DIRECT MEASUREMENT OF SILICATE HEATS OF MELTING.

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ABSTRACT.

The reluctance of most silicates to crystallize when once melted makes it difficult to obtain their heats of melting when using calorimeters operated at room temperatures. It is here shown that with a suitable high-temperature calorimeter we may measure the energy actually absorbed by the silicate in the act of melting, as is often done at low temperatures, and so obtain data of usable precision. Determinations are described using pure K_2SO_4 and somewhat impure Na_2SiO_3, whose melting points are 1069° and 1089°.

The past two or three years have witnessed a rapidly growing interest in thermochemical investigations in many different fields. At the Geophysical Laboratory, extensive phase rule studies of silicate equilibria have been in progress ever since the Laboratory was established; application of these investigations to geologic problems has brought about a more and more urgent demand for thermal data, particularly heats of melting, which has now to be met. Since existing data are scanty, the present need is not so much for a few determinations of high precision as it is for the ability to obtain data of adequate precision in the majority of cases that present themselves. This consideration is an important factor in the choice of method and equipment.

THE PROBLEM IN GENERAL.

If we plot the internal energy of a pure substance as a function of temperature we obtain a curve like ABCD in Fig. 1; the vertical portion BC represents energy absorbed isothermally during the melting process and is the quantity we want to determine.

If the substance contains a small amount of an impurity that forms a eutectic with it, the energy curve resembles AEE′C′D. A vertical portion EE′ appears at the eutectic temperature. It represents the energy needed to melt all the impurity and enough of the pure substance to form a saturated solution, together with a generally much smaller heat of dilution. The initial slope of E′C′ is greater than that of AB and increases

more and more rapidly until the end of melting at C′. If the impurity forms a solid solution the transition from AB to A′D is confined to the short temperature interval between liquidus and solidus, and the energy curve more nearly resembles ABCD.

Above and below the melting interval E to C′, the change in total energy caused by the small impurity is a second order

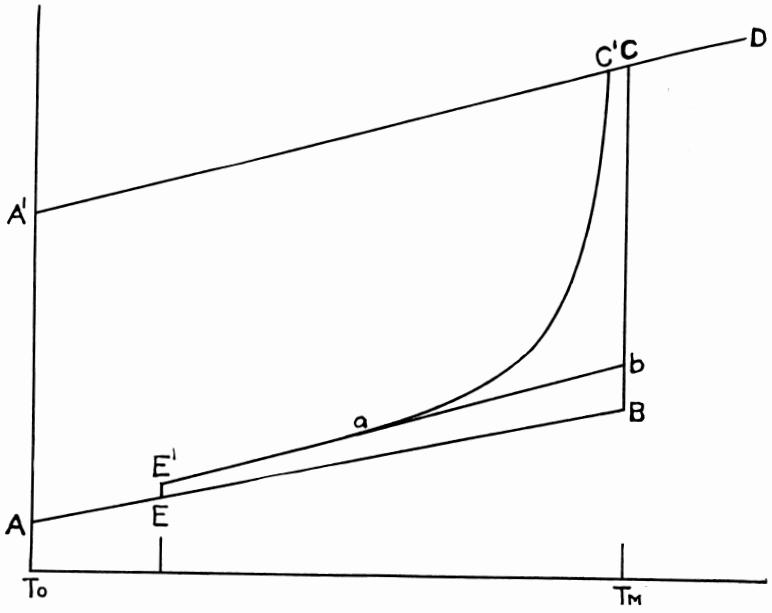

Fig. 1. Hypothetical "energy vs. temperature" curves. ABCD for a pure substance. AEE′C′D for a substance containing a small quantity of eutectic forming impurity. AB gives the heat of the solid; A′D of the liquid. For *ab* see text.

effect and may here be neglected. Consequently we may consider the curves as coincident from A to E and from C to D. Then, from the practical determination, we may define the heat of melting as the vertical distance between the extrapolated curve AE and the curve C′D, measured at the melting temperature of the pure substance.

The metals and many other substances follow these curves very faithfully even when cooled rapidly from temperatures above the melting point. There is nearly always undercooling,

i.e. a short digression toward A′ before crystallization begins; but once started, crystallization proceeds rapidly to completion.

For determinations with these substances the dropping method affords, probably, the most satisfactory and precise means of tracing the energy curve. The cooling takes place in a calorimeter whose temperature rise gives the difference between the energy content of the sample at the initial temperature, before dropping it into the calorimeter, and that at the final temperature of the calorimeter. Since only differences are given, the energy curve thus obtained represents relative and not absolute values.

The silicates, however, are characterized as a class by extreme undercooling. When once melted, most of them fail to crystallize at all unless cooled very slowly, and the heat of melting remains in the sample because from the energy standpoint, as well as the structural, the sample is still a liquid. For them the dropping method gives only the energy curve of the liquid, curve A′D in the figure, located an undetermined distance AA′ above AB. This quantity AA′ includes the heat of melting. Several investigators have evaluated it by taking the difference between determinations of heat of solution of the glassy and of the crystalline form in some suitable solvent. The determination is complicated and is particularly subject to uncertainties that are difficult to evaluate.

When all these considerations were taken into account it appeared that it would be a great deal simpler and possibly, in the long run, nearly as accurate to determine the energy actually absorbed by the silicate in the act of melting and to subtract from this the energy needed merely to raise its temperature. In the method adopted the greater part of the energy needed is supplied by an electric heater surrounded by the sample being melted. The method is an old one and the desirability of electric heating has been pointed out by many workers, although few have employed it at high temperatures. White[1] investigated it at this Laboratory as a possible method for specific heats but he abandoned it in favor of the dropping method which, for that purpose, is undoubtedly superior. The most recent application of the heater at higher temperatures seems to be that of Moser,[2] who has used it very successfully for heat capacity measurements up to 700°.

[1] White, W. P.: J. Phys. Chem., 34, 1121-1136, 1930.
[2] Moser, H.: Physik. Z., 36, 737-753, 1936.

APPARATUS.

Calorimeter and Jacket.

Figure 2 is a drawing of part of the furnace F with the calorimeter in place. The charge is contained in the Pt crucible

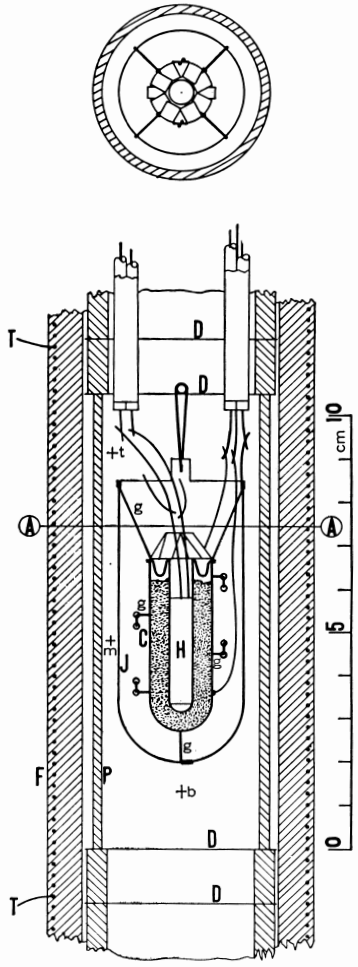

Fig. 2. Calorimeter and part of the furnace. The upper view is a section at the level A-A.

C which is provided with a central well or sheath for the electric heater H. Two lugs at the top of the sheath are bent

outward and welded to corresponding lugs near the top of the crucible. Above this level the crucible is divided into narrow strips by longitudinal saw cuts. After the charge is filled in, these strips are bent inward, leaving a small central opening through which the heater leads pass. The assembly, crucible, sheath, and heater will be referred to as the calorimeter.

The calorimeter is held in position inside the Pt jacket J by 11 guy wires g of 0.2 mm. PtRh. These are spot welded to the outside of the calorimeter and are tied to the jacket by threading through pairs of holes drilled in it. Taken together they form the composite thermocouple which measures temperature difference between calorimeter and jacket and are therefore distributed over the air-gap so as to give an average value of thermal head.

The top of the jacket is cut into strips which, like those at the top of the calorimeter, are bent inward to close the end, leaving 2 small windows for the heater and thermocouple leads.

The jacket hangs in a chamber formed by the porcelain tube P located at the center of the furnace. The ends of the chamber are closed by discs D of thin platinum; and similar platinum discs, alternating with 12 mm. spacers cut from an alundum tube, fill all of the furnace tube above and below the calorimeter chamber.

Furnace and Temperature Regulator.

The furnace core is an alundum tube 394 mm. long, 45 mm. inside, and 57 mm. outside diameter. On this are wound 136 turns of 0.8 mm. Pt wire with a winding pitch of 0.1 inch (2.54 mm.). Electrical leads are brought out from a point on the 43d turn and from a point on the 93d. Thus the winding is divided into a middle section of 50 turns with 2 end sections of 43 turns each. The position of these taps relative to the calorimeter chamber is as indicated at T in Fig. 1. The axial temperature distribution within the calorimeter chamber may be made nearly uniform by adjusting the ratios of the voltages across the 3 sections. The 7 cm. space between the core and the outer case is filled with calcined magnesia for thermal insulation.

The temperature regulator is of the type described elsewhere[3] but freed of moving contacts by replacing the rectifier, galvanometer, relay, etc. of the 1925 edition with an amplifier and

[3] Roberts, H. S.: J Optical Soc. Am., 11, 171-186, 1925.

thyratron. A slide wire connected into the regulator, and having its movable contact driven by a synchronous clock motor, provides for heating or cooling at a fairly uniform rate.

Calorimeter Heater.

The heater consists of 35 turns of 0.16 mm. PtRh wire wound on a porcelain tube. The ends of the winding are welded to 0.4 mm. Pt leads, one passing through the center of the tube and the other held by ties of Pt wire in a longitudinal groove in the outside. The heater is insulated from the Pt well by a coating of alundum cement.

It is supplied with low voltage alternating current from a transformer that serves to insulate the heater circuit from the power line. Power is measured by a suspension type dynamometer whose stationary coil carries the whole heater current and whose moving coil is connected through a suitable resistance to potential taps close to the heater.

The heater current produces heat in the leads to the heater as well as in the heater itself. Since the pair of leads runs for 13 mm. through the air-gap, part of the heat produced there is transferred to the calorimeter and the remainder chiefly to the jacket. The calorimeter's share would appear to be somewhat less than half. Accordingly the leads that feed the potential circuit of the wattmeter are welded to the current leads about 5 mm. above the top of the calorimeter. Since the total heat produced in these 26 mm. of current leads is only about 1 per cent of that produced in the heater, the exact location of the potential taps is not very important.

When the heater is first turned on, its resistance increases rapidly and the power would suffer a corresponding decrease if connection were made directly to the transformer. The effect of this increase is minimized by connecting a rheostat in series with the heater and adjusting it, before starting an experiment, to such a value that the heater receives half the voltage of the transformer. When this is done the heater resistance may be changed to 95 per cent or 105 per cent of its original resistance without changing the watts by more than 0.25 per cent.

The energy in joules given to the change by the heater is the integrated product of watts and seconds. Since the voltage of our power supply can be held within 0.1 per cent by a suitable regulator it seemed best in our situation to keep the watts

constant and to record the total time. The laboratory was already provided with a clock that sends out a short electrical impulse each second, and these impulses are used to turn the heater on or off. This requires two quick-acting telephone relays and a switch. When the switch is turned to the "high" position nothing happens until the next impulse from the clock closes the main relay contact, and so connects the heater to the transformer. The relay then remains closed until immediately after the switch is turned back to the "low" position when the contact is opened by the next impulse from the clock. Thus the time of heating is always an integral number of seconds, recorded automatically by an electrical "message counter." The electrical energy that has been supplied to the heater is then equal to the product wattmeter reading $\times$ counter reading.

Since the relay does not open or close instantaneously there is a small error in timing due to the difference between the delay on closing and the delay on opening. Another small error may be caused by electrical transients in the heater circuit at the beginning of each heating period.

For determining the leakage modulus and to reduce the thermal head during determinations of heat of melting, a steady heat is needed of much lower power than that used for melting. This is obtained by having the back contacts of the main relay connect the heater to another transformer of lower voltage. This voltage may be varied by means of an adjustable ratio autotransformer[4] in the primary circuit. Thus the heater operates at the lower voltage when the main relay is open and at the higher when it is closed.

When both the steady "low" heat and the intermittent "high" heat are used in the same experiment, it is a simplification to treat the high heat increments as superposed on the low. We therefore subtract the low watts from the high and multiply the difference by the counter reading.

Temperature Measurements.

Temperatures are given by the emf's of Pt-PtRh couples measured with a White double potentiometer in conjunction with a sensitive galvanometer. The composite couple for thermal head readings has already been described. The junction giving calorimeter temperature is made by spot welding a

[4] A General Radio Co. Variac.

PtRh wire to the outside of the platinum crucible, the other wire of the couple being a pure platinum wire welded to the top of the crucible. This platinum wire and a similar platinum wire welded to the jacket form the couple for measuring thermal head. Other Pt-PtRh junctions at b, m, and t in the space outside the calorimeter provide for measuring temperature distribution over the length of the calorimeter chamber.

Between the calorimeter chamber and the top of the furnace the thermocouple leads are insulated with porcelain capillaries tied into a bundle and covered with a shield of Pt foil. The shield is connected by a short wire to the top of the jacket and to a similar shield surrounding the four heater leads.

Outside the furnace the single PtRh lead is extended to a glass-enclosed junction with Pt which is immersed in a vacuum bottle filled with ice. This Pt wire and the four coming direct from the calorimeter chamber are joined, inside an isothermal junction box, to the Cu wires leading to the potentiometer.

The whole measuring system is rather carefully insulated and shielded[5] to minimize effects of electrical leakage. The maximum irregularity in temperature indications, which may originate in the furnace temperature regulator, potentiometer—in fact nearly anywhere in the system—seems to be about $\pm$ 0.2 μv for periods of half an hour or so. For longer periods there are sometimes changes as great as 1 or 2 μv apparently connected with the temperature of the laboratory, as well as a slow downward drift of about 1 μv per day when the furnace stays for long periods in the neighborhood of 1100°.

Thermal head readings made with the furnace temperature stationary about 1100° seem to be free from temporary irregularities greater than 0.1 μv, while the change from day to day appears to be very much less than that of the temperature readings.

DETERMINATIONS WITH SHARPLY MELTING K_2SO_4.

The first determinations were made with a charge of 7.10 grams of K_2SO_4. In another investigation[6] this material had been found to melt very sharply at 1069°. The energy curve must therefore have nearly the same form as ABCD in Fig. 1. Since K_2SO_4 crystallizes very promptly, determinations could be repeated as needed. The reversible transformation at

[5] White, W. P.: J. Am. Chem. Soc., 36, 1856-1885 and 2011-2020, 1914.
[6] Roberts, H. S.: Phys. Rev., 23, 386, 1924.

583° was utilized in a study of the calorimeter at this low temperature.

The charge was melted several times under various schedules. Data for two meltings under the schedule finally adopted are plotted in Fig. 3. In these determinations continuous heating by the calorimeter heater was not employed. The furnace was held about 2° below the melting point until temperatures became stationary and then the regulator setting was changed by an amount that would raise the temperature to about 2° above the melting point. While the temperature was rising the thermal head reading was recorded at 15 second intervals and was kept as small as possible by intermittent operation of the heater. The thermal head readings are plotted at I and II in the figure. The data for Curves III-θ and III-ϕ were obtained at a later date with a charge of molten Na_2SiO_3, but they give an approximate picture of the temperature rise for I and II and of what the thermal head curve might have been if melting had not taken place and the calorimeter heater therefore had not been turned on.

The straight line connecting initial and final values of ϕ in I and II is here assumed to represent, at any temperature, the correction that must be subtracted from the thermal head reading to give the true thermal head. Multiplying the net area between this line and the jagged curve by the leakage modulus k gives the net leakage of energy from calorimeter to furnace. The area, lying below the straight line, represents energy, *b*, gained by the calorimeter; the area lying above represents energy, *c*, lost.

If *a* is the total energy obtained from the heater, then the quantity, $a + b - c$, is the energy retained by the calorimeter and its contents; a part, *d*, going to raise the temperature of the whole, and the remainder, *e*, to melting the charge. The part *d* was taken as the product of temperature rise in μv by the heat capacity C determined at a lower temperature where the amount of melting would be insignificant. Strictly, this value of C is applicable only below the melting point and a different value, to be determined with the charge molten, should be used above the melting point. Over this short temperature interval, however, the difference is negligible.

Thermal head data for a determination of k and C are given as Curves IV-k and IV-C of Fig. 3. In IV-k an input of 13.9 joules per minute (0.232 watts) from the heater caused an increase of 11.1 μv in the thermal head ϕ, the temperature

being stationary at 10227 μv. At this temperature k is therefore 1.26 joules-per-minute per μv rise in ϕ.

In IV-C a heating rate of 10.1 μv per minute caused ϕ to decrease 9.5 μv, corresponding to an input of 12.0 joules per

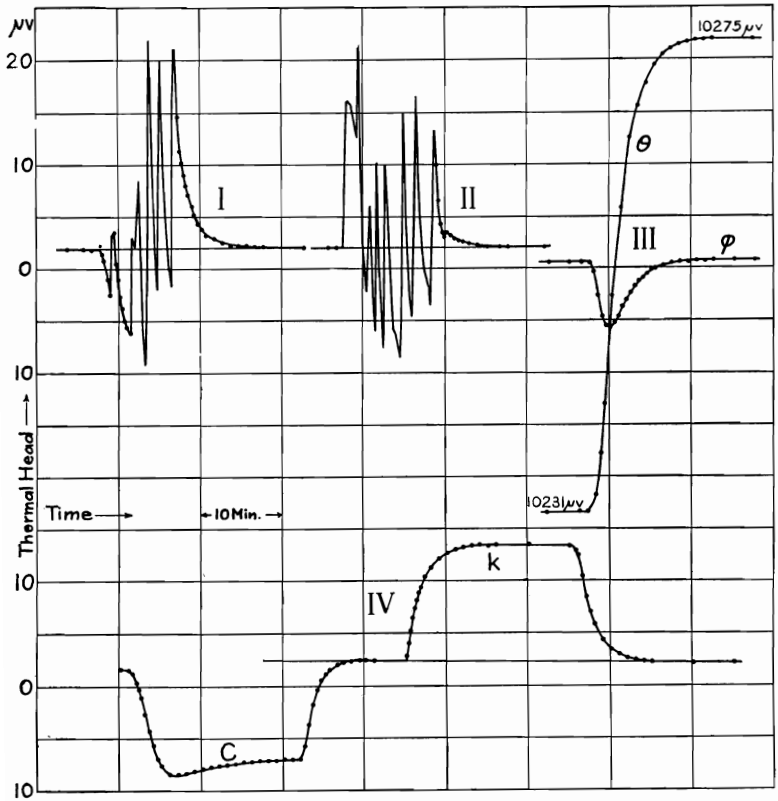

Fig. 3. I, II, IV, thermal head curves for K_2SO_4. III, thermal head and temperature curves for Na_2SiO_3.

minute from the furnace, the heater input being zero. In the neighborhood of 10100 μv, therefore, C =1.2 joules per μv rise in the temperature of the calorimeter. Since the thermal head correction is more uncertain with changing than with stationary temperature, the determined value of C is subject to a greater percentage error than that of k.

Table I is a summary of the quantities measured and calculated in determinations of heat of melting and heat of inversion of the sample of K_2SO_4.

TABLE I.

K_2SO_4 Latent Heats.

		Melting		Inversion		
k, joules/min. μv		1.26			0.4	
C, joules/μv		1.2			0.95	
Final temperature	μv	10411	10411	5101	5108	5104
Initial temperature	μv	10367	10363	5032	5036	5032
Temperature interval	μv	44	48	69	72	72
Watts in heater		5.71	8.76	7.75	9.53	1.18
Seconds heater was on		258	168	43	40	289
a, Input from heater	joules	1473	1471	333	381	323
b, " " furnace	"	27	35	6	0	9
Total input	"	1500	1506	339	381	332
c, Loss to furnace	"	64	72	10	48	3
d. To raise temperature	"	49	53	65	68	68
e, Balance, latent heat for 7.10 g.		1387	1381	264	265	261
Mean ΔH		—195 joules/g.			—37.0 joules/g.	
		—46.5 calories/g.			—8.8 calories/g.	
Estimated uncertainty		2%			7%	

Of the four quantities, *a*, *b*, *c*, and *d*, whose algebraic sum is the heat of melting, *a* has by far the least absolute uncertainty, since it is the product of electrical watts and time. Frequent checking of the wattmeter over a two-month period disclosed an irregular variation less than 0.2 per cent of full scale deflection. The nature of the timing error has already been discussed; it may here be as large as 0.01 second in each of perhaps 20 intervals.

The significant uncertainty of *b* and *c* comes from the choice of thermal head correction used in determining k; the uncertainty is probably considerably less than 10 per cent. The thermal head correction is still more uncertain in determinations of C, and since the value of k is included in C, we may expect a possible uncertainty of 20 per cent in the quantity *d*.

In estimating the uncertainty of the final result we must expect that occasionally the contributing errors may all have the same sign. The estimated uncertainty given in Table I is therefore the sum of the individual estimates taken without regard to sign.

The uncertainty introduced by use of the factor C might have been avoided if C had been determined by following the procedure used for the latent heat determination. At the end of the latter determination the regulator might again have been

set forward so as to cause the temperature to rise through a second interval of the same length as the first. We should then have obtained a thermal head curve similar to III-ϕ in Fig. 3. The thermal head corrections should be very nearly the same for the new as for the original interval. Then, if we imagine this new thermal head superposed on the original curve (Curve I or II in the figure), it can easily be shown that the area between the new curve and the old would have given at once, when multiplied by k, the whole of the correction *b-c-d* to be added to the electrical input. This method of estimating the correction would have been more satisfactory than the method that was actually employed. It is, in principle, what was employed in the following investigation of impure Na_2SiO_3.

DETERMINATIONS WITH IMPURE Na_2SiO_3.

Application of the method to somewhat impure material was studied with a 4.91 gram sample of Na_2SiO_3 that contained a small excess of silica. Since this heat of melting is to be determined in the near future with a much purer sample of Na_2SiO_3, the present investigation is to be considered as merely a critical study of the method to be used in the actual determination.

The charge was found to crystallize readily when cooled to 950° and it apparently reached an equilibrium between crystals and liquid when held at this temperature over night.

The preliminary study showed that measurements would need to be made over a wide temperature interval and that, for such an interval, we should not be justified in taking the thermal head corrections from a straight line drawn as it was in the K_2SO_4 determination. Since there appears to be no way to determine the magnitude of the correction, except at constant temperature, it was eliminated by running a duplicate experiment with the charge molten and subtracting the thermal head readings so obtained from the corresponding readings obtained with the charge in the act of melting.

The data for Fig. 4 were obtained with the temperature regulator automatically raising the temperature at a rate that varied from 9.7 μv per minute at the lowest temperature to 10.6 at the highest. A mistake (now remedied) in the design of the regulator limited the temperature interval that could be covered in a single run to about 600 μv, so the data had to be obtained in two stages.

The charge was held over night at the initial temperature for the run and at a definite time the next day the regulator was started raising the temperature; about 20 seconds later enough power was turned into the calorimeter heater to bring the thermal head reading to a low value. The "steady heat" was

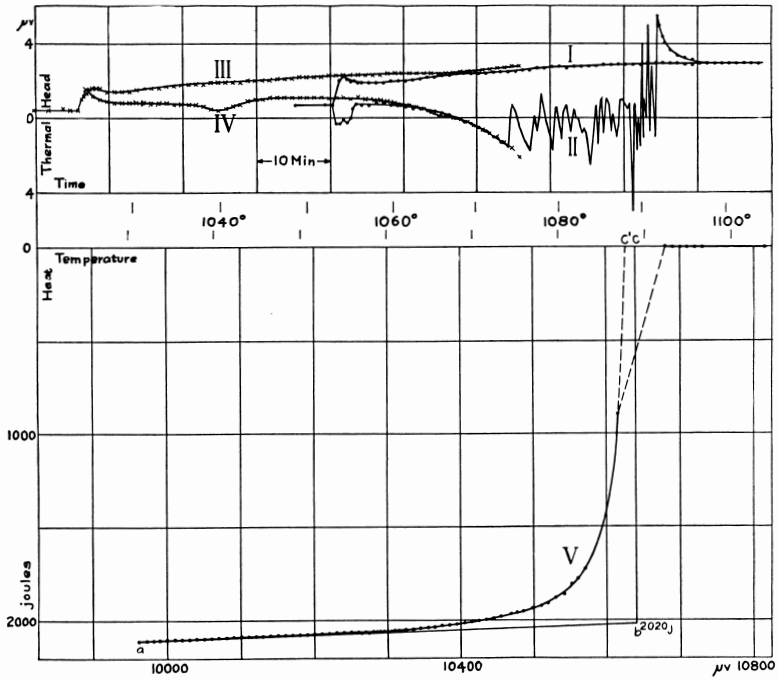

Fig. 4. Thermal head and energy curves for Na_2SiO_3 with small excess SiO_2. The energy curve differs from the curves of Fig. 1 in that ordinates here represent differences between the total energy of the melting charge and that obtained in a second experiment with the charge still molten. The ordinate *Cb*, divided by the weight of the charge, is taken as the latent heat of melting. This value, 412 joules per gram, may need considerable revision when the latent heat of the pure compound is determined.

then maintained at its initial value (0.160 watts) throughout all four runs. During the period of rapid melting (Curve I in Fig. 4) additional large increments of energy were put in exactly as was done during the melting of K_2SO_4. Thermal head data so obtained are plotted in Fig. 4, Curves I and III being for the solid, II and IV for the liquid. The distance from I to II, or III to IV, along any ordinate represents the

difference between the two leakage rates at corresponding times. The area enclosed between these two curves and any two ordinates gives, when multiplied by the leakage modulus, the difference between the total energy received from the furnace by the melting charge and that received by the molten charge, while passing through a particular temperature interval. To this are to be added such increments of energy as may have been received during the same interval from the heater. (The steady heat does not contribute to the difference.) Energy data for Curve V were obtained in this way, omitting the data obtained during the first 10 minutes of each run.

Curve V corresponds to what would be obtained in Fig. 1 by subtracting the ordinates of A′D from those of *a*C′D. The tangent *ab* at the beginning of the curve corresponds to *ab* in Fig. 1 and the 1089° ordinate to T_MC. Since we have no data for the pure solid, the curve corresponding to AB of Fig. 1 cannot be included in Fig. 4 and we must take the intercept *b*C as the heat of melting.

The undetermined quantity corresponding to B*b* in Fig. 1 must usually remain undetermined. It is made up of two parts, the heat of melting for the quantity of liquid actually present at *a*, plus the amount that *ab* has deviated from AB. Both parts may be diminished by starting at a lower temperature. However, too long an extrapolation of *ab* may invalidate our tacit assumption of a constant difference between solid and liquid specific heats.

The sources of error in this determination are of the same kind as those already discussed under K_2SO_4 with greater emphasis, however, on those that increase with the temperature interval or with time.

The failure of solid and liquid to attain equilibrium here leads to an uncertainty that may be turned to good account. We have heretofore considered the energy curve as that of the solid and a homogeneous liquid in equilibrium. With rising temperature, however, equilibrium is shifted during the melting process because the newly dissolved solid cannot instantaneously distribute itself through the melt. Thus the quantity of liquid formed is always less than it would be at equilibrium and, during the early part of the experiment, the rate of melting must also be less. Since divergence of *ab* from AB is proportional to the initial rate of melting, the lower rate leads to a smaller value of the undetermined quantity B*b*.

CONCLUSIONS.

Experience gained with these two samples indicates that the apparatus is entirely adequate to supply usable latent heat data for at least a considerable number of the silicates. The difficulty and uncertainty of the determination will undoubtedly increase at the higher temperatures and reach a point where the determination ceases to have any value. There is nothing at present to indicate how far above 1100° this limiting temperature lies; its location will depend to some extent on the nature and purity of the sample to be employed.

It has already been shown that the energy curve in Fig. 4 lies below the curve that would give energy vs. temperature with solid and liquid in equilibrium. However, it was found to be practicable to cover at least part of the melting interval in small steps, measuring energy input and allowing the charge to come to equilibrium between steps. This procedure gives the quantity dQ/dT as a function of temperature and may be useful in investigating processes of solution or dilution.

It may not always be possible to eliminate the thermal head correction by means of a second heating curve with the charge liquid. It appears, however, that the *change* in the correction during the significant part of the experiment may be calculated from measurements of temperature distribution within the calorimeter chamber. In the case of Curves I and III, Fig. 4, this change seems to be about 1/5 of the temperature difference between points t and m in Fig. 2. Additional work is needed to determine the effect of heating rate, especially if the latter is not uniform.