	9997.4	10005.8	+8.4
910.5 (3)	9987.2	10025.3	+38.1
910.9	9994.6	10033.2	+38.6
913.9	10141.3	10091.9	−49.4
936.1 (2)	10541.0	10528.8	−12.2
937.1	10532.8	10548.6	+15.8
937.3	10538.2	10552.5	+14.3
938.0 (4)	10552.4	10566.4	+14.0
973.1	11179.5	11266.0	+86.5
1021.6	12269.2	12249.3	−19.9
1048.9	12927.0	12811.1	−115.9
1076.4 (2)	13380.9	13383.1	+2.2

Table 2. Heat of solution ΔH_s of beryllium fluoride at 298.15 K[a)]

T is the temperature at which the glass is maintained. $cal_{th}=4.184$ J

T/K	ΔH_s/cal_{th} mol^{-1}
quenched galss	
853.5	4645.8
853.5	4623.4
904.3	4644.1
958.1	4639.0
998.2	4573.8
998.2	4602.6
1063.1	4654.0
1133.1	4610.2
slowly cooled galss	
573.5	4635.4
675.3	4587.0
770.4	4613.5
crystal (α-quartz form)	
	3576.5
	3550.2
	3540.0

a) As for the solution, see the text.

for these enthalpy increments of the glassy through liquid beryllium fluoride:

$$\{H(T)-H(\text{glass}, 298.15\text{K})\}/(\text{cal}_{\text{th}}\ \text{mol}^{-1})$$
$$= (13.452\pm0.936)\times(T/\text{K}) + (3.6314\pm0.4260)$$
$$\times10^{-3}(T/\text{K})^2 + (4.1861\pm1.5849)$$
$$\times10^5(\text{K}/T) - (5692.5\pm674.7)$$
$$(450\text{K}<T<1083\text{K}) \qquad (1)$$

The standard deviation is 39 $cal_{th}mol^{-1}$. The enthalpy increments calculated from Eq. (1) and the deviations are listed in Table 1. Some thermodynamic functions were derived from Eq. (1) with well-known equations; they are tabulated in Table 3. Fig. 4 shows the derived heat capacities as well as those of other phases.

Table 3. Thermodynamic functions of beryllium fluoride ($cal_{th}=4.184$ J)

T/K	$H°(T)-H°$(α-q, 298.15 K)[a)]/cal_{th} mol^{-1}	$C_p°$/cal_{th} $K^{-1}\cdot mol^{-1}$	$S°$/cal_{th} $K^{-1}\cdot mol^{-1}$	$-\{G°(T)-H°$(α-q, 298.15 K)$\}/T$/cal_{th} $K^{-1}\cdot mol^{-1}$
Glassy through liquid state				
450	3161	14.65	19.87	12.84
500	3913	15.41	21.45	13.62
550	4700	16.06	22.95	14.41
600	5518	16.65	24.38	15.18
650	6364	17.18	25.73	15.94
700	7236	17.68	27.02	16.68
750	*8132*	*18.15*	*28.26*	*17.41*
800	9051	18.61	29.44	18.13
823(m.p.)	9481	18.81	29.97[b)]	18.45
850	9992	19.05	30.58	18.83
900	10955	19.47	31.69	19.51
950	11939	19.89	32.75	20.18
1000	12944	20.30	33.78	20.84
1050	13969	20.70	34.78	21.48
1100	15014	21.10	35.75	22.10

a) $H°$(glass, 298.15 K)$-H°$ (α-q, 298.15 K)$=1135$ cal_{th} mol^{-1} from Ref. 8 is used. b) estimated from the entropy of β-quartz form of BeF_2 at the melting point[8)] and the present enthalpy data of the liquid.

Discussion

The present experimental results indicate two interesting facts: (1) the glass transition was not observed, and (2) the heat capacity and the temperature dependence of the entropy of the supercooled liquid are quite similar to those of the crystal. Figure 5 illustrates the entropies of the crystalline, glassy, and liquid forms as functions of the temperature. Here the entropy of fusion, ΔS_f°, was quoted from our previous work,[8)] while the residual entropy of the glass at 0 K, S_{res}°, was quoted from Ref. 12. The heat capacity data of the crystal and glass at low temperatures were also quoted from the literature.[7,13)] For a closer examination, the data of the residual entropy, the entropy of fusion, and the heat-capacity differences between the liquid and glassy states of various glass-forming liquids are tabulated in Table 4. The first column shows the heat-capacity differences between the liquid and glassy states as a basis for a later discussion of the glass transition. The second column is the value of $\Delta C_p/n$, where n is the number of beads defined as the smallest molecular units, whose movements may change the molecular configuration.[14)] Though it is a concept devised for chain polymers, it is tentatively set at 2 for beryllium fluoride. The fact

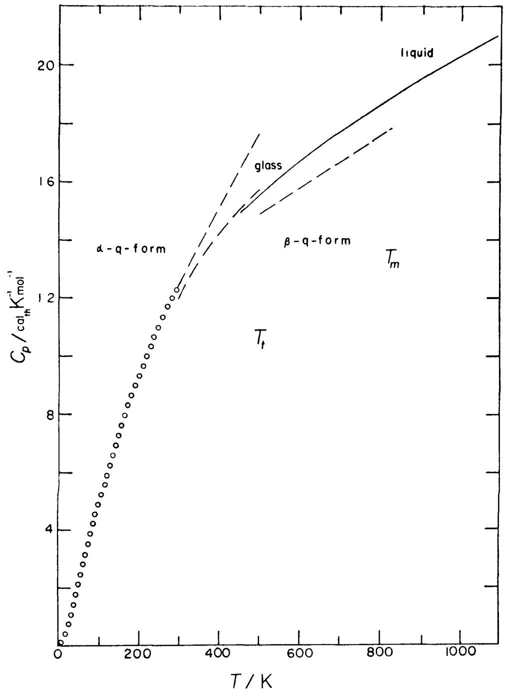

Fig. 4. Heat capacities of beryllium fluoride.

○: α-quartz form, by adiabatic calorimetry (Ref. 7),
— • —: α-quartz form, by drop calorimetry (Ref. 7),
—••—: glassy state, by drop calorimetry (Ref. 7),
------: β-quartz form, our previous work (Ref. 8),
———: glassy through liquid state, Present work.

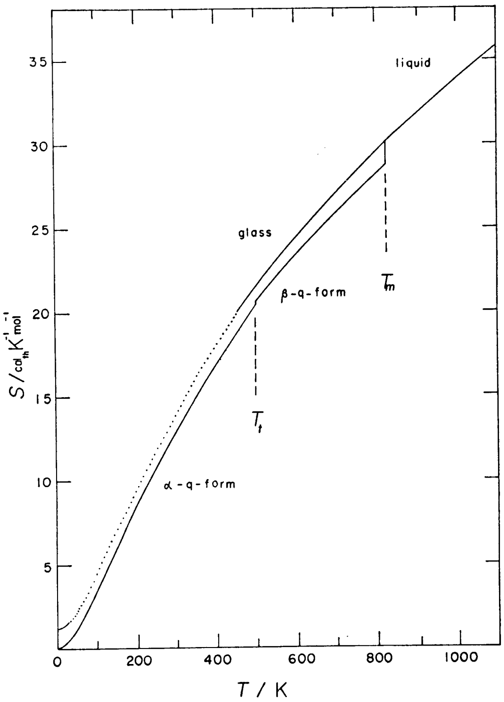

Fig. 5. Entropies of beryllium fluoride.
·········: have not been measured.

that the heat capacity of the supercooled liquid of beryllium fluoride is quite similar to that of the crystal is reflected in the similarity of the entropy trends, as may be seen in Fig. 5. ΔS_f° (T_m) is kept nearly constant down to S°_{res} at 0 K. These facts seem to be closely related to the viscosity-temperature curve of this system.

As is well known, the viscosities of liquids in a temperature range considerably above their melting points obey a two-parameter Arrhenius equation of this form:

$$\eta = A \exp (E_\eta/RT) \qquad (2)$$

where η is the viscosity, A is a constant, R is the gas constant, and E_η is the activation energy of the viscous flow. However, this equation is not applicable to the group of liquids with high viscosities or to the supercooled liquids with a glass-forming tendency. For these liquids, Fulcher[15] and Tammann and Hesse[16] found an empirical equation of the form:

$$\eta = B \exp \{C/(T-T_0)\} \qquad (3)$$

where B, C, and T_0 are constants.

Meanwhile, according to Adam and Gibbs,[17] the temperature dependence of such transport properties as viscosity is given by an equation of this form:

$$\eta = D \exp (\Delta\mu s_c^*/kTS(T)^{\mathrm{config}}) \qquad (4)$$

where D is a temperature-independent factor, k is Boltzmann's constant, $\Delta\mu$ is the potential energy barrier impending over the cooperative rearrangement, s_c^* is the critical configurational entropy, and $S(T)^{\mathrm{config}}$ is the configurational entropy of liquids. Since the temperature dependence of $\Delta\mu$ is so small as to be safely neglected,[17] the above equation explicitly explains the temperature dependence of the viscosity (Eqs. 2 and 3) in terms of the configurational entropy of the glass-forming liquids. From the standpoint of the modern lattice theory of the liquid state,[18,19] any thermodynamic function of the supercooled liquid may be separated into two terms: vibrational and configurational. Thus, the entropy of the liquid, $S(T)^{\mathrm{liq}}$, is given by $S(T)^{\mathrm{liq}}=S(T)^{\mathrm{vib}}+S(T)^{\mathrm{config}}$, and since $S(T)^{\mathrm{vib}}$ is approximately equal to the entropy of the crystal, $S(T)^{\mathrm{cryst}}$, at the same temperature, the following equation is obtained:

$$S(T)^{\mathrm{config}} \approx S(T)^{\mathrm{liq}} - S(T)^{\mathrm{cryst}} \equiv \Delta S_f(T) \qquad (5)$$

It is very interesting to note that Kishimoto, Suga and Seki compared the T_0 (dynamic) in Eq. 3 with the T_2 (static) estimated in their study and found a consistency between these values.[20] Here T_2 is the temperature, as proposed by Gibbs and DiMarzio,[21] at which the configurational entropy, $S(T_2)^{\mathrm{config}}$, of a liquid would vanish *via* a second-order thermodynamic transition if it were possible to cool the liquid in a metastable equilibrium state to T_2.

On the other hand, beryllium fluoride is also different from nearly all other glass-forming liquids in that the viscosity shows Arrhenius behaviour over a wide range of more than 10 orders of magnitude, as is shown in Fig. 6.[5,6] This behaviour is analogous to that of silicon dioxide.[1,2] This unusual viscosity behaviour of beryllium fluoride can be understood when the configura-

Table 4. Heat capacities and entropies of glass-forming liquids

	ΔC_p° [a] / $\mathrm{cal_{th}\,K^{-1}\,mol^{-1}}$	$\Delta C_p^\circ/n$ [b] / $\mathrm{cal_{th}\,K^{-1}\,mol^{-1}}$	$\Delta S_f^\circ(T_m)$ / $\mathrm{cal_{th}\,K^{-1}\,mol^{-1}}$	S°_{res}(gl, 0 K) / $\mathrm{cal_{th}\,K^{-1}\,mol^{-1}}$		$\Delta S_f^\circ(T_m)$ / S°_{res} (gl, 0 K)
				obsd	calcd	
BeF_2	0.93	0.47	1.33	—	1.08[12]	1.25
SiO_2	2.1[24]	1.1	1.25[25]	0.9[26]	1.04[12]	1.20
Se	3.5[27]	3.5	3.1[29]	0.94[28]	0.78[12]	3.9_7
	3.3[28]	3.3		0.86[28]		
				0.66[30]		
B_2O_3	1.66[31]	0.55	7.3_3[32]	—	—	—
Isopentane	16.8[33]	4.2	10.9[33]	3.3_0[33]	—	3.3_0
Isopropylbenzene	15.9[20]	4.0	9.9[20]	2.8_7[20]	—	3.44

a) $\Delta C_p^\circ \equiv C_p^\circ(\mathrm{l}, T_g) - C_p^\circ(\mathrm{gl}, T_g)$ The values of $C_p^\circ(\mathrm{l}, T_m) - C_p^\circ(\mathrm{c}, T_m)$, and $C_p^\circ(\mathrm{gl}, T_m) - C_p^\circ(\mathrm{c}, T_m)$ are used for BeF_2 and SiO_2 respectively since $C_p^\circ(\mathrm{l}, T_g) - C_p^\circ(\mathrm{gl}, T_g)$ has not yet been obtained. The state symbols are l, liquid form; gl, glassy form; c, crystal form. b) n is the number of beads proposed by Wunderlich.[14]

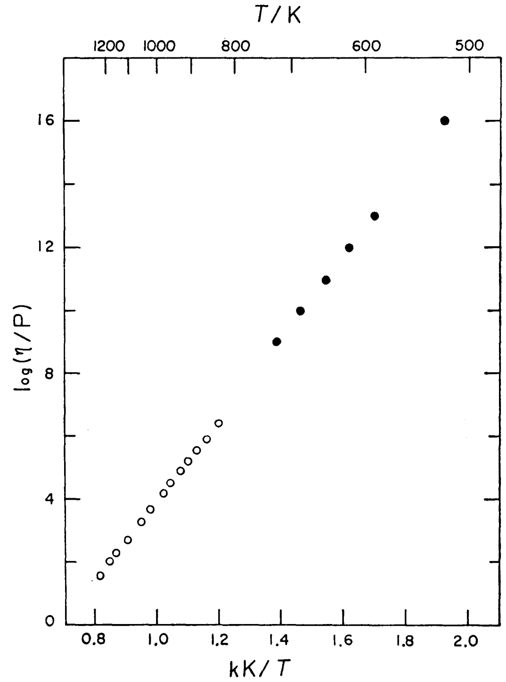

Fig. 6. Arrhenius plot of viscosity.
○: cited from Ref. 5, ●: cited from Ref. 6.

tional entropy of a liquid is independent of the temperature, as in the present work (see ΔC_p in Table 4); then Eq. 4 turns into Eq. 2. In other words, it is very difficult to estimate T_2 because $S(T)^{\text{config}}$ shows little temperature-dependence. If T_2 were estimated, it might be quite low. It is also difficult to estimate T_g because the entropy of fusion is small, comparable with the residual entropy. The small entropy of fusion implies that the structure of the liquid is not very different from that of the crystal. Thus, any heat-capacity increase at the glass-transition temperature would be negligibly small.

In conclusion, the present data, if coupled with the heat of fusion and the unusual viscosity behaviour, suggest that the structures of the crystal, glass, and liquid states are similar to each other. This is consistent with the similarities of their spectroscopic data.[22,23] No distinction between glass and the supercooled liquid of beryllium fluoride is appreciable in the present work.

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