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The Linear Thermal Expansion of Sodium Tungstate Between 20° and 600°

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(1) The linear thermal expansion of anhydrous sodium tungstate has been determined between 20° and 600°C by means of an interferometer, with results given by the following equations:

$$\begin{aligned}v &= v_{20}[1 + 53.194(t-20)10^{-6} + 41.5(t-20)^2 10^{-9}], \\ \Delta l/l_{20} &= 17.73(t-20)10^{-6} + 13.83(t-20)^2 10^{-9}, \\ \alpha_m &= 17.73 \times 10^{-6} + 13.83(t-20)10^{-9}, \\ \alpha_t &= 17.73 \times 10^{-6} + 27.66(t-20)10^{-9}.\end{aligned}$$

(2) The results show that at atmospheric pressure the salt is trimorphous. Modification III is stable on heating up to 585° at which temperature it transforms to II with an increase in volume of 17.4 percent. Form II is stable over a very short temperature interval, whose exact extent could not be determined, and then transforms to Na₂WO₄ I with a decrease in volume of 0.12 percent.

IN the course of an investigation of the linear thermal expansion of tridymite prepared by heating powdered quartz with Na₂WO₄ it became desirable to know the expansion of the flux alone. Since such information is not available in the literature we have determined the dilatation of Na₂WO₄ between 20° and 600°C by means of an interferometer previously described.¹ In addition to providing values of the expansion coefficient, the results confirm the phase relations in this system as recently reported by Goranson and Kracek.² Thus, it is shown that at atmospheric pressure, anhydrous Na₂WO₄ exists in three crystalline forms which, following Goranson and Kracek, are designated III, II and I in the order of their stability range with increasing temperature. Na₂WO₄ III, is stable up to 585°C, at which temperature it transforms to Na₂WO₄ II with an increase in volume of approximately 17 percent. Na₂WO₄ II then changes to modification I a few degrees above the transition III→II, but in this case there is a decrease in volume of 0.12 percent. These transitions lie so close together that on heating under our experimental conditions the second one was always masked by the large change of volume accompanying the first. It was, on the other hand possible to separate them on cooling because of their different tendencies to undercool. Thus, on cooling from 600°C, Na₂WO₄ I transforms to Na₂WO₄ II at approximately

580°C, the exact temperature depending on the rate of cooling; modification II then persists in metastable equilibrium to some lower temperature which again depends on the rate of cooling. At a rate of 3°C per min. the transition II→III was observed to take place close to 525°C, or 60°C below the equilibrium temperature. This behavior provides another convincing example of the error which may be introduced into a determination of phase equilibria in solids by approaching the equilibrium from one side only, particularly if this approach is by cooling, as is often the case.

MATERIAL

A good grade of commercial Na₂WO₄, further purified by recrystallization from water, was fused in gold and was allowed to solidify into a block from which three specimens, approximately 3 mm in height and 3 mm in diameter, could easily be cut. No measurements were made on single crystals because we were not able to prepare suitable ones; Na₂WO₄ could not be made to form well-defined anhydrous crystals of satisfactory size from aqueous solution, and all attempts to grow a single crystal from the melt failed because a crystal formed on cooling was invariably shattered on cooling through the inversion II→III.

RESULTS. THERMAL EXPANSION BELOW 585°C

Up to approximately 400° the salt showed a normal reversible thermal expansion (see Fig. 1) but just above 400° the expansion coefficient

¹ Austin and Pierce, J. Am. Chem. Soc. **55**, 661 (1933). For a complete description of the method see Merritt, Bur. Standards J. Research **10**, 159 (1933).

² Goranson and Kracek, J. Chem. Phys. **3**, 87 (1935).

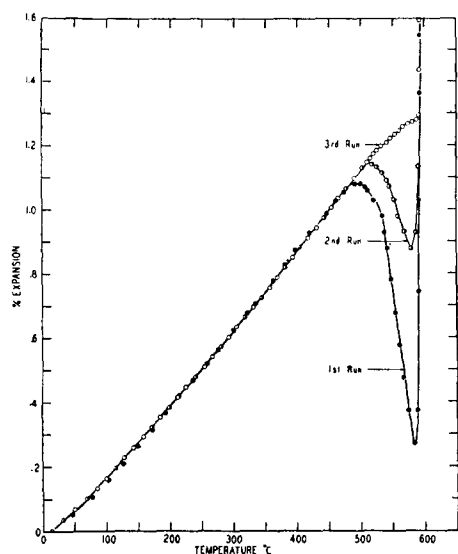


FIG. 1. The linear thermal expansion of Na_2WO_4 up to 585° as determined on three successive runs on the same sample under a load of 63 grams.

appeared to pass through a maximum and began to decrease, the rate of decrease varying considerably with the experimental conditions. In many cases an actual contraction of the specimens was observed as indicated by the typical curves given in Figs. 1 and 2. The latter gives the length-temperature curves for two sets of measurements in which the specimens were under the load of the upper interferometer plate alone (6 grams). Fig. 2a shows the results for a run in which heating was stopped just short of the inversion and indicates that there was a permanent contraction represented by the length Δl_0 , which correspond to 0.30 percent of the length at 20° . In the run shown in Fig. 2b, however, the heating was stopped just as the inversion started (see inset); after cooling to 500° the temperature was again raised to that of the inversion. In this case the apparent irreversible shrinkage was 0.20 percent of the length at 20° .

Although there was little doubt that these permanent changes in length were due to softening or shifting of crystallites in the aggregate it seemed desirable to demonstrate it beyond question, and at the same time to determine whether or not the shrinkage could be reduced or elimi-

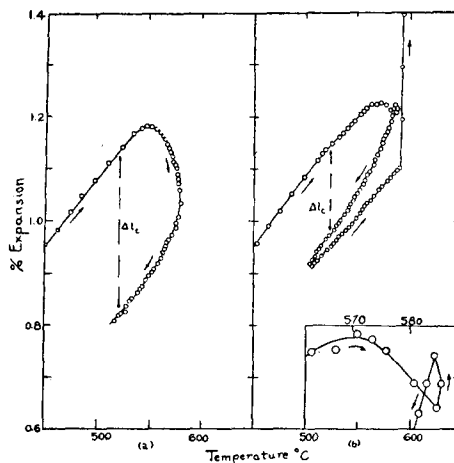


FIG. 2. Curves showing the linear thermal expansion of two samples of Na_2WO_4 in the neighborhood of the III \rightarrow II inversion.

nated, by observing the expansion of the same specimens during successive heatings under load. Accordingly, a brass ring weighing 57 grams was placed on the upper plate of the interferometer, bringing the total load to 63 grams. The results for three successive runs, given in Fig. 1, show that on first heating the contraction between 500° and the inversion was very nearly as large as the total increase in length between 20° and 500° ; and that on the succeeding runs the shrinkage was much less, as was expected. Since it was not possible to obtain reproducible data from 450° to the inversion point, an extrapolation was made from 400°C to 585°C based on a quadratic equation representing the points below 400°C .

Although the data below 400° showed a reasonable consistency, a careful examination of the individual runs revealed that in every case the length-temperature curve was not strictly a smooth curve but showed an irregular waviness which was not reproducible and which was greater in some cases than in others. In order to eliminate the effect of these undulations all the observations were plotted on a large scale and averaged graphically by drawing a smooth curve through them. That this correction was a very slight one is evident from Fig. 1 which shows how nearly the experimental points fall on the curve below 400°C .

Values of the expansion taken from this smooth curve were used by Goranson and Kracek² to derive a least-square quadratic for the volume as a function of temperature on the assumption that the specimens were aggregates of randomly-oriented grains. Their equation is:

$$v - v_{20} = v_{20} [53.194(t-20)10^{-6} + 41.5(t-20)^2 10^{-9}].$$

(The equation as printed in their paper erroneously gives the coefficient of the term containing $(t-20)^2$ as 41.5×10^{-8} instead of 10^{-9} .) The corresponding equations for α_m , the mean linear expansion coefficient between 20° and t° , for α_t , the instantaneous linear expansion coefficient at t° , and for $\Delta l/l_{20}$ the increase in length per unit length at 20° are, respectively:

$$\begin{aligned}\alpha_m &= 17.73 \times 10^{-6} + 13.83(t-20) \times 10^{-9}, \\ \alpha_t &= 17.73 \times 10^{-6} + 27.66(t-20) \times 10^{-9}, \\ \Delta l/l_{20} &= 17.73(t-20) \times 10^{-6} \\ &\quad + 13.83(t-20)^2 \times 10^{-9}.\end{aligned}$$

As a further check on the values of the instantaneous coefficient, the slope of the several length-temperature curves at several temperatures was determined by means of an optical "tangent-meter." Considering the difficulty involved in obtaining high precision with this instrument on a slightly wavy curve the results are in satisfactory agreement with those given by the equation. In two runs, however, the coefficients were slightly greater than in the others although the variation with temperature was substantially the same in all cases. A similar displacement has been observed in crystalline aggregates of substances which have a highly anisotropic expansion, such as polycrystalline zinc, which suggests that the thermal expansion of single-crystal Na_2WO_4 may vary considerably in different orientations.

CRYSTAL INVERSIONS

The transition from III to II at 585° is accompanied by such an extraordinarily large change in volume, and therefore in length, that in most cases the relative height of the specimens was altered to an extent which spoiled the fringes and prevented further observation. This difficulty was in some measure overcome by cutting down the size of the specimens or by loading the upper plate as previously described, so that three

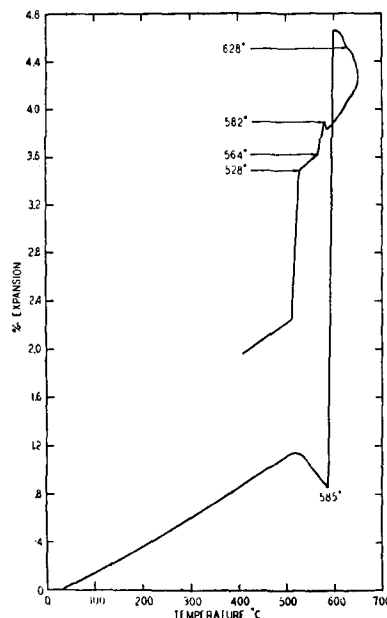


FIG. 3. Typical curve showing the linear thermal expansion of Na_2WO_4 on heating and on cooling.

runs were finally obtained in which it was possible to follow the expansion above the inversion, and two of these were carried through it again on cooling. A curve showing the linear expansion *versus* temperature for one of these runs is given in Fig. 3.

The temperature at which the III to II inversion starts, as determined from all the observations which were carried to this point, is $585^\circ \pm 2^\circ\text{C}$, which is in good agreement with the value 587.6° observed by Goranson and Kracek. The transition II to I found at 588.8° by Goranson and Kracek was not detected on heating because it is masked by the transformation III to II, which at the rate of heating of 3°C per minute, is still going on. In one run, however, the rate of passage of the fringes was appreciably less at 590° than either above or below this temperature, which may be an indication of the occurrence of the transformation $\text{II} \rightarrow \text{I}$. The cooling curve, which is discussed below, indicates, however, that both transformations must have occurred.

In every case the specimens contracted after the transformation had apparently been com-

pleted (see Fig. 3) but this shrinkage was irreversible and was probably due to a softening or settling of the aggregate after the disturbance during the inversion. In the three cases in which heating was carried above the transitions the maximum temperature did not exceed 635° because it was considered inadvisable to carry the samples too close to their melting point (695.5°). In two cases a faint but definite irregularity was found at 628° . Since this temperature coincides with that of the eutectic in the system $\text{Na}_2\text{WO}_4 - \text{Na}_2\text{W}_2\text{O}_7$ as reported by Hoermann³ it is likely that the "dip" is associated with the presence of a trace of excess WO_3 .

In the two runs from which satisfactory cooling curves were obtained a small but definite expansion characterizing the transition I to II was observed close to 582° . This temperature is lower than that found by Goranson and Kracek for equilibrium and indicates that with a rate of cooling of 3° to 4°C per minute the transformation undercools approximately 6° .

On further cooling, there is a rather rapid shrinkage followed by a contraction which is presumably that of the reversible expansion of Na_2WO_4 II. Unfortunately the results in this range are not very reproducible and are not suitable for deriving a precise coefficient. About all that can be said is that α_t for Na_2WO_4 II in the neighborhood of 550°C appears to be much larger, perhaps almost twice as large as α_t for Na_2WO_4 III in the same temperature range. The transformation II to III did not occur until the specimens had cooled to approximately 525° , indicating that at a rate of cooling of 3°C per minute this transition undercools by 60°C . In no case was the total contraction on cooling as great as the expansion at 585° on heating, but this behavior is generally observed in crystalline aggregates of anisotropic materials.⁴

LENGTH AND VOLUME CHANGE AT THE INVERSIONS

Three measurements were made of $\Delta l/l_{20}$ at the III to II inversion on heating, namely, 3.75, 4.30 and 5.63 percent. Of these the last is believed to be the best for two reasons: (1) This run was the last of the three in which the brass ring was

used to weight the upper plate and the specimens seemed to be the most compact of any examined; (2) in counting a large number of fringes passing the reference mark rapidly the observer is more likely to miss a few than to count too many, hence the highest value of $\Delta l/l_{20}$ is the most trustworthy. We have accordingly selected 5.63 as the best value, keeping in mind that even this may be somewhat low. The corresponding volume increase is 17.4 percent, which, so far as we are aware is the largest increase yet reported at a solid transition. By using Goranson and Kracek's value of 0.194 cm^3 per gram for the specific volume of Na_2WO_4 III at 20° , the increase in volume at the inversion is 0.034 cm^3 per gram, which is in satisfactory agreement with the value of 0.035 cm^3 per gram calculated by Goranson and Kracek from the effect of pressure on the transition temperature.

Both measurements of $\Delta l/l_{20}$ accompanying the transformation I to II on cooling, showed an increase of 0.04 percent, which, assuming random orientation of the grains, corresponds to a volume change of 0.12 percent or 0.00023 cm^3 per gram. Combining this result with the heat of transition obtained by Goranson and Kracek, the change in transition temperature with pressure calculated by means of the Clausius-Clapeyron equation is approximately -0.0014 degree per bar. This appears to be close to the limit of error of Goranson and Kracek's measurements and explains why they observed no change in the inversion temperature with pressure.

The relatively large undercooling of the transition II to III at a rate of 3° per min. suggested that rapid cooling might preserve form II to room temperature and thus make possible a determination of its optical properties. An attempt to do this has been made by the usual method of quenching into mercury. One procedure employed was to heat the tungstate above its melting point, cool it in the furnace at a rate of approximately 3° per min. to 570°C , and then quench; another was to quench the salt directly from the melt. In each case the optical properties of the quenched samples, for the determination of which we are indebted to Dr. O. Andersen, corresponded to those given by Goranson and Kracek for Na_2WO_4 III, indicating that the usual quenching technique does not provide sufficiently rapid cooling.

³ Hoermann, *Zeits. f. anorg. allgem. Chemie* **177**, 145 (1928).

⁴ See, for example, Sosman, *The Properties of Silica* (Chemical Catalog Co., New York, 1927), p. 388.