be worth noting is the apparent discrepancy that occurs when one compares the fraction double bond character with the corresponding value obtained from Pauling's equation[8] using covalent radii of the atoms involved. The discrepancy can be partially removed by combining the Pauling equation with an equation suggested by Schomaker and Stevenson[9] which attempts to account for shortening of a bond due to a difference in electronegativities of the atoms involved. This correction has been reviewed critically by Wells.[10] If one considers the possible simultaneous effect on bond length of the ionic and double bond characters and combines the Pauling and Schomaker equations one then obtains an expression

$$R = R_1 - \frac{(R_1 - R_2)3\pi}{(2\pi + 1)} - 0.09(X_X - X_B) \qquad (5)$$

where R = observed bond distance, R_1 = sum of covalent radii[8] and R_2 = sum of double bond radii.[8] If this expression is now used to get the π-bond character from observed bond distances the agreement with quadrupole data is reasonable. For example the fraction double bond character from bond distances[8,11,12] is 0.05, 0.16 and 0.20 whereas the quadrupole data give 0.06, 0.12 and 0.16 for BCl_3, BBr_3 and BI_3, respectively. Of course, equations such as (5) should be taken with considerable reservation. However, we felt that it was of interest to point out that if a sufficient number of effects are taken into consideration the conclusions drawn from observed bond distances are not necessarily in conflict with quadrupole data.

In addition, one can make some qualitative comments on the crystal structure of BI_3 relative to the other boron trihalides whose structures are known. It has been determined that the resonance in BI_3 consists of a doublet with an intensity ratio of one to four. The doublet separation is 25.5 ± kc./sec. in the lower frequency transition. In the other trihalides this doublet has been attributed to a boron isotope effect. The magnitude of the splitting and the intensity ratio obtained for the BI_3 case suggests that the same interpretation can be given for the splitting as in BCl_3 and BBr_3. Furthermore, since the resonance in BI_3 is the same except for absolute magnitude of the frequency and splitting, it can be concluded that its crystal structure is very probably the same as that of BBr_3 which is known. All of the iodines are in equivalent positions and the molecule is planar.

The authors are indebted to Dr. Frank J. Adrian for a very informative discussion on the molecular orbital aspects of these compounds.

BALTIMORE, MARYLAND

[8] L. Pauling, "Nature of Chemical Bond," Cornell University Press, Ithaca, New York, 1948.

[9] V. Schomaker and D. P. Stevenson, THIS JOURNAL, **63**, 37 (1941).

[10] A. F. Wells, *J. Chem. Soc.*, 55 (1949).

[11] P. W. Allen and L. E. Sutton, *Acta Cryst.*, **3**, 46 (1950).

[12] M. Atoji and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 195 (1957).

[CONTRIBUTION FROM THE WATSON LABORATORIES OF INTERNATIONAL BUSINESS MACHINES CORPORATION]

Further Comments on the Polymorphism of Nb_2O_5. The High Temperature Metastable Phase ϵ

BY ARNOLD REISMAN AND FREDERIC HOLTZBERG

RECEIVED NOVEMBER 18, 1958

Experimental evidence is presented which indicates the existence of a high temperature metastable phase of Nb_2O_5, ϵ. Attempts at correlating the available information with the proposed stability diagram of Shafer and Roy were unsuccessful, and their interpretation is analyzed.

Introduction

In 1957,[1] the authors published an article describing the polymorphic behavior of Nb_2O. During an investigation of the system Nb_2O_5–Ta_2O_5, anomalies in the cooling behavior of Nb_2O_5 rich melts indicated the existence of a new high temperature polymorph of the pentoxide. Since the effect on the equilibrium diagram Nb_2O_5–Ta_2O_5 would depend on whether this new phase was enantiomorphic or not, a separate study of its thermal properties was undertaken, and the results indicate that the new phase, ϵ, is metastable, relative to α. Recently,[2] Shafer and Roy postulated the existence of a new Nb_2O_5 phase, I (high), stable in the temperature interval 1285° to the melting point and also proposed that the β-phase has a definite interval of stability. Since the existence of the (I high) form was not substantiated in the present investigation and since the arguments presented in support of a stable β-region are not self consistent, the stability diagram was reevaluated.

Experimental Procedure

The DTA equipment has been described previously.[1,3] Heating and cooling experiments were conducted in the appropriate apparati using a gain of 5 to 10 μv./inch and a temperature variation of 2–3°/minute. High purity Nb_2O_5 containing <0.2% Ta_2O_5 as the major contaminant was dried in platinum at 1100° for 24 hr. prior to use. The diffraction pattern of the ignited oxide corresponded to that of the α-form,[1] and gave an experimental density[4] of 4.548 ± 0.002 g./cm.³ at 25°, in good agreement with the X-ray density of 4.52 g./cm.³ at the same temperature.[1] The freezing point of the pentoxide was found to be 1491 ± 2°.

---

[1] F. Holtzberg, A. Reisman, M. Berry and M. Berkenblit, THIS JOURNAL, **79**, 2039 (1957).

[2] M. W. Shafer and R. Roy, *Z. Krist.*, **110**, 241 (1958).

[3] A. Reisman, F. Holtzberg and E. Banks, THIS JOURNAL, **80**, 37 (1958).

[4] A. Reisman, F. Holtzberg, M. Berkenblit and M. Berry, *ibid.*, **78**, 4514 (1956).

Discussion

A. The Thermal Behavior of the High Temperature Phase, ε.—ε has been observed to crystallize exothermally from molten Nb_2O_5 without supercooling at *ca.* 1435°, and then transform spontaneously, with the liberation of heat, to α-Nb_2O_5 anywhere from 1200 to 1400°. The transformation to the stable α-phase is so striking that during microscopic examination on a hot wire[5] the crystallized sample becomes incandescent due to the rapid heat evolution.

The relative stability of ε to α is clearly demonstrated by the following sequence of experiments. If molten Nb_2O_5 is seeded with α, through the freezing point, a normal crystallization exotherm is observed at 1491°, with no subsequent heat effects. The cooled melt then consists of a highly crystalline transparent mass which gives an α-Nb_2O_5 diffraction pattern. In the absence of seeding, cooling traces resemble Figs. 1 or 2. In the first, ε crystallizes without supercooling and in the second case, with supercooling, and then transforms exothermally to α, anywhere from 1200° to just below the ε freezing point. The cooled specimen again gives the pattern of α-Nb_2O_5 but no longer possesses a definable crystalline habit, being opaque and severely fragmented, attesting to the violence of the ε → α transformation. Heating curves of the α-solid whether formed directly from the liquid, or indirectly from the ε solid, are identical and show no evidence of a solid state thermal anomaly from room temperature to the melting point.

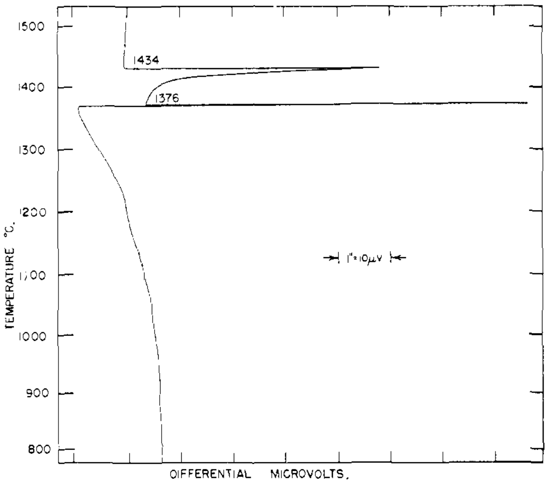

Fig. 1.—Differential thermal analysis cooling curve of Nb_2O_5 showing formation and inversion of the ε-phase.

In order to first determine the relative stability of ε below its freezing point, an Nb_2O_5 melt was permitted to crystallize in the ε-form, and the temperature then was maintained at 1400° for several hours. During this time ε did not invert to α, since subsequent cooling showed an ε → α irreversible exotherm at *ca.* 1350°. Having demonstrated that ε could be maintained for a sufficient time period just below its freezing point, the sample was remelted and once again ε was permitted to crystallize. The metastable solid was cooled to 1400° and then reheated at 3°/minute, Fig. 3. First the endothermic melting of ε was observed at 1435°, peak "a." As soon as the ε melting was concluded, a minute seed of α was dropped into the melt. Immediately, an almost adiabatic exotherm resulted which raised the sample temperature above that of the reference sample, peak "b." The adiabatic nature of the exotherm was occasioned by the spontaneity of the non-equilibrium ε → α inversion, and as seen from the shape of the exotherm the sample subsequently cooled to approximately the reference sample temperature before further increase in temperature occurred. Finally the "equilibrium" melting of α was observed at 1491°. In order that none of the important features of this heating curve be obscured, it was necessary to reduce the gain to 25 μv./inch because of the size of the ε → α inversion peak.

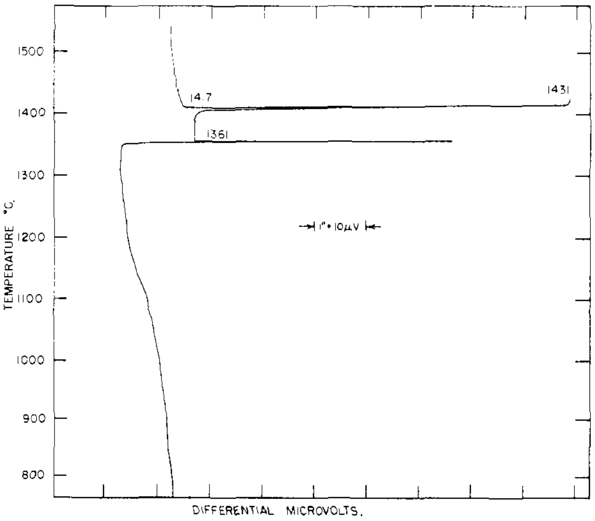

Fig. 2.—DTA cooling trace showing supercooling of the ε-phase.

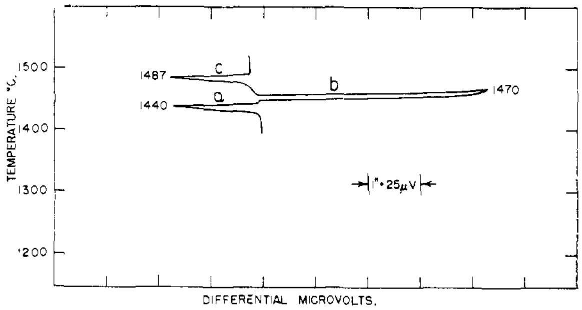

Fig. 3.—DTA heating trace of the ε-phase: (a) ε → metastable liquid; (b) metastable liquid → α; (c) α → liquid.

In several other experiments of the same type, the seeding with α above the ε melting point was omitted. In a few cases no further heat effect was observed. In another case the ε → α inversion occurred during the melting of ε and the melting of α subsequently was observed.

B. The High Temperature Stability Diagram of Nb_2O_5.—In referring to the I (high) phase, Shafer and Roy state, "A *reversible endothermic* heat effect corresponding to a high ⇄ low transition

---

[5] F. Ordway, *J. Research Natl. Bur. Standards*, **48**, 152 (1952).

was observed at 1285°." The pentoxide has been used as a freezing point standard in these laboratories for nearly five years during which time the authors have studied over one hundred samples of Nb_2O_5 in both heating and cooling cycles of materials purchased from a number of sources. None has shown the presence of a "reversible endothermic" transformation anywhere in the interval—room temperature to the melting point. Included in the studies were samples of amorphous as well as crystalline Nb_2O_5. Furthermore, investigation of the systems Li_2O–,[6] K_2O–,[7] Na_2O–[3] and Rb_2O–Nb_2O_5[8] failed to reveal discontinuities in the Nb_2O_5 liquid fields attributable to an Nb_2O_5 enantromorphic transition.[9]

From the above, and the previous data referred to, there is no evidence confirming the existence of a "reversible endothermic" transition, α to some higher form, at any temperature. If one were able to reconcile the discrepancies between the thermal data observed for ϵ and I (high), and considered them to be the same phase, it is evident that this phase must be metastable relative to α at all temperatures. Firstly, α freezes at a higher temperature than ϵ, therefore at the melting point α is the stable phase. Secondly, ϵ, when permitted to crystallize, spontaneously reverts to α, indicating that ϵ is metastable relative to α in any temperature interval in which they are both known to exist. Thirdly, if α is heated to just below the melting point and then cooled, no anomaly representing the $\epsilon \rightarrow \alpha$ transformation is observed. ϵ has only been observed upon crystallization from the liquid phase.

Since ϵ cannot be formed from crystalline α, it is evident that the X-ray data obtained by Shafer and Roy are not related to the ϵ phase. Furthermore, since their thermal findings could not be duplicated, it is not clear what their X-ray data verify. It is not inconceivable that their powder data for the I (high) form are really for α at high temperatures. Significantly, it appears that there is some confusion as to the interpretation of the high temperature X-ray measurements, since it is not obvious how twinning can be suggested in their I (high) form when only powder studies have been made or how the absence of twinning in α can be related to a questionable twinning in their I (high) form, *cf.* p. 248, ref. 2.

C. The Low Temperature Stability Diagram of Nb_2O_5.—Using hydrothermal techniques, Shafer and Roy report the synthesis of their II form in a crystalline state. It is implied that the "*d*" spacings for this form are similar to those reported by Brauer[10] but include resolved doublets. A comparison of their data with Brauer's shows no correlation between their II form and Brauer's M form. For example, Shafer and Roy find the strongest reflection at 4.178 Å., a spacing not observed by any other investigator.

The statement made by Shafer and Roy to the effect that experiments performed hydrothermally at pressures approximating 3000 lb. /sq. in. enable better approach to equilibrium conditions is unsubstantiated by their results. Firstly, the degree of crystallinity one obtains is in no way indicative of the relative stability of a phase, *viz.*, diamond at 1 atmosphere. Secondly, an important criterion of relative stability when more than one phase is known, namely, reversibility of phases, was not satisfied even by the "more equilibrium hydrothermal techniques." Shafer and Roy were apparently troubled by the inability to effect reversal, *viz.*, footnote 14, ref. 2.

Probably most significant, however, are the results of a comparison of their wet and dry data. Whereas 30 hr. at 1000° starting with amorphous material yielded "probably all high Nb_2O_5," the supposedly more equilibrium hydrothermal technique yielded only the medium phase after treatment at 1035° for 72 hr., a mixture of medium and high after 48 hr. at 1060°, and "practically all high" after 48 hr. at 1075°. These data do not corroborate their statements to the effect that the hydrothermal technique enables closer approximation to equilibrium conditions. As a matter of fact, the use of hydrothermal techniques appears to have induced an unfortunate line of reasoning, *cf.* p. 248, ref. 2.

Since none of the criteria for stability of any phase other than α has been satisfied, one must at present conclude that α is the only stable phase of Nb_2O_5 at one atmosphere pressure in the temperature interval surveyed.

Acknowledgment.—The authors wish to thank Mrs. R. Mineo and Miss C. Linde for assisting with the experiments.

NEW YORK, NEW YORK

---

(6) A. Reisman and F. Holtzberg, *J. Research Natl. Bur. Standards*, **80**, 6503 (1958).

(7) A. Reisman and F. Holtzberg, *ibid.*, **77**, 2115 (1955).

(8) A. Reisman and F. Holtzberg, to be published.

(9) See for example a relevant discussion in ref. 3, p. 38–40.

(10) G. Brauer, *Z. anorg. allgem. Chem.*, **248**, 1 (1941).