1 and 4 above. At ionic strength 0.028 the rate constant for step 1, the bimolecular reaction between Ni^{++} and $NiY^{=}$, is 5×10^{-5} l./mole/sec. whereas for step 4, the bimolecular reaction between Ni^{++} and $HNiY^{-}$, the rate constant is 0.003. The greater reactivity of $HNiY^{-}$ is quite understandable since addition of a proton should decrease the stability of the complex ion. Similarly we would expect the rates for the unimolecular decompositions of $HNiY^{-}$, H_2NiY and H_3NiY^{+} to be increasingly larger for the more highly protonated species. A comparison for somewhat similar bimolecular steps has been given by Ackermann and Schwarzenbach[12] who report that cupric ion reacts 20-fold more rapidly with $HCdY^{-}$ than with $CdY^{=}$.

Complexity of exchange behavior seems to be typical of the MeY complexes studied thus far. In the *p*H region four to seven the cobaltous complex, $CoY^{=}$, exchanges with cobaltous ion according to[5]

$$R_t = k_1(Co^{++})(CoY^{=})_t + k_2(H^{+})(CoY^{=})_t$$

The exchange between ferric ion and FeY^{-} at hydrogen ion concentrations of from 0.003 to 0.3 *M* has been shown to follow the law

$$R_t = k_1(FeOH^{++})(FeY^{-}) + k_2(Fe^{+++})(FeY^{-}) + k_3(H^{+})^3(FeY^{-})$$

with indications of a possible contribution from a term that is first order in hydrogen ion.[4] The terms in these rate laws, with the exception of the term in ($FeOH^{++}$), are similar to those for the nickelous–$NiY^{=}$ exchange. Reactions of the type $A^{++} + BY^{-} = AY^{=} + B^{++}$ also exhibit rate laws with several terms[12,13] and these have been interpreted by mechanisms which are closely related to the one suggested here.

ITHACA, N. Y.
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[CONTRIBUTION FROM THE WATSON LABORATORIES OF INTERNATIONAL BUSINESS MACHINES]

Reactions of the Group VB Pentoxides with Alkali Oxides and Carbonates. VII. Heterogeneous Equilibria in the System Na_2O or Na_2CO_3–Nb_2O_5

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The heterogeneous equilibria in the system Na_2O or Na_2CO_3 with Nb_2O_5 have been investigated using differential thermal analysis, X-ray analysis and density measurements. Four compounds corresponding to the formulas (I) $Na_2O·14Nb_2O_5$, (II) $Na_2O·4Nb_2O_5$, (III) $Na_2O·Nb_2O_5$ and (IV) $3Na_2O·Nb_2O_5$, have been identified. Compounds I and II melt incongruently at 1309 and 1277°, respectively, and compounds III and IV melt congruently at 1422 and 997°, respectively. The polymorphism of compound III has been reinvestigated, and results indicate the existence of four phases with transitions at 640, 562 and 354°. The 562° transition was observable, as a sharp heat effect at this temperature, only after extensive annealing. In a reëxamination of the polymorphic behavior of Na_2CO_3, latent heat anomalies were observed at 485 and 355°. X-Ray powder data have been obtained for compounds I, II, III and IV.

Introduction

Although the preparation and chemistry of the sodium niobates have been the subject of a considerable number of papers, dating back to 1812, the major emphasis has been placed on the study of those salts derived from aqueous media. In 1897, Holmquist[2] reported that the anhydrous compounds $2Na_2O·Nb_2O_5$ and $Na_2O·Nb_2O_5$ resulted from the reaction of stoichiometric quantities of Na_2CO_3 and Nb_2O_5 in the presence of NaF flux. Subsequently, Barth,[3] in determining the lattice constants of $Na_2O·Nb_2O_5$, provided the first X-ray confirmation of any of the sodium niobates. In an investigation of the reactivity of $NaNbO_3$ with molten Na_2CO_3 Lapitskiĭ[4] concluded that the meta salt was unreactive toward the molten alkali and consequently more basic niobates do not exist. The anomalous dielectric behavior of $NaNbO_3$ was discovered in 1949,[5] and since that time the transition temperatures and accompanying structural changes have been studied extensively.[6-11] The only other anhydrous sodium niobate reported is the compound $5Na_2O·Nb_2O_5$.[12]

In this, the seventh paper in a series involving the reactions of alkali oxides and group VB pentoxides, the heterogeneous equilibria in the anhydrous system Na_2O or Na_2CO_3–Nb_2O_5 have been investigated in order to resolve the ambiguities concerning the number of compounds formed and their stoichiometries. Included is a study of the polymorphic behavior of $NaNbO_3$ and Na_2CO_3.

Experimental Procedure

1. **Reagents.**—The Na_2CO_3 used in this study was Mallinckrodt analytical reagent. Prior to use, the carbonate was dried to constant weight at 400° and stored in a desiccator over drierite. The niobium pentoxide was obtained from two sources, the Fansteel Metallurgical Co. and the Var-lac-oid Co. These reagents were of the highest purity available, containing as a maximum contaminant 0.2% Ta.

[1a] This paper represents part of a thesis submitted by A. Reisman to the Graduate School of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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X-Ray fluorescence analysis of both materials showed trace amounts of iron and nickel and less than 0.2% Ta. The original Fansteel pentoxide gave a diffraction pattern characteristic of partially crystallized α-Nb_2O_5,[13] and the Varlac-oid material gave the pattern of the intermediate α-phase. After drying to constant weight at 1100°, both reagents were completely converted to the α-form.

2. **Preparation of Samples. a. Thermal Analysis Cooling Curves, 0–75 Mole % Na_2O.**—Charges were weighed so as to give predetermined quantities of melt after completion of reaction. In this way the length of eutectic halts and composition could be correlated. The components were weighed to the nearest 0.2 mg., rolled in a vial for 30 minutes and then loaded into 10-cc. platinum crucibles. As the reaction between an alkali carbonate and Nb_2O_5 is violent at elevated temperatures, the charges were placed in a furnace at 800° and then heated at 100°/hr. until molten. When this technique is used, the reaction proceeds smoothly with a minimum of spattering, and samples exhibited a maximum excess weight loss of 4 mg. Since the samples had a final weight of 8 g., the excess weight loss was well within the limits of experimental detection, even if such losses were attributable to one component. Fluorescence analysis of samples selected from different portions of the diagram showed the presence of trace quantities of dissolved platinum.

b. **Thermal Analysis Cooling Curves 75–100 Mole % Na_2CO_3.**—In the region 75–100 mole % Na_2O, platinum ware is severely attacked by molten alkali. In attempting to carry out the reactions in gold crucibles, it was found that unreacted solid remained at the bottom of the crucible after prolonged treatment at 1025°. Furthermore, fluorescence analysis indicated contamination of the charges with gold after 24 hr. at 1025°. Difficulty in attaining complete reactions also had been noted in the high alkali regions in the K_2O–Nb_2O_5, Ta_2O_5 and V_2O_5 systems.[14–16] A satisfactory solution to this problem was found in the use of gold–20% palladium crucibles. The alloy was resistant to molten alkali, as proved by fluorescence analysis, and could be heated to 1300°. Charges weighed into gold–palladium crucibles were heated to 1200°. Reaction began at about 800° and at approximately 1100° the samples appeared completely molten. Further heating resulted in partial resolidification followed by a gas evolution and complete melting. Weight loss experiments indicated that the reaction was not complete until the second melting and gas evolution were observed, and only then did the ratio of the number of moles of CO_2 lost to the number of moles of Nb_2O_5 present become constant.

c. **X-Ray Analysis, Heating Curves and Density Determinations.**—Completely reacted, homogeneous samples were prepared by thorough mixing of the components which were then heated three times at temperatures 25–50° below the solidus as determined from cooling data. All samples were maintained at the appropriate temperature for 24 hr. In order to minimize strain and approach equilibrium conditions, heating and cooling rates were programmed at 1°/min. Single crystals for X-ray analysis were obtained from molten charges.

3. **Differential Thermal Analysis.**—The Na_2O–Nb_2O_5 system was investigated using the method of differential thermal analysis with the following modifications of previously described apparatus.[13–17] Gold–20% palladium thermocouple protective capsules, grounding wires, bubbling tubes and crucibles were used in the high alkali regions. Thirteen mil Pt–10 Rh thermocouple wire was replaced by 20 mil wire since the heavier wire was found to have a longer noise-free lifetime. A heating curve furnace based on an earlier design[13] was constructed to provide higher operating temperatures. The barrel loading feature was the same except that the thermocouple protecting capsules were not permanently attached to the grounding wire, and after each run the crucible and capsule were removed as a unit for cleaning. Differential e.m.f. signals were amplified 15×, and heating and cooling rates were of the order of 2°/min.

4. **X-Rays.**—The stoichiometry of the incongruently melting compound I could not be determined by the method of differential thermal analysis since it was difficult to achieve equilibrium through two consecutive incongruent halts. Consequently an X-ray phase diagram was constructed by plotting the variation of "intensities" of selected diffraction maxima as a function of composition.[16] Loading and reloading samples indicated little or no orientation effects. All X-ray data were obtained using a Norelco diffractometer with Ni filtered Cu radiation, a scintillation counter and the Atomic pulse height analyzer. Single crystal data were obtained with Supper precession and Weissenberg cameras.

5. **Density Measurements.**—In order to provide an independent method of establishing the stoichiometry of compound I, a density phase diagram was determined. The powder pycnometer and density measuring technique previously described[17] were used for all measurements.

Discussion of Experimental Results

The "equilibrium" curves, Figs. 1, 2, 3, are based on the data tabulated in the corresponding tables. The region from 25–100 mole % Nb_2O_5, Fig. 1, represents equilibrium between Na_2O and Nb_2O_5. From 0–25 mole %, Na_2CO_3 behaves as a binary component. Therefore this region may be treated as a separate phase diagram, since it represents the only field in which Na_2CO_3 can exist in equilibrium with a sodium niobate. As Na_2O and Na_2CO_3 are molecularly equivalent, no discontinuity arises in moving from one portion of the diagram to the other. The data indicate the existence of four compounds corresponding to the formulas (I) $Na_2O \cdot 14Nb_2O_5$, (II) $Na_2O \cdot 4Nb_2O_5$, (III) $Na_2O \cdot Nb_2O_5$ and (IV) $3Na_2O \cdot Nb_2O_5$.

In the liquidus region 0–19 mole % Na_2O, α-Nb_2O_5 occurs as the primary crystallization. The Nb_2O_5 liquidus terminates incongruently at 19 mole % and 1309°. Between 0 and $6^2/_3$ mole % Na_2O, the solidus region represents equilibrium between the incongruently melting compound I and α-Nb_2O_5. The dotted line at 830° represents the boundary of the hypothetical α-, γ-Nb_2O_5, compound I fields. Since the starting Nb_2O_5 was received as the α-polymorph which cannot be inverted to the γ-form,[13] the latter's field of existence is purely speculative.

In the region $6^2/_3$ to $21^1/_3$ mole %, α-Nb_2O_5 undergoes a transformation at 1309° to compound I plus liquid. The compound I liquidus terminates incongruently at $21^1/_3$ mole % and 1277°. Between $6^2/_3$ and 20 mole % Na_2O, the solidus region represents equilibrium between I and II. In attempting to define the isoplethal boundary of the 1277° transformation, an anomalous behavior was observed. All cooling experiments in the region 0.5–17 mole % showed persistence of the 1277° transformation, which apparently would preclude the existence of a compound intermediate in composition between Nb_2O_5 and $Na_2O \cdot 4Nb_2O_5$. It was noted further that the length of the incongruent halt could not be correlated with composition, and a preliminary X-ray survey of quenched samples in the region 0–20 mole % Na_2O showed the existence of unaccountable diffraction lines. The data either indicated the presence of a possible new high temperature phase of Nb_2O_5 stabilized by the presence of the liquid phase or the formation of a new compound. If a new phase of Nb_2O_5 existed above 1309°, solid state reaction of samples below the

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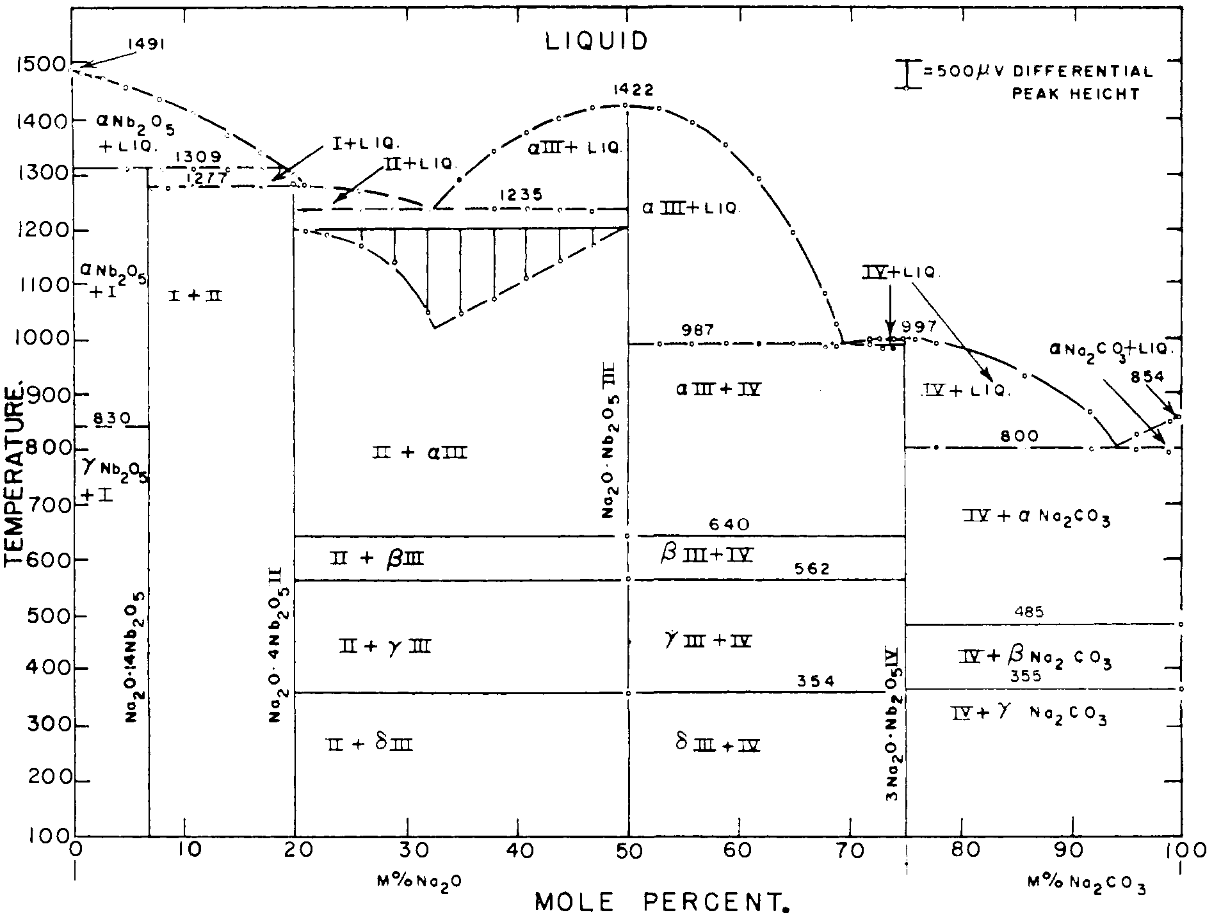

Fig. 1.—Phase diagram of system Na_2O or Na_2CO_3-Nb_2O_5.

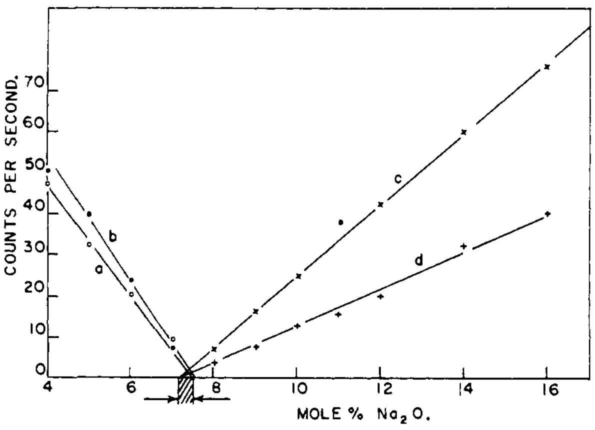

Fig. 2.—Partial X-ray phase diagram of system Na_2O-Nb_2O_5. Nb_2O_5—a, $2\theta = 23.75°$; b, $2\theta = 25.52°$. Compound II—c, $2\theta = 22.46°$; d, $2\theta = 22.69°$.

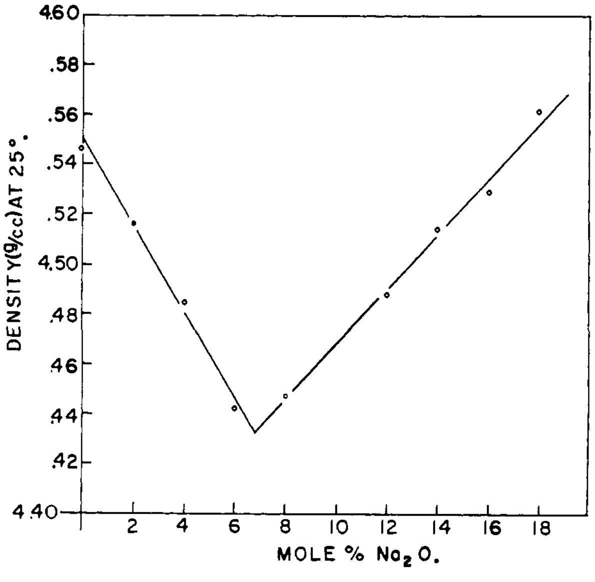

Fig. 3.—Partial density phase diagram of system N_2O-N_2O_5.

1277° transition would definitely preclude the formation of this phase. In such a case the extra lines would not be observed in the solid state reacted samples. On the other hand, if the undefined X-ray lines were attributable to an intermediate compound, the additional diffraction maxima would persist. A series of solid state reacted samples, in the composition range 0–20 mole %, was prepared for X-ray examination as described in the Experimental section. The persistence of the extra diffraction lines proved the existence of an intermediate compound, and an X-ray phase diagram was determined. The extrapolation of the Nb_2O_5 and compound II lines to zero intensity established the stoichiometry of compound I to within ±0.50 mole %, Fig. 2, Further confirmation of the existence and stoichiometry of compound I was obtained with heating curves and density measurements. Heating curve experiments showed the disappearance of the 1277° transformation at approximately 8 mole % Na_2O. The densities of a series of samples ranging in composition from 0–18 mole % Na_2O were determined at 25°. The data listed in Table III and plotted in Fig. 3 show a minimum at 6.7 mole %, corresponding to the density of compound I. Within the limits of experimental error of the X-ray and density measurements, the smallest integral ratio corresponds to $Na_2O \cdot 14Nb_2O_5$. Based on the above evidence, the anomalous cooling behavior can be explained by considering what occurs in the freezing process. When a crystallite of Nb_2O_5 interacts with the liquid phase at 1309° the reaction proceeds from the exterior to the interior of the crystal, the process being diffusion controlled. As the temperature is continually lowered during the experiment, sufficient time is not available for the entire bulk of the crystallized Nb_2O_5 to come into equilibrium with the melt. The net effect is the withdrawal of Nb_2O_5 from the reaction mixture, shifting the effective composition toward higher Na_2O concentration. That the shift is not insignificant is shown by the fact that a gap of up to $6^2/_3$ mole % is created. It is evident that the dynamic determination of binary fields can result at best in quasi equilibrium, the approach to true equilibrium depending on the complexity of the fields, the nature of the interacting components, and the temperature.

TABLE I

THERMAL DATA FOR THE SYSTEM Na_2CO_3–Nb_2O_5

Na_2CO_3, mole %	Nb_2O_5	Liquidus	Solidus	Transition	M.p., °C.	Primary phase
100	0			485, 355	854	Na_2CO_3
99	1	849	793	486, 358		Na_2CO_3
96	4	823	799	492, 360		Na_2CO_3
92	8	867	798	490, 360		IV
86	14	932	802	490, 359		IV
78	22	993	801	491, 358		IV
76	24	997				IV
75	25				997	IV
74	26	996	980			IV
73	27	996	984			IV
72	28	995	989			IV
69	31	1026	986			III
68	32	1079	986			III
65	35	1190	987			III
62	38	1289	988			III
59	41	1352	988			III
56	44	1393	989			III
53	47	1415	987			III
50	50			640, 562, 354	1422	III
47	53	1417	1229			III
44	56	1397	1234			III
41	59	1373	1235			III
38	62	1337	1234			III
35	65	1291	1236			III
32	68		1235			
29	71	1256	1237			II
26	74	1269	1234			II
23	77	1274	1234			II
21	79	1281	1233	1277		I
20	80	1298	1277			I
17	83	1341	1275	1309		Nb_2O_5
14	86	1367	1277	1309		Nb_2O_5
11	89	1407	1277	1308		Nb_2O_5
9	91		1277			
8	92	1435		1307		Nb_2O_5
5	95	1459	1308			Nb_2O_5
3	97	1473	1298			Nb_2O_5
2	98	1480				Nb_2O_5
1	99	1486				Nb_2O_5
0	100				1491	Nb_2O_5

TABLE II

"INTENSITY" DATA FOR SELECTED DIFFRACTION MAXIMA AS A FUNCTION OF M % Na_2O

		Counts per second			
Na_2O, mole %	Nb_2O_5	Nb_2O_5 2θ = 23.75°	Nb_2O_5 2θ = 25.52°	Compound II 2θ = 22.46°	Compound III 2θ = 22.69°
16	84			76	40
14	86			60	32
12	88			42	20
11	89			38	16
10	90			25	13
9	91			16	8
8	92			7	4
7	93	9	7		
6	94	20	23		
5	95	39	32		
4	96	47	50		

TABLE III

DENSITY DATA FOR THE SYSTEM Na_2O–Nb_2O_5 AT 25°

Na_2O, mole %	Nb_2O_5	Density, av. of 2 detns., g./cc.
18	82	4.561 ± 0.002
16	84	4.529 ± .008
14	86	4.514 ± .004
12	88	4.488 ± .000
8	92	4.447 ± .000
6	94	4.442 ± .006
4	96	4.484 ± .002
2	98	4.516 ± .000
0	100	4.547 ± .000

The compound II liquidus field extends from $21^1/_3$ mole % to the 1235° eutectic at 32.5 mole % Na_2O. The disappearance of the 1235° solidus heat effect at 20 mole % establishes the base to acid ratio of compound II. A plot of the height of differential thermal maxima of the eutectic halt, Fig. 1, fixed the isobaric invariant point at 32.5 ± 0.25 mole % and the compound III location at 50 mole %. The solidus region from 20–50 mole % Na_2O represents equilibrium between II and III. Using single crystal and powder diffraction data, II was indexed on the basis of an orthorhombic unit cell with a = 12.39, b = 36.98 and c = 3.97 Å. The lattice constants and the pycnometric density of 4.62 g./cm.^{3} at 25° require 4.5 molecules of $Na_2O \cdot 4Nb_2O_5$ per unit cell. Assuming that this is the correct unit cell, then according to the systematic extinctions the space group is P--a with the selected a and b having 2 or m symmetry operations. The basic unit would contain 9 sodium, 36 niobium and 94.5 oxygen atoms, which is prohibited by the space group. Even though precession, Weissenberg and rotation photographs show no evidence of twinning, it is believed that the single crystals are microscopically twinned and therefore exhibit a higher symmetry than is present. The fact that the powder photograph can be indexed does not prove the correct choice of crystal class, since large lattice constants facilitate the fitting of powder data. Detailed single crystal studies of compound II are being conducted, and the results will be presented at a later date.

Compound III melts congruently at 1422°. Its liquidus field extends from the 32.5 mole % eutectic to the 987° eutectic at 69.5 mole %. Solid state phase transformations in sodium metaniobate have been found by several investigators.[6–9,11] The transition temperatures were determined by light optical and/or X-ray methods. Although the nature of these transformations was the subject of considerable controversy, the temperatures of transitions were essentially the same, *i.e.*, 360, 480 and 640°. Except for Shirane's[8] reference to an unpublished work, the results of differential thermal analysis on sodium niobate have not been reported. Twenty separate sets of D.T.A. cooling and heating experiments were run on solid state reacted samples as well as on material crystallized from molten $NaNbO_3$. Three distinct latent heat anomalies were observed at 354 ± 1, 562 ± 1 and 640 ± 4° for all samples. The estimated latent heats associated with these transitions are 150, 50 and 75 cal./mole, respectively. There is excellent agreement of thermal data with previous values for the low and high temperature transitions; however, the middle transition is considerably different from that previously reported. It is interesting to note that the first several D.T.A. cycles, using either crystalline or solid state reacted samples failed to reveal the upper two transitions. After five or six cycles the upper transitions became detectable with the middle heat effect spread over approximately a 100° range. Subsequent recycling to 1150° at 1°/minute increased the sharpness of the heat effect, and the temperature of the middle transition increased to a reproducible value at 562°. Since such behavior was observed in all samples, it would appear that the middle phase transformation is subject to strain and only by repeated annealing could consistent results be obtained. It is believed that on the basis of the thermal behavior, the ambiguities between optical and X-ray behavior can be explained. Shirane found that at 430° the material was essentially cubic to X-rays, and it was evidently assumed that in the range 430 to 640° the structure converged to the cubic phase since in this critical range no data are presented. However, Francombe reported that somewhere between 480 and 505° true tetragonal splitting reappeared on the diffraction pattern and that the tetragonal splitting becomes sharpest at 560°. The unusual X-ray behavior between 480 and 560° would appear to result from strain, as has been demonstrated with differential thermal analysis. This picture is consistent with Francombe's data which indicate a maximum in tetragonal splitting at 560°.

The solidus region between 50 and 75 mole % Na_2O represents equilibrium between compounds III and IV. IV melts congruently at 997° and its liquidus field extends from 69.5 to the 800° eutectic at 94 mole % Na_2O. Compound IV and Na_2CO_3 are in equilibrium in the solidus region from 75–100 mole % Na_2CO_3. In the "equilibrium" diagram, there is no evidence of the 5:1 compound reported by Lapitskiĭ.[12] In the author's discussion of the 5:1 salt, the statement is made, "The melts obtained were not transparent in all cases, and a solid phase was always found in the liquid melts.[18]" From this description, it is difficult to understand how the stoichiometry of this compound was determined, in view of the fact that alkali-rich niobates crystallize poorly from the melts and are not readily separable. The peculiarities of the reaction melts in the high alkaline region have been discussed in the Experimental section. From the results obtained, it appears probable that Lapitskiĭ's experiments were conducted on partially reacted melts. It was found that cooling curves recorded immediately after the first fusion at approximately 1100° showed a eutectic type halt at 750° instead of the "equilibrium" arrest at 800°. It is conceivable that if a 5:1 compound exists, it is the product of a metastable equilibrium, but since the liquidus temperatures for the partially reacted samples depended on the degree of reaction and gave inconsistent data, the metastable diagram could not be resolved.

Using D.T.A. Makarov and Shulgina[19] found that Na_2CO_3 exists in four polymorphic forms with transitions at 356, 486 and 618°. Transition temperatures were chosen at peak maxima rather than at points of maximum inflection. Figure 4a shows a differential heating curve starting with "anhydrous" Na_2CO_3. Experiments were run in Au–20% Pd since even in the solid state Na_2CO_3 reacts appreciably with platinum ware. The low temperature endotherm corresponds to a loss of water. As the temperature is increased, two broad endotherms develop at approximately 300 and 400° as determined from extrapolation of maximum inflection to the base line. After the sample became molten a differential cooling curve was recorded, using a CO_2 atmosphere, Fig. 4b. Two distinct transitions were observed at 485 ± 3 and 354 ± 3° both rather sluggish. If this sample were then permitted to equilibrate at room temperature for several hours without being protected from moisture the heating curve was again that of 4a. However, if the sample were protected from moisture and then taken through a heating cycle the trace shown in 4c resulted. Comparison of Fig. 4c with 4b shows that attempting to choose the upper and lower transition temperatures from heating data gave non-reproducible results. Selecting peak maxima on heating curves gave reproducible results consistent with cooling data obtained with the extrapolation method. This particular apparatus has been calibrated with standard materials, and it has always been found that the extrapolation method, as expected, gave consistent heating and cooling data. Selection of the transition tem-

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[18] Translation from the Russian of ref. 12.

[19] S. Makarov and M. P. Shulgina, *Bull. Acad. Sci. U.R.S.S.*, **5**, 691 (1940).

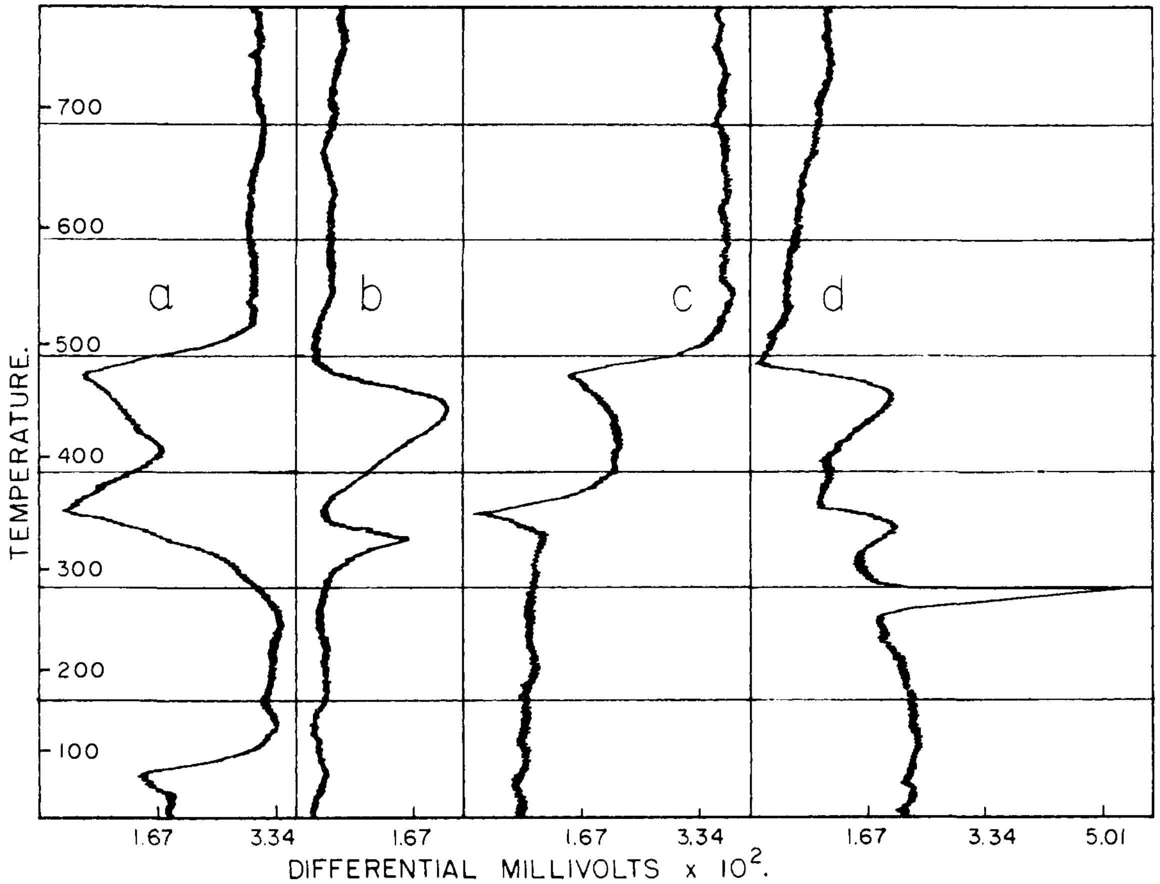

Fig. 4.—DTA traces of Na_2CO_3.

peratures at the differential peak maxima is meaningless because it ignores the continuous heat effect which has been occurring up until that point. The reported temperatures were obtained from cooling data using the extrapolation method. The anomalous heating behavior observed in Na_2CO_3 is believed to be due to strain developed in the cooling cycle. This belief is supported by the rather broad heat effects shown in Fig. 4b.

Neither heating nor cooling curves gave any indication of a transition in the neighborhood of 600°, which is strange since, based on the magnitude of the heat effects, the present equipment appears to be much more sensitive. In order to determine the effect on the DTA traces caused by decomposition of the Na_2CO_3, cooling traces were taken in an oxygen atmosphere, Fig. 4d. The sharp exotherm observed at 288° probably represents a phase transformation in Na_2O since if the sample were not protected from moisture pickup the subsequent heating curve is similar to Fig. 4a indicating a conversion of Na_2O to NaOH. In this case Fig. 4d can be regenerated by first making the sample molten. As the two Na_2CO_3 transitions are not affected by the decomposition product the indications are that the high Na_2CO_3 region of the interaction Na_2CO_3–Na_2O is of the eutectic type.

Interplanar spacings for all the anhydrous compounds are presented elsewhere.[20]

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