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Citation: [The Journal of Chemical Physics](#) **3**, 87 (1935); doi: 10.1063/1.1749613

View online: <http://dx.doi.org/10.1063/1.1749613>

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An Experimental Investigation of the Effect of Pressure on Phase Equilibria of Sodium Tungstate and of Related Thermodynamic Properties

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(Received December 7, 1934)

In order to clarify some uncertainties concerning the physical properties of sodium tungstate the effect of pressure on phase equilibria to 1000 bars, the heats of inversion and of melting, and the specific volume (density) at 30° were determined. Sodium tungstate is trimorphous at atmospheric pressure, form I being stable from 695.5° (melting point) to 588.8°, form II stable from 588.8° to just below 587.6°, and form III stable below this temperature. The I=II inversion is estimated to take place at 588.8° with a heat change of 14 joules/gram but no volume change (independent of pressure). Because of the large amount of undercooling in the I=III inversion, the II=I transition could be obtained metastably to 613 bars. The III=I inversion takes place promptly and reproducibly on heating but not so on cooling, the temperature change being dependent in large measure on the past history of the charge. Heating curve values lead to the expression

$t = 588.8 + 0.025(p - 40)$ with a heat change of 105 joules/gram and volume change of 0.035 cm³/gram. The triple point lies at $t = 588.8^\circ$ and $p = 40$ to 80 bars. The II=III inversion is very similar in behavior to the I=III inversion; here $t = 587.6 + 0.029 p$ on the heating curve. In order to represent specific volume as a function of temperature from 20° to 1300° the data of Jaeger and of Austin were also utilized. The published density of sodium tungstate was found to be in error and therefore a redetermination was made. The value obtained by us, 5.13 ± 0.01 , is 20 percent higher than that given by F. W. Clarke (J. L. Davis). The low-temperature modification expands from 0.195₂ cm³/gram at 30° to 0.203₂ cm³/gram at 587.6°. The salt inverts at this temperature, attaining the volume 0.238₂ cm³/gram, and finally, it again increases in volume at the melting point, 695.5°, to 0.256₂ cm³/gram.

INTRODUCTION

Scope of the investigation

Three crystalline forms of (anhydrous) sodium tungstate are known to exist but the exact relationship between these phases at atmospheric pressure is still somewhat in doubt, no work having been done at other pressures. The temperature-pressure-phase equilibria relations of these three solid phases and of the liquid phase were therefore determined to 1000 bars (10⁹ dynes/cm²) pressure. In order to utilize these data to obtain other thermodynamic properties of sodium tungstate the heats of inversion and of melting and the density at 30°C were re-determined. From these data, together with Jaeger's liquid density data and Austin's thermal expansion data from 20° to 500°C, the specific volume could be evaluated as a function of temperature from 20° to 1300°C.

Description of the material used

A pure grade of sodium tungstate was recrystallized either by cooling a hot saturated solution or by precipitating it by the addition of 95 percent ethyl alcohol to a nearly saturated solution. The resulting sodium tungstate dihydrate was dried at 125°, yielding very finely

powdered sodium tungstate which, however, was not completely anhydrous.¹ The last traces of water were removed by melting the salt.

Boeke² states that the low-temperature modification of sodium tungstate is optically isotropic. The material was found to have a weak birefringence, however, and examination of x-ray powder photographs shows that the symmetry is not that of the cubic system.³ It has a mean refractive index ($\lambda = 547\text{m}\mu$) of 1.678.

TEMPERATURE-PRESSURE PHASE EQUILIBRIA

The three crystalline modifications of sodium tungstate will be designated I, II and III, to denote the high, intermediate, and the low temperature forms, respectively. The liquid phase will be designated as *L*.

Previous work

The results recorded in the literature⁴ show that on cooling two breaks are obtained in the

¹ F. Hoermann, *Zeits. f. anorg. allgem. Chemie* **177**, 150 (1929) states that the dihydrate can be dehydrated at 100°. It was found, however, that material dried at 125° retained up to 0.5 percent of water.

² H. E. Boeke, *Zeits. f. anorg. allgem. Chemie* **50**, 359 (1906).

³ We are indebted to Mr. C. J. Ksanda of this Laboratory for the x-ray photographs.

⁴ The literature to 1929 is given in Gmelin's *Handbuch der anorg. Chemie*, Wolfram system No. 52, 212 (1933).

curve: (a) a small heat effect in the range between 590° and 576°, and (b) a large heat effect in the range between 583° and 560°. On heating there appears to be only a single arrest at about 588°. Van Klooster and Germs found that if cooling was arrested at 584° there was on subsequent reheating an arrest at 591°. Kracek⁵ made further measurements and found that the small heat effect took place at 586° on cooling and that it could be reversed readily, provided the temperature did not fall low enough for the large heat effect to begin, taking place at 592° on reheating. The large heat effect was observed to take place with considerable undercooling, and reheating afterwards gave an apparently single arrest at 588°. This behavior is almost an exact parallel to that of potassium nitrate, and the modifications were accordingly numbered in the Smithsonian Tables to agree with Bridgman's nomenclature for the latter substance,⁶ assuming the intermediate form to be metastable at atmospheric pressure. Boeke observed with a heating microscope that the melt crystallizes in birefringent dendritic crystals which transform at 590° to a still more birefringent form and then invert at 584° to become optically isotropic. On reheating, the phenomena are said to occur in reverse order. Boeke's observations would indicate that the intermediate form of sodium tungstate has a temperature range of stable existence at atmospheric pressure instead of coming in metastably as was supposed by Kracek.

The results of this paper establish, among other things, the validity of Boeke's observations, and also show that, with proper technique, both arrests can be observed on heating as well as on cooling.

Experimental procedure

The pressure investigation was carried out in a water-jacketed steel bomb containing a platinum-rhodium resistance furnace. A detailed description of the bomb has been given in an earlier paper.⁷ Pressures were measured with a resistance gauge consisting of a hundred ohm coil of manganin wire immersed in the pressure

fluid but kept at room temperature (25°). The coil is connected to the apparatus for measuring the resistance through a pressure-tight electrically insulated packing. The sensitivity in measuring changes in resistance (about 0.2 ohm per kilobar) was such that one scale division corresponds to about one bar. The scale for this electrical pressure gauge was calibrated by comparison with an absolute gauge of the free-piston type. The pressure medium used was nitrogen gas.

Temperatures were measured with Pt-PtRh thermocouples. The leads are carried out of the bomb through pressure-tight electrically insulated packings in the bomb lid. The scale for these thermocouples was obtained by calibration at several fixed points and interpolated from the table of L. H. Adams.⁸

The differential temperature, i.e., the difference in temperature between the inert body, in this case silica glass, and the sodium tungstate charge, was measured with PtRh-AuPd-PtRh thermocouples.

The inversion and melting temperatures were obtained from differential heating and cooling curves.

Some of the measurements at atmospheric pressure were made in an ordinary platinum resistance furnace in connection with the calorimetric data.

Experimental results

The accuracy of the determination of the temperature-pressure-phase *equilibrium curves* for the III \rightleftharpoons II and III \rightleftharpoons I inversions is limited by the rather wide passive regions within which the rate of transition is not measurable. The upper bound (heating curve values) of these regions is reproducible to within 0.5°, taking place promptly but not isothermally. The lower bound (cooling curve values), although prompt when initiated, is nevertheless variable and not readily reproducible because it depends in a large measure on the past history of the sodium tungstate charge. It was found that if the powder was first sintered or melted to a cake it would react more or less as a single crystal, i.e., the individual crystalline grains, by this procedure, seem to have been brought into contact intimate

⁵ Kracek, Smithsonian Physical Tables, 8th Edition, p. 261 (1933).

⁶ P. W. Bridgman, Proc. Am. Acad. 51, 579 (1916); F. C. Kracek, J. Phys. Chem. 34, 225 (1930).

⁷ Roy W. Goranson, Am. J. Sci. 22, 481 (1931).

⁸ L. H. Adams, Int. Crit. Tab. 1, 59 (1926).

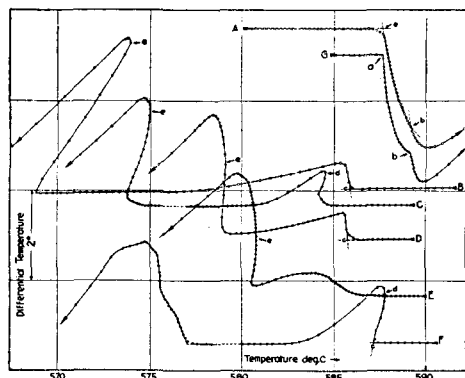


Fig. 1. Typical differential heating (A, G) and cooling curves (B to F inclusive) through the two inversions.

enough to initiate the reaction in their neighbors. Moreover, this procedure of first sintering or fusing to a cake increases the thermal conductivity and thereby lessens temperature gradients in the charge; the unfused precipitate, dehydrated at 125°, is an extremely fine powder and a good thermal insulator, and such a charge would therefore have high temperature gradients when heating or cooling. Differential cooling curves yield a lower bound averaging about 6° below the upper bound, and undercooling of as much as 15° has been observed. By repeated reversals of the heating and cooling curves before the transition was complete the undercooling could be apparently largely eliminated, but even with this technique the maximum value obtained at atmospheric pressure for the inversion temperature on the cooling curve was still 5° below the inversion temperature on the heating curve; at 420 bars pressure this technique was able to bring the cooling curve value to within 1° of the heating curve value. The essential characteristics of the differential heating and cooling curves do not vary appreciably with pressure, but the curves do become more reproducible at high pressures, perhaps as a result of increased efficiency in heat transference. Such curves are reproduced in Fig. 1; they represent runs made at one bar pressure, but the shapes of the transition curves are typical of any of the pressure runs. The curves of Fig. 1 were all obtained with the same sample; cooling curves B to F inclusive demonstrate the variability in

TABLE I. Temperature-pressure relations of the $\text{III} \rightleftharpoons \text{II}$ and $\text{III} \rightleftharpoons \text{I}$ inversions. "H" denotes the beginning of inversion on heating and "C" the beginning on cooling. The asterisk value is calculated (as shown later in the text).

Pressure in bars	Temperature H	C	Pressure in bars	Temperature H	C
1	587.6*	—	440	598.5	—
1	587.5	581.1	625	603.9	599.4
40	588.8	582.6	715	606.0	598.8
90	589.3	582.7	740	605.5	—
175	592.4	583.6	890	—	605.2
276	594.6	—	923	611.3	—
301	595.5	592.5	990	613.0	606.4
410	599.2	—	1030	614.0	—
418	599.2	597.7			

values, indicated by "e," obtained for the $\text{II} \rightarrow \text{III}$ inversion.

The experimental results for the $\text{III} \rightleftharpoons \text{II}$ and the $\text{III} \rightleftharpoons \text{I}$ inversions are tabulated in Table I.

The $\text{II} \rightarrow \text{I}$ inversion, when it follows immediately upon the $\text{III} \rightarrow \text{II}$ inversion, is not readily detectable on the differential heating curve because it takes place only one and a half degrees above the beginning of the $\text{III} \rightarrow \text{II}$ inversion at atmospheric pressure and with only about one-seventh the heat effect of the latter. With careful technique the break can be obtained (Fig. 1, points "b" on curves A and G) and this break can be easily accentuated by reversing the cooling curve before the $\text{II} \rightarrow \text{III}$ transition has been completed. This inversion is prompt but not isothermal; superheating and undercooling of about one-half degree each have been observed for this transition. Because of the large amount of undercooling in the $\text{I} \rightarrow \text{III}$ transition it was found that ordinarily the transitions would take place metastably in the order $\text{I} \rightarrow \text{II} \rightarrow \text{III}$ up to 613 bars pressure. It was also possible to reverse the cooling curve before the $\text{II} \rightarrow \text{III}$ transition occurred and so to obtain the metastable $\text{II} \rightarrow \text{I}$ transition up to 300 bars pressure. Typical records of such reversal curves are presented in Fig. 2 and were made in the order as numbered. The metastable prolongation of the $\text{I} \rightleftharpoons \text{II}$ pressure-inversion curve was therefore determined to 613 bars pressure. The experimental results for the $\text{II} \rightleftharpoons \text{I}$ inversion are collected in Table II.

The temperature-pressure results given in Table I for the $\text{III} \rightarrow \text{I}$ (heating curve values) transition can be represented, within the accu-

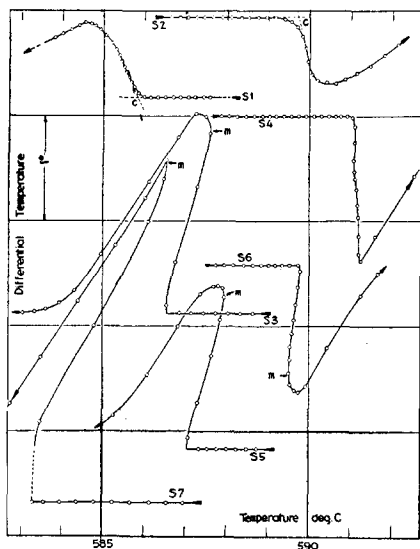


FIG. 2. Typical differential heating and cooling curves of the I=II inversion made in the order as numbered without going through the II=III inversion.

racy of the experiments, by the slope $dt/dp = 0.025$ or, if no account be taken of stable and metastable states and extrapolated to one bar, by the equation

$$t_{III \rightarrow I} = 587.8 + 0.025p,$$

where t denotes temperature in degrees C, and p pressure in bars.

For reasons already given, the cooling curve values (I \rightarrow III) were not used in the calculation, especially as in a number of the experiments the cooling curve values represent the metastable II \rightarrow III rather than the stable I \rightarrow III transition.

TABLE II. Temperature-pressure relations of the II=I inversion. "H" and "C" denote the beginning of inversion on the differential heating and cooling curves, respectively.

Pressure in bars	H	Temperature C	Mean
1	589.5	588.0	588.8
1	589.1	588.5	588.8
40	589.9	588.1	589.0
90	588.6	588.7	588.6
175	588.5	588.8	588.7
276	589.4	587.6	588.4
300	589.5	588.5	589.0
410	—	588.9	588.9
613	—	589.2	589.2

The temperature-pressure curve for the II=I inversion, as can be seen by inspection of Table II, is independent of pressure, within the experimental error; that is,

$$t_{II \rightarrow I} = 588.8 + 0.000p.$$

The location of the triple point can be evaluated only within limits from the data available. The intersection of the III \rightarrow I and the II=I curves yields $p = 40$ bars at 588.8° . This must be regarded as the lower pressure limit. The true location of this point depends, obviously, upon the location of the true equilibrium temperature-pressure curve for the III=I inversion, and, hence, lies at a somewhat higher pressure. Now, since at 420 bars the III=I band was found to be only one degree wide, and if we suppose that this width would persist to lower pressures if the I \rightarrow III transition could take place without the metastable intervention of the sequence I \rightarrow II \rightarrow III, it may be estimated from the data that the upper limiting value of pressure for the triple point is 80 bars at 588.8° . Hence,

$$\text{Na}_2\text{WO}_4(\text{I, II, III}): t = 588.8^\circ \\ p = 40 \text{ to } 80 \text{ bars.}$$

Melting curve

The temperature of melting is taken as the end of melting and the temperature of freezing as the beginning of crystallization or as the maximum where undercooling occurs. The experimental values are presented in Table III.

TABLE III. Pressure melting of Na_2WO_4 . "H" denotes the end of melting and "C" the beginning of crystallization. The lower four values denote a single sequence and are used in calculating the slope of the curve.

Pressure in bars	H	Temperature C	Mean
1			695.5
1	695.0	695.0	695.0
500	705.7	705.4	705.5
706	711.4	712.0	711.7
1040	715.6	716.6	716.1

The pressure-melting relations, where temperature represents the mean of the melting and freezing temperatures, was represented as a least square quadratic passed through the points and is given by the following equation:

$$t_{I \rightarrow L} = 695.5 + 0.0219p - 1.18 \times 10^{-6}p^2,$$

Specific volume of the liquid

Jaeger¹¹ has measured the density of liquid sodium tungstate at three temperatures. His values are: 3.685 at 917°, 3.502 at 1128°, and 3.356 at 1330°. A recalculation of these points was made in terms of specific volume yielding the equation

$$v = 0.2714 + 0.703(t - 917)10^{-4} - 1.423(t - 917)^2 10^{-8}$$

where v denotes the specific volume of the liquid which, from this equation, is 0.257 at the melting point.

Specific volume of the crystals at room temperature

The only published value of the density of anhydrous sodium tungstate at room temperature is that by Clarke and Davis,¹² who give 4.1833 at 18.5° and 4.1743 at 20.5°. From these data and those of Jaeger the change in specific volume from solid at 20° to liquid at 695° is calculated to be 0.017. This result is inconsistent with the data of Table IV from which the specific volume change due to the transitions and melting alone is calculated to be 0.053₂. Accordingly, the density at room temperature was re-determined.

The density results on the very fine-grained powder resulting from dehydration of Na₂WO₄·2H₂O clustered about the value 4.82, with deviations of about 0.01, while those on the fused material were in the neighborhood of 5.10, and depended on the grain size, the coarsest size used (10–24 mesh) yielding the highest value. This variability resulted from an imperfect removal of the air trapped in the sample. Consequently the ordinary technique was modified by squeezing toluene (the displacement fluid) into the pores of the grains under a pressure of 6000 bars for about one-half to one hour; this additional treatment increased the measured density by about two parts in 500. Accordingly, the density of sodium tungstate is taken to be 5.13±0.01 at 30°. The corresponding specific volume is 0.195±0.0004 cm³/gram.

¹¹ F. M. Jaeger, *Zeits. f. anorg. Chemie* **101**, 183 (1917).

¹² F. W. Clarke (J. L. Davis), *Am. J. Sci.* (3), **14**, 283 (1877).

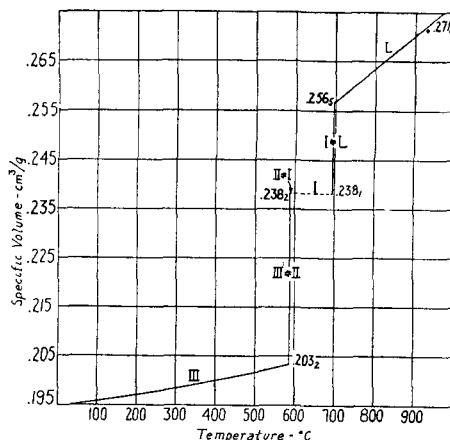


FIG. 4. The specific volume of sodium tungstate as a function of temperature.

Thermal expansion of sodium tungstate

The linear thermal expansion of sodium tungstate has been determined by J. B. Austin¹³ from 20° to the inversion temperature. We have calculated a least square quadratic for the volume expansion of modification III from his data to 500° on the assumption that his samples represent aggregates of randomly oriented crystalline grains. The equation is

$$v - v_{20} = v_{20} [53.194(t - 20)10^{-6} + 41.5(t - 20)^2 10^{-8}],$$

which, if the measured value of the specific volume at 30° be inserted, becomes

$$v = 0.1947 + 10.4(t - 20)10^{-6} + 8(t - 20)^2 10^{-9},$$

v denoting specific volume.

Specific volume as a function of temperature

By combining the various data we can finally express the specific volume of sodium tungstate as a function of temperature from 20° to 1300° at atmospheric pressure. In this temperature interval there are two discontinuities, the III→II transition at 587.6° with $\Delta v = 0.035_0$ and the I→L transition at 695.5° with $\Delta v = 0.018_2$. These results are represented graphically in Fig. 4.

¹³ We are indebted to Dr. Austin for allowing us to use his results before publication.